Bifunctional Oxygen Reduction/Evolution Catalysts for Rechargeable Metal-Air Batteries and Regenerative Alkaline Fuel Cells

by

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Abstract

The electrocatalysis of oxygen reduction and evolution reactions (ORR and OER, respectively) on the same catalyst surface is among the long-standing challenges in electrochemistry with paramount significance for a variety of electrochemical systems including regenerative fuel cells and rechargeable metal-air batteries. Non-precious group metals (non-PGMs) and their oxides, such as manganese oxides, are the alternative cost-effective solutions for the next generation of high-performance bifunctional oxygen catalyst materials.

Here, initial stage electrocatalytic activity and long-term durability of four non-PGM oxides and their combinations, i.e. MnO₂, perovskites (LaCoO₃ and LaNiO₃) and fluorite-type oxide (Nd₃IrO₇), were investigated for ORR and OER in alkaline media. The combination of structurally diverse oxides revealed synergistic catalytic effect by improved bifunctional activity compared to the individual oxide components.

Next, the novel role of alkali-metal ion insertion and the mechanism involved for performance promotion of oxide catalysts were investigated. Potassium insertion in the oxide structures enhanced both ORR and OER performances, e.g. 110 and 75 mV decrease in the OER (5 mAcm⁻²) and ORR (-2 mAcm²⁻) overpotentials (in absolute values) of MnO₂-LaCoO₃, respectively, during galvanostatic polarization tests. In addition, the stability of K⁺ activated catalysts was improved compared to unactivated samples.

Further, a factorial design study has been performed to find an active nanostructured manganese oxide for both ORR and OER, synthesized via a surfactant-assisted anodic electrodeposition method. Two-hour-long galvanostatic polarization at 5 mAcm⁻² showed the lowest OER degradation rate of 5 mVh⁻¹ for the electrodeposited MnOₓ with 270 mV lower OER overpotential compared to the commercial γ-MnO₂ electrode.
Lastly, the effect of carbon addition to the catalyst layer, e.g. Vulcan XC-72, carbon nanotubes and graphene-based materials, was examined on the ORR/OER bifunctional activity and durability of MnO$_2$-LaCoO$_3$. The highest ORR and OER mass activities of -6.7 and 15.5 A g$^{-1}$ at 850 and 1650 mV$\text{RHE}$, respectively, were achieved for MnO$_2$-LaCoO$_3$-multi_walled_carbon_nanotube-graphene, outperforming a commercial Pt electrode. The factors affecting the durability of mixed-oxide catalysts were discussed, mainly attributing the performance degradation to Mn valence changes during ORR/OER. A wide range of surface analyses were employed to support the presented electrochemical results as well as the proposed mechanisms.
Preface

The materials presented in the following dissertation are confidential and subject to United States and Canadian patent applications.

The research work presented in this thesis including literature review, research proposal, experimental work, data interpretation, proposed hypothesis and preparation of this dissertation, four research manuscripts, five conference presentations along with one provisional and one U.S./Canadian patent applications are completed by Pooya Hosseini-Benhangi under the direct supervision of Professors Előd Gyenge and Akram Alfantazi at the Department of Chemical & Biological Engineering Department, the University of British Columbia.

The following publications, manuscripts, presentations and patent applications are developed form the work presented in this dissertation:

A version of chapter 3 and 4 was published and presented in:


A version of chapter 5 is in preparation for publication and was presented at a conference:

6) P. Hosseini-Benhangi, A. Alfantazi, E. Gyenge, “Surfactant-assisted electrodeposition of Mn oxides as promising ORR/OER bifunctional non-PGM electrocatalysts: Factorial design study of the electrodeposition factors”, to be submitted.


A version of chapter 6 is in preparation for publication and was presented at a conference:

8) P. Hosseini-Benhangi, M. A. Garcia-Contreras, A. Alfantazi, E. Gyenge, “Carbon support effect on ORR/OER bifunctional activity and durability of non-PGM mixed-oxide catalyst: Graphene vs. commercial carbon materials”, to be submitted.

For the items 1 to 9, all of the experiments were performed by Pooya Hosseini-Benhangi and the manuscripts were co-authored by Előd Gyenge with the support from Akram Alfantazi. For items 2, 8 and 9, the experiments were performed by Pooya Hosseini-Benhangi with laboratory recommendations from Dr. Miguel Angel Garcia-Contreras. The manuscripts and presentations mentioned in items 2, 8 and 9 were also co-authored by Dr. Miguel Angel Garcia-Contreras.

Parts of chapters 2, 3, 4, 5 and 6 from this dissertation were filed as United States and Canadian patent applications:


where all of the experiments for this intellectual property were performed by Pooya Hosseini-Benhangi. The U.S. and Canadian patent applications were co-authored by Előd Gyenge and Brian Yat-Ming Lee (Patent Attorney).
Table of Contents

Chapter 1: Introduction ............................................................................................................ 1
  1.1 Summary .......................................................................................................................... 1
  1.2 Bifunctional catalysts for ORR and OER in alkaline batteries and fuel cells .............. 9
    1.2.1 Nobel metals and their alloys .................................................................................. 10
    1.2.2 Manganese dioxide ................................................................................................. 11
      1.2.2.1 Electro-reduction of MnO₂ ................................................................................. 15
      1.2.2.2 Oxygen reduction reaction on manganese oxides ........................................... 20
      1.2.2.3 Oxygen evolution reaction on manganese oxides ........................................... 29
      1.2.2.4 Density Functional Theory (DFT) studies on manganese oxides catalyzing both ORR and OER ...................................................................................................... 35
      1.2.2.5 Dopants for manganese dioxide as cathode material in alkaline fuel cells and metal-air batteries ................................................................................................. 37
      1.2.2.6 Nanostructured manganese oxides ..................................................................... 38
1.2.3 Perovskite-type oxides ................................................................. 56
1.2.4 Fluorite-type oxides ................................................................. 58
1.2.5 Carbon support for ORR/OER bifunctional catalysts ................... 59
1.3 Knowledge gap and research objectives ........................................... 61
1.3.1 Knowledge gap ........................................................................ 61
1.3.2 Research objectives .................................................................. 62

Chapter 2: Experimental methods, apparatus and materials ..........................65

2.1 Material preparation ........................................................................ 65
  2.1.1 Catalyst powders ....................................................................... 65
    2.1.1.1 Perovskites ........................................................................ 65
    2.1.1.2 Nd₃IrO₇ ............................................................................... 65
    2.1.1.3 Manganese dioxide .............................................................. 66
    2.1.1.4 Carbonaceous materials ...................................................... 66
    2.1.1.5 Platinum ............................................................................. 66
  2.1.2 Catalyst layer preparation ............................................................. 66
  2.1.3 Gas diffusion electrode preparation ................................ .......... 67
  2.1.4 Anodic electrodeposition of manganese oxides ............................ 69
  2.1.5 Surface modification: K⁺ intercalation ......................................... 73
  2.2 Surface and structural characterization ............................................. 74
  2.3 Electrochemical measurements ....................................................... 75

Chapter 3: Comprehensive studies on the ORR/OER electrocatalytic activity and durability of individual (MnO₂, LaCoO₃, LaNiO₃ and Nd₃IrO₇) and mixed-oxide (MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇) catalysts .................................................................80
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>80</td>
</tr>
<tr>
<td>3.2</td>
<td>Results and discussions</td>
<td>81</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Characterization of oxide catalysts</td>
<td>81</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Initial stage electrocatalytic activity of oxide catalysts</td>
<td>86</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Accelerated degradation testing of oxide catalysts in flooded test setup</td>
<td>96</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Long-term ORR durability of oxide catalysts in a flow-by test setup</td>
<td>97</td>
</tr>
<tr>
<td>3.3</td>
<td>Conclusion</td>
<td>103</td>
</tr>
</tbody>
</table>

**Chapter 4: Oxide catalyst activation by alkali-metal ion intercalation** ...........................................106

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>106</td>
</tr>
<tr>
<td>4.2</td>
<td>Results and Discussion</td>
<td>107</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Oxide catalyst layer activation by open-circuit potential (OCP) K⁺ intercalation</td>
<td>107</td>
</tr>
<tr>
<td>4.2.1.1</td>
<td>Healing effect</td>
<td>107</td>
</tr>
<tr>
<td>4.2.1.2</td>
<td>Activation of fresh catalysts</td>
<td>116</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Oxide catalyst layer activation by potential driven intercalation (PDI) of K⁺</td>
<td>129</td>
</tr>
<tr>
<td>4.2.2.1</td>
<td>Initial stage electrocatalytic activity of PDI activated mixed-oxide catalysts</td>
<td>129</td>
</tr>
<tr>
<td>4.2.2.2</td>
<td>Initial stage electrocatalytic activity of PDI activated individual oxides</td>
<td>133</td>
</tr>
<tr>
<td>4.2.2.3</td>
<td>Galvanostatic long-term durability testing of unactivated and PDI activated mixed-oxide catalysts</td>
<td>138</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Comparison of Bifunctional ORR/OER Activities: present work vs. literature</td>
<td>141</td>
</tr>
<tr>
<td>4.3</td>
<td>Conclusion</td>
<td>144</td>
</tr>
</tbody>
</table>
Chapter 5: Surfactant-assisted electrodeposition of Mn oxides as promising ORR/OER bifunctional non-PGM electrocatalysts: Factorial design study of the electrodeposition factors

5.1 Introduction ........................................................................................................................................ 146
5.2 Results and discussion ..................................................................................................................... 147
  5.2.1 Anodic electrodeposition behavior of Mn oxides with and without surfactants .................. 147
  5.2.2 Characterization of the electrodeposited samples ................................................................... 150
  5.2.3 Factorial design experiments .................................................................................................. 154
    5.2.3.1 Triton X-100 surfactant-assisted electrodeposition ...................................................... 156
    5.2.3.2 SDS surfactant-assisted electrodeposition ..................................................................... 160
    5.2.3.3 CTAB surfactant-assisted electrodeposition ................................................................... 164
  5.2.4 ORR/OER performance comparison ....................................................................................... 168
  5.2.5 Galvanostatic long-term durability testing of deposited MnO_x ........................................ 173
5.3 Conclusion ...................................................................................................................................... 174

Chapter 6: Carbon support effect on ORR/OER bifunctional activity and durability of non-PGM mixed-oxide catalyst: Graphene vs. commercial carbon materials

6.1 Introduction ...................................................................................................................................... 177
6.2 Results and discussion ..................................................................................................................... 178
  6.2.1 Microstructural studies of catalyst and support materials .................................................... 178
  6.2.2 RRDE studies of carbonaceous materials for ORR ............................................................. 181
  6.2.3 ORR/OER bifunctional electrocatalytic activity measurements: Carbonaceous materials as oxygen catalysts ........................................................................................................... 184
6.2.4 ORR/OER bifunctional electrocatalytic activity measurements of non-PGM oxide oxygen catalyst: MnO$_2$-LaCoO$_3$ supported on carbonaceous materials .......................... 190

6.2.5 Bifunctional accelerated degradation testing: MnO$_2$-LaCoO$_3$ supported on MWCNT-Graphene or Vulcan XC-72.................................................................................... 197

6.3 Conclusion .......................................................................................................................... 200

Chapter 7: Conclusions and recommendations for future work........................................... 203

7.1 Conclusions ..................................................................................................................... 203

7.1.1 ORR/OER electrocatalytic activity and durability of individual and mixed-oxide catalysts ......................................................................................................................... 203

7.1.2 Oxide catalyst activation by alkali-metal ion intercalation............................................ 204

7.1.3 Surfactant-assisted electrodeposition of Mn oxides: Factorial design study of the electrodeposition factors ........................................................................................................ 205

7.1.4 The effect of carbon supports: Graphene vs. commercial carbon materials... 206

7.2 Contributions to knowledge ............................................................................................. 207

7.3 Recommendation for future work .................................................................................. 209

Bibliography ............................................................................................................................. 211

Appendices ............................................................................................................................... 228

Appendix A: Electrode kinetics: The Butler-Erdey-Grúz-Volmer (BE-GV) equation .. 228

Appendix B: The rotating disk and ring disk electrode (RDE and RRDE) ............... 231

Appendix C: Break-in protocol test results for GDE flow-by cell ................................. 235

Appendix D: The effect of inter-stage OCP activation......................................................... 237

Appendix E: Factorial design study ....................................................................................... 240

xi
List of Tables

Table 1.1 MnO$_2$ crystal structure evolution at several electrode potentials in fractional composition. Other conditions idem to Figure 1.10. Reprinted with permission from [45]........ 18
Table 1.2 Possible ORR pathways in alkaline media [2, 17, 45, 98-100]. ........................................... 21
Table 2.1 Experimental design factors and their levels for $2^{4-1}$+3 factorial design runs. .......... 70
Table 3.1 XRD structural analysis of: Commercial MnO$_2$, synthesized LaCoO$_3$, synthesized LaNiO$_3$ and synthesized Nd$_3$IrO$_7$. The XRD spectrum of the powders are presented in Figure 3.2. The bold 2θ and Miller indices show overlapped peaks for different crystallographic plans. ..... 85
Table 3.2 BET surface area of single and mixed oxide catalyst layers. ................................................... 90
Table 3.3 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated GDEs with fresh catalysts. O$_2$ saturated 6 M KOH. 293 K. P$_{O_2}$ of 1 atm. The exchange current densities are expressed per geometric area. The standard error of the mean calculated based on six replicates is indicated for each catalyst. ......................... 95
Table 5.1 XPS peak analysis of electrodeposited MnO$_x$ samples (T1, T9 and T10). The deconvoluted data for Mn 2p, Mn 3s and O 1s is presented. The error associated with binding energy of peak position is ±0.1 eV. Other conditions idem to Figure 5.2. ......................... 152
Table 5.2 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of Triton X-100. Other conditions idem to Table 2.1.157
Table 5.3 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of SDS. Other conditions idem to Table 2.1. ........ 161
Table 5.4 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of CTAB. Other conditions idem to Table 2.1. ....... 165
Table 6.1 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated carbonaceous catalyst materials in Figure 6.3. The exchange current densities are expressed per geometric area. The apparent Tafel slope and exchange current density values are obtained over a potential range of min. 50 mV on six replicates. Other conditions idem to Figure 6.3.

Table 6.2 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated catalyst materials in Figure 6.5. The exchange current densities are expressed per geometric area. The apparent Tafel slope and exchange current density values are obtained over a potential range of min. 50 mV on six replicates. Other conditions idem to Figure 6.5.
**List of Figures**

Figure 1.1 Schematic illustration of electrically rechargeable metal-air batteries with its operating principle and bifunctional cathode. Reprinted with permission from [16]................................. 3

Figure 1.2 Schematic polarization curve of rechargeable Zn-air battery. The equilibrium potential of the Zn-air battery (black line) is 1.65 V, but the practical voltage (red line) in discharge is lower than 1.65 V due to the sluggish ORR. A large potential is needed to charge Zn-air battery, higher than the equilibrium potential (blue line). Reprinted with permission from [11]................................. 4

Figure 1.3 Challenges facing rechargeable aqueous Li-air batteries. Reprinted with permission from [21]................................................................. 4

Figure 1.4 a) Discharge polarization curves of gas diffusion electrodes containing graphene nanosheets (GNSs), 20 wt% Pt/C and acetylene black at 0.5 mA cm$^{-2}$, b) Galvanostatic discharge-charge cycle curves of heat-treated GNSs at 0.5 mA cm$^{-2}$. 1 M LiClO$_4$/ED/DEC was used as the organic electrolyte and 1 M LiNO$_3$ + 0.5 M LiOH was used as the aqueous electrolyte. A solid-state electrolyte Li$_{1+x+y}$Al$_x$Ti$_2$Si$_3$P$_3$O$_{12}$ (LISICON) film was used as a separating membrane between the organic and aqueous electrolytes to prevent intermixing of the two solutions. The discharge-charge performance was carried out at a current density of 0.5 mA cm$^{-2}$ between 2 and 4.8 V vs. Li/Li$^+$ for 2 hrs per each cycle. 298 K. Reprinted with permission from [24]. ........................................................................................................................................................................ 5

Figure 1.5 Schematic representation of an anion exchange membrane-unitised regenerative fuel cell (AEM-URFC) as an energy storage unit. The AEM-URFC stores renewable energy as H$_2$ while in electrolyzer mode and then uses that H$_2$ to generate electric energy on-demand when in fuel cell mode. Reprinted with permission from [32]................................................................. 7
Figure 1.6 Polarization curves for the AEM-URFC under eight fuel cell/electrolyzer cycles. MEA: Fumapem FAA-3, Fumatech as Anion exchange memberane. Gas diffusion electrodes: 6 mg_{cat} cm^{-2} Ni/C for the H_2 electrode and 4 mg_{cat} cm^{-2} MnO_x/GC:Ni/C (5:1 weight ratio) for the O_2 electrode. An alkaline ionomer (1.8 μL per 1 mg catalyst, Fumion FAA-3, Fumatech) was added to each of the electrodes. 20 min per each cycle. 335 K. H_2/O_2 gas flow rates of 300 Standard Cubic Centimeters per Minute (SCCM). All potentials are reported vs. reversible hydrogen electrode (RHE). Reprinted with permission from [32].

Figure 1.7 A comparison between bifunctional oxygen performance of different catalyst materials in alkaline media. The ORR and OER overpotentials were calculated at superficial current densities specified on the graph. Reprinted with permission from [4].

Figure 1.8 Schematic representation of five different crystal structures of MnO_2: A) Pyrolusite (β-MnO_2): Rutile structure with an infinite chain of MnO_6 octahedra sharing opposite edges. Each chain is corner-linked with four similar chains, B) Ramsdellite (α-MnO_2): Cross-linking of double or triple chains of the MnO_6 octahedra resulting in two-dimensional tunnels within the lattice, C) Birnessite (δ-MnO_2): Layered structure containing infinite two-dimensional sheets of edge-shared MnO_6 octahedra, D) Spinel (λ-MnO_2): A 3D spinel structure and E) Electrolytic manganese dioxide (γ-MnO_2): An intergrowth of pyrolusite in ramsdellite matrix. Each MnO_6 octahedra composes of oxygen and manganese atoms in the corners and center, respectively. Reprinted with permission from [85, 88, 89].

Figure 1.9 Linear sweep voltammetry of 0.2 mg MnO_2 on Ni mesh in N_2 saturated 10.2 M KOH. 0.05 mV s^{-1}. 298 K.

Figure 1.10 Cyclic voltammograms of different manganese oxides supported on carbon in N_2 saturated 1 M KOH at 20 mV s^{-1} and 298 K. Samples labeled as A, B and C are MnO_2/C,
Mn$_2$O$_3$/C and Mn$_3$O$_4$/C, respectively. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [45].

Figure 1.11 Cyclic voltammograms of four different commercially available MnO$_2$ powders supported on carbon in N$_2$-purged 6 M KOH at 2 mV s$^{-1}$. 295 K. Third cycle is presented. The potentials are reported vs. mercury-mercury oxide reference electrode (MOE). Reprinted with permission from [90].

Figure 1.12 ORR polarization curves of various catalysts following 2e$^-$ or 4e$^-$ pathways in 0.1 M KOH. Theoretical limiting current densities for the 2e$^-$ or 4e$^-$ pathways are indicated by solid lines together with a ±10% margin (dashed lines). Currents are normalized to the geometrical area of the disk. 1600 rpm. 298 K. P$_O_2$ equals to 1 atm. Reprinted with permission from [107].

Figure 1.13 Possible ORR pathways on manganese oxides in alkaline media: A) Four-electron pathway reducing O$_2$ to hydroxide, B) Two-electron pathway reducing O$_2$ to peroxide ion and C) Two-electron reduction of peroxide ions. Orange denotes species on the catalyst surface, and blue/purple denotes species in solution. Reprinted with permission from [107].

Figure 1.14 Linear sweep voltammograms of four types of manganese dioxide: A) α-MnO$_2$ (ramsdellite), B) β-MnO$_2$, C) γ-MnO$_2$ and D) ε-MnO$_2$. N$_2$ saturated 7 N KOH. 0.003 mV s$^{-1}$. 298 K. Solid and dotted lines represent mass activity (I, currents normalized by the catalyst loading) and the fraction of one electron capacity expressed in percentage, respectively, vs. potential. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [41].

Figure 1.15 Linear voltammograms of MnO$_2$-catalyzed air electrode in: A) Argon and B) Air. The catalysts are labelled as follows: 1) α-MnO$_2$, 2) β-MnO$_2$, 3) γ-MnO$_2$, 4) λ-MnO$_2$ and 5) δ-MnO$_2$. The reduction current is defined as positive (American current polarity convention). 6 M KOH.
298 K. 1 mV s\(^{-1}\). Currents are normalized by the catalyst loading, presenting mass activity values. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [48]. .......................................................... 28

Figure 1.16 Oxygen reduction polarization curves recorded in a flow cell for four types of commercially available MnO\(_2\) powders: Tronox (\(\gamma\)-MnO\(_2\)), Riedel (\(\beta\)-MnO\(_2\)), Merck (\(\gamma\)-MnO\(_2\)) and Sigma (\(\gamma\)-MnO\(_2\) with high portion of \(\alpha\)-MnO\(_2\)). Gas diffusion electrodes are employed at a loading of 0.25 mg cm\(^{-2}\) for MnO\(_2\) mixed with Vulcan XC-72 (1:1 weight ratio). 6 M KOH. 293 K. Currents are normalized to the geometrical area of the electrode. The potentials are reported vs. mercury-mercury oxide reference electrode (MOE). Reprinted with permission from [90]. ............... 29

Figure 1.17 OER mechanisms proposed for crystalline oxide surfaces in alkaline electrolytes: A) Four-step reaction mechanism proposed by Rossmeisl et al. for the OER on noble metal catalysts and oxide surfaces [124, 125], B) Four-step reaction mechanism proposed by Goodenough et al. for the OER on perovskite surfaces [126], C) Acid–base mechanism proposed for first-row transition-metal oxides [127], D) Reaction mechanism proposed by Faria et al. involving recombination of oxygen atoms to produce O\(_2\) [128] and E) Reaction mechanism proposed by Gerken et al. for electrodeposited cobalt oxides [129]. The orange and blue denote species on the catalyst surface and in solution, respectively. Reprinted with permission from [123]............... 32

Figure 1.18 A comparison between the OER activity and durability of wide range of catalysts in 1 M NaOH: The x-axis is the overpotential required to achieve 10 mA cm\(^{-2}\) at time equal to 0 s. The y-axis is the overpotential required to achieve 10 mA cm\(^{-2}\) after two hrs of testing. The dashed diagonal line indicates where the stable catalysts would be. Catalyst loadings are 0.8 mg cm\(^{-2}\) for each case. 298 K. P\(_{O_2}\) of 1 atm. Reprinted with permission from [130]....................... 33
Figure 1.19 A comparison between the OER overpotentials (at 10 mA cm\(^{-2}\)) for four different types of manganese oxides in alkaline media: \(\alpha\), \(\beta\), \(\delta\)-MnO\(_2\) and amorphous MnO\(_x\). 0.1 M KOH. 1600 rpm. 298 K. Reprinted with permission from [105].

Figure 1.20 OER cyclic voltammograms of various catalysts in O\(_2\) saturated 0.1 M KOH: As-deposited 500 ALD MnO, annealed Mn\(_2\)O\(_3\), glassy carbon, 20 wt% Ru/C and 20 wt% Pt/C. 20 mV s\(^{-1}\). 1600 rpm. 298 K. Reprinted with permission from [67].

Figure 1.21 A) Free-energy diagram for ORR (in reverse direction) and OER on an ideal catalyst. The vertical solid arrow shows \(\Delta G_{HOO(ads)} - \Delta G_{HO(ads)}\) on a perfect crystal which is 2.46 eV. B) Adsorption energy of HOO\(_{(ads)}\) plotted against the adsorption energy of HO\(_{(ads)}\) on the clean surfaces: Perovskites (○), rutiles (▲), Mn\(_x\)O\(_y\) (□), TiO\(_2\) (◇) and Co\(_3\)O\(_4\) (+). The best fit of all points is \(\Delta E_{HOO(ads)} = \Delta E_{HO(ads)} + 3.20\) eV. The red star indicates where the binding energies need to be for an ideal catalyst. Reprinted with permissions from [121, 124].

Figure 1.22 Cyclic voltammetry on platinum working electrode in 2 M H\(_2\)SO\(_4\), with varying Mn\(^{2+}\) concentrations of 0.018 M to 0.73 M at 308 K and 1 mV s\(^{-1}\) [156]. The potentials are reported vs. mercury-mercurous sulfate reference electrode (MSE). Reprinted with permission from [156].

Figure 1.23 SEM plan-view and cross-sectional images of manganese oxide deposits synthesized from: A) 3 mM Mn(CH\(_3\)COO)\(_2\) solution at 0.25 mA cm\(^{-2}\), B) 5 mM, C) 7 mM, D) 10 mM, E) 20 mM and F) 30 mM Mn(CH\(_3\)COO)\(_2\) solutions at 5 mA cm\(^{-2}\). 10 min per each deposition. 373 K and pH of 7.5. Reprinted with permission from [155].

Figure 1.24 Schematic diagram showing the morphological evolution of electrodeposited manganese oxides (from left to right: thin sheets, rods, aggregated rods and non-uniform continuous coating) with increasing the Mn\(^{2+}\) concentration during anodic electrodeposition process. Reprinted with permission from [155]
Figure 1.25 XRD patterns of MnO$_x$ electrodeposited at different anodic potentials (0.5 to 0.95 V$_{SCE}$) in 0.25 M manganese acetate solution at 298 K. Arrowed peaks (at 20 = 37.1° and 66.3°) correspond to the oxides formed on the carbon substrates. Potentials are versus saturated calomel reference electrode (SCE). Reprinted with permission from [158].

Figure 1.26 SEM micrographs showing the surface morphologies of manganese oxides electrodeposited at A) 0.5, B) 0.65, C) 0.8 and D) 0.95 V$_{SCE}$ characterized in Figure 1.25. Reprinted with permission from [158].

Figure 1.27 Levich plots calculated from anodic electrodeposition of manganese dioxide in 0.1 M MnSO$_4$+5 M H$_2$SO$_4$ at different temperatures. Reprinted with permission from [86].

Figure 1.28 SEM plan-view and cross-sectional images of manganese oxides deposited from 10 mM Mn(CH$_3$COO)$_2$ at 5 mA cm$^{-2}$ for 10 min and pH of 7.5: A) 298 K, B) 333 K, C) 358 K. Reprinted with permission from [155].

Figure 1.29 Surfactant classifications based on the charge of head group. Reprinted with permission from [169].

Figure 1.30 Molecular structure of: A) Cationic cetyltrimethylammonium bromide (CTAB), B) Anionic sodium $n$-dodecylbenzenesulfonate (SDBS) and C) Non-ionic $n$-octyl phenoxypolyethoxyethanol (Triton X-100). Reprinted with permission from [161].

Figure 1.31 FESEM images of the manganese oxide (EMD) samples in the presence of various concentrations of SDS (in ppm) as anionic surfactants. Reprinted with permission from [162].

Figure 1.32 SEM images of MnO$_2$ thin film prepared in: A) Absence and B) presence of Triton X-100. Reprinted with permission from [172].

Figure 1.33 SEM images of electrodeposited manganese dioxide in presence of: a) 5.1 mM Triton X-100 and 9 mM CTAB. Reprinted with permission from [161].
Figure 1.34 Surfactant aggregation to form micelle at critical micelle concentration (CMC). Reprinted with permission from [175]................................. 55

Figure 1.35 Geometrical shapes of surfactant micelles in aqueous solutions. Reprinted with permission from [176]........................................................................... 55

Figure 1.36 Schematic representation of perovskite-type oxides with the general formula of ABO$_3$ where A sites includes rare-earth metal ions while B sites are transition-metal ions. Reprinted with permission from [184]........................................................................... 56

Figure 1.37 Volcano-type graphs showing the comparison between the electrocatalytic activity of various perovskite-type oxides for: A) ORR and B) OER. Figures reveal the ORR/OER overpotentials at 50 μA cm$^{-2}$ in alkaline media as a function of $e_g$ electron occupancy at 298 K. Reprinted with permission from [123]......................................................................................... 58

Figure 1.38 Schematic representation of Nd$_3$IrO$_7$ with an orthorhombic crystal structure (space group Cmcm). Reprinted with permission from [195, 196].................................................................................. 59

Figure 2.1 CNC controlled sprayer machine with IWATA air brusher (50 ml capacity). ........ 68

Figure 2.2 Gas diffusion electrodes consist of catalyst inks sprayed on: 1) 40 wt% PTFE treated carbon cloth from Fuel Cell Earth Co. and 2) PTFE treated carbon substrate supported on a Ni mesh (as current collector) from ZincNyx Energy Solution Inc........................................... 69

Figure 2.3 Schematic diagram of three-electrode electrochemical half-cell setup used in this study. ................................................................................................................................. 72

Figure 2.4 Components of a quick-fit exchangeable sample holder (left) from radio Radiometer Analytical (#A35T450) with sample opening of 6 mm in diameter. The samples (right) were placed on a glassy carbon disk as a backing layer prior to be placed on the tip. .......................... 72
Figure 2.5 Computer-controlled VoltaLab 80 potentiostat with its associated RDE setup and the electrochemical three-electrode cell. .......................................................... 73

Figure 2.6 A Pine jacketed electrochemical cell connected to a water bath in the three-electrode RDE half-cell test setup used for electrochemical measurements in this study. ....................... 76

Figure 2.7 Flow-by electrochemical test cell (HZ-PP01) and its components from Gaskatel GmbH used for ORR GDE tests: PTFE body, built-in platinum counter electrode, built-in Luggin-Haber capillary for the reference electrode. .......................................................... 79

Figure 3.1 SEM images of A) Commercial Sigma-Aldrich MnO₂ powder (pillar and sphere-like particles are shown using dashed oval and circle shapes, respectively), B) Synthesized LaCoO₃ powder, C) Synthesized LaNiO₃ powder and D) Synthesized Nd₃IrO₇ powder. The black arrow in B and C points out the flakes in SEM morphology of studied oxides. ........................................ 82

Figure 3.2 XRD spectra of: A) Commercial MnO₂, B) Synthesized LaCoO₃, C) Synthesized LaNiO₃ and D) Synthesized Nd₃IrO₇. (*), (▼), (▌) and (♦) present major peaks corresponding to MnO₂, LaCoO₃, LaNiO₃ and Nd₃IrO₇, respectively. .......................................................... 84

Figure 3.3 EDX spectra of commercial and synthesized catalyst powders: A) MnO₂, B) LaCoO₃, C) LaNiO₃ and D) Nd₃IrO₇. .............................................................................................................................................. 86

Figure 3.4 IR-corrected cyclic voltammograms of GDEs with MnO₂, LaCoO₃, LaNiO₃, Nd₃IrO₇, MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇ catalysts. A) MnO₂, LaCoO₃, LaNiO₃ and Nd₃IrO₇, B) MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇. Electrolyte: N₂ saturated 6 M KOH at 293 K and P N₂ of 1 atm. The oxide loadings were 0.5 mg cm⁻² each. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s⁻¹, respectively. Cycle number five is reported in all cases........................................................................................................... 88
Figure 3.5 SEM images of the GDE consisting of MnO$_2$:LaCoO$_3$:Vulcan XC-72:Nafion:PTFE (weight ratio of 1:1:1:0.6:0.6) sprayed on 40% PTFE treated carbon cloth.

Figure 3.6 Initial stage IR-corrected bifunctional ORR/OER Tafel-lines of GDEs with MnO$_2$, LaCoO$_3$, LaNiO$_3$, Nd$_3$IrO$_7$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts. A) ORR, B) OER. Electrolyte: O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Electrode potential scanning between 233 to 1683 mV. The oxide loadings were 0.5 mg cm$^{-2}$ each. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s$^{-1}$, respectively. Cycle number five is reported in all cases. The numbers associated with each line represent the respective apparent Tafel slopes.

Figure 3.7 Electrocatalytic durability testing of GDEs with MnO$_2$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts: A) ORR at cycle one, B) OER at cycle one, C) ORR at cycle one hundred, D) OER at cycle one hundred. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1633 mV for one hundred cycles (accelerated degradation testing) in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Other conditions idem to Figure 3.6.

Figure 3.8 Long-term ORR durability testing of fresh GDEs containing Pt, MnO$_2$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts compared with commercial MnO$_x$ GDE from Gaskatel GmbH: A) With air at -40 mA cm$^{-2}$ and B) With oxygen at -100 mA cm$^{-2}$. IR-corrected galvanostatic polarization curves obtained in 11.7 M (45 wt%) KOH at 323 K for 24 hrs with either air (CO$_2$ removed) or oxygen flowing through the gas chamber of a flow-by cell from Gaskatel GmbH after 24 hrs of break-in protocol explained in section 2.3 and Appendix C. The absolute gas pressure and flow rate were fixed at 1 atm and 1.51×10$^{-3}$ SLPM. The catalyst(s) loadings were 2 mg cm$^{-2}$ each (except for Pt with 0.5 mg cm$^{-2}$) with final weight ratio of 1:1:2:0.6:0.6 for MnO$_2$. xxii
or Pt:co-catalyst (if present): Vulcan XC-72:Nafion:PTFE in the catalyst layer. The catalyst loading for the commercial MnO$_x$ from Gaskatel was 20 mg cm$^{-2}$. The standard error of the mean calculated based on min. two replicates is indicated for each data point. ................................. 102

Figure 3.9 Comparison between the XRD spectrum of the MnO$_2$ catalyst: 1) Fresh electrode (black dotted line) and 2) After 48 hrs of galvanostatic tests (24 hrs at -67 mA cm$^{-2}$ followed by 24 hrs at -100 mA cm$^{-2}$) with O$_2$ as feed gas in an unflooded flow-by test setup. ................................. 103

Figure 4.1 The effect of rest-time at open-circuit potential in 6 M KOH at 293 K following accelerated degradation testing in the flooded test setup (i.e. one hundred potential cycles between 633 to 1633 mV in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm): A) ORR polarization curve for MnO$_2$, B) OER polarization curve for MnO$_2$, C) ORR polarization curve for MnO$_2$-LaCoO$_3$ and D) OER polarization curve for MnO$_2$-LaCoO$_3$. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1683 mV in O$_2$ saturated 6 M KOH at 400 rpm, 293 K and P$_{O_2}$ of 1 atm. Other conditions idem to Figure 3.6. .............................................................. 109

Figure 4.2 The effect of rest-time at open-circuit potential in 6 M KOH at 293 K following accelerated degradation testing in the flooded test setup (i.e. one hundred potential cycles between 633 to 1633 mV in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm): A) ORR polarization curve for MnO$_2$-LaNiO$_3$, B) OER polarization curve for MnO$_2$-LaNiO$_3$, C) ORR polarization curve for MnO$_2$-Nd$_3$IrO$_7$ and D) OER polarization curve for MnO$_2$-Nd$_3$IrO$_7$. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1683 mV in O$_2$ saturated 6 M KOH at 400 rpm, 293 K and P$_{O_2}$ of 1 atm. Other conditions idem to Figure 3.6. ......................... 110

Figure 4.3 Comparison between the XRD spectrum of the MnO$_2$-LaCoO$_3$ catalyst: 1) Fresh GDE (black dotted line) and 2) After accelerated degradation testing for one hundred cycles in the
potential range of 633 to 1633 mV followed by resting for six days at open-circuit in 6 M KOH at 293 K (red solid line) in a flooded test setup ................................................................. 113

Figure 4.4 XPS spectra of MnO$_2$ GDE: A) Fresh, C) After accelerated degradation testing for one hundred cycles in the potential range of 633 to 1633 mV and rested for six days at open-circuit in 6 M KOH at 293 K .................................................................................................................. 115

Figure 4.5 Bifunctional activation effect of long-term (i.e. six days) exposure of MnO$_2$-LaCoO$_3$ to alkali-metal hydroxide solutions: LiOH, NaOH, KOH, CsOH. Initial stage IR-corrected polarization curves obtained by potential scanning between 633 to 1483 mV in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Other conditions idem to Figure 3.6 ........................................... 118

Figure 4.6 Electrocatalytic durability testing of fresh activated MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ GDEs: A) ORR polarization curves and B) OER polarization curves. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1483 mV for one hundred cycles (accelerated degradation testing) in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Catalysts were activated by six-day-long exposure to 6 M KOH at 313 K and 400 rpm and open-circuit. Other conditions idem to Figure 3.6 .................................................................................................................. 121

Figure 4.7 XPS spectra of MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ before and after long-term exposure to 6 M KOH: A) MnO$_2$-LaCoO$_3$ fresh electrode, B) MnO$_2$-LaCoO$_3$ activated electrode, C) MnO$_2$-Nd$_3$IrO$_7$ fresh electrode, D) MnO$_2$-Nd$_3$IrO$_7$ electrode. Other conditions idem to Figure 4.6. ... 123

Figure 4.8 EDX spectra of the activated catalyst layers after six days of exposure to 6 M KOH: A) MnO$_2$-LaCoO$_3$, B) MnO$_2$-Nd$_3$IrO$_7$. Conditions idem to Figure 4.6 ................................................................. 124

Figure 4.9 EELS analysis of MnO$_2$-LaCoO$_3$: A) EELS spectrum showing Mn (L$_{2,3}$) edges, B) EELS spectrum showing O (K) edges, C) L$_3$:L$_2$ Branching ratio versus valence state for Mn oxides. The sample was tested under three different conditions: 1) Initial stage, 2) After being activated in
KOH for six days (idem to Figure 4.6) and cycled between the ORR and OER regions for ten cycles, 3) After being activated in KOH for six days and cycled between the ORR and OER regions for one hundred cycles (accelerated degradation test idem to Figure 4.6). The (■) and (▲) symbols represent reference data points obtained from literature [228] and the ones calculated directly from EELS spectrum for each sample, respectively. The standard error of the mean associated with Mn valence state, L₃:L₂ branching ratio and energy loss are ± 0.2, ± 0.001 and ± 0.1 eV, respectively.

Figure 4.10 Cell potential profile during potential driven K⁺ intercalation (PDI) on A) MnO₂-LaCoO₃ and B) MnO₂-Nd₃IrO₇ as catalyst layers. 5.4 mA cm⁻² was cathodically applied to each GDE in the RDE setup in a 0.036 M K₂SO₄ solution for 30 min up to seven times. The rotation speed and temperature were 400 rpm and 343 K, respectively. A platinum mesh was employed as both reference and counter electrode. The figure indicates the cell potential for the third round of PDI in each case.

Figure 4.11 XPS spectra of the potential driven K⁺ intercalation (PDI) activated catalyst layers: A) MnO₂-LaCoO₃ electrode after seven rounds of PDI activation, B) MnO₂-Nd₃IrO₇ electrode after six rounds of PDI activation.

Figure 4.12 The effect of potential driven K⁺ intercalation on the initial stage bifunctional polarization of mixed-oxide catalysts: A) ORR on MnO₂-LaCoO₃, B) OER on MnO₂-LaCoO₃, C) ORR on MnO₂-Nd₃IrO₇ and D) OER on MnO₂-Nd₃IrO₇. Other conditions idem to Figure 3.6.

Figure 4.13 The effect of potential driven K⁺ intercalation on the initial stage bifunctional polarization of individual oxides: MnO₂, LaCoO₃ and Nd₃IrO₇. A) ORR, B) OER. Other conditions idem to Figure 3.6.
Figure 4.14 XPS spectra of the PDI activated catalyst layers: A) MnO$_2$ after five rounds of K$^+$ PDI activation, B) LaCoO$_3$ after five rounds of K$^+$ PDI activation and C) Nd$_3$IrO$_7$ after five rounds of K$^+$ PDI activation.

Figure 4.15 Galvanostatic polarization of mixed-oxide catalysts without and with potential driven K$^+$ intercalation activation: A) MnO$_2$-LaCoO$_3$ and B) MnO$_2$-Nd$_3$IrO$_7$. Tests started with 5 mA cm$^{-2}$ anodically applied to each GDE for 2 hrs followed by -2 mA cm$^{-2}$ applied cathodically for 30 min in O$_2$ saturated 6 M KOH using a flooded test setup. The rotation speed and temperature were 400 rpm and 293 K, respectively. P$_{O_2}$ was 1 atm. The oxide loadings were 0.5 mg cm$^{-2}$ each.

Figure 4.16 Comparison between the ORR and OER overpotential values of the catalyst materials investigated here (shown as (▲)) with those reported in the literature for other bifunctional electrodes (shown as (♦)) [4, 64, 67, 71, 72, 74, 76, 121, 259, 260]. For the catalyst investigated here: a) Fresh catalyst without activation. b) Activation by K$^+$ insertion at open-circuit potential (OCP), c) Activation by K$^+$ insertion using five rounds of potential driven intercalation (PDI), d) Activation by K$^+$ insertion using six rounds of potential driven intercalation (PDI), e) Activation by K$^+$ insertion using three rounds of PDI. The max error associated with overpotential values is ±5 mV.

Figure 5.1 IR-corrected linear sweep voltammograms of nitric acid pre-treated 40 wt% PTFE treated carbon cloth starting from 0 to 2500 mV$_{MOE}$ in presence of: A) 5 vol% and B) 10 vol% of Triton X-100, SDS and CTAB. The solution was made of 0.2 M Mn(CH$_3$COO)$_2$ and 0.1 M Na$_2$SO$_4$ at 293 K. The scan rate and rotation speed were 5 mV s$^{-1}$ and 400 rpm, respectively.

Figure 5.2 XPS spectra of three representative electrodeposited MnO$_x$ samples at Mn 2p, Mn 3s and O 1s regions. The electrodeposition factors for each sample are as follows: T1 (C: 0.3 M, T:
295 K, S: Triton, 10 vol%, E: 800 mV_{MOE}), T9 (C: 0.1 M, T: 343 K, S: Triton, 10 vol%, E: 800 mV_{MOE}), T10 (C: 0.3 M, T: 295 K, S: Triton, 0 vol%, E: 1600 mV_{MOE}).

Figure 5.3 FT-IR spectra of MnO\textsubscript{x} samples (after IPA washing) electrodeposited on the pre-treated carbon cloth as substrate in presence of Triton X-100, SDS and CTAB. The electrodeposition factors for each sample are as follows: Carbon cloth (no electrodeposited material), Triton (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV_{MOE}), SDS (C: 0.3 M, T: 295 K, S: 10 vol%, E: 800 mV_{MOE}), CTAB (C: 0.3 M, T: 343 K, S: 10 vol%, E: 1600 mV_{MOE}).

Figure 5.4 Surface plots for 2\textsuperscript{4}+1\textsuperscript{3} factorial design in presence of Triton X-100 including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm\textsuperscript{-2}, respectively. Details of each run has been given in Table 5.2. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively.

Figure 5.5 Surface plots for 2\textsuperscript{4}+1\textsuperscript{3} factorial design in presence of SDS including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm\textsuperscript{-2}, respectively. Details of each run has been given in Table 5.3. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively.

Figure 5.6 Surface plots for 2\textsuperscript{4}+1\textsuperscript{3} factorial design in presence of CTAB including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm\textsuperscript{-2}, respectively. Details of each run has been given in Table
5.4. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively. ................................................................. 167

Figure 5.7 IR-corrected bifunctional performance comparison of electrodeposited MnOx in presence of different surfactants, i.e. Triton X-100, SDS and CTAB: A) ORR, B) OER. The electrodeposition factors for each sample are as follows: Carbon cloth substrate (no electrodeposited material), CTAB-Run no. 6 (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV\text{MOE}), SDS-Run no. 1 (C: 0.3 M, T: 295 K, S: 10 vol%, E: 800 mV\text{MOE}), Triton-Run no. 9 (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV\text{MOE}). Electrolyte: O2 saturated 6 M KOH at 293 K and P\text{O}_2 of 1 atm. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s\textsuperscript{-1}, respectively. Cycle number five is reported in all cases. ................................................................. 171

Figure 5.8 SEM micrographs of best performing electrodeposited MnOx oxides on nitric acid pre-treated carbon cloth: A and B) Triton run no. 9, C and D) SDS run no. 1, E and F) CTAB run no. 6. The electrodeposition factors are stated in Figure 5.7. ................................................................. 172

Figure 5.9 Galvanostatic polarization comparison of in-house made and commercial manganese oxide GDEs: I) Manganese oxide/C GDE from Gaskatel GmbH (20 mg cm\textsuperscript{-2}), II) γ-MnO\textsubscript{2}/C from Sigma Aldrich (loading 5.6 mg cm\textsuperscript{-2}) and III) Triton run no. 9 (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV\text{MOE}) (calculated loading 17.5 mg cm\textsuperscript{-2}). The galvanostatic polarization started at 5 mA cm\textsuperscript{-2} anodically applied to each GDE for 2 hrs followed by -2 mA cm\textsuperscript{-2} applied cathodically for 30 min in O\textsubscript{2} saturated 6 M KOH. The rotation speed and temperature were 400 rpm and 293 K, respectively. P\text{O}_2 was 1 atm. ........................................................................................................ 174

Figure 6.1 TEM images of materials investigated in this chapter as oxygen catalyst or catalyst support: A) Graphene, B) N-doped graphene, C) Vulcan XC-72, D) MWCNT, E) MnO\textsubscript{2} and F) LaCoO\textsubscript{3}. ........................................................................................................ 180
Figure 6.2 Rotating ring disk electrode results for ORR on Graphene (I), N-doped Graphene (II), MWCNT (III) and Vulcan XC-72 (IV): A) O₂ reduction current densities obtained from disk electrode (i_ν) when polarized from 1170 to 500 mV (bottom) and the corresponding oxidation current densities on the ring at 1353 mV (i_r) as a function of disc potentials (top). B) Calculated percentage of hydrogen peroxide ions produced during ORR (%HO₂⁻). C) Calculated number of electrons transferred per molecule of oxygen during ORR (n). Carbon loadings of 0.5 mg cm⁻² each. O₂ saturated 6 M KOH. 5 mV s⁻¹. 293 K. P₀₂ of 1 atm.

Figure 6.3 Bifunctional ORR/OER performance of carbonaceous materials, i.e. Graphene, N-doped graphene, MWCNT, Vulcan XC-72, MWCNT-Graphene and MWCNT-N-doped graphene: A) ORR, B) OER. Initial stage IR-corrected polarization curves obtained by potential scanning between 475 to 1673 mV, starting with anodic polarization. Carbon loadings are fixed at 0.5 mg cm⁻², each. In cases where two materials were mixed, a weight ratio of 1:1 was used. Cycle number five is reported in all cases. O₂ saturated 6 M KOH. 293 K. 400 rpm. 5 mV s⁻¹. P₀₂ of 1 atm.

Figure 6.4 IR-corrected bifunctional ORR/OER Tafel-lines of investigated carbonaceous catalyst materials: A) ORR, B) OER. The numbers associated with each line represent the respective apparent Tafel slopes. Cycle number five is reported in all cases. The N₂-baseline is subtracted from the ORR part for all samples. For the OER part, capacitive background current at open circuit potential is removed from each corresponding voltammogram. Other conditions idem to Figure 6.3.

Figure 6.5 Bifunctional ORR/OER performance of MnO₂-LaCoO₃ catalyst supported on various carbonaceous materials: A) Graphene and N-doped graphene, B) MWCNT and Vulcan XC-72, C) MWCNT-Graphene and MWCNT-N-doped graphene. The 50 wt% Pt/Graphitized carbon is being shown as the baseline for comparison (Pt loading of 0.25 mg cm⁻²). The oxide and carbon loadings
were 0.5 mg cm\(^{-2}\) each. A weight ratio of 1:1:1:1 for MnO\(_2\):LaCoO\(_3\):Carbon1:Carbon2 (if available) was used. Cycle number five is reported in all cases. Other conditions idem to Figure 6.3................................................................. 191

Figure 6.6 IR-corrected bifunctional ORR/OER Tafel-lines of investigated MnO\(_2\)-LaCoO\(_3\) catalyst supported on various carbonaceous materials studied in Figure 6.5 (50 wt% Pt/Graphitized carbon as the baseline): A) ORR, B) OER. The numbers associated with each line represent the respective apparent Tafel slopes. Cycle number five is reported in all cases. The N\(_2\)-baseline is subtracted from the ORR part for all samples. For the OER part, capacitive background current at open circuit potential is removed from each corresponding voltammogram. Other conditions idem to Figure 6.5........................................................................................................... 195

Figure 6.7 Electrocatalytic durability testing: ORR (bottom) and OER (top) current densities at 800 mV and 1750 mV, respectively, during one hundred successive potential cycling between 673 to 1873 mV on MnO\(_2\)-LaCoO\(_3\)-MWCNT-Graphene (weight ratio 1:1:1:1) and MnO\(_2\)-LaCoO\(_3\)-Vulcan XC-72 (weight ratio 1:1:1) GDEs in flooded test setup. The oxide and carbon loadings were kept at 0.5 mg cm\(^{-2}\), each, spayed on a 40 wt% PTFE treated carbon cloth as porous substrate. The error associated with ORR and OER current densities was found to be between 2% and 10%. Other conditions idem to Figure 6.3 .............................................................................................................................................. 199

Figure A.1 Effect of the symmetry factor (\(\beta\)) on the symmetry of the current-overpotential curve described by the BE-GV equation (eq. 40). .............................................................................................................. 230

Figure B.1 Typical cathodic polarization curves obtained by a RDE as a function of angular velocity (\(\omega\)). \(\omega_1 < \omega_2 < \omega_3\).............................................................................................................................................. 231

Figure C.1 Long-term ORR durability testing of fresh GDEs containing Pt, MnO\(_2\), MnO\(_2\)-LaCoO\(_3\), MnO\(_2\)-LaNiO\(_3\) and MnO\(_2\)-Nd\(_3\)IrO\(_7\) catalysts compared with commercial MnO\(_x\) GDE from xxx
Gaskatel GmbH: A) With air at \(-33\) mA cm\(^{-2}\) and B) With oxygen at \(-67\) mA cm\(^{-2}\). IR-corrected galvanostatic polarization curves obtained in 11.7 M (45 wt%) KOH at 323 K for 24 hrs with either air (CO\(_2\) removed) or oxygen flowing through the gas chamber of a flow-by cell from Gaskatel GmbH as twenty-four-hour-long break-in protocol. The absolute gas pressure and flow rate were fixed at 1 atm and 1.51\(\times\)10\(^{-3}\) SLPM. The catalyst(s) loadings were 2 mg cm\(^{-2}\) each (except for Pt with 0.5 mg cm\(^{-2}\)) with final weight ratio of 1:1:2:0.6:0.6 for MnO\(_2\) or Pt:co-catalyst (if present):Vulcan XC-72:Nafion:PTFE in the catalyst layer. The catalyst loading for the commercial MnO\(_x\) from Gaskatel was 20 mg cm\(^{-2}\). The standard error of the mean calculated based on min. two replicates is indicated for each data point.

Figure D.1 The effect of inter-stage OCP activation: ORR and OER polarization curves of the activated MnO\(_2\)-LaCoO\(_3\) electrodes tested for three hundred cycles with OCP activation in between, A) ORR polarization curves, B) OER polarization curves. The samples are kept at OCP in 6 M KOH solution for 12 hrs at 293 K and a rotation speed of 400 rpm after each one hundred cycles of durability testing. Other conditions are same as Figure 3.6.

Figure E.1 Pareto plot of estimates for the effects of four main factors (i.e. surfactant concentration (S), temperature (T), Mn concentration (C) and applied anodic potential (E)) and three aliased two-factor interactions on the ORR mass activity in the \(2^{4-1}+3\) factorial design study on the anodic electrodeposition of MnO\(_x\) in presence of Triton X-100.
## Nomenclature

<table>
<thead>
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<th>Symbol</th>
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<td>$a_j$</td>
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<td>$C$</td>
<td>$\text{Mn}^{2+}$ concentration</td>
<td>mol L$^{-1}$</td>
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<tr>
<td>$C_j$</td>
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<td>m$^{2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential</td>
<td>$V_{\text{MOE}, V_{\text{RHE}}}$</td>
</tr>
<tr>
<td>$E^0_{298K}$</td>
<td>Standard equilibrium potential at 298 K</td>
<td>$V_{\text{SHE}}$</td>
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<td>Binding energy</td>
<td>eV</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant (96500)</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$i$</td>
<td>Measured current density</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$i_d$</td>
<td>Disk current density in a RRDE test setup</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$i_k$</td>
<td>Pure electrode kinetic current density</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$i_L$</td>
<td>Limiting current density</td>
<td>mA cm$^{-2}$</td>
</tr>
<tr>
<td>$i_{0,OER}$</td>
<td>Apparent exchange current density calculated from the OER part</td>
<td>$\mu$A cm$^{-2}$</td>
</tr>
</tbody>
</table>

xxxii
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i_{0,\text{ORR}})</td>
<td>Apparent exchange current density calculated from the ORR part</td>
<td>(\mu\text{A cm}^{-2})</td>
</tr>
<tr>
<td>(i_r)</td>
<td>Ring current density in a RRDE test setup</td>
<td>(\text{mA cm}^{-2})</td>
</tr>
<tr>
<td>(I(L_3))</td>
<td>Normalized intensity of Mn(L(^3)) edge in a Mn EELS spectrum</td>
<td>-</td>
</tr>
<tr>
<td>(I(L_2))</td>
<td>Normalized intensity of Mn(L(^2)) edge in a Mn EELS spectrum</td>
<td>-</td>
</tr>
<tr>
<td>(K^0)</td>
<td>Standard heterogeneous rate constant</td>
<td>(\text{mol m}^2\text{s}^{-1})</td>
</tr>
<tr>
<td>(K_{m,j})</td>
<td>Mass transfer coefficient of species (j)</td>
<td>(\text{m s}^{-1})</td>
</tr>
<tr>
<td>(M)</td>
<td>Molarity</td>
<td>(\text{mol L}^{-1})</td>
</tr>
<tr>
<td>(m_j)</td>
<td>A power expressing the concentration/pressure dependence of the activity for species (j)</td>
<td>-</td>
</tr>
<tr>
<td>(n)</td>
<td>Electron stoichiometry coefficient</td>
<td>-</td>
</tr>
<tr>
<td>(N)</td>
<td>Collection efficiency of the ring in a RRDE test setup</td>
<td>-</td>
</tr>
<tr>
<td>(O_\varnothing^x)</td>
<td>An oxygen ion sitting on an oxygen lattice site with neutral charge in the Kröger-Vink notation</td>
<td>-</td>
</tr>
<tr>
<td>(P_\text{O}_2)</td>
<td>Absolute partial pressure of oxygen</td>
<td>(\text{atm})</td>
</tr>
<tr>
<td>(P_{\text{gas}})</td>
<td>Absolute gas pressure</td>
<td>(\text{atm})</td>
</tr>
<tr>
<td>(R)</td>
<td>Gas constant (8.314)</td>
<td>(\text{J mol}^{-1}\text{ K}^{-1})</td>
</tr>
<tr>
<td>(Re)</td>
<td>Reynolds number</td>
<td>-</td>
</tr>
<tr>
<td>(S)</td>
<td>Surfactant concentration</td>
<td>(\text{vol}%)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>------</td>
</tr>
<tr>
<td>$s_j$</td>
<td>Stoichiometric coefficient of species $j$</td>
<td>-</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$V'_{x//}$</td>
<td>Cation vacancy in the Schottky notation</td>
<td>-</td>
</tr>
<tr>
<td>$V_{0^-}$</td>
<td>Lattice oxygen vacancy with double positive charge in the Kröger-Vink notation</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Transfer coefficient</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha_a$</td>
<td>Anodic transfer coefficient</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>Cathodic transfer coefficient</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Symmetry factor</td>
<td>-</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Diffusion layer thickness</td>
<td>m</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
<td>mV</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>Diffraction angle</td>
<td>degree (°)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Kinematic viscosity of the electrolyte</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular velocity</td>
<td>radian s⁻¹</td>
</tr>
<tr>
<td>$\Pi_j$</td>
<td>Multiplication operator symbol</td>
<td>-</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>ARFCs</td>
<td>Alkaline Regenerative Fuel Cells</td>
<td></td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
<td></td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
<td></td>
</tr>
<tr>
<td>CNC</td>
<td>Computer Numerical Control</td>
<td></td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
<td></td>
</tr>
<tr>
<td>ECSA</td>
<td>Electrochemically Active Surface Area</td>
<td></td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>FT-IR ATR</td>
<td>Fourier Transfer-Infrared Spectroscopy with Attenuated Total Reflectance</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
<td></td>
</tr>
<tr>
<td>GDE</td>
<td>Gas Diffusion Electrode</td>
<td></td>
</tr>
<tr>
<td>GNS</td>
<td>Graphene Nano Sheet</td>
<td></td>
</tr>
<tr>
<td>IPA</td>
<td>Iso-Propyl Alcohol</td>
<td></td>
</tr>
<tr>
<td>IR-corrected</td>
<td>Ohmic Drop Compensated</td>
<td></td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
<td></td>
</tr>
<tr>
<td>MOE</td>
<td>Mercury-Mercury Oxide Reference Electrode</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>MSE</td>
<td>Mercury-Mercurous Sulfate Reference Electrode</td>
<td></td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-Walled Carbon Nanotubes</td>
<td></td>
</tr>
<tr>
<td>Non-PGM</td>
<td>Non-Precious Group Metal</td>
<td></td>
</tr>
<tr>
<td>OCP</td>
<td>Open-Circuit Potential</td>
<td></td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen Evolution Reaction</td>
<td></td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
<td></td>
</tr>
<tr>
<td>PDI</td>
<td>Potential Driven Intercalation</td>
<td></td>
</tr>
<tr>
<td>PGM</td>
<td>Precious Group Metal</td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly-Tetra-Fluoro-Ethylene</td>
<td></td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating Disk Electrode</td>
<td></td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Reference Electrode</td>
<td></td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating Ring Disk Electrode</td>
<td></td>
</tr>
<tr>
<td>RTIL</td>
<td>Room Temperature Ionic Liquid</td>
<td></td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Reference Electrode</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
<td></td>
</tr>
<tr>
<td>SLPM</td>
<td>Standard Liter Per Minute</td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
<td></td>
</tr>
<tr>
<td>URFC</td>
<td>Unitised Regenerative Fuel Cell</td>
<td></td>
</tr>
<tr>
<td>Wt%</td>
<td>Weight Percentage</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
<td></td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
<td></td>
</tr>
<tr>
<td>Vol%</td>
<td>Volume Percentage</td>
<td></td>
</tr>
<tr>
<td>VPSEM</td>
<td>Variable Pressure Scanning Electron</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microscopy</td>
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</table>
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Let me start with saying that I had an amazing experience at the University of British Columbia and will always be grateful for the opportunity to pursue my Ph.D. studies here in Vancouver.

This is going to be a quite different acknowledgment, neither formal nor informal. I have spent many hours, nights and days to come up with something that truly express my appreciation to all the people who have helped and empowered me to be who I am right now. But who am I kidding? I am neither a writer nor a poet. I am just a person who thinks everything in a scientific manner. It is such a strange feeling for me to write this section at this particular moment. One part of me wants to rush it while the other part tells me to put down every single word carefully from the bottom of my heart. I can say the nostalgic song that I am listening to right now will have a huge effect on the following paragraphs.

I am digging deeper and deeper into my memory and soul, asking myself where to start; The moment my aunt called me “Mr. Doctor” for the first time, my indescribable feelings of joy and satisfaction which I have always experienced during my many years at school, my mother who I always adored for being a loving and patient physician, my father who is always proud of me, inspired me to pursue my passion and encouraged me to invent something useful, the laughs and support of my lovely sister, the moment I almost wanted to quit in the middle of the university entrance exam, the unsuccessful attempts to pursue my M.Sc. studies in Canada which almost crushed me, the moment I saw Maryam and something clicked in my heart, my first publication in the Journal of Power Sources, the very moment Akram replied to my email with an admission to UBC, the moment I had my study permit in one hand and Maryam’s rejected visa in the other, the awkward moment I left my hometown for Vancouver almost five years ago, my first meeting with
Elod at CHBE, shaking as I was excited and frightened at the same time or the relentless one-and-half-year-long wait till my precious wife could finally join me in Canada (Oh, I was relieved). Like others, I have gone through many ups and downs in my life. Those experiences have helped me grow so very much both mentally and physically, especially during the past five years.

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Finally, I would like to acknowledge the University of British Columbia, Natural Sciences and Engineering Research Council of Canada (NSERC) and Electrochemical Society for giving me the opportunity to pursue my passion in science and engineering through their generous support, funding, travel grants and fellowships.
To my beautiful wife, Maryam,

Your everlasting love and support sustains me. Your nurturing being completes me.

To my beloved parents and sister, Zohreh, Hossein and Parastoo,

Whose unceasing and unconditional love, compassion and thoughts empower me.

And,

To my childhood nanny, Maryam Khanoom, who is in heaven now,

You are always in my heart. I miss you each day, every day, all the times.
Chapter 1: Introduction

1.1 Summary

Oxygen electrochemistry, i.e. electrochemical oxygen reduction (ORR) and oxygen evolution reactions (OER), is known to be the heart of various electrochemical processes from renewable energy generation such as hydrogen-oxygen fuel cells, rechargeable metal-air and metal hydride-air batteries to chemical production technologies such as NaCl electrolysis along with hydrogen, hydrogen peroxide and chlorine production [1-6]. The development of a bifunctional catalyst for both ORR and OER reactions (cathodic and anodic directions, respectively, for eqs. 1 and 2) is of great interest due to their involvement in energy conversion systems such as regenerative fuel cells and rechargeable metal-air batteries, remaining an important challenge for electrochemists [2, 7, 8].

\[
O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O \quad (E_{298K}^0 = 1.229 \text{ V}_{SHE}) \quad (1)
\]

\[
O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad (E_{298K}^0 = 0.401 \text{ V}_{SHE}) \quad (2)
\]

Based on pH, two types of electrolytes, i.e. acid and alkaline, are currently used in fuel cells and batteries depending on the oxygen evolution/reduction reactions rates and the type of the metal catalyst. Alkaline electrolytes (such as 6-14 M KOH) are the primary choice for both ORR and OER in metal-air batteries such as Zn-air and Mg-air.

Metal-air batteries are being used in wide range of applications due to a combination of favorable properties such as low cost (Zn and Mg are the fourth and seventh most abundant metals in the earth’s crust, respectively [9, 10]), high safety due to non-flammable electrolyte and relatively high energy density as well as equilibrium cell voltage [10-13]. While the Zn-air battery
provides a standard equilibrium cell potential of 1.65 V (298 K) with theoretical energy density of 1330 Wh kg\(^{-1}\)\(^*\). Mg-air battery is characterized by a higher standard cell potential of 3.09 V (298 K) as well as high theoretical energy density of 6813 Wh kg\(^{-1}\)\(^*\) [14]. However, the practical energy density of the existing metal-air batteries are low, e.g. 500 and 680 Wh kg\(^{-1}\)\(^*\) for the Zn-air and Mg-air batteries, respectively [15, 16], limiting their commercial applications because of similar challenges, i.e. low utilization efficiency of the anode due to passivation and corrosion, sluggish kinetics of the cathode, sensitivity to contaminants from air (e.g. CO\(_2\)) and electrolyte evaporation due to their open cathode structure [10, 13].

Electrically rechargeable metal-air batteries such as rechargeable Zn-air and Li-air operate based on the similar principle as of primary metal-air batteries except for the bifunctional cathode material which catalyzes both ORR and OER during discharging and charging, respectively, while the anode material is oxidized during discharge mode and reduced during the charge mode (Figure 1.1) [10, 11, 14, 16-18]. Figure 1.2 shows schematic polarization curve of a rechargeable Zn-air battery. Similar challenges to the primary metal-air batteries impede the commercialization of rechargeable Zn-air batteries such as low conversion rate of anode, i.e. Zn, dendrite formation on the anode and lack of active as well as durable bifunctional catalyst for both ORR and OER [11, 16, 19]. In 2007, Visco and Nimon introduced a protected anode for non-aqueous Li-air batteries which paved the way for development of rechargeable aqueous Li-air batteries [20, 21]. In theory, Li-air batteries could provide very high energy density of 11148 Wh kg\(^{-1}\)\(^*\), however, the practical energy density is much lower due to combination of challenges facing the aqueous Li-air batteries

\[ \text{**Per kg of the metal. Calculated from the electrochemical equivalents of the metals and the cell electromotive forces based on the overall reaction in the battery.} \]
such as low cycling efficiency, LiOH crystallization, CO₂ contamination leading to Li₂CO₃ formation as well as lack of active and durable ORR/OER bifunctional catalyst (Figure 1.3) [11, 16, 17, 21-23].

Figure 1.1 Schematic illustration of electrically rechargeable metal-air batteries with its operating principle and bifunctional cathode. Reprinted with permission from [16].
Figure 1.2 Schematic polarization curve of rechargeable Zn-air battery. The equilibrium potential of the Zn-air battery (black line) is 1.65 V, but the practical voltage (red line) in discharge is lower than 1.65 V due to the sluggish ORR. A large potential is needed to charge Zn-air battery, higher than the equilibrium potential (blue line). Reprinted with permission from [11].

Figure 1.3 Challenges facing rechargeable aqueous Li-air batteries. Reprinted with permission from [21].
A typical discharge polarization and galvanostatic discharge-charge cycle curves are shown in Figure 1.4 for a rechargeable Li-air battery with a hybrid aqueous/organic electrolyte and various air electrodes. Yoo and Zhou introduced metal-free graphene nanosheets (GNSs) as air cathode with similar performances to Pt/C cathode as well as enhanced cycling ability, i.e. discharge and charge potential deviation of less than 0.2 V after 200 hrs of testing at 0.5 mA cm$^{-2}$ [24].

Figure 1.4 a) Discharge polarization curves of gas diffusion electrodes containing graphene nanosheets (GNSs), 20 wt% Pt/C and acetylene black at 0.5 mA cm$^{-2}$, b) Galvanostatic discharge-charge cycle curves of heat-treated GNSs at 0.5 mA cm$^{-2}$. 1 M LiClO$_4$/ED/DEC was used as the organic electrolyte and 1 M LiNO$_3$ + 0.5 M LiOH was used as the aqueous electrolyte. A solid-state electrolyte Li$_{1+x+y}$Al$_x$(Ti,Ge)$_{2-x}$Si$_y$P$_3$O$_{12}$ (LISICON) film was used as a separating membrane between the organic and aqueous electrolytes to prevent intermixing of the two solutions. The discharge-charge performance was carried out at a current density of 0.5 mA cm$^{-2}$ between 2 and 4.8 V vs. Li/Li$^+$ for 2 hrs per each cycle. 298 K. Reprinted with permission from [24].
Alkaline fuel cells such as the alkaline hydrogen-oxygen fuel cell, direct borohydride fuel cells and others (e.g. methanol and formate fuel cells) have also received significant attention [25-28]. Particularly, alkaline regenerative fuel cells (ARFCs) are promising candidates as alternative energy storage technologies which in principle, include an electrolyzer and a fuel cell, employing hydrogen as energy carrier [29]. The electrolyzer is responsible for hydrogen production during the charging mode while the fuel cell part combines the hydrogen and oxygen (from air) to generate electricity during discharge mode [29-31]. A smaller and compact version of this unit is called unitised regenerative fuel cell (URFC) which both electrolyzer and fuel cell parts are combined into one cell, effectively reducing the costs and decrease the complexity of the system (Figure 1.5) [30-32]. Such a unit provides wide range of advantages including environmental friendliness of employed chemistries, i.e. hydrogen, oxygen and water, potentially high energy density due to use of H\textsubscript{2} and customizable in size to appeal to variety of applications including grid-scale energy storage, centralized commercial/residential energy storage, transportation as well as space exploration [30-33]. However, issues such as low round-trip power efficiency\textsuperscript{†} (less than 40%) and relatively high capital costs comparing to pumped hydroelectric and compressed air ($4000 USD per kW) hinder their wide-spread commercialization [30-32]. Figure 1.6 presents a typical polarization curve for an anion exchange membrane-unitised regenerative fuel cell (AEM-URFC) with Ni/C+MnO\textsubscript{x}/GC as O\textsubscript{2} electrode and Ni/C as H\textsubscript{2} electrode, providing round-trip power efficiencies of 34 to 40\% at 10 mA cm\textsuperscript{-2} and a peak power density of 17 mW cm\textsuperscript{-2} in fuel cell mode [32].

\textsuperscript{†} The round-trip power efficiency is defined as the power density in fuel cell mode over the power density in electrolyzer mode, both at certain current density. Here, the round-trip power efficiency was calculated at 10 mA cm\textsuperscript{-2}. 
Figure 1.5 Schematic representation of an anion exchange membrane-unitised regenerative fuel cell (AEM-URFC) as an energy storage unit. The AEM-URFC stores renewable energy as H₂ while in electrolyzer mode and then uses that H₂ to generate electric energy on-demand when in fuel cell mode.
Reprinted with permission from [32].
Figure 1.6 Polarization curves for the AEM-URFC under eight fuel cell/electrolyzer cycles. MEA: Fumapem FAA-3, Fumatech as Anion exchange membrane. Gas diffusion electrodes: 6 mg\textsubscript{cat} cm\textsuperscript{-2} Ni/C for the H\textsubscript{2} electrode and 4 mg\textsubscript{cat} cm\textsuperscript{-2} MnO\textsubscript{x}/GC:Ni/C (5:1 weight ratio) for the O\textsubscript{2} electrode. An alkaline ionomer (1.8 μL per 1 mg catalyst, Fumion FAA-3, Fumatech) was added to each of the electrodes. 20 min per each cycle. 335 K. H\textsubscript{2}/O\textsubscript{2} gas flow rates of 300 Standard Cubic Centimeters per Minute (SCCM). All potentials are reported vs. reversible hydrogen electrode (RHE). Reprinted with permission from [32].

The alkaline electrolyte offers two significant advantages for the oxygen (or air) cathode: 1) Higher exchange current densities of oxygen reduction/evolution reactions compared to acidic media [2] and 2) The possibility of employing less expensive non-precious metal catalysts (e.g. transition metal oxides, perovskite or fluorite-type oxides) [34-37]. In acidic electrolytes, however, the use of noble metal catalysts seems inevitable at present for commercial applications of PEM fuel cells [38].
Manganese dioxide was found to be a potentially suitable catalyst for ORR in alkaline batteries and fuel cells due to a unique combination of properties, i.e. low cost, abundance, environmental friendliness, low self-discharge rate (open-circuit state) and fairly stable performance over a wide temperature range [39]. With regards to the oxygen electro-reduction mechanism, one of its major advantages is that it can facilitate the reduction of the peroxide ions (formed in ORR as an intermediate in neutral and alkaline media), reaching the theoretical four electrons per oxygen molecule exchanged during ORR [40-48]. However, some challenging issues such as low electrocatalytic activity for OER and poor rechargeability due to the conversion of MnO₂ to non-rechargeable discharge products like Mn(OH)₂, Mn₂O₃ and Mn₃O₄ limit the application of manganese dioxide as a lone bifunctional catalyst for both ORR and OER in rechargeable metal-air batteries and alkaline regenerative fuel cells [49, 50].

This work aims at developing active and durable MnOₓ-based catalysts for both ORR and OER in alkaline media, by modifying the microstructure and crystal structure of the manganese dioxide as well as introduction of co-catalysts to enhance its electrocatalytic activity and stability for both ORR and OER.

1.2 Bifunctional catalysts for ORR and OER in alkaline batteries and fuel cells

In theory, it could be possible to develop an ideal, reversible, oxygen electrode with low ORR as well as OER overpotentials. In practice, a suitable catalyst should have certain characteristics, i.e. minimum changes in surface structure during the operation and the ability to fluctuate between the two reactions in a small potential window near the oxygen electrode equilibrium potential. The high activation overvoltage of the oxygen electrode in aqueous solutions, which implies a strong irreversible system, limits the choice of catalysts for the oxygen electrode to four major groups of
materials: 1) Pt, Ag, Ni, 2) Mixed valence oxides of Co, Ni and Mn with spinel\textsuperscript{4} or perovskite\textsuperscript{8} crystal structures, 3) Metal sulfides, nitrides and carbides, and 4) Mixed metal oxides catalysts containing Pt, Ir, Ru, Os and/or Rh [7, 51-53].

1.2.1 Nobel metals and their alloys

Noble metals and their alloys such as Pd [2], Ag [54], Pt [55], Pt-Au [56] and Pt-Co [57] have been extensively investigated for ORR in alkaline media but their lower electrocatalytic activity toward OER as well as high price compared to non-precious group metals (non-PGM) such as perovskite-type oxides (e.g. LaNiO\textsubscript{3} and LaCoO\textsubscript{3}) [2, 4, 58-63] and Co oxides [64, 65], limit their widespread use as cost-effective bifunctional oxygen electrode catalysts. Moreover, other noble metals and their oxides such as Ru [66, 67], Ir [68, 69], RuO\textsubscript{2} and IrO\textsubscript{2} [2, 70], which are known as benchmarks for OER electrocatalysis, exhibit poor ORR electrocatalytic activity compared to MnO\textsubscript{x} [4, 67] and Pt [2, 55, 67], hindering their development as bifunctional oxygen electrocatalysts as well. Figure 1.7 summarizes the ORR and OER overpotentials of some candidates for bifunctional oxygen electrodes from the literature. For instance, high ORR overpotentials of -662, -502 and -444 mV (at -2 mA cm\textsuperscript{-2}) have been reported for 83 wt\% RuO\textsubscript{2}/C [71], 20 wt\% Ru/C [67, 69] and 20 wt\% Ir/C [69], respectively, while much lower values of -375, -365 and -284 mV (at -2 mA cm\textsuperscript{-2}) were obtained for activated MnO\textsubscript{2} [4], MnO\textsubscript{2}/Nitrogen doped carbon nano tube [72] and nano particulate Pt/C [73], respectively. In the OER region, 20 wt\% Pt/C [67], Pt/TiO\textsubscript{2} [74] and nano-sized Ag [75] have been reported to generate high OER overpotentials of 526, 473 and 464 mV (at 2 mA cm\textsuperscript{-2}), respectively, comparing to lower values

\textsuperscript{4} The spinels have the general formula of A\textsuperscript{2+}B\textsuperscript{3+}X\textsubscript{4}\textsuperscript{2-} where A and B are cations and X is an anion such as O, S, Se and Te. They crystallize with the same structure as the mineral spinel, i.e. MgAl\textsubscript{2}O\textsubscript{4} [51] K.E. Sickafus, J.M. Wills, N.W. Grimes, Structure of Spinel, Journal of the American Ceramic Society, 82 (1999) 3279-3292.

\textsuperscript{8} Please go to 1.2.3.
of 329, 252 and 206 mV (at 2 mA cm\(^{-2}\)) for Core-Corona Structured Bifunctional Catalyst (CCBC) [76], nano-sized Co\(_3\)O\(_4\) [65] and MnO\(_2\)-LaCoO\(_3\) [4], respectively.

![Graph showing ORR and OER overpotentials for different catalyst materials.](image)

Figure 1.7 A comparison between bifunctional oxygen performance of different catalyst materials in alkaline media. The ORR and OER overpotentials were calculated at superficial current densities specified on the graph. Reprinted with permission from [4].

1.2.2 Manganese dioxide

A considerable amount of work has been done on manganese dioxide since its introduction as depolarizing agent in the Zinc-Ammonium Chloride-Carbon battery by Leclanché in 1866 [39]. The use of chemically-synthesized manganese dioxide proposed by Glemser, instead of natural MnO\(_2\) first used by Leclanché, substantially enhanced its performance in the so called Leclanché
battery [39]. The next major step was in 1952 when Herbert introduced the application of electrochemically prepared MnO₂, first proposed by Van Arsdale and Maier in 1918, in a concentrated KOH solution for commercial batteries [77]. In 1973, Zoltowski et al. showed that carbon supported air electrodes with manganese dioxide catalyst could improve the reversibility of the ORR, or in other words, it could enhance the performance of rechargeable metal-air batteries [44]. For 20 wt% MnO₂/C, high ORR electrocatalytic activity was reported, close to the performance of 20 wt% Pt/C catalyst, i.e. a current density of about -3.5 mA cm⁻² for both aforementioned catalysts at -300 mV_MOE in 1 M KOH at 298 K and 1600 rpm [45].

Various synthesis methods of manganese oxides have been reported in the literature including hydrothermal synthesis, sol-gel synthesis, thermal decomposition, chemical co-precipitation and electrodeposition methods, leading to a number of different morphologies and crystal structures for synthesized Mn oxides [78-85]. Electrodeposition methods, in particular, have gained much attention due to several merits including ease of processing, low production cost, environmental compatibility, better control over properties of deposited materials such as morphology and crystallographic structure, high degree of reproducibility and high yield [84, 86, 87].

MnO₂ exists in several crystallographic forms, which are known as α (Ramsdellite), β (Pyrolusite), γ (Electrolytic), δ (Birnessite), ε and λ (Spinel type) forms. The α, β, and γ forms possess 1D tunnels in their structures while the δ is a 2D layered compound and the λ is a 3D spinel structure (Figure 1.8) [85, 88, 89]. The physico-chemical and electrochemical properties of MnOₓ species depend very much on its crystallographic features [39].

Since the reduction potential of MnO₂ is close to the oxygen reduction potential in alkaline media (between -110 and -126 mV_SHE depending on the electrolyte’s composition and the crystal structure of manganese dioxide [90, 91]), the electro-reduction of manganese dioxide may occur
simultaneously with ORR (or at a more positive potentials due to the higher overpotential for the ORR). Cao et al. reported that the ORR happens in parallel with the reduction of MnO$_2$ to MnOOH and the electrocatalytic activity of MnO$_2$ for ORR is dependent on its electrochemical activity for reduction in alkaline media [48]. This further underlines the importance of Mn valence changes on the performance of MnO$_x$-containing bifunctional electrodes which catalyze both ORR and OER.
Figure 1.8 Schematic representation of five different crystal structures of MnO₂: A) Pyrolusite (β-MnO₂): Rutile structure with an infinite chain of MnO₆ octahedra sharing opposite edges. Each chain is corner-linked with four similar chains, B) Ramsdellite (α-MnO₂): Cross-linking of double or triple chains of the MnO₆ octahedra resulting in two-dimensional tunnels within the lattice, C) Birnessite (δ-MnO₂): Layered structure containing infinite two-dimensional sheets of edge-shared MnO₆ octahedra, D) Spinel (λ-MnO₂): A 3D spinel structure and E) Electrolytic manganese dioxide (γ-MnO₂): An intergrowth of pyrolusite in ramsdellite matrix. Each MnO₆ octahedra composes of oxygen and manganese atoms in the corners and center, respectively. Reprinted with permission from [85, 88, 89].
1.2.2.1 Electro-reduction of MnO₂

In 1966, Kozawa and Powers proposed a two-step mechanism for the reduction of electrolytic MnO₂ [92]:

\[ MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^- \quad (E_{298K}^0 = -0.022 \, V_{SHE}) \]  \hspace{1cm} (3)
\[ MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^- \quad (E_{298K}^0 = -0.072 \, V_{SHE}) \]  \hspace{1cm} (4)

The first step begins with the formation of MnOOH in a solid-phase reaction without any changes in the basic structure of MnO₂ [92]. During this step, protons are associated with the manganese dioxide lattice, while the reduction of Mn⁴⁺ into Mn³⁺ ions occurs on the surface [92]. It is reported that this discharge reaction is theoretically finished at an oxygen index of 1.5 in MnOₓ [92]. In addition to this reaction, parts of MnOOH are then converted to the Mn(OH)₂, also known as deep-discharge process, which limits the rechargeability of MnO₂ [92]. During the recharge process of the deep-discharged γ-MnO₂, Mn(OH)₂ is transformed to δ-MnO₂ (layered birnessite structure) [92]. The reduction of birnessite during the subsequent cycles results in excessive formation of hausmannite (Mn₃O₄) which has been regarded as the main reason for the poor rechargeability of manganese dioxide [40, 41, 93].

For Leclanché-type Zn-MnO₂ batteries in which MnO₂ is being reduced as the cathode material, two solutions have been suggested in practice to avoid the deep discharge: 1) Limiting the discharge voltage of MnO₂ and 2) Applying a limit to the capacity of the zinc anode electrode [42]. Moreover, other methods such as chemical or physical modifications of MnO₂ cathodes have been reported to further improve the recharging ability of manganese dioxide [43, 94]. The feasibility of these methods for MnO₂ acting as ORR catalyst have not been reported in the
literature thus far. This could arise from the fact that the ORR happens at more negative potentials compared to the potentials needed for Mn valence changes in alkaline media which makes it hard to limit the potential regime [48, 90, 91].

In 1976, Ruetschi investigated the discharge mechanism of γ-MnO$_2$ deposited on fine Ni or Pt screens in 10.2 M KOH electrolyte. The following reaction mechanism was proposed [46]:

\[
\begin{align*}
MnO_2 + H_2O + e^- & \rightarrow MnOOH + OH^- & (5) \\
MnOOH + H_2O + OH^- & \rightarrow Mn(OH)_4^- & (6) \\
Mn(OH)_4^- + e^- & \rightarrow Mn(OH)_4^{2-} & (7) \\
Mn(OH)_4^{2-} & \rightarrow Mn(OH)_2 + 2OH^- & (8)
\end{align*}
\]

According to Ruetschi, Mn$^{4+}$ is reduced to Mn$^{3+}$ in MnOOH (eq. 5) and then, the manganese (III) oxy-hydroxide dissolves in water (eq. 6) [46]. Afterwards, the hydrated Mn$^{3+}$ ions are further reduced to Mn$^{2+}$ (eq. 7) and crystalized to produce stable manganese hydroxide (eq. 8) [46]. Therefore, two cathodic peaks were reported for the sequential reduction of Mn$^{4+}$ to Mn$^{2+}$ according to the aforementioned simplified mechanism (Figure 1.9) [46]. The reduction steps in reality are far more complex for manganese dioxide mainly due to the crystal structure changes during the discharge-charge processes [42, 45, 90, 94-98]. Lima et al. studied the redox performance of different manganese oxides supported on carbon in conjunction with in-situ X-ray Absorption Near Edge Structure (XANES) in alkaline media, showing high redox electrochemical activity for MnO$_2$ and to lower extend for Mn$_2$O$_3$ and then Mn$_3$O$_4$ (Figure 1.10) [45]. In the cathodic direction, the reduction of MnO$_2$ to MnOOH starts around 200 mV$_{MOE}$, converting almost
40% of the MnO₂ to MnOOH at -100 mV MOE (Figure 1.10 and Table 1.1) [45]. Further decrease in the potential leads to the formation of Mn₃O₄ and Mn(OH)₂ starting at -300 and -700 mV MOE, respectively (Figure 1.10 and Table 1.1) [45]. In the anodic direction, the reduced MnO₂, i.e. majorly Mn(OH)₂, converts to Mn₂O₃ (slowly) and MnOOH at -300 and 0 mV MOE, respectively, followed by the oxidation of Mn³⁺ species, i.e. MnOOH, to MnO₂ at 400 mV MOE while the generated Mn₃O₄ during cathodic polarization step stays intact in the anodic potential region investigated (Figure 1.10 and Table 1.1) [45].

Figure 1.9 Linear sweep voltammetry of 0.2 mg MnO₂ on Ni mesh in N₂ saturated 10.2 M KOH. 0.05 mV s⁻¹. 298 K.
Figure 1.10 Cyclic voltammograms of different manganese oxides supported on carbon in N$_2$ saturated 1 M KOH at 20 mV s$^{-1}$ and 298 K. Samples labeled as A, B and C are MnO$_2$/C, Mn$_3$O$_4$/C and Mn$_2$O$_3$/C, respectively. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [45].

Table 1.1 MnO$_2$ crystal structure evolution at several electrode potentials in fractional composition. Other conditions idem to Figure 1.10. Reprinted with permission from [45].
Gyenge and Drillet further reported the existence of similar anodic and cathodic peaks for various commercially available MnO₂ catalysts in alkaline media, depicting some deviations in the peak potentials of these reduction and oxidation peaks compared to the literature, mainly due to differences in the experimental protocols such as MnO₂ synthesis method, electrolyte composition and scan rate (Figure 1.11) [90]. Moreover, they have shown other small scan-rate-dependent peaks around the two major anodic and cathodic peaks in the cyclic voltammograms of all investigated MnO₂ samples which they have contributed the existence of such peaks to the electrochemical, structural and physico-chemical phenomena (e.g. adsorption) together with the carbon support effect (Figure 1.11) [90].
Figure 1.11 Cyclic voltammograms of four different commercially available MnO$_2$ powders supported on carbon in N$_2$-purged 6 M KOH at 2 mV s$^{-1}$. 295 K. Third cycle is presented. The potentials are reported vs. mercury-mercury oxide reference electrode (MOE). Reprinted with permission from [90].

1.2.2.2 Oxygen reduction reaction on manganese oxides

The electro-reduction of oxygen in alkaline media is composed of series of complex electrochemical reactions. It is believed that the oxygen reduction reaction kinetics are governed by the binding energies between the catalyst and oxygen containing intermediates, i.e. O$_2^-$, HO$_2^-$ and OH$^-$ [2, 17, 90, 99, 100]. Generally, two mechanisms have been proposed for ORR in alkaline
media [2, 17, 45, 98-100]: a) Four-electron pathway (direct or indirect) and b) Two-electron pathway. Table 1.2 summarizes the possible pathways for ORR on catalysts in alkaline media.

**Table 1.2 Possible ORR pathways in alkaline media [2, 17, 45, 98-100].**

<table>
<thead>
<tr>
<th>Four-electron pathway (Direct)</th>
<th>$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$ ($E_{298K}^0 = 0.401 \text{ V}_{\text{SHE}}$) (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-electron pathway</td>
<td>$O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^-$ ($E_{298K}^0 = -0.076 \text{ V}_{\text{SHE}}$) (9)</td>
</tr>
</tbody>
</table>
| Four-electron pathway (Indirect) | 1) $O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^-$ ($E_{298K}^0 = -0.076 \text{ V}_{\text{SHE}}$) (9)  
2) $HO_2^- + H_2O + 2e^- \leftrightarrow 3OH^-$ ($E_{298K}^0 = 0.878 \text{ V}_{\text{SHE}}$) (10)  
Or  
3) $2HO_2^- \rightarrow O_2 + 2OH^-$ (11) |

The ORR mechanism is mainly affected by the configuration of adsorbed oxygen on the catalyst’s active sites, which itself depends on two factors: 1) Surface geometry of the catalyst and, 2) Oxygen binding energies on the catalyst (or the formation energy of lattice oxygen vacancies) [101, 102]. In cases where a single atom of the adsorbed oxygen is perpendicularly coordinated to the surface, two-electron pathway mainly prevails, generating peroxide ions (eq. 9) [17]. This process can be further explained in details via eqs. 12, 13 and 14 [17, 90, 99]:

\[ O_2 \rightarrow O_{2,(ads)} \]  \hspace{1cm} (12)

\[ O_{2,(ads)} + H_2O + e^- \rightarrow HO_{2,(ads)} + OH^- \]  \hspace{1cm} (13)

\[ HO_{2,(ads)} + e^- \rightarrow HO_2^- \]  \hspace{1cm} (14)
On some ORR catalyst surfaces the two-electron oxygen reduction reaction (eq. 9) could be followed by either the two-electron reduction of hydrogen peroxide ions (eq. 10) or a disproportionation reaction of HO$_2^-$ (eq. 11), leading to indirect four-electron pathway, also known as $2 \times 2e^-$ [17, 45, 90, 98].

Different mechanism is proposed when both of the adsorbed oxygen atoms are coordinated parallel to the catalyst surface [17, 99, 101, 102]. This configuration of adsorbed oxygen favors O$_2$ dissociation, leading to the direct four-electron pathway via eqs. 12, 15 and 16 (overall eq. 2):

\begin{align*}
O_2 & \rightarrow O_{2,(ads)} \\
O_{2,(ads)} + 2H_2O + 2e^- & \rightarrow 2OH_{(ads)} + 2OH^- \\
2OH_{(ads)} + 2e^- & \rightarrow 2OH^-
\end{align*}

Figure 1.12 shows typical ORR polarization curves for a variety of catalysts in alkaline media. The ORR limiting current densities ($i_{L,j}$)$^\text{**}$ in 0.1 M KOH solution were found to be around -5.8 mA cm$^{-2}$ for catalysts following a 4e$^-$ pathway such as Pt/C, MnO$_x$, LaMn$_{0.5}$Cu$_{0.5}$O$_3$ and α-MnO$_2$ while half of that, i.e. 2.9 mA cm$^{-2}$, was reported as $i_L$ for ORR catalysts showing 2e$^-$ pathway, e.g. glassy carbon and δ-MnO$_2$ [104-107]. ORR Tafel slopes and exchange current densities of between -80 to -120 mV dec$^{-1}$ and 0.02 µA cm$^{-2}$, respectively, were shown for carbon-based ORR catalysts which follow 2e$^-$ pathway, while Tafel slopes as low as -40 mV dec$^{-1}$ and

\text{** The limiting current density for a reactant is the current density under pure mass transfer control which is the max. current density that can be supported by that reactant [103] C. Oloman, Electrochemical processing for the pulp and paper industry, The Electrochemical Consultancy, Romsey, Hants, UK, 1996.}
exchange current densities as high as 0.63 μA cm\(^{-2}\) were reported for catalysts following a 4e\(^-\) pathway such as Pt, γ-MnO\(_2\) and α-MnO\(_2\) [5, 90, 104-109].

Figure 1.12 ORR polarization curves of various catalysts following 2e\(^-\) or 4e\(^-\) pathways in 0.1 M KOH. Theoretical limiting current densities for the 2e\(^-\) or 4e\(^-\) pathways are indicated by solid lines together with a ±10% margin (dashed lines). Currents are normalized to the geometrical area of the disk. 1600 rpm. 298 K. P\(_{O_2}\) equals to 1 atm. Reprinted with permission from [107].

Manganese dioxide has been intensely investigated as a catalyst for ORR in alkaline batteries and fuel cells due to a unique combination of properties, i.e., low cost, abundance, environmental friendliness and promising electrocatalytic activity for ORR [27, 39, 47, 90]. The study by Lima et al. reveals that the ORR on carbon supported manganese oxides (MnO\(_x\)/C) in 1 M KOH undergoes a 2e\(^-\) pathway [49]. According to this mechanism, Mn\(^{4+}\) ions rapidly reduce to Mn\(^{3+}\) while oxygen is promptly being adsorbed without splitting (eqs. 12 and 17) [49]. The rate determining step for overall ORR is reported to be the electron transfer of Mn\(^{3+}\) to the adsorbed
oxygen without molecular splitting (eq. 18) [49]. The speedy oxidation of water and formation of
OH$^-$ and HO$_2$$^-$ ions (eq. 19) are the final steps in the proposed 2e$^-$ pathway for ORR on MnO$_x$/C
[49, 110]:

\[
\begin{align*}
Mn^{4+} + e^- & \leftrightarrow Mn^{3+} \quad (fast) \quad (17) \\
O_2 & \leftrightarrow O_{2,ads} \quad (fast) \quad (12) \\
Mn^{3+} + O_{2,ads} & \leftrightarrow Mn^{4+} + O_{2,ads}^- \quad (slow) \quad (18) \\
O_{2,ads}^- + H_2O + e^- & \rightarrow HO_2^- + OH^- \quad (fast) \quad (19)
\end{align*}
\]

Mao et al., however, proposed an overall four-electron mechanism for the reduction of O$_2$ on
MnO$_x$ catalysts in alkaline solutions [111]. It starts with the reduction of oxygen to hydrogen
peroxide ions (eqs. 17 to 19) and continues with the disproportionation of HO$_2$$^-$ on MnO$_x$ surfaces
leading to O$_2$ and OH$^-$ (eq. 11) when the regenerated oxygen gets to reduce again in the same first
reduction steps (eqs. 17 to 19), resulting in a $2 \times 2e^-$ pathway for ORR [111].

Although Lima et al. proposed a two-electron mechanism for ORR on γ-MnO$_2$, they have
reported that under certain conditions of low rotation rates and/or low overpotentials, a complete
disproportionation reaction of HO$_2$$^-$ at the Mn$_y$O$_x$ sites could follow the main reaction which
results in an overall 4e$^-$ process per O$_2$ molecule, as suggested by Mao et al. and others [37, 45,
49, 50, 110, 111]. Figure 1.13 summarizes the ORR mechanisms on manganese oxides, revealing
4e$^-$ (Figure 1.13-A), 2e$^-$ (Figure 1.13-B) and $2 \times 2e^-$ pathways (Figure 1.13-B and C).
Figure 1.13 Possible ORR pathways on manganese oxides in alkaline media: A) Four-electron pathway reducing O\textsubscript{2} to hydroxide, B) Two-electron pathway reducing O\textsubscript{2} to peroxide ion and C) Two-electron reduction of peroxide ions. Orange denotes species on the catalyst surface, and blue/purple denotes species in solution. Reprinted with permission from [107].

It is worth mentioning that a competition between 2e\textsuperscript{−} and 4e\textsuperscript{−} mechanisms is reported for ORR on manganese dioxide/carbon electrodes in alkaline solutions which is unanimously believed to depend on the carbon content of the catalyst layer as well as the applied electrode potential [45, 48-50, 111]. Increasing the carbon support content of the catalyst layer enhances the two-electron mechanism for ORR [45, 111].
The ORR electrocatalytic activity and reduction ability of different crystallographic types of manganese oxides have been intensively studied [39, 41, 48, 90]. Poinsignon et al. studied the electrochemical reduction of four allotropic forms of manganese dioxide, i.e. α, β, γ and ε-MnO₂, in KOH solutions [41]. They have shown that the γ and ε types of manganese dioxide are reduced to MnOOH (eq. 5) at more positive potentials compared to either ramsdellite (α-MnO₂) or pyrolusite (β-MnO₂) in 7 N KOH solution (Figure 1.14) [41].

Further studies by Cao et al. revealed that not only the reduction currents of different crystallographic forms of MnO₂ increases from β < λ < γ < α ≈ δ in argon saturated KOH solution but also the currents from ORR on manganese dioxide follow the same trend, showing a relationship between the ORR electrocatalytic activity of MnO₂ and its electro-reduction (Figure 1.15) [48]. For instance, the γ-MnO₂, an intergrowth of pyrolusite (β-MnO₂) in the ramsdellite (α-MnO₂) matrix [39, 112], is known as one of the most electrocatalytically active crystal structures of manganese dioxide for ORR in alkaline media, e.g. modest ORR Tafel slope of 40 mV dec⁻¹ (Figure 1.16) and exceptionally low ORR overpotential of -375 mV (at -2 mA cm⁻²), while its facile reduction during ORR was reported in many studies [4, 39, 46, 48, 90, 113].
Figure 1.14 Linear sweep voltammograms of four types of manganese dioxide: A) α-MnO₂ (ramsdellite), B) β-MnO₂, C) γ-MnO₂ and D) ε-MnO₂. N₂ saturated 7 N KOH. 0.003 mV s⁻¹. 298 K. Solid and dotted lines represent mass activity (I, currents normalized by the catalyst loading) and the fraction of one electron capacity expressed in percentage, respectively, vs. potential. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [41].
Figure 1.15 Linear voltammograms of MnO$_2$-catalyzed air electrode in: A) Argon and B) Air. The catalysts are labelled as follows: 1) $\alpha$-MnO$_2$, 2) $\beta$-MnO$_2$, 3) $\gamma$-MnO$_2$, 4) $\lambda$-MnO$_2$ and 5) $\delta$-MnO$_2$. The reduction current is defined as positive (American current polarity convention). 6 M KOH. 298 K. 1 mV s$^{-1}$. Currents are normalized by the catalyst loading, presenting mass activity values. The potentials are reported vs. mercury-mercury oxide reference electrode (Hg/HgO). Reprinted with permission from [48].
Figure 1.16 Oxygen reduction polarization curves recorded in a flow cell for four types of commercially available MnO₂ powders: Tronox (γ-MnO₂), Riedel (β-MnO₂), Merck (γ-MnO₂) and Sigma (γ-MnO₂ with high portion of α-MnO₂). Gas diffusion electrodes are employed at a loading of 0.25 mg cm⁻² for MnO₂ mixed with Vulcan XC-72 (1:1 weight ratio). 6 M KOH. 293 K. Currents are normalized to the geometrical area of the electrode. The potentials are reported vs. mercury-mercury oxide reference electrode (MOE). Reprinted with permission from [90].

1.2.2.3 Oxygen evolution reaction on manganese oxides

The mechanism originally proposed by Krasil’shchikov to describe the OER on nickel (or nickel oxide) and cobalt (or cobalt oxide) seems to inspire other researchers to introduce various complex pathways with distinctive rate determining steps and intermediates on variety of surfaces from perovskite-type oxides to MnOOH, NiOOH, NiCo₂O₄, Li-doped Co₃O₄, iron oxide and cobalt [52, 59, 114-121]. The complexity of these mechanisms arises from the several reaction intermediates with no available method to clearly identify them on different surfaces during OER
Figure 1.17 summarizes the proposed OER mechanisms in the literature for variety of metal and oxide surfaces. The OER mechanism described in Figure 1.17-A is based on an extensive computational work on ORR/OER pathways for metals which was extended to oxide surfaces such as perovskites and rutile structures, (also referred to as acid-base mechanism) in which \( \text{OH}^- \) (Lewis base) attacks a metal-bound electrophilic oxygen surface species (Lewis acid) [124, 125]. This mechanism will be discussed in details in the following sections. Goodenough et al. further proposed similar mechanism for OER on pyrochlores \((\text{Pb}_2(\text{Ir or Ru})_{2-x}\text{Pb}_x\text{O}_{7-y})\), perovskites \((\text{Sr}_{1-x}\text{NbO}_{3-\delta})\) and rutile oxides \((\text{RuO}_2 \text{ and IrO}_2)\) (Figure 1.17-B) [126]. Computational works of Mavros et al. confirmed similar acid-base OER mechanism for first-row transition-metal oxides (Figure 1.17-C) [127]. The only difference between the first proposed OER mechanism (Figure 1.17-A) and the other two (Figure 1.17-B and C) is that the first one involves a step with a bare catalyst surface unlike the other two (Figure 1.17-A). Nevertheless, oxide surfaces are more likely to adsorb negatively charged species such as \( \text{OH}^* \), \( \text{OOH}^* \) and \( \text{O}^* \) in alkaline media [126]. Figure 1.17-D describes a two-site reaction mechanism for OER on RuO\(_2\) surfaces, based on the work of Faria et al., which one involves the typical acid-base pathway while the recombination of surface oxygen species to produce oxygen molecules happens at the other site [128]. Moreover, Figure 1.17-E represents the OER mechanism proposed by Gerken et al. for electrodeposited cobalt oxides [129].

Jung et al. performed a systematic study on the OER electrocatalytic activity of wide range of catalysts in alkaline media, based on the primary work of McCoy et al. in which they evaluated the performance of oxygen-evolving catalysts under standardized protocol, i.e. OER overpotential measurements at the beginning and after 2 hrs of testing at 10 mA cm\(^{-2}\), 298 K and \( P_{\text{O}_2} \) of 1 atm [130, 131]. Figure 1.18 depicts a graphical representation of activity and stability comparison.
between different OER catalysts. Although IrO$_2$, RuO$_2$ and NiCoO$_2$ provided the lowest OER overpotentials (at 10 mA cm$_{geo}^{-2}$) of 380 to 390 mV at the beginning, the OER overpotential values of IrO$_2$ and RuO$_2$ increased by 50 mV after two hrs of testing (Figure 1.18) [130]. Moreover, other catalysts such as LiNiO$_2$, Mn$_3$O$_4$ and NiO provided stable OER overpotentials of 420 mV during the two-hour-long tests at 10 mA cm$_{geo}^{-2}$ (Figure 1.18) [130].
Figure 1.17 OER mechanisms proposed for crystalline oxide surfaces in alkaline electrolytes: A) Four-step reaction mechanism proposed by Rossmeisl et al. for the OER on noble metal catalysts and oxide surfaces [124, 125], B) Four-step reaction mechanism proposed by Goodenough et al. for the OER on perovskite surfaces [126], C) Acid–base mechanism proposed for first-row transition-metal oxides [127], D) Reaction mechanism proposed by Faria et al. involving recombination of oxygen atoms to produce O₂ [128] and E) Reaction mechanism proposed by Gerken et al. for electrodeposited cobalt oxides [129]. The orange and blue denote species on the catalyst surface and in solution, respectively. Reprinted with permission from [123].
Figure 1.18 A comparison between the OER activity and durability of wide range of catalysts in 1 M NaOH: The x-axis is the overpotential required to achieve 10 mA cm\(^{-2}\) at time equal to 0 s. The y-axis is the overpotential required to achieve 10 mA cm\(^{-2}\) after two hrs of testing. The dashed diagonal line indicates where the stable catalysts would be. Catalyst loadings are 0.8 mg cm\(^{-2}\) for each case. 298 K, P\(_O_2\) of 1 atm. Reprinted with permission from [130].

Further, Meng et al. investigated the bifunctional electrocatalytic activity of manganese oxides with various crystallographic structures ($\alpha$, $\beta$, $\delta$-MnO\(_2\) and amorphous) in alkaline media, proposing an OER mechanism similar to the acid-base mechanism based on Rossmeisl et al. work [105]. They have shown that the OER electrocatalytic activity of investigated manganese oxides increases in the following sequence: $\delta$-MnO\(_2\) < $\beta$-MnO\(_2\) < Amorphous MnO\(_x\) < $\alpha$-MnO\(_2\), with $\alpha$-MnO\(_2\) providing OER overpotential (at 10 mA cm\(^{-2}\)) and Tafel slope of 490 mV (about 100 mV
higher than 20 wt% Ir/C, 20 wt% Ru/C and RuO$_2$) and 77.5 mV dec$^{-1}$, respectively (Figure 1.19) [105]. Furthermore, other studies have reported modest OER electrocatalytic activities for different types of manganese oxides including MnO and Mn$_3$O$_4$ when being used as either bifunctional or oxygen-evolving catalysts in alkaline media (Figure 1.20) [32, 67, 69, 104, 113, 121, 130].

![Figure 1.19 A comparison between the OER overpotentials (at 10 mA cm$^{-2}$) for four different types of manganese oxides in alkaline media: α, β, δ-MnO$_2$ and amorphous MnO$_x$. 0.1 M KOH. 1600 rpm. 298 K. Reprinted with permission from [105].](image-url)
Figure 1.20 OER cyclic voltammograms of various catalysts in O\textsubscript{2} saturated 0.1 M KOH: As-deposited 500 ALD MnO, annealed Mn\textsubscript{2}O\textsubscript{3}, glassy carbon, 20 wt% Ru/C and 20 wt% Pt/C. 20 mV s\textsuperscript{-1}. 1600 rpm. 298 K. Reprinted with permission from [67].

However, difficulties associated with the synthesis of pure crystalline manganese oxides and the structural changes during reduction/oxidation cycles, express the need for more fundamental studies on these oxides during both ORR and OER.

1.2.2.4 Density Functional Theory (DFT) studies on manganese oxides catalyzing both ORR and OER

Recent DFT studies have shown that the following simplified mechanism occurs for ORR (eqs. 20-23) and OER (eqs. 23-20) on oxide surfaces in alkaline media (Figure 1.21-A) [5, 16, 107, 121, 123, 132]:

\[
O_2 + H_2O + e^- \leftrightarrow HOO_{(ads)} + OH^- \quad (20)
\]
where $\text{HOO}_{(ads)}$, $\text{HO}_{(ads)}$ and $\text{O}_{(ads)}$ are the oxygen containing intermediates binding to active sites through their oxygen atoms [121]. It is worth mentioning that this mechanism was developed with the assumptions of: 1) The reactions occur on a perfect single metal site without any defects, and 2) The possibility of oxygen recombination on any metal surfaces is excluded [121, 123]. Hence, it fails to address the challenging effects of crystal structure transformations as well as the existing and newly-formed defects, i.e. intertwined structures, twinnings and numerous types of vacancies, during ORR and OER which is the case in commercial scenarios [5, 39, 121]. The constant difference between the binding energy levels of the $\text{HOO}_{(ads)}$ and $\text{HO}_{(ads)}$ intermediates for many metals and their oxides, also known as universal scaling relationship, contributes largely to the overpotential of both ORR and OER (Figure 1.21-B) [121, 124, 133]. Breaking away from this linear scaling relationship (red star in Figure 1.21-B) via modification of catalyst surfaces, enhances its activity for both ORR and OER, significantly lowers the reaction overpotentials.
Figure 1.21 A) Free-energy diagram for ORR (in reverse direction) and OER on an ideal catalyst. The vertical solid arrow shows $\Delta G_{\text{HOO(ad)}} - \Delta G_{\text{HO(ad)}}$ on a perfect crystal which is 2.46 eV.

B) Adsorption energy of HOO(ad) plotted against the adsorption energy of HO(ad) on the clean surfaces: Perovskites (○), rutiles (▵), Mn$_x$O$_y$ (□), TiO$_2$ (◊) and Co$_3$O$_4$ (+). The best fit of all points is $\Delta E_{\text{HOO(ad)}} = \Delta E_{\text{HO(ad)}} + 3.20$ eV. The red star indicates where the binding energies need to be for an ideal catalyst. Reprinted with permissions from [121, 124].

In a study by Su et al. on DFT calculations of MnO$_x$ single crystals catalyzing oxygen reduction and evolution reactions in alkaline media, it has been reported that HO(ad) covered α-Mn$_2$O$_3$ and O(ad) covered β-MnO$_2$ sites are the most active surfaces for ORR and OER, respectively, among Mn$_3$O$_4$ (001), α-Mn$_2$O$_3$ (110) and β-MnO$_2$ (110) single crystals [121].

1.2.2.5 Dopants for manganese dioxide as cathode material in alkaline fuel cells and metal-air batteries

There have not been many intensive studies on the effect of dopants and co-catalysts to enhance the ORR/OER bifunctional electrocatalytic activity of manganese oxides. Sun et al. showed that the core-shell like combination of β-MnO$_2$ nano-rods (40-50 nm in diameter and
500-1000 nm in length) with 8.7 wt% Pd coating could shift positively the ORR onset and half-wave potentials by more than 250 mV compared to pure manganese dioxide in alkaline media [134]. In another study, Klápště et al. investigated the activity of MnOx/C composites doped with divalent and trivalent ions, such as Ca2+, Mg2+, Ni2+, Bi3+ and Cr3+, for ORR in alkaline solutions [135]. While alkali earth metals like Ca and Mg did not enhance the ORR electrocatalytic activity compared to the un-doped manganese oxide samples, transition metal ions such as Ni2+ or Cr3+ shifted positively the ORR half-wave potential by 50 to 60 mV [135]. The authors hypothesized that this could be due to the ability of transition metal ions to exist in several states of valence, mainly facilitating the charge transfer to oxygen [135].

1.2.2.6 Nanostructured manganese oxides

When it comes to the particle size, nanostructured MnOx generally outperforms the micro-sized particles mainly due to its higher specific surface area. Hence, more active sites are available for nanostructured MnOx to facilitate the O2 reduction/oxidation reactions. The higher porosity for nanostructured manganese oxides also leads to extra space for oxygen bubbles to evolve and avoid entrapment [17, 67, 136, 137]. Recent studies showed promising ORR and OER electrocatalytic activities for electrochemically deposited nanostructured manganese oxides in alkaline media, i.e. ORR and OER overpotential of -311 mV (at -2 mA cm\(^{-2}\)) and 405 mV (at 2 mA cm\(^{-2}\)) [136, 137].

While several synthesis methods such as hydrothermal synthesis, sol-gel synthesis, thermal decomposition and chemical co-precipitation have been studied for production of nano-sized MnOx, the electrodeposition techniques provided huge opportunity in the synthesis of nanostructured manganese oxides by introducing an easy process with low production costs, environmental compatibility, enhanced control over properties of deposited material such as morphology and crystallographic structure, high degree of reproducibility and high yields [78-87].
Using electrochemical deposition methods, MnO$_2$ can be either synthesized via cathodic reduction of Mn$^{7+}$ species or anodic oxidation of Mn$^{2+}$ [87].

**Cathodic electrodeposition of MnO$_2$ from anionic MnO$_4^-$ (Mn$^{7+}$) species**

The overall reaction for cathodic electro-reduction of MnO$_4^-$ ions to deposit MnO$_2$ can be represented as follows in acidic (eq. 24) and neutral (eq. 25) media [87, 138, 139]:

\[
\text{MnO}_4^- + 4H^+ + 3e^- \rightarrow \text{MnO}_2 + 2H_2O \quad (E_{298K}^0 = 1.679 V_{SHE}) \quad (24)
\]

\[
\text{MnO}_4^- + 2H_2O + 3e^- \rightarrow \text{MnO}_2 + 4OH^- \quad (E_{298K}^0 = 0.595 V_{SHE}) \quad (25)
\]

It is noteworthy to mention that the kinetic pathway of Mn$^{7+}$ reduction to Mn$^{4+}$ depends on a number of factors such as electrode potential (as described in eqs. 26 and 27), pH, concentration of MnO$_4^-$ and other species available in the solution [87, 138, 139]. Moreover, Nguyen et al. argued that the deposition factors such as applied potential, electrolyte concentration, applied charge and post-thermal treatments, can significantly affect the surface morphology and electrochemical response of the cathodically electrodeposited MnO$_x$ [140].

\[
E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Mn}O_4^-}.a_{H_2O}^4}{a_{\text{MnO}_2}.a_{H_2O}^2} \quad (26)
\]

\[
E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{Mn}O_4^-}.a_{H_2O}^2}{a_{\text{MnO}_2}.a_{OH^-}^4} \quad (27)
\]

The cathodic electrodeposition process from Mn$^{7+}$ draws some attention as the method of choice for the synthesis of nanostructured MnO$_x$ since it provides the opportunity to modify the composition of the catalyst layer by either chemical doping or co-deposition of other oxides for
fabrication of enhanced composite catalysts [87, 139]. Moreover, other advantages include avoiding anodic oxidation and dissolution of metallic substrates, no passivation of anode and low risk of product contamination [87, 139, 141].

**Anodic electrodeposition of MnO₂ from cationic Mn²⁺ species**

Anodic electrodeposition of MnO₂ has recently gained more attention mainly due to its flexibility at scale and control on the morphology as well as crystallographic phases of the final deposited MnOₓ [86, 137, 142-144]. This electrochemical deposition of manganese dioxide involves oxidation of Mn²⁺ species on the anode while hydrogen evolution is happening on the cathode in aqueous media of manganese salt as described by eq. 28 [84]. A wide range of electrochemical techniques have been reported in the literature for deposition of MnO₂ anodically, including galvanostatic, potentiostatic, potentiodynamic and pulse deposition methods [84, 87, 145-148].

\[
Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (E_{298K}^0 = 1.23 \text{ V}_{SHE})
\]  

(28)

Recent study by Clark et al. revealed that the complex electrochemical oxidation of Mn²⁺ to MnO₂ can proceed via two different multistep mechanisms: 1) Disproportionation and 2) Hydrolysis [86]. The first mechanism, i.e. disproportionation, consists of the following reactions (eqs. 29 to 31) [86, 149]:

\[
Mn^{2+} \rightarrow Mn^{3+} + e^- \quad (electrochemical oxidation)
\]  

(29)

\[
2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+} \quad (disproportionation)
\]  

(30)

\[
Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+ \quad (hydrolysis)
\]  

(31)
This mechanism is believed to occur in concentrated acidic media where soluble Mn$^{3+}$ ions are more stable. The second mechanism (i.e. hydrolysis), first introduced by Fleischmann et al. and further developed by Catwright and Paul, mainly starts in low acidic and neutral media [86, 150-154]. This helps un-stabilize the soluble Mn$^{3+}$, allowing the MnOOH to precipitate on the electrode surface. Next, the MnOOH oxidizes to MnO$_2$ as follows (eqs. 32 to 34) [86]:

\[
\begin{align*}
Mn^{2+} & \rightarrow Mn^{3+} + e^- \quad (electrochemical \, oxidation) \quad (32) \\
Mn^{3+} + 2H_2O & \rightarrow MnOOH + 3H^+ (hydrolysis) \quad (33) \\
MnOOH & \rightarrow MnO_2 + H^+ + e^- \quad (electrochemical \, oxidation) \quad (34)
\end{align*}
\]

The deposition of solid MnO$_2$ from Mn$^{2+}$ ions follows different pathways as mentioned in each of the proposed mechanisms which is expected to be the reason behind distinctive morphology of any deposited product [86, 149].

**Experimental factors affecting the electrosynthesis of nanostructured MnO$_x$ via anodic electrodeposition method**

While many factors affect the electrodeposition process for manganese oxides, some important ones are being reviewed here from the literature. Any changes in these factors could substantially alter the physical properties of deposited Mn oxides, i.e. crystal structure, morphology, pore density and Mn valence, leading to diverse ORR/OER electrocatalytic activity and durability for the deposited materials.

Many researchers tried to study the individual effect of these electrodeposition factors, i.e. Mn$^{2+}$ concentration, applied potential, temperature and surfactant content, on the morphology and
later the electrochemical properties of electrodeposited manganese oxides. However, the important yet ignored piece in all of these studies is the complex interactions between all of the electrodeposition operating factors. These complicated interactions are crucial to more reliable predictions of the effect each factor has on electrochemical properties of the deposited manganese oxides in presence of other variable factors.

*Manganese ion concentration*

Mn$^{2+}$ concentration is one of the important factors that can affect morphology, crystal structure and the mechanism by which manganese oxides deposit on the substrate during anodic electrodeposition process [155, 156]. In a study of Mn$^{2+}$ oxidation on Pt electrodes in 2 M H$_2$SO$_4$ solution with various Mn ion concentrations, Nijer et al. reported two anodic peaks representing Mn$^{2+}$ oxidation to Mn$^{3+}$ (around 0.8 mV$_{MSE}$, eq. 32) followed by MnOOH oxidation to MnO$_2$ (around 0.9 V$_{MSE}$, eq. 34) (Figure 1.22) [156]. At high concentrations of Mn$^{2+}$ ions in the solution (over 90 mM), the first sharp anodic peak (around 0.8 mV$_{MSE}$) represented facile oxidation of Mn$^{2+}$ to Mn$^{3+}$ (Figure 1.22) [156]. The decrease in the peak current density of second anodic peak was attributed to the slow electrochemical oxidation of MnOOH to MnO$_2$, leaving a combination of MnOOH and MnO$_2$ as the final deposited product on Pt substrate (Figure 1.22) [156]. Moreover, they have proposed that the decrease in current density after the first sharp peak may be due to formation of intermediates such as MnOOH on the electrode which inhibit further oxidation of Mn$^{2+}$ [156]. Nonetheless, the intermediate species may oxidize to MnO$_2$ at higher potentials, justifying the existence of second anodic peak (Figure 1.22) [156]. At low Mn$^{2+}$ concentrations (less than 90 mM), the two oxidation peaks seem to overlap, meaning similar Mn$^{2+}$/Mn$^{3+}$ oxidation rate to that of MnOOH/MnO$_2$ step (the rate determining step). This leads to high contents of MnO$_2$ in the final deposited layer (Figure 1.22) [156].
Figure 1.22 Cyclic voltammetry on platinum working electrode in 2 M H₂SO₄, with varying Mn²⁺ concentrations of 0.018 M to 0.73 M at 308 K and 1 mV s⁻¹ [156]. The potentials are reported vs. mercury-mercurous sulfate reference electrode (MSE). Reprinted with permission from [156].

Babakhani and Ivey further studied the significance of Mn²⁺ concentration as an electrodeposition factor on the morphology of anodically deposited manganese oxides (Figure 1.23) [155]. At extreme low manganese concentrations (3 to 5 mM for Mn²⁺ ions), discrete oxide clusters were reported to grow vertically on the substrate as thin sheets (Figure 1.23-A and B). Increasing the Mn²⁺ concentration to 10 mM leaded to free-standing MnOₓ rods with fibrous surfaces (Figure 1.23-C and D) [155]. Manganese ion concentrations of over 50 mM were shown to be unfavorable mainly due to the poor adhesion of deposited manganese oxides to the substrate [155]. Figure 1.24 shows schematically this morphological evolution of electrodeposited
manganese oxides from thin sheets to rod-like structure and continuous coating with increasing the Mn$^{2+}$ concentration, as studied by Babakhani and Ivey [155].

Figure 1.23 SEM plan-view and cross-sectional images of manganese oxide deposits synthesized from: A) 3 mM Mn(CH$_3$COO)$_2$ solution at 0.25 mA cm$^{-2}$, B) 5 mM, C) 7 mM, D) 10 mM, E) 20 mM and F) 30 mM Mn(CH$_3$COO)$_2$ solutions at 5 mA cm$^{-2}$. 10 min per each deposition. 373 K and pH of 7.5. Reprinted with permission from [155].
Figure 1.24 Schematic diagram showing the morphological evolution of electrodeposited manganese oxides (from left to right: thin sheets, rods, aggregated rods and non-uniform continuous coating) with increasing the Mn$^{2+}$ concentration during anodic electrodeposition process. Reprinted with permission from [155].

**Applied anodic potential and current density**

The applied anodic charge can also alter the crystallinity, surface morphology and coverage, pore density and more importantly, Mn valence of the electrodeposited materials during anodic electrodeposition of MnO$_x$ [147, 157-159]. Chang and Tsai showed that the XRD peak intensity of electrodeposited manganese oxides (at 2θ equals to 37.1° and 66.3°) increases marginally when the deposition potential decreases, signifying formation of higher crystallinity at lower applied potentials (Figure 1.25) [158]. The higher crystallinity is attributed to the slower rate of oxide deposition at low anodic potentials, allowing more time for the formation of highly aligned and uniform MnO$_x$ nanostructures [158]. SEM images of electrodeposited MnO$_x$ in Figure 1.25 clearly demonstrate the changes in their surface morphologies with applied potentials (Figure 1.26). While high density for small-sized pores in the microstructure of electrodeposited MnO$_x$ is observed at low anodic potentials, the low pore density at high potentials results in formation of uniform, compact and dense manganese oxide layer (Figure 1.26) [158]. Moreover, Chang and Tsai study revealed that based on the XPS analysis of the electrodeposited manganese oxides at various
applied anodic potentials, Mn$^{4+}$ is present at higher potentials above 0.65 V$_{SCE}$ whereas Mn$^{3+}$/Mn$^{4+}$ are formed in the deposit at lower deposition potential [158].

Figure 1.25 XRD patterns of MnO$_x$ electrodeposited at different anodic potentials (0.5 to 0.95 V$_{SCE}$) in 0.25 M manganese acetate solution at 298 K. Arrowed peaks (at $2\theta = 37.1^\circ$ and 66.3$^\circ$) correspond to the oxides formed on the carbon substrates. Potentials are versus saturated calomel reference electrode (SCE). Reprinted with permission from [158].
Figure 1.26 SEM micrographs showing the surface morphologies of manganese oxides electrodeposited at A) 0.5, B) 0.65, C) 0.8 and D) 0.95 V\textsubscript{SCE} characterized in Figure 1.25. Reprinted with permission from [158].

Deposition temperature

Temperature is another factor that can play a paramount role on the nucleation and growth rates as well as morphology of the final electrodeposited MnO\textsubscript{x} [155, 160]. Clark et al. studied the effect of temperature on anodic electrodeposition behavior of manganese dioxide in acidic electrolyte, showing the deposition rate is charge transfer controlled at low temperatures (295 to 333 K), i.e. plateau line presenting the dependence of limiting current density and rotation speed
in Levich plot, while the process is mass transfer limited at high temperatures (i.e. 343 to 363 K), as demonstrated by Levich plots in Figure 1.27 [86]. The significant mass transport limitations at high temperatures might seem contradictory given the diffusion rate of species in electrolyte enhances with increased temperature, however, this can be interpreted in terms of an increase in electrocatalytic activity of electrode at elevated temperatures forcing more demands on mass transport for effective charge transfer, Clark et al. argued [86].

![Levich plots](image)

Figure 1.27 Levich plots calculated from anodic electrodeposition of manganese dioxide in 0.1 M MnSO$_4$+5 M H$_2$SO$_4$ at different temperatures. Reprinted with permission from [86].
Babakhani et al. further investigated the effect of deposition temperature on anodically electrodeposited manganese oxides using SEM surface morphology analysis (Figure 1.28) [155]. They have shown that at room temperature, the nucleation rate for electrodeposition of MnO\(_x\) is low, resulting in discrete oxide particles with cracks while well-ordered rod-like structure (1-3 µm in diameter) and aggregated rods with fibrous feature can form at 333 K and 358 K, respectively (Figure 1.28) [155].

Figure 1.28 SEM plan-view and cross-sectional images of manganese oxides deposited from 10 mM Mn(CH\(_3\)COO)\(_2\) at 5 mA cm\(^{-2}\) for 10 min and pH of 7.5: A) 298 K, B) 333 K, C) 358 K. Reprinted with permission from [155].
**Surfactants**

Surfactants can significantly change the surface coverage and morphology of electrodeposited materials by mainly adsorbing to the solid/liquid interface, acting as a deposition template, reducing the interfacial energy and controlling the nucleation/growth of the particles which result in distinctive electrochemical activities for the deposited particles [150, 161-166]. Surfactants are amphiphilic organic compounds consisting of a hydrophilic head group attached to a long aliphatic hydrocarbon chain, generally classified into four main classes according to the charge of head group: 1) Non-ionic surfactant (absence of charge on the head group), 2) Anionic surfactant (with negatively charged head group), 3) Cationic surfactant (with positively charged head group) and 4) Zwitter-ionic surfactant (the head group has either a positive or negative charge depending on the pH of solution), as shown in Figure 1.29 [167-169]. The molecular structure of some commonly used ionic and non-ionic surfactants in electrodeposition processes are displayed in Figure 1.30 as an example.

![Surfactant classifications based on the charge of head group](image-url)

*Figure 1.29 Surfactant classifications based on the charge of head group. Reprinted with permission from [169].*
Surfactant-assisted electrodeposition methods have gained much attention lately as the methods of choice for synthesis of nanostructured manganese oxides with diverse morphologies and electrochemical properties for wide range of applications such as batteries and electrochemical capacitors [150, 161, 162, 170, 171].

Biswal et al. studied the effect of anionic surfactants on the morphology and electrochemical performance of anodically electrodeposited electrolytic manganese dioxide (γ-MnO₂ or EMD) [162]. They have reported that the addition of sodium dodecyl sulfate (SDS) at its optimum concentration (about 50 ppm) during electrodeposition of γ-MnO₂ significantly enhances its surface area (BET surface area of 130 m² g⁻¹ comparing to 100 m² g⁻¹ in the absence of SDS) and galvanostatic charge-discharge cycle life [162]. Moreover, they have shown a variety of morphologies for the different concentrations of SDS in the solution during anodic electrodeposition of manganese oxide from a porous structure with narrow needle-like particles (SDS: 10 ppm) to smaller narrow needle-like particles (within a size range of 50-100 nm) with...
high surface area (SDS: 50 ppm) and platy morphology with randomly oriented particles (net-like appearance) (SDS: 100 ppm) (Figure 1.31) [162].

Figure 1.31 FESEM images of the manganese oxide (EMD) samples in the presence of various concentrations of SDS (in ppm) as anionic surfactants. Reprinted with permission from [162].

Further studies by Dubal et al. explored the effects of t-octyl phenoxy polyethoxyethanol (Triton X-100) as non-ionic surfactant on the morphological property and electrochemical performance of anodically electrodeposited manganese dioxide [172]. The sample deposited in presence of Triton X-100 (1 wt% in the final deposition solution) showed more uniform and porous
morphology with smaller particles compared to the MnO$_2$ deposited without any surfactant, Dubal et al. argued (Figure 1.32) [172]. They have also reported enhanced supercapacitance of 278 F g$^{-1}$ (at 100 mV s$^{-1}$ and 298 K based on cyclic voltammetry tests in alkaline media) for the MnO$_2$ deposited in presence of Triton X-100, about 70 F g$^{-1}$ higher than the case without any surfactant [172].

![Figure 1.32 SEM images of MnO$_2$ thin film prepared in: A) Absence and B) presence of Triton X-100. Reprinted with permission from [172].](image)

Similar studies targeting the effect of cationic cetyltrimethylammonium bromide (CTAB) and non-ionic Triton X-100 surfactants on the morphology and electrochemical behavior of electrodeposited $\gamma$-MnO$_2$ revealed characteristic morphologies with enhanced activity in rechargeable alkaline batteries for these samples [161]. Better discharge performance and lower degradation rates were reported when optimum Triton X-100 concentration of 5.1 mM were employed to deposit manganese dioxide, leading to a morphology of small needle-like fibers roughly packed to each other with excellent orientation and high surface area (Figure
Moreover, CTAB at optimum concentration of 9 mM slightly promoted the charge/discharge cycle behavior of the deposited MnO$_2$, Ghaemi et al reported [161]. The morphology of these CTAB assisted electrodeposited MnO$_2$ showed rather rod-like crystals, smaller and more perpendicular to the electrode surface compared to Triton X-100 case (Figure 1.33).

![Figure 1.33 SEM images of electrodeposited manganese dioxide in presence of : a) 5.1 mM Triton X-100 and 9 mM CTAB. Reprinted with permission from [161].](image)

When the surfactant concentration reaches a certain level in the solution, known as the critical micelle concentration (CMC), they tend to aggregate to form micelles (Figure 1.34) [173-175]. The formation of micelles is governed by the molecular interactions such as the van der Waals and electrostatic forces, making different conformations for their arrangements [173, 175]. Some examples of these arrangements are: spherical, cylindrical, hexagonal, cubic and lamellar (bilayer) structures as demonstrated in Figure 1.35 [176]. At concentrations lower than CMC, surfactant molecules adsorb on the solid/liquid interface and effectively enhance the growth of deposits.
whereas at concentrations higher than CMC, its molecules tend to form aggregates, lowering the surfactant concentration at the interface and hence, compromising the effectiveness of surfactant on directing growth of deposited materials such as nano-sized MnO$_x$ [171, 177].

![Figure 1.34](image1.png)

**Figure 1.34** Surfactant aggregation to form micelle at critical micelle concentration (CMC). Reprinted with permission from [175].

![Figure 1.35](image2.png)

**Figure 1.35** Geometrical shapes of surfactant micelles in aqueous solutions. Reprinted with permission from [176].

Many factors such as temperature, pressure, pH, ionic strength and the properties of surfactant species like hydrophobic volume, chain length, head group area, etc., can affect the micellization [178]. Among them, temperature has shown substantial influence on CMC where their relationship largely depends on the surfactant systems [178-182]. For most non-ionic surfactants, it has been
reported that the CMC decreases with an increase in temperature mainly due to enhanced hydrophobicity coming from the destruction of hydrogen bonds between the hydrophilic head groups of surfactant and water molecules [178]. On the other hand, for ionic surfactants, the CMC shows a U-shaped dependence on temperature where CMC decreases to a min. point with increasing temperature and then keeps ascending with any further increase in temperature [178, 179, 182]. However, experimental results for some non-ionic surfactants showed similar U-type temperature dependence of CMC to ionic surfactants [181].

1.2.3 Perovskite-type oxides

Another important class of non-precious metal oxide electrocatalysts for oxygen cathodes is perovskites, with the general formula of ABO$_3$, (where A and B correspond to rare-earth metal and transition-metal ions, respectively) (Figure 1.36) [13, 183].

![Figure 1.36 Schematic representation of perovskite-type oxides with the general formula of ABO$_3$, where A sites includes rare-earth metal ions while B sites are transition-metal ions. Reprinted with permission from [184].](image)
These are catalysts of great diversity because of the wide range of ions and valences that the structure can accommodate [17, 185]. Different types of perovskites have been synthesized and reported to possess improved physical properties as well as good electrocatalytic activity for ORR and OER in alkaline electrolytes [59, 60, 184, 186]. Lee et al. revealed that La$_{0.6}$Ca$_{0.4}$CoO$_3$ prepared by the amorphous citrate precursor process, calcined at 923 K and then rapidly quenched, has a high surface area of 33 m$^2$ g$^{-1}$ [61]. They reported that 10 mg cm$^{-2}$ of this catalyst can provide a significant bifunctional performance, i.e. -280 mA cm$^{-2}$ for ORR and 300 mA cm$^{-2}$ for OER at 600 and 1600 mV$_{\text{RHE}}$ in 30 wt% KOH at 298 K, respectively, when the gas diffusion electrodes (GDEs) are exposed to pure oxygen [61]. In another study, Li et al. reported fast ORR kinetics for La$_{0.6}$Ca$_{0.4}$CoO$_3$-carbon composites with low Tafel slope of -60 mV dec$^{-1}$ and relatively high exchange current density of 5.8×10$^{-8}$ mA cm$^{-2}$ in O$_2$ saturated 6 M KOH [187]. Although 0.17 mg cm$^{-2}$ of this perovskite-type catalyst reveals good electrocatalytic activity toward OER in both O$_2$ and N$_2$ saturated 4 M KOH solutions at 1600 rpm, i.e. 10 mA cm$^{-2}$ at 1600 mV$_{\text{RHE}}$, it provides poor ORR electrocatalystic activity of 1-2 mA cm$^{-2}$ at 600 mV$_{\text{RHE}}$ comparing to γ-MnO$_2$ [90, 187]. Promising electrocatalytic activity for OER have been also reported for other types of perovskites such as Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ [63], LaNiO$_3$ [188, 189], LaCoO$_3$ [58, 190] and layered LaSr$_3$Fe$_3$O$_{10}$ [191] in alkaline media. Figure 1.37 summarizes the ORR and OER overpotentials as a function of e$_g$ electron occupancy on a variety of perovskite-type oxides in alkaline solutions. Even though perovskite-type oxides show high electrocatalytic activity for OER, their relatively low electrical conductivity (e.g. 1-10 S cm$^{-1}$ for LaCoO$_3$ [58] comparing to 1.7×10$^4$ S cm$^{-1}$ for IrO$_2$ [192] at 298 K) and surface area (e.g. 12.6 m$^2$ g$^{-1}$ for LaCoO$_3$ [58] comparing to 200 m$^2$ g$^{-1}$ for Vulcan XC-72 [193]), as well as poor electrocatalytic activity toward ORR, compared to other
non-precious compounds like MnO\textsubscript{x}, limit their use as bifunctional electrodes in concentrated alkaline solutions [4, 59, 60, 90, 184, 187, 194].

![Volcano-type graphs showing the comparison between the electrocatalytic activity of various perovskite-type oxides for: A) ORR and B) OER. Figures reveal the ORR/OER overpotentials at 50 μA cm\textsuperscript{-2} in alkaline media as a function of e\textsubscript{g} electron occupancy at 298 K. Reprinted with permission from [123].](image)

1.2.4 Fluorite-type oxides

Oxides with fluorite-related structure, such as Nd\textsubscript{3}IrO\textsubscript{7} with an orthorhombic structure (space group Cmcm) (Figure 1.38), were also investigated as bifunctional oxygen electrode catalyst in the literature [108, 195]. According to the author’s knowledge, the study by Kortenaar et al. was the only investigation available in the literature on exploring these potentially active oxygen catalysts in alkaline media. Tafel slopes and exchange current densities for OER of 25 mV dec\textsuperscript{-1} and 1.5×10\textsuperscript{15} μA cm\textsuperscript{-2}, respectively, and 63 mV dec\textsuperscript{-1} and 8.5 μA cm\textsuperscript{-2} for ORR, were reported in
45 wt% KOH [108]. The very low exchange current density for OER compared to ORR renders unlikely the practical possibility of using Nd$_3$IrO$_7$ or other IrO$_6$ or IrO$_7$-containing compounds as a lone bifunctional catalyst [108].

![Figure 1.38 Schematic representation of Nd$_3$IrO$_7$ with an orthorhombic crystal structure (space group $Cmcm$). Reprinted with permission from [195, 196].](image)

1.2.5 Carbon support for ORR/OER bifunctional catalysts

Non-precious group metals (non-PGMs) and their oxides are the alternative cost-effective solution for next-generation catalyst materials, showing similar, and in some cases, superior activity and long-term stability comparing to the noble metal catalysts [4-6, 17, 197]. While low
cost ($0.95 USD per kg for MnO₂ ††), ease of synthesis, high abundancy and environmental friendliness make these oxides favorable to be used as bifunctional oxygen catalysts, their inherent low electrical conductivity (10⁻⁵-10⁻⁶ S cm⁻¹ for MnO₂ [198]) is one of the major drawbacks toward their use for oxygen electrocatalysis [4, 5, 10, 39, 199]. To alleviate the low electrical conductivity of transition metal oxides and perovskites in ORR and OER applications, carbon-based materials are widely being used as catalyst supports [4, 5, 10, 17, 107, 122, 200]. Carbons provide favorable merits including low cost ($0.95 USD per kg for carbon black ‡‡), abundance, wettability, large active surface area (200 m² g⁻¹ for Vulcan XC-72 [193]), enhanced electrical conductivity (2.70×10⁻¹ S cm⁻¹ for Vulcan XC-72 [193]) and good stability in harsh concentrated acidic and alkaline media [17, 38]. It is believed that carbons with large meso-pores and thick crystalline walls provide more favorable properties such as high electrical conductivity and oxidation resistivity for ORR/OER applications [201].

However, carbonaceous materials alone are not the catalysts of choice to be used as ORR/OER bifunctional electrodes in aqueous solutions due to low electrocatalytic activity for both ORR and OER as well as durability issues mainly caused by carbon corrosion at the high anodic potentials [10, 17, 29, 137, 202-205]. Carbon structure modifications such as graphitization or hetero-atom (e.g. S, P and N) doping can boost the durability of carbon materials to enhance their role as either catalyst support or even ORR/OER bifunctional catalyst itself, mainly by increasing the defects and edge plan sites in graphitic matrix [10, 17, 203, 206-208]. Zhang et al. reported high ORR/OER electrocatalytic activity and durability for mesoporous carbon foams co-doped with N and P in

†† From Alibaba.com on September 8th, 2016. ‡‡ From Alibaba.com on September 8th, 2016.
alkaline media, showing similar ORR electrocatalytic activity to commercial Pt/C catalyst as well as lower OER onset potential (up to 1700 mV<sub>RHE</sub>) comparing to Ru/C [206]. Using DFT calculations, they revealed that the most active sites for ORR and OER are N-dopant sites near the graphene edges and N/P co-doped graphene edges, respectively [206].

Although Vulcan XC-72 is known as the most conventional ORR catalyst support, it has been rarely used as either catalyst or support for OER due to the aforementioned carbon corrosion issues at high anodic potentials [2, 4, 5, 10, 17, 90, 202, 203]. Nanostructured carbons such as carbon nanotubes, graphene and especially N-doped graphene, however, showed promising performances as effective support or highly electrocatalytically active catalysts for ORR and OER, reviving the hope of finding durable, cheap, abundant and noble-metal-free oxygen catalysts [10, 17, 209-214]. In a study by Chen et al., it has been shown that the addition of nitrogen doped carbon nanotubes (NCNT) as support for MnO<sub>2</sub> nanotubes could significantly boost both ORR and OER electrocatalytic activity of the catalyst, i.e. compare ORR overpotentials of -832 and -365 mV (at -2 mA cm<sup>-2</sup>) for MnO<sub>2</sub> and MnO<sub>2</sub>-NCNT, respectively, as well as OER overpotentials of 482 and 395 mV (at 2 mA cm<sup>-2</sup>) for MnO<sub>2</sub> and MnO<sub>2</sub>-NCNT, respectively [72]. They have also reported better durability for MnO<sub>2</sub>-NCNT in a homemade Zn-air battery [72].

1.3 Knowledge gap and research objectives

1.3.1 Knowledge gap

The knowledge gap in the literature can be summarized as follows:

1) Talking about an ideal bifunctional catalyst for both ORR and OER, it is important to look at the initial stage electrocatalytic activity and long-term stability of the oxygen catalysts as inter-connected properties rather than two distinct un-related ones. This approach is not the case for most of the studies in the literature on non-PGM oxides (such as manganese oxides,
perovskites and fluorite-type oxides and their combinations) as ORR/OER bifunctional catalysts in alkaline media. Often times, the focus of these studies is only on the initial activity, neglecting the long-term durability of these oxides during ORR and OER. Moreover, it seems that there is a lack of sufficient experimental data on the structural evolution of the aforementioned non-PGM oxides to propose and support degradation mechanisms explaining the ORR/OER performance loss of these catalysts in operation.

2) The roles of surface treatments and possible elemental doping on the ORR/OER electrocatalytic activity and durability of aforementioned non-PGM oxides are other topics that have not been intensively investigated in the literature.

3) The studies on the electrosynthesis of manganese oxides, with diverse morphologies and crystal structures, as ORR/OER bifunctional catalysts neglect the complex interactions between different electrodeposition operating factors, e.g. temperature, applied current, Mn concentration, surfactant type and concentration, etcetera. The interactions between these factors need to be investigated comprehensively and systematically using factorial design studies to give better predictions for the effects of these tangled factors on the final electrochemical performance of deposited materials.

1.3.2 Research objectives

The main goal of this study is to develop electrochemically active and durable MnO$_x$-based bifunctional catalysts for both ORR and OER in alkaline media, by first, incorporating active OER co-catalysts and second, microstructural and surface modifications of manganese oxides using surfactant-assisted electrodeposition methods as well as alkali-metal ion intercalation techniques. The objectives can be further detailed as follows:
1) A comprehensive study on the ORR/OER electrocatalytic activity and durability of commercial MnO₂/co-catalyst electrodes:
   a. To investigate the synergistic effects of synthesized active OER co-catalysts, e.g. LaCoO₃, LaNiO₃ and Nd₃IrO₇, when physically mixed with commercial MnO₂ for the oxygen electrocatalysis.
   c. To study the ORR/OER performances of individual and mixed-oxide catalysts using fundamental-study methods (flooded test setup) and commercial test protocols (flow-by Gas Diffusion Electrode (GDE) half-cell test setup).

2) A study on the effect of surface modifications on the ORR/OER electrocatalytic activity and durability of mixed oxides:
   a. To investigate the effect of alkali-metal ions on the ORR/OER performance of oxide catalysts.
   b. To develop time- and cost-effective alkali-metal ion intercalation methods for employing any beneficial effects provided by alkali-metal ion intercalation on the ORR and OER performance of oxide catalysts.

3) A systematic study on finding an electrochemically active nanostructured manganese oxide as a non-PGM binder-free ORR/OER bifunctional electrode, synthesized via anodic electrodeposition method on a pre-treated carbon cloth:
a. To investigate the main effects and important interaction effects of key operating factors, i.e. Mn$^{2+}$ concentration, applied potential, temperature, surfactant type and concentration, that significantly influence the electrosynthesis of manganese oxides on the catalyst response for ORR and OER using a two-level half-fraction factorial design.

4) An investigation on the carbonaceous materials as catalyst support/additive for mixed-oxide non-PGM oxygen catalysts or as lone ORR/OER bifunctional catalyst:

a. To study the electrochemical behavior of four carbonaceous materials, i.e. commercial Vulcan XC-72, commercial multi-walled carbon nanotubes (MWCNT), in-house made graphene and N-doped graphene, while catalyzing both ORR and OER or supporting highly active bifunctional non-PGM oxides, i.e. MnO$_2$-LaCoO$_3$.

b. To find a cost-effective, active and durable catalyst/support combination for oxygen cathodes in alkaline metal-air batteries, regenerative fuel cells and electrolyzers.
Chapter 2: Experimental methods, apparatus and materials

2.1 Material preparation

2.1.1 Catalyst powders

2.1.1.1 Perovskites

LaNiO$_3$ and LaCoO$_3$ were synthesized via a co-precipitation method [215]. The LaNiO$_3$ powder was made by preparing a solution of 0.2 M lanthanum (III) nitrate hexahydrate (Sigma-Aldrich) and 0.2 M nickel(II) nitrate hexahydrate (Sigma-Aldrich) and adding ammonium hydroxide 30% (Fisher Scientific) as a precipitating agent until the pH reached 9.25. The solution was then heated for 2 hrs at 343 K followed by a heating sequence of: 3 hrs at 383 K, 1 hr at 573 K and another 2 hrs at 973 K in air using a box furnace ($P_{\text{air}}$ equals to 1 atm). Afterwards, the sample was left to cool to room temperature in the furnace. The heating rate for all segments was set at 5 K min$^{-1}$. For LaCoO$_3$ synthesis, a similar procedure was carried out except that Ni(NO$_3$)$_2$·6 H$_2$O was replaced with cobalt(II) nitrate hexahydrate (Sigma-Aldrich).

2.1.1.2 Nd$_3$IrO$_7$

Nd$_3$IrO$_7$ was made by a direct solid-state synthesis method [195]. Neodymium (III) oxide (Sigma-Aldrich) and iridium metal (Alfa Aesar) powders were mixed with a molar ratio of 1:1 in a glass mortar. The mixture was then heated for 12 hrs at 1323 K in an oxygen atmosphere ($P_{\text{O}_2}$ equals to 1 atm) using a tube furnace and then left to cool down to room temperature in the furnace. Afterwards, the sample was grinded and heated again for 15 hrs at 1323 K under oxygen. The last step was cooling the sample in the furnace. The heating rate for all segments was kept at 5 K min$^{-1}$. To avoid pyrochlore-type compound formation, i.e. Nd$_2$Ir$_2$O$_7$, the excess oxygen from oxygen atmosphere was crucial during heat treatments [216].
2.1.1.3 Manganese dioxide

Manganese (IV) dioxide (reagent grade, ≥90%) was purchased from Sigma-Aldrich. This MnO₂ is structurally a γ-MnO₂, i.e. an intergrowth of pyrolusite (β-MnO₂) into a ramsdellite (α-MnO₂) matrix, and has higher ORR electrocatalytic activity in alkaline media compared to other commercially readily available MnO₂ samples [90].

2.1.1.4 Carbonaceous materials

The in-house-made graphene and N-doped graphene sheets were acquired from Gyenge’s lab at the University of British Columbia. They were made using electrochemical exfoliation of graphite, assisted by ionic liquids (ILs), extensively explained elsewhere [217]. Vulcan XC-72 was acquired from Cabot. MWCNT (>95%) was purchased from Sigma-Aldrich.

2.1.1.5 Platinum

50 wt% Pt on Graphitized Carbon was acquired from Tanaka Kikinzoku Kogyo K.K. in Japan. Pt powder (assay 98%) was also purchased from Alfa Aesar.

2.1.2 Catalyst layer preparation

To check the electrochemical performance of aforementioned carbonaceous materials (2.1.1.4) as support for MnO₂-LaCoO₃ (weight ratio of 1:1) or oxygen catalyst alone, a mixture of oxides (if present), carbonaceous material(s), isopropyl alcohol (IPA) and 5 wt% Nafion solution was sonicated for 1 hr. Next, a specified volume of the catalyst ink (5-15 µL) was drop-casted on a polished glassy carbon (GC) electrode to reach a loading of 0.5 mg cm⁻² for the carbonaceous material(s) or oxides, whichever was present, and left in air to dry for another hour.

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§§ Note that throughout the entire experimental work performed in this thesis, the carbonaceous materials labeled as support for a non-PGM catalyst were added to the catalyst ink prior to its deposition on a substrate.
at 293 K. The final weight ratio of MnO$_2$ (if present):LaCoO$_3$ (if present):carbon(s):Nafion in the catalyst layer was 1:1:1:0.6. In all cases where more than one carbonaceous material was used, either as the catalyst or support, the loading of each carbon component was kept at 0.5 mg cm$^{-2}$.

### 2.1.3 Gas diffusion electrode preparation

Catalyst inks were prepared by 1 hr sonication of a mixture composed of catalyst material(s) (i.e. Pt, MnO$_2$, LaCoO$_3$, LaNiO$_3$ and Nd$_3$IrO$_7$), carbon(s), IPA, water, 5 wt% Nafion solution and 60 wt% polytetrafluoroethylene (PTFE) suspension at 293 K. The carbon:isopropanol:water weight ratio was fixed at 1:50:16 in all catalyst inks based on previous studies aimed at finding the right catalyst ink composition for spraying using the CNC sprayer machine (Figure 2.1). The PTFE and dry Nafion content of the catalyst layer was the same for all samples, namely 0.3 mg cm$^{-2}$ each. The catalyst inks were then sprayed on a 4×4 cm (16 cm$^2$ geometric area) piece of 40 wt% PTFE treated carbon cloth from Fuel Cell Earth Co. using the CNC sprayer machine (Figure 2.1) to achieve main catalyst (i.e. MnO$_2$ or Pt) and co-catalyst (i.e. LaCoO$_3$, LaNiO$_3$ and Nd$_3$IrO$_7$, if present) loadings of 0.5 mg cm$^{-2}$ each.

For GDE half-cell experiments in a flow-by-test cell (Gaskatel Half Cell HZ-PP01), a PTFE treated carbon substrate supported on a Ni mesh (as current collector) from ZincNyx Energy Solution Inc. was employed to stand the vigorous GDE durability testing protocols during the course of 48 hrs at 323 K and P$_{\text{gas}}$ of 1 atm (either O$_2$ or purified air). In these cases, the final weight ratio of main catalyst (i.e. MnO$_2$ or Pt):co-catalyst (i.e. LaCoO$_3$, LaNiO$_3$ and Nd$_3$IrO$_7$, if present):Vulcan XC-72:Nafion:PTFE in the catalyst layer was 1:1:2:0.6:0.6. Catalyst ink preparation and spraying procedures were similar to the aforementioned steps. The final loadings of main catalysts, i.e. MnO$_2$ or Pt, were set at 2 and 0.5 mg cm$^{-2}$, respectively. Figure 2.2 shows
a representative image of the GDEs with catalyst inks sprayed on 40 wt% PTFE treated carbon cloth from Fuel Cell Earth Co. and ZincNyx’s PTFE treated carbon substrate.

Further specifications of the employed GDEs are described in each corresponding chapter.

Figure 2.1 CNC controlled sprayer machine with IWATA air brusher (50 ml capacity).
Figure 2.2 Gas diffusion electrodes consist of catalyst inks sprayed on: 1) 40 wt% PTFE treated carbon cloth from Fuel Cell Earth Co. and 2) PTFE treated carbon substrate supported on a Ni mesh (as current collector) from ZineNyx Energy Solution Inc.

2.1.4 Anodic electrodeposition of manganese oxides

Manganese oxides were electrodeposited onto a 6 mm in-diameter 40 wt% PTFE treated carbon cloth substrate (from Fuel Cell Earth Co.). The investigated electrodeposition factors and corresponding ranges are outlined in Table 2.1. Three different types of surfactants were used, i.e. Sodium dodecyl sulfate (SDS) as anionic, hexadecyl-trimethyl-ammonium bromide (CTAB, also known as cetrimonium bromide) as cationic and Triton X-100 as non-ionic surfactants. The critical micelle concentration (CMC) values of SDS, CTAB and Triton X-100 at 298 K are 7-10, 1-3 and
0.2-0.3 mM ***. The surfactant concentrations employed in this study, i.e. 5 or 10 vol%, were over the CMC in all cases. The electrolyte solution contained various concentrations of manganese (II) acetate tetrahydrate (Mn(CH$_3$COO)$_2$.4H$_2$O) and 0.1 M sodium sulphate (Na$_2$SO$_4$) solution. A half-fraction $2^n$ factorial design was constructed using the statistical software JMP 11. For a half-fraction factorial design of four factors (Table 2.1) with three center-points, the number of experimental runs required for each surfactant type was 11, compiling to a total of 33 random runs for the entire screening design experiments.

**Table 2.1 Experimental design factors and their levels for $2^{4-1+3}$ factorial design runs.**

<table>
<thead>
<tr>
<th>Factors (symbol, unit)*</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low (-)</td>
</tr>
<tr>
<td>Mn(CH$_3$COO)$_2$.4H$_2$O concentration (C, M)</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature (T, K)</td>
<td>295</td>
</tr>
<tr>
<td>Surfactant concentration (S, vol%)</td>
<td>0</td>
</tr>
<tr>
<td>Applied anodic potential (E, mV$_{MOE}$)</td>
<td>800</td>
</tr>
</tbody>
</table>

* $P_{air}$ is 1 atm.

Prior to the electrodeposition process, the carbon substrate was pre-treated using nitric acid to reduce the hydrophobicity of the carbon cloth and remove any remaining impurity as well as surface oxides on the carbon fiber surfaces. The 40 wt% PTFE treated carbon cloth was dipped in acetone for 5 min and then washed thoroughly with DI water. Next, the substrate was soaked in 1 M nitric acid at 333 K for 30 min. Afterwards, the samples were washed thoroughly with 18 mΩ DI water and left to dry overnight at 343 K in an oven.

*** All CMC values are obtained from Sigma-Aldrich website, the supplier of the three surfactants.
A conventional three-electrode electrochemical half-cell setup was used for the electrodeposition process (Figure 2.3). The working electrode was a punch-cut circular pre-treated carbon cloth piece with geometric surface area of 0.283 cm$^2$ in a quick-fit exchangeable sample holder from Radiometer Analytical (#A35T450), attached to a rotating disk electrode (RDE) setup (Figure 2.4). The reference and counter electrodes were Hg/HgO/20 wt% KOH (MOE) and platinized titanium plate, respectively. The electrodes were connected to a computer-controlled VoltaLab 80 potentiostat in its associated RDE setup (Figure 2.5). The anodic electrodeposition was performed under different conditions as outlined in Table 2.1 using a potentiostatic method at rotation speed of 400 rpm and $P_{\text{air}}$ of 1 atm for 30 minutes per each run. After the completion of electrodeposition process, the working electrode was washed thoroughly with DI water. In the case where a surfactant was used, the surfactant residue was removed by dipping the sample in IPA at 343 K for 15 minutes at 400 rpm. The catalyst-coated carbon cloth was then rinsed with DI water again.
Figure 2.3 Schematic diagram of three-electrode electrochemical half-cell setup used in this study.

Figure 2.4 Components of a quick-fit exchangeable sample holder (left) from radio Radiometer Analytical (#A35T450) with sample opening of 6 mm in diameter. The samples (right) were placed on a glassy carbon disk as a backing layer prior to be placed on the tip.
2.1.5 Surface modification: K⁺ intercalation

Two methods of K⁺ intercalation was investigated: open-circuit potential intercalation (OCP) and potential driven (electrophoretic) intercalation (PDI). In the open-circuit potential (OCP) method, each GDE was exposed to 6 M KOH solution for up to six days at 313 K under a rotation speed of 400 rpm. The samples were then thoroughly washed in 18 mΩ DI water for further electrochemical investigations. The same OCP method was also applied using LiOH, NaOH and CsOH to study comparatively the effect of exposure of the oxide catalysts to diverse alkali-metal ions.
In the potential driven intercalation (PDI) method, a constant cathodic current density of -5.4 mA cm\(^{-2}\) was applied for 30 min. to the electrodes under investigation in the RDE setup (at 400 rpm) in a 0.036 M K\(_2\)SO\(_4\) solution at 343 K. The cathodic current density was selected such that to provide the necessary potential gradient for K\(^+\) migration toward the cathode while avoiding excessive H\(_2\) gas evolution. A platinum plate was used as a counter electrode. Next, the samples were thoroughly washed in DI water before further electrochemical investigations. The PDI procedure was repeated up to seven times to investigate the cumulative effect of the treatment method on the bifunctional performance. Each repeated PDI treatment was carried out using fresh K\(_2\)SO\(_4\) solution.

### 2.2 Surface and structural characterization

The catalyst powders as well as GDEs were characterized by one or more of the following techniques: X-Ray Diffraction (XRD, D8 Advance Bruker diffractometer), X-ray Photoelectron Spectroscopy (XPS, Leybold Max 200 and Kratos AXIS Ultra), Energy Dispersive X-ray analysis (EDX, Hitachi S-2600N Variable Pressure Scanning Electron Microscope (VPSEM) equipped with an X-ray detector), Electron Energy Loss Spectroscopy (EELS, FEI Titan 80-300 LB equipped with a energy loss spectrometer Gatan 865 model), Field Emission Scanning Electron Microscopy (FESEM, Hitachi S-4700), Transmission Electron Microscope (TEM, FEI Tecnai G2 200kV), Fourier Transfer-Infrared spectroscopy with Attenuated Total Reflectance (FT-IR ATR, PerkinElmer Frontier) and Brunauer-Emmet-Teller analysis (BET, Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer). The operating conditions for XRD were as follows: generator set at 40 kV and 40 mA; Cu as X-ray source; wavelength of 1.54439 Å K\(_{α1}\); step size of 0.04˚ (2θ); step time of 230.4 s; range: between 5˚ to 90˚ for 2θ. The XPS source was monochromatic Al K\(_α\). The manganese oxidation state was determined from the multiplet splitting
of Mn 3s and the corresponding separation of peak energies at the XPS spectrum for the electrodeposited samples only. The EDX accelerating voltage was 10 kV. FT-IR analysis was used to confirm the efficiency of the surfactant removal technique on the catalyst-coated carbon clothes. The FT-IR ATR operating conditions were as follows: an aperture setting of 4 cm\(^{-1}\); wavenumber range of 4000-600 cm\(^{-1}\); 64 scans per sample at a scan speed of 2.5 kHz.

### 2.3 Electrochemical measurements

A conventional three-electrode RDE half-cell setup was used for the electrochemical analysis of the catalyst materials (Figure 2.6). Two different types of working electrodes were employed to test the electrocatalytic activity and durability of materials investigated here:

1. Catalyst ink drop-casted on a 5-mm-in-diameter polished GC.
2. A circular 8-mm-in-diameter punch-cut GDE fitted in a quick-fit exchangeable sample holder from Radiometer Analytical (#A35T450) with a geometric area of 0.283 cm\(^2\) exposed to the electrolyte.

The reference and counter electrodes were Hg/HgO/0.1 M KOH (MOE) from Radiometer Analytical (XR400) and platinum mesh, respectively. The electrodes were connected to a computer-controlled VoltaLab 80 potentiostat in its associated RDE setup (Figure 2.5). The potential of MOE reference electrode was measured to be 977 and 1037 mV vs. RHE in 6 and 11.7 M (45 wt\%) KOH solutions at 293 K, respectively, using the reversible hydrogen reference electrode (HydroFlex) from Gaskatel GmbH. All potentials are reported vs. RHE unless otherwise specified. All currents are normalized by the geometric surface area of the electrodes. All gas pressures specified in this study are absolute pressures. The equilibrium oxygen electrode potential in 6 and 11.7 M KOH solutions was calculated to be 1168 mV\(_{\text{RHE}}\) (191 mV\(_{\text{MOE}}\)) and 1153 mV\(_{\text{RHE}}\) (116 mV\(_{\text{MOE}}\)), respectively, at 293 K.
Figure 2.6 A Pine jacketed electrochemical cell connected to a water bath in the three-electrode RDE half-cell test setup used for electrochemical measurements in this study.

To study the electrode kinetics, rotating ring disc electrode (RRDE) measurements were performed by a Pine RRDE electrode (AFE6R1GCPK) with a GC disk (5.7 mm in diameter) and ring (6.4 mm inner and 7.8 mm outer diameter) using linear sweep voltammetry (LSV) tests in O₂ saturated 6 M KOH at 293 K and P_O₂ of 1 atm, starting with cathodic polarization from 1173 to 398 mV at 5 mV s⁻¹ and various rotation speeds (check Appendix A and Appendix B). The collection efficiency of the RRDE was 0.34 and the potential of the ring electrode was held at 1353 mV during the RRDE measurements.
To investigate the electrocatalytic activity and durability of the catalysts, cyclic voltammetry (CV) tests up to one hundred successive potential cycles were employed on catalyst materials, either deposited on GC or 40 wt% PTFE treated carbon cloth, in 6 M KOH between 373 and 1823 mV, starting with anodic polarization, using a flooded test setup at 5 mV s\(^{-1}\), 293 K, 400 rpm and \(P_{\text{gas}}\) of 1 atm (either O\(_2\) or N\(_2\)). In some cases, shorter potential range was adopted to avoid catalyst loss, specially for samples deposited on GC.

To further study the durability of the catalysts, galvanostatic polarization experiments (i.e. chronopotentiometry) were performed on GDEs as working electrodes in O\(_2\) saturated 6 M KOH at 293 K, 400 rpm and \(P_{\text{O}_2}\) of 1 atm by applying a constant current density (per geometric area) of 5 mA cm\(^{-2}\) for 2 hrs followed by -2 mA cm\(^{-2}\) for 30 min. The current densities were chosen to avoid mass transport limitations in the flooded electrode half-cell arrangement used in this study during galvanostatic longer-term experiments.

To test the ORR performance and stability of catalyst oxides developed here in commercial scenarios, a galvanostatic test protocol (i.e. chronopotentiometry) was employed in a flow-by test cell from Gaskatel GmbH (Half Cell HZ-PP01) as shown in Figure 2.7. Fresh GDEs composed of oxide containing catalyst layer on ZincNyx’s carbon substrate (see 2.1.3) were polarized at -100 mA (-34 mA cm\(^{-2}\)) for 24 hrs followed by -120 mA (-40 mA cm\(^{-2}\)) for another 24 hrs in 11.7 M (45 wt%) KOH at 323 K with air (CO\(_2\) removed) flowing through the gas chamber. In presence of pure oxygen, constant currents of -200 mA (-67 mA cm\(^{-2}\)) for 24 hrs followed by -300 mA (-100 mA cm\(^{-2}\)) for another 24 hrs were applied on the fresh electrodes with the same
conditions as air. The absolute gas pressure and flow rate were fixed at 1 atm and $1.51 \times 10^{-3}$ SLPM$^{\dagger \dagger \dagger}$.

Prior to the reported electrocatalytic performance tests, each electrode was subjected to a break-in polarization protocol composed of five potential cycles between 233 and 1683 mV at 5 mV s$^{-1}$ and 400 rpm, starting with anodic polarization. For GDEs in the Gaskatel flow-by cell, the potential cycle for break-in polarization protocol was started at 373 mV to 1173 mV. All cyclic and linear sweep voltammograms have been repeated for at least five times to ensure the reproducibility of the presented results. For the galvanostatic measurements in the flooded test setup, min. three replicates were produced for each catalyst. In the case of ORR galvanostatic polarizations for 48 hrs in the flow-by cell, min. two replicates were employed to calculate the standard error of the mean for each sample.

In an electrochemical cell under operating conditions, the movement of ionic species in the electrolyte can bring about a number of sectional potential drops between the working and reference electrodes. When current is flowing between the working and counter electrodes, the movement of anions and cations at unequal rates in opposing directions under the imposed electric field sets up a total ohmic potential drop (IR-drop) in the electrolyte, mainly due to electrode/electrolyte contact resistance, ionic resistance of the electrolyte and diffusion limitations at the porous frit tips of the Luggin-Haber capillary and the reference electrode [218, 219]. Here, all cyclic and linear sweep voltammograms as well as galvanostatic polarization results are IR-drop corrected using “Static Manual” ohmic drop compensation feature of the VoltaLab 80 potentiostat.

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$^{\dagger \dagger \dagger}$ Standard liter per minute (SLPM): Volumetric flow rate of a gas corrected to ”standardized” conditions of temperature and pressure, i.e. temperature of 273.15 K and an absolute pressure of 100 kPa.
Figure 2.7 Flow-by electrochemical test cell (HZ-PP01) and its components from Gaskatel GmbH used for ORR GDE tests: PTFE body, built-in platinum counter electrode, built-in Luggin-Haber capillary for the reference electrode.
Chapter 3: Comprehensive studies on the ORR/OER electrocatalytic activity and durability of individual (MnO$_2$, LaCoO$_3$, LaNiO$_3$ and Nd$_3$IrO$_7$) and mixed-oxide (MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$) catalysts

3.1 Introduction

Non-precious metal bifunctional oxygen reduction and oxygen evolution reactions catalysts are of great interest for rechargeable metal-air batteries and regenerative alkaline fuel cells. In this chapter, both the initial stage electrocatalytic activities and the catalytic durability of novel bifunctional catalysts composed of MnO$_2$ with perovskite (LaCoO$_3$ or LaNiO$_3$) or fluorite-type oxide (Nd$_3$IrO$_7$) as co-catalysts were studied. Gas diffusion electrodes (GDE) with a catalyst layer composed of MnO$_2$:co-catalyst (LaCoO$_3$, LaNiO$_3$ or Nd$_3$IrO$_7$);Vulcan XC-72 were prepared and studied in alkaline media using two different cell configurations, i.e. flooded and flow-by test setups. The catalyst powders were carefully characterized before the electrochemical tests.

The initial stage bifunctional activities of mixed-oxide catalysts, i.e. MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ are markedly superior compared to either MnO$_2$ or individual co-catalysts, demonstrating a synergistic effect. However, the activity degradation during extensive potential cycling is more severe for all mixed-oxide formulations than MnO$_2$ itself. MnO$_2$-LaNiO$_3$ revealed the best initial stage ORR/OER electrocatalytic activity whereas showing the worst long-

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‡‡‡ Parts of this chapter have been published and filed as United States and Canadian patent applications:

80
term ORR/OER performance during accelerated degradation testing of one hundred cycles in flooded test setup.

Long-term ORR galvanostatic polarization curves of fresh MnO$_2$ and mixed-oxide GDEs compared with commercial Pt and MnO$_x$ were obtained in a flow-by cell over the course of 24 hrs in 11.7 M KOH at 323 K and $P_{\text{gas}}$ of 1 atm with either air (CO$_2$ removed) or oxygen to resemble the commercial scenarios. MnO$_2$-Nd$_3$IrO$_7$ possessed the lowest ORR overpotentials with both air and oxygen flowing through the gas chamber, followed by MnO$_2$-LaCoO$_3$ as the second best, both outperforming the commercial Pt and MnO$_x$ GDEs. An insight on the structural changes of GDEs during these long-term ORR durability tests was given. Further in-depth structural studies on the investigated catalysts during both ORR and OER are given in the next chapters.

3.2 Results and discussions

3.2.1 Characterization of oxide catalysts

Figure 3.1 shows representative SEM images of the synthesized LaCoO$_3$, LaNiO$_3$, Nd$_3$IrO$_7$ and commercial MnO$_2$ powders used in the catalyst layer preparation. The Sigma-Aldrich MnO$_2$ powder clearly shows agglomerates of pillar and sphere-like particles (Figure 3.1-A). The size range of these agglomerates was found to be between 0.5 and 3 µm based on the SEM images (Figure 3.1-A). The synthesized perovskite powders, i.e. LaCoO$_3$ and LaNiO$_3$, have shown flaky and porous morphology with sharp edges (Figure 3.1-B and-C). Nd$_3$IrO$_7$, on the other hand, possesses particles with soft edges and round shapes comparing to perovskites’ morphology (Figure 3.1-D). All particles have shown great tendency to form agglomerates.
Figure 3.1 SEM images of A) Commercial Sigma-Aldrich MnO$_2$ powder (pillar and sphere-like particles are shown using dashed oval and circle shapes, respectively), B) Synthesized LaCoO$_3$ powder, C) Synthesized LaNiO$_3$ powder and D) Synthesized Nd$_3$IrO$_7$ powder. The black arrow in B and C points out the flakes in SEM morphology of studied oxides.

The structural analysis of synthesized LaCoO$_3$, LaNiO$_3$, Nd$_3$IrO$_7$ and commercial MnO$_2$ powders is presented in Figure 3.2 and Table 3.1, showing major peaks for the corresponding oxides. The diffraction pattern of Sigma-Aldrich MnO$_2$ reveals that it can be structurally characterized as $\gamma$-MnO$_2$, an intergrowth of pyrolusite in the ramsdellite matrix (Figure 3.2-A and Table 3.1) [39].
The EDX elemental analysis obtained from commercial and synthesized powders, previously shown in the SEM images of Figure 3.1, further confirms the existence of constituent elements for compounds reported by XRD results of each powder (Figure 3.2), i.e. Mn/O, La/Co/O, La/Ni/O and Nd/Ir/O for commercial manganese oxide, synthesized lanthanum cobalt oxide, lanthanum nickel oxide and neodymium iridium oxide, respectively (Figure 3.3). Due to the presence of other compounds and impurities in the synthesized powders, the atomic percentage of each element calculated from EDX results cannot be linked to the chemical formula found for major compounds in each powder via XRD analysis.
Figure 3.2 XRD spectra of: A) Commercial MnO₂, B) Synthesized LaCoO₃, C) Synthesized LaNiO₃ and D) Synthesized Nd₃IrO₇. (▲), (▼), (▌) and (♦) present major peaks corresponding to MnO₂, LaCoO₃, LaNiO₃ and Nd₃IrO₇, respectively.
Table 3.1 XRD structural analysis of: Commercial MnO₂, synthesized LaCoO₃, synthesized LaNiO₃ and synthesized Nd₃IrO₇. The XRD spectrum of the powders are presented in Figure 3.2. The bold 2θ and Miller indices show overlapped peaks for different crystallographic plans.

<table>
<thead>
<tr>
<th>Catalyst powder</th>
<th>2θ (hkl)</th>
<th>Crystal structure</th>
</tr>
</thead>
</table>
| MnO₂            | 1) 28.5° (110), 37.5° (101), 41° (200), 43° (111), 56.5° (211), 59.5° (220), 65° (002), 67.5° (310) and 72° (301) (marked as (*) in Figure 3.2-A)  
2) 33° (marked as ▶️) in Figure 3.2-A  
3) 37.5° (201), 43° (211) and 56.5° (221) | 1) Pyrolusite (β-MnO₂) phase with a tetragonal Bravais lattice system (a=b=4.3999 Å, c=2.8740 Å)  
2) Mn₂O₃  
3) Ramsdellite (α-MnO₂) |
| LaCoO₃          | 1) 23.3° (012), 33° (110), 33.5° (104), 40° (202), 47.5° (024) and 59° (214) (marked as (▼) in Figure 3.2-B) corresponding to (012), (110), (104), (202), (024) and (214)  
2) 15.6°, 27.3°, 28°, 39° and 48.5° (marked as (●) in Figure 3.2-B) | 1) LaCoO₃ with a rhombohedral Bravais lattice system (a=b=c=5.3778 Å, α=β=γ=60.798°)  
2) La(OH)₃ with a hexagonal Bravais lattice system (a=b=6.5286 Å, c=3.8588 Å, α=β=90°, γ=120°) |
| LaNiO₃          | 1) 23.5° (012), 33° (110), 47.5° (024) and 59° (214) (marked as (▌) in Figure 3.2-C)  
2) 15.6°, 27.3°, 28°, 39° and 48.5° (marked as (●) in Figure 3.2-C) | 1) LaNiO₃ with rhombohedral Bravais lattice system (a=b=5.4510 Å, c=6.5640 Å, α=β=90°, γ=120°)  
2) La(OH)₃ with a hexagonal Bravais lattice system (a=b=6.5286 Å, c=3.8588 Å, α=β=90°, γ=120°) |
| Nd₃IrO₇         | 1) 14.4° (110), 26.7° (021), 28.9° (220)/(202), 31.4° (221), 32.8° (400), 33.9° (022), 47.9° (422), 48.5° (004), 56.3° (620)/(602) and 57.6° (224)/(531) (marked as (♦) in Figure 3.2-D) | 1) Nd₃IrO₇ with an orthorhombic Bravais lattice system (a=10.8903 Å, b=7.4400 Å, c=7.4893 Å, α=β=γ=90°) |
Figure 3.3 EDX spectra of commercial and synthesized catalyst powders: A) MnO$_2$, B) LaCoO$_3$, C) LaNiO$_3$ and D) Nd$_3$IrO$_7$.

### 3.2.2 Initial stage electrocatalytic activity of oxide catalysts

Figure 3.4 presents the cyclic voltammograms of the investigated oxide electrodes recorded in N$_2$ saturated 6 M KOH. The upper potential limit in Figure 3.4 was selected such that to be lower than the oxygen equilibrium potential in order to reveal at this stage only the intrinsic responses of the oxides themselves and to avoid as much as possible interferences by dissolved oxygen. The reduction waves for MnO$_2$ and Nd$_3$IrO$_7$ reach their respective peak currents at 300 and 500 mV, respectively (Figure 3.4-A). The features of MnO$_2$ cyclic voltammograms and the
role of Mn$^{4+}$, Mn$^{3+}$ and Mn$^{2+}$ species, in the 2×2 e$^-$ ORR electrocatalysis was extensively discussed in section 1.2.2.2. For iridium oxide compounds with structures related to Nd$_3$IrO$_7$, similar voltammetry response to that shown by Figure 3.4-A at high pH was attributed to the Ir$^{5+}$/Ir$^{4+}$ couple [126]. The reduction onset potential for both MnO$_2$ and Nd$_3$IrO$_7$ is the same, about 750 mV. Compared to MnO$_2$ and Nd$_3$IrO$_7$, either oxidation or reduction waves associated with perovskites alone, i.e. LaCoO$_3$ and LaNiO$_3$, are virtually absent (Figure 3.4-A), corroborating previous reports of sluggish intrinsic electron transfer to or from LaCoO$_3$ and LaNiO$_3$ [123, 220].

For MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ (Figure 3.4-B), the reduction peak potential is observed at about 480 mV, which is characteristic mainly for Mn$^{4+}$/Mn$^{3+}$ reduction as opposed to Mn$^{3+}$/Mn$^{2+}$ reduction occurring at lower potentials (i.e. 300 mV in Figure 3.4-A). Furthermore, the reduction current densities for these two mixed oxides were larger than for each of the individual components, suggesting more extensive reduction in the catalyst layer (of mostly MnO$_2$ and Nd$_3$IrO$_7$ where applicable).

The MnO$_2$-LaNiO$_3$, however, shows a weak reduction wave starting at about 625 mV with no characteristic peak, mainly due to the scarce reduction of Mn$^{4+}$ to Mn$^{3+}$ and later Mn$^{2+}$ (Figure 3.4-B). The low reduction current densities of MnO$_2$-LaNiO$_3$ comparing to MnO$_2$ and the other two mixed-oxide formulations infer low reduction of its components, supposedly lower than MnO$_2$ alone too (Figure 3.4-A and B).
Figure 3.4 IR-corrected cyclic voltammograms of GDEs with MnO$_2$, LaCoO$_3$, LaNiO$_3$, Nd$_3$IrO$_7$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts. A) MnO$_2$, LaCoO$_3$, LaNiO$_3$ and Nd$_3$IrO$_7$, B) MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$. Electrolyte: N$_2$ saturated 6 M KOH at 293 K and P$_{N_2}$ of 1 atm. The oxide loadings were 0.5 mg cm$^{-2}$ each. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s$^{-1}$, respectively. Cycle number five is reported in all cases.
Figure 3.5 presents representative SEM micrographs of the mixed-oxide GDEs studied here with MnO$_2$:LaCoO$_3$:Vulcan:Nafion:PTFE (weight ratio of 1:1:1:0.6:0.6) as catalyst layer, sprayed on 40% PTFE treated carbon cloth. The SEM images reveal homogenized catalyst layer with an average thickness of about 25 µm, attached to carbon fibers as the substrates (Figure 3.5).

![SEM images of the GDE consisting of MnO$_2$:LaCoO$_3$:Vulcan XC-72:Nafion:PTFE (weight ratio of 1:1:1:0.6:0.6) sprayed on 40% PTFE treated carbon cloth.](image)

Figure 3.5 SEM images of the GDE consisting of MnO$_2$:LaCoO$_3$:Vulcan XC-72:Nafion:PTFE (weight ratio of 1:1:1:0.6:0.6) sprayed on 40% PTFE treated carbon cloth.
Next, the BET surface areas of catalyst layers investigated here are reported in Table 3.2. The oxide(s) and Vulcan XC-72 were physically mixed with a weight ratio of 1:1 or 1:1:1 (in case of mixed oxides) and sonicated for 1 hr in IPA. Each solution was then left in open air to dry over night before taking to the BET analyzer. The mixed oxide formulations have very similar BET surface areas between 53.7 and 55.1 m² g⁻¹.

With regard to Figure 3.4, it is noted that in a few reports, the electric double-layer portion of cyclic voltammograms for various oxides was used to estimate the electrochemically active surface area (ECSA) of these oxide catalysts [65, 131]. However, equating the total charged surface area obtained from electric double-layer capacitance measurements with the area of bifunctionally active sites for oxides with complex structures and involving various oxidation states with different activities, is unwarranted. In such cases, with respect to ECSA, the area obtained from electric capacitance measurements is hardly more accurate than the total BET area (Table 3.2). Hence, none of them are utilized here to represent the ECSA.

Table 3.2 BET surface area of single and mixed oxide catalyst layers.

<table>
<thead>
<tr>
<th>Catalyst layer (component weight ratios 1:1 or 1:1:1)</th>
<th>BET Surface Area (m² g⁻¹oxide)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂-Vulcan</td>
<td>84.6</td>
</tr>
<tr>
<td>LaCoO₃-Vulcan</td>
<td>107.5</td>
</tr>
<tr>
<td>LaNiO₃-Vulcan</td>
<td>106.7</td>
</tr>
<tr>
<td>Nd₃IrO₇-Vulcan</td>
<td>104.6</td>
</tr>
<tr>
<td>MnO₂-LaCoO₃-Vulcan</td>
<td>55.2</td>
</tr>
<tr>
<td>MnO₂-LaNiO₃-Vulcan</td>
<td>54.3</td>
</tr>
<tr>
<td>MnO₂-Nd₃IrO₇-Vulcan</td>
<td>53.7</td>
</tr>
</tbody>
</table>
The polarization curves for ORR and OER were recorded by potential scanning between 233 to 1683 mV in O\textsubscript{2} saturated 6 M KOH at 293 K and P\textsubscript{O\textsubscript{2}} of 1 atm, with a scan rate of 5 mV s\textsuperscript{-1}. The results, representative for the initial stage electrocatalytic activity, are presented as Tafel plots in Figure 3.6, whereas Table 3.3 summarizes the calculated apparent exchange current densities and Tafel slopes (check Appendix A for more details on the electrode kinetic theory). With respect to ORR, among the individual oxides, MnO\textsubscript{2} has the highest activity, followed by LaCoO\textsubscript{3}, LaNiO\textsubscript{3} and lastly Nd\textsubscript{3}IrO\textsubscript{7} (Figure 3.6-A). Considering for comparison an overpotential of -350 mV, the ORR current density on MnO\textsubscript{2} was 3, 9 and 20 times the ones on LaCoO\textsubscript{3}, LaNiO\textsubscript{3} and Nd\textsubscript{3}IrO\textsubscript{7}, respectively. Furthermore, the combination of MnO\textsubscript{2} with Nd\textsubscript{3}IrO\textsubscript{7} (in a 1:1 weight ratio) increased the apparent exchange current density compared with either of the individual oxides, i.e. by 1.25 times vs. MnO\textsubscript{2} alone and by over two-orders of magnitude vs. Nd\textsubscript{3}IrO\textsubscript{7} alone (Table 3.3). The Tafel slope of the mixed oxide MnO\textsubscript{2}-Nd\textsubscript{3}IrO\textsubscript{7} catalyst remained virtually the same as for MnO\textsubscript{2} alone. The synergistic effect between MnO\textsubscript{2} and Nd\textsubscript{3}IrO\textsubscript{7} impacting the apparent exchange current density, brought about the highest initial stage ORR current densities among the investigated catalysts followed by MnO\textsubscript{2}-LaNiO\textsubscript{3} for overpotentials greater than -500 mV (Figure 3.6-A). At overpotentials lower than -500 mV, the MnO\textsubscript{2}-LaCoO\textsubscript{3} combination prevailed due to lower Tafel slope, i.e. -84 mV dec\textsuperscript{-1} vs. -125 mV dec\textsuperscript{-1} for MnO\textsubscript{2}-Nd\textsubscript{3}IrO\textsubscript{7} (Figure 3.6-A).

In the OER part of the polarization curve, the Tafel lines and the associated kinetic parameters are potential dependent (Figure 3.6-B and Table 3.3), a phenomenon well-known in the literature and usually attributed to changes in the rate determining step [221-223]. At overpotentials lower than 360 mV, the apparent Tafel slopes were between 69 mV dec\textsuperscript{-1} (LaNiO\textsubscript{3}) and 115 mV dec\textsuperscript{-1} (MnO\textsubscript{2}), whereas above 360 mV the Tafel slopes varied between 103 mV dec\textsuperscript{-1} (MnO\textsubscript{2}-LaCoO\textsubscript{3}) and 201 mV dec\textsuperscript{-1} (Nd\textsubscript{3}IrO\textsubscript{7}). In the high overpotential region, abnormal Tafel slopes such as 147...
to 201 mV dec\(^{-1}\) in Figure 3.6-B, have been reported by others as well [224, 225], and it is due to hampered growth and detachment of O\(_2\) gas bubbles. In other words, at high overpotentials, there are many surface sites available for gas bubble nucleation but due to surface irregularities and other morphological features of the porous electrode causing entrapment, the bubble growth and break-off are inhibited, thereby, shielding the catalytic surface [226]. These effects are manifested as abnormally high apparent Tafel slopes in polarization experiments at high overpotentials.

Considering as basis for comparison an OER current density of 10 mA cm\(^{-2}\) as per the benchmarking study of McCrory et al. [131], the corresponding overpotentials on the mixed-oxide catalysts were 425, 440 and 501 mV on MnO\(_2\)-LaNiO\(_3\), MnO\(_2\)-LaCoO\(_3\) and MnO\(_2\)-Nd\(_3\)IrO\(_7\), respectively (Figure 3.6-B). The latter overpotentials, representative for the initial stage activities, are significantly lower than for any of the individual oxides investigated, demonstrating clearly a strong beneficial synergistic electrocatalytic effect between the two components. Table 3.3 reveals that in the low OER overpotential region, the combination of MnO\(_2\) with LaCoO\(_3\) decreased the Tafel slope to 69 mV dec\(^{-1}\) from 115 and 98 mV dec\(^{-1}\), respectively, whereas the combination of MnO\(_2\) with Nd\(_3\)IrO\(_7\) increased the exchange current density from 0.60 µA cm\(^{-2}\) for MnO\(_2\) to 0.79 µA cm\(^{-2}\) for MnO\(_2\)-Nd\(_3\)IrO\(_7\). However, MnO\(_2\)-LaNiO\(_3\) possesses the best OER electrocatalytic activity with an OER Tafel slope and exchange current density of 93 mV dec\(^{-1}\) and 0.43 µA cm\(^{-2}\), respectively, at overpotentials lower than 360 mV (Table 3.3).

The prevailing modern theoretical concept regarding the oxygen electrode mechanism is based on the scaling relationships, indicating that the binding energies of intermediates, such as HOO\(_{\text{ads}}\) and HO\(_{\text{ads}}\), are linearly correlated regardless of the binding site. Both species adsorb on the same sites on the oxide surface with a single bond between O and the surface [124]. This so-called universal scaling relationship, i.e. approximately constant difference of 3.2 eV between the binding
energy levels of $\text{HOO}_{\text{ads}}$ and $\text{HO}_{\text{ads}}$ for various catalyst surfaces, leads to minimum “theoretical overpotential” of about 370 mV for the ORR and the OER on a variety of defect free materials. The practical translation of these results for “designing” the oxide catalytic surfaces is complicated by the fact that the synthesized oxides, such as $\text{MnO}_2$, have a very complex crystallographic structure (ranging from $\alpha$ to $\varepsilon$), with the possibility of intertwined structures, numerous types of vacancies, disorders and lattice defects and changes in the oxidation states during battery cycling [39]. In spite of the virtual impossibility of considering all these effects in a first principles model, a comparison between theoretically calculated and experimentally measured initial stage ORR and OER current densities for $\alpha$-$\text{Mn}_2\text{O}_3$ showed promising fit, specially in the ORR region, whereas some deviations are noted in case of OER [121]. The $\text{MnO}_2$ used in the present work is of $\gamma$-type, which is a combination of $\alpha$ and $\beta$ structures, and it was previously shown to provide good ORR activity compared to other commercial sources of $\text{MnO}_2$ [90]. Theoretical studies suggest the need to break the scaling relationship between the $\text{HOO}_{\text{ads}}$ and $\text{HO}_{\text{ads}}$ binding energies in order to improve the bifunctional activity by favoring weaker $\text{HO}_{\text{ads}}$ binding. It is hypothesized that combining oxides with different structural features such as $\text{MnO}_2$ and perovskites or $\text{MnO}_2$ with fluorite-type structures, provides different binding sites and binding energies for $\text{HOO}_{\text{ads}}$ and $\text{HO}_{\text{ads}}$, that contribute to the observed synergistic electrocatalytic effect presented by Figure 3.6 and Table 3.3.
Figure 3.6 Initial stage IR-corrected bifunctional ORR/OER Tafel-lines of GDEs with MnO₂, LaCoO₃, LaNiO₃, Nd₃IrO₇, MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇ catalysts. A) ORR, B) OER. Electrolyte: O₂ saturated 6 M KOH at 293 K and P₀₂ of 1 atm. Electrode potential scanning between 233 to 1683 mV. The oxide loadings were 0.5 mg cm⁻² each. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s⁻¹, respectively. Cycle number five is reported in all cases. The numbers associated with each line represent the respective apparent Tafel slopes.
Table 3.3 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated GDEs with fresh catalysts. O₂ saturated 6 M KOH. 293 K. P₀₂ of 1 atm. The exchange current densities are expressed per geometric area. The standard error of the mean calculated based on six replicates is indicated for each catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( \text{b}_{\text{OER}} ) ((\eta&lt; 360 \text{ mV}) ) (mV dec(^{-1}))</th>
<th>( \text{i}_{0,\text{OER}} ) ((\eta&lt; 360 \text{ mV}) ) (µA cm(^{-2}))</th>
<th>( \text{b}_{\text{OER}} ) ((\eta&gt; 360 \text{ mV}) ) (mV dec(^{-1}))</th>
<th>( \text{i}_{0,\text{OER}} ) ((\eta&gt; 360 \text{ mV}) ) (µA cm(^{-2}))</th>
<th>( \text{b}_{\text{ORR}} ) (mV dec(^{-1}))</th>
<th>( \text{i}_{0,\text{ORR}} ) (µA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>115 ±2</td>
<td>0.63 ±0.01</td>
<td>187 ±4</td>
<td>9.0 ±0.2</td>
<td>-125 ±3</td>
<td>0.63 ±0.01</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>98 ±2</td>
<td>0.20 ±4×10(^{-3})</td>
<td>105 ±2</td>
<td>0.39 ±8×10(^{-3})</td>
<td>-126 ±3</td>
<td>0.20 ±4×10(^{-3})</td>
</tr>
<tr>
<td>LaNiO₃</td>
<td>69 ±1</td>
<td>1.5×10(^{-2}) ±3×10(^{-4})</td>
<td>147 ±3</td>
<td>9.4 ±0.2</td>
<td>-101 ±2</td>
<td>1.5×10(^{-2}) ±3×10(^{-4})</td>
</tr>
<tr>
<td>Nd₃IrO₇</td>
<td>70 ±1</td>
<td>2.5×10(^{-3}) ±0.05×10(^{-3})</td>
<td>201 ±4</td>
<td>5.0 ±0.1</td>
<td>-90 ±2</td>
<td>2.5×10(^{-3}) ±0.05×10(^{-3})</td>
</tr>
<tr>
<td>MnO₂-LaCoO₃</td>
<td>69 ±1</td>
<td>1.0×10(^{-2}) ±0.02×10(^{-2})</td>
<td>103 ±2</td>
<td>0.56 ±0.01</td>
<td>-84 ±2</td>
<td>1.0×10(^{-2}) ±0.02×10(^{-2})</td>
</tr>
<tr>
<td>MnO₂-LaNiO₃</td>
<td>93 ±2</td>
<td>0.43 ±9×10(^{-3})</td>
<td>129 ±3</td>
<td>5.2 ±0.1</td>
<td>117 ±2</td>
<td>0.43 ±9×10(^{-3})</td>
</tr>
<tr>
<td>MnO₂-Nd₃IrO₇</td>
<td>108 ±2</td>
<td>0.79 ±0.02</td>
<td>182 ±4</td>
<td>18 ±0.4</td>
<td>-125 ±3</td>
<td>0.79 ±0.02</td>
</tr>
</tbody>
</table>
3.2.3 Accelerated degradation testing of oxide catalysts in flooded test setup

Long-term durability investigations are of outmost importance for practical applicability of electrocatalysts. Unfortunately, many studies dealing with non-precious metal ORR or OER catalysts in alkaline media have focused only on the initial stage activities of fresh electrodes.

The electrocatalytic long-term durability performances of MnO$_2$ (as baseline) and mixed-oxide GDEs were investigated by performing one hundred continuous potential cycles between 633 and 1633 mV in O$_2$ saturated 6 M KOH at 293 K and P$_O$, of 1 atm, using a flooded test setup. Figure 3.7 presents the ORR and OER polarization curves of the investigated GDEs at cycle one and one hundred, after continuous potential cycling.

Extensive cycling for one hundred continuous cycles caused significant drop in the ORR and OER electrocatalytic activities of all mixed-oxide catalysts (Figure 3.7). While the addition of perovskites and fluorite-type oxides to MnO$_2$ enhances significantly both the ORR and OER initial stage electrocatalytic activities (as confirmed by Tafel plots in Figure 3.6), the activity degradation during one hundred cycles of accelerated degradation test is more severe than MnO$_2$ alone for all mixed-oxide formulations. MnO$_2$-LaNiO$_3$ revealed the best initial stage ORR/OER electrocatalytic activity whereas showing the worst long-term ORR/OER performance during accelerated degradation testing of one hundred cycles in the flooded test setup (Figure 3.6 and Figure 3.7).

While it can be inferred that the perovskite and fluorite-type oxides as co-catalysts are most likely responsible for the degradation of the ORR/OER electrocatalytic activity of mixed-oxide catalysts during potential cycling, an insight on the factors involving this complex degradation phenomenon is given in section 6.2.5 following further in-depth structural and electrochemical studies in the next chapters.
Figure 3.7 Electrocatalytic durability testing of GDEs with MnO$_2$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts: A) ORR at cycle one, B) OER at cycle one, C) ORR at cycle one hundred, D) OER at cycle one hundred. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1633 mV for one hundred cycles (accelerated degradation testing) in O$_2$ saturated 6 M KOH at 293 K and P$_O_2$ of 1 atm. Other conditions idem to Figure 3.6.

3.2.4 Long-term ORR durability of oxide catalysts in a flow-by test setup

Figure 3.8 shows the long-term ORR galvanostatic polarization curves of fresh GDEs over the course of 24 hrs in 11.7 M (45 wt%) KOH at 323 K with either air (CO$_2$ removed) or oxygen flowing through the gas chamber of the Gaskatel flow-by cell. The GDE consisting of Pt powder from Alfa Aesar sprayed on Zincnyx’s PTFE treated carbon substrate was used to compare the
performances of investigated catalysts to a commercial PGM catalyst norm. A MnO$_x$ GDE from Gaskatel was also used to compare the results to a non-PGM commercial electrode currently being used for industrial ORR applications. The first 24 hrs of applying low current densities in each case (i.e. -33 mA cm$^{-2}$ in air or -67 mA cm$^{-2}$ in oxygen) were adopted as a break-in protocol for the fresh GDEs (see section 2.3 and Appendix C ). With air as feed gas at -40 mA cm$^{-2}$, MnO$_2$-Nd$_3$IrO$_7$ catalyst possessed the lowest average ORR overpotential of about -290 mV with a potential loss of -29 mV during 24 hrs of testing (Figure 3.8-A). MnO$_2$-perovskite mixed oxides showed the next lowest ORR overpotentials, closely tailing the MnO$_2$-Nd$_3$IrO$_7$ sample (Figure 3.8-A). With an average ORR overpotential and potential loss of -370 and -30 mV, respectively, for the in-house MnO$_2$ sample, the synergistic effect of oxide co-catalysts on the ORR performance of MnO$_2$ catalyst layer can be further confirmed at high cathodic current densities in an unflooded test setup (Figure 3.8-A). As mentioned in section 3.2.2, this synergistic effect could be as a result of breaking away from the universal scaling relationship between the HOO$_{(ads)}$ and HO$_{(ads)}$ binding energies with new binding sites available through the mixed-oxide catalysts. In terms of stability, however, it seems that perovskite-type oxides (specially LaNiO$_3$) better enhance the long-term durability of MnO$_2$ catalyst layer compared to Nd$_3$IrO$_7$ (Figure 3.8-A). Comparing the ORR performances of the in-house MnO$_2$ with commercial PGM and non-PGM GDEs, Gaskatel MnO$_x$ and Pt samples showed more negative overpotentials (about -10 mV and -40 to -50 mV, respectively) comparing to the in-house MnO$_2$ GDE during the course of 24 hrs (Figure 3.8-A). The overall potential losses of commercial Pt and MnO$_x$ GDEs were found to be similar to the in-house MnO$_2$ sample, i.e. about -30 mV (Figure 3.8-A).

In the case of pure oxygen as feed gas, severe potential losses were observed during the one-day-long ORR durability tests except for MnO$_2$-Nd$_3$IrO$_7$ sample (Figure 3.8-B). With an average
ORR overpotential of -248 mV and potential loss of -15 mV during 24 hrs of testing, MnO$_2$-Nd$_3$IrO$_7$ is the best performing GDE at -100 mA cm$^{-2}$ with oxygen feed, about 110 mV more positive than the commercial Pt after 23 hrs of testing (Figure 3.8-B). Contrary to the air feed case, the MnO$_2$-LaNiO$_3$ showed the highest ORR overpotentials as well as most drastic potential loss during 24 hrs of testing (Figure 3.8-B). Looking at the galvanostatic polarization curves in presence of oxygen, a considerable synergistic effect specially after 9 hrs of testing is observed for MnO$_2$-Nd$_3$IrO$_7$ and MnO$_2$-LaCoO$_3$ samples, showing more positive ORR overpotentials compared to the in-house MnO$_2$ GDE (Figure 3.8-B). Moreover, both commercial GDEs were unable to tolerate 24 hrs of durability tests with Gaskatel MnO$_x$ failing after 10 min. into the test while Pt sample failed after 23 hrs of testing (Figure 3.8-B). This could be related to the loss of active materials or the blockage in GDE pores, which are necessary for gas supply, during the previous testing conditions, i.e. break-in protocols.

Comparing the results in air and oxygen, the trend in ORR electrocatalytic activity of samples is quite the same except for MnO$_2$-LaNiO$_3$ and commercial MnO$_x$ which could not tolerate high current density of -100 mA cm$^{-2}$ (Figure 3.8-A and B). Looking at the stability performances of MnO$_2$-based GDEs in both air and oxygen cases, it can be inferred that the decay in ORR electrocatalytic activity of mixed-oxide catalysts is mainly due to MnO$_2$ degradation since performance losses for mixed oxides happen at about the same time MnO$_2$ GDE starts to degrade, i.e. after 3 and 7 hrs of testing for air and oxygen tests, respectively (Figure 3.8-A and B). This can be backed by the literature studies which found less active Mn species, such as Mn(OH)$_2$ and Mn$_3$O$_4$, toward ORR on cathodically polarized MnO$_2$ catalysts for prolonged times, as further explained in section 1.2.2.2 [4, 5, 39, 45, 46, 67, 90, 98, 113, 227].
To further study the role of MnO$_2$ in ORR performance loss of mixed-oxide catalysts, XRD characterization has been performed on MnO$_2$ catalyst layer at two stages: 1) Fresh and 2) After 48 hrs of galvanostatic polarization tests (including the break-in protocol) (Figure 3.9). Due to the high contents of PTFE in both catalyst layer and carbon substrate leading to low signal-to-noise ratio, it is extremely hard to detect any small structural changes in the XRD spectrum of the investigated mixed-oxide catalyst during the long-term durability tests. Some even argue that other characterization methods such as EELS are more effective for Mn valence determination when it comes to complex catalyst layers with more than one component [228, 229]. Hence, the in-house made MnO$_2$ GDE was chosen to avoid further complexity by other co-catalysts during the experiments. Section 4.2.1.2 will touch more on the EELS characterization method for the catalyst layer degradation of MnO$_2$-based mixed oxides during ORR/OER accelerated degradation tests.

Regarding the fresh MnO$_2$ electrode, the peaks at $2\theta = 18^\circ$, $28.5^\circ$, $41^\circ$, $59.5^\circ$, $65^\circ$, $67.5^\circ$ and $72^\circ$ correspond to PTFE, $\beta$-MnO$_2$ (110), $\beta$-MnO$_2$ (200), $\beta$-MnO$_2$ (220), $\beta$-MnO$_2$ (002), $\beta$-MnO$_2$ (310) and $\beta$-MnO$_2$ (301), respectively (Figure 3.9). The broad peak at $25^\circ$ is mainly due to an overlap of peaks corresponding to $\alpha$-MnO$_2$ (110) and graphite (Vulcan XC-72) (100). Other peaks around $37.5^\circ$, $43^\circ$ and $56.5^\circ$ represent both $\beta$-MnO$_2$ (101)/$\alpha$-MnO$_2$ (201), $\beta$-MnO$_2$ (111)/$\alpha$-MnO$_2$ (211) and $\beta$-MnO$_2$ (211)/$\alpha$-MnO$_2$ (221), respectively. After 48 hrs of galvanostatic durability testing, five new and relatively small peaks appear at $2\theta = 17.6^\circ$, $26.4^\circ$, $30.4^\circ$, $36.2^\circ$ and $60.6^\circ$ corresponding to MnOOH (010), MnOOH (111), Mn$_3$O$_4$ (112), Mn(OH)$_2$ (311) and MnOOH (-123)/Mn$_3$O$_4$ (215). Hence, the XRD results further confirm the gradual reduction of MnO$_2$ to Mn$^{3+}$/Mn$^{2+}$ species, attributing the ORR performance loss of mixed-oxide catalysts to formation of less active Mn species toward ORR during long-term galvanostatic measurements at cathodic currents.
The results here are contrary to the findings from the flooded experiments where the degradation of co-catalyst materials, i.e. perovskite and fluorite-type oxides, was likely the reason behind the performance loss of mixed-oxide GDEs for oxygen electrocatalysis during accelerated degradation tests (section 3.2.3). However, it should be noted that the test protocols and applied currents are totally different in each case, enabling different phenomena which can significantly affect the durability behavior of studied catalysts. In the flooded test setup, the GDEs were polarized between both ORR and OER regions where other phenomena such as MnO\(_2\) electro-corrosion, carbon corrosion and even Mn valence evolution at high anodic currents can influence the overall performance of mixed-oxide catalysts [48, 141, 203-205, 230]. In the unflooded experiments (flow-by cell), however, the currents were applied cathodically enabling ORR and MnO\(_2\) reduction/dissolution reactions only (eqs. 5 to 19).
Figure 3.8 Long-term ORR durability testing of fresh GDEs containing Pt, MnO₂, MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇ catalysts compared with commercial MnOₓ GDE from Gaskatel GmbH: A) With air at -40 mA cm⁻² and B) With oxygen at -100 mA cm⁻². IR-corrected galvanostatic polarization curves obtained in 11.7 M (45 wt%) KOH at 323 K for 24 hrs with either air (CO₂ removed) or oxygen flowing through the gas chamber of a flow-by cell from Gaskatel GmbH after 24 hrs of break-in protocol explained in section 2.3 and Appendix C. The absolute gas pressure and flow rate were fixed at 1 atm and 1.51×10⁻³ SLPM. The catalyst(s) loadings were 2 mg cm⁻² each (except for Pt with 0.5 mg cm⁻²) with final weight ratio of 1:1:2:0.6:0.6 for MnO₂ or Pt:co-catalyst (if present):Vulcan XC-72:Nafion:PTFE in the catalyst layer. The catalyst loading for the commercial MnOₓ from Gaskatel was 20 mg cm⁻². The standard error of the mean calculated based on min. two replicates is indicated for each data point.
Figure 3.9 Comparison between the XRD spectrum of the MnO$_2$ catalyst: 1) Fresh electrode (black dotted line) and 2) After 48 hrs of galvanostatic tests (24 hrs at -67 mA cm$^{-2}$ followed by 24 hrs at -100 mA cm$^{-2}$) with O$_2$ as feed gas in an unflooded flow-by test setup.

In the next chapters, further discussions are made on the complex degradation phenomena of mixed-oxide catalysts using in-depth structural analysis coupled with electrochemical studies.

### 3.3 Conclusion

The electrocatalytic activities for ORR and OER on individual and mixed-oxide catalysts, i.e. MnO$_2$, LaCoO$_3$, LaNiO$_3$, Nd$_3$IrO$_7$ and their combinations, were studied. A positive synergistic electrode kinetic effect between the oxide components was found as shown by either a decrease in the apparent Tafel slope or an increase in the apparent exchange current density for the mixed-oxide formulations compared to the respective individual oxide catalysts. The mechanism for the
mixed oxides’ synergistic electrocatalytic effect could be rationalized in terms of the linear scaling relationship between HOO$_{\text{(ads)}}$ and HO$_{\text{(ads)}}$ binding energies. The structurally diverse oxide combinations provide different binding energies for the key intermediates, thus, “breaking” away from the linear scaling relationship. However, further studies, both theoretical and experimental, are required to validate the proposed hypothesis.

Furthermore, the bifunctional durability of catalysts was investigated by carrying out one hundred potential cycles between 633 and 1683 mV in a flooded test setup. The degradations in electrocatalytic activity of all mixed-oxide catalysts were found to be higher than MnO$_2$ alone. MnO$_2$-LaNiO$_3$ revealed the best initial stage ORR/OER electrocatalytic activity whereas showing the worst long-term ORR/OER performance during accelerated degradation testing of one hundred cycles in the flooded test setup. The perovskite and fluorite-type oxides as co-catalysts are likely to be one of the reasons behind the degradation in the ORR/OER electrocatalytic activity of mixed-oxide catalysts. However, further in-depth structural and electrochemical studies are needed to investigate this complex phenomenon.

The ORR long-term performances of fresh MnO$_2$ and mixed-oxide GDEs in commercial scenarios were tested using twenty-four-hour-long galvanostatic polarizations in 11.7 M KOH at 323 K and $P_{\text{gas}}$ of 1 atm with either air or oxygen flowing through a flow-by test cell. MnO$_2$-Nd$_3$IrO$_7$ revealed the highest ORR activity and good stability followed by MnO$_2$-LaCoO$_3$ as the second best, both outperforming the commercial Pt and MnO$_x$ GDEs with up to 100 mV (air) and 150 mV (oxygen) more positive ORR overpotentials during 24 hrs of galvanostatic testing. The structural analysis on the MnO$_2$-based GDEs during ORR galvanostatic polarization tests showed that the gradual transformation of MnO$_2$ to less active forms of manganese species (i.e.
Mn$^{3+}$/Mn$^{2+}$) during ORR could attribute to the ORR performance degradation of the mixed-oxide catalysts.
Chapter 4: Oxide catalyst activation by alkali-metal ion intercalation

4.1 Introduction

The present chapter discusses the effect of alkali-metal ions (Li\(^+\), Na\(^+\), K\(^+\) and Cs\(^+\)), specially potassium ions, on the electrocatalytic activity and durability of oxide catalysts, i.e. MnO\(_2\), LaCoO\(_3\), Nd\(_3\)IrO\(_7\), MnO\(_2\)-LaCoO\(_3\) and MnO\(_2\)-Nd\(_3\)IrO\(_7\), for ORR and OER with wide range of in-depth structural and electrochemical characterizations.

The degradation of bifunctional electrocatalytic activity for the mixed-oxide catalysts, i.e. MnO\(_2\) with either perovskites or fluorite-type oxides, during extensive potential cycling is shown to be fully restored by long-term exposure to 6 M KOH at open-circuit. Insertion of potassium ion in the oxide structure either by longer-term exposure to 6 M KOH or by an accelerated potential driven intercalation method, has been found to be effective in enhancing the ORR and OER electrocatalytic activity of the investigated oxide catalysts. In addition, the stability of the potassium ion activated catalysts is reported to be improved. The electrode kinetic results presented here are supported by extensive surface analysis.

Lastly, a thorough comparison of the results obtained in the present work with those reported in the literature for a variety of bifunctional catalysts is shown, demonstrating the effectiveness of

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\(\text{§§§ Parts of this chapter have been published and filed as United States and Canadian patent applications:} \)
potassium activation methods on enhancing the ORR and OER electrocatalytic activity of both individual and mixed-oxide catalysts.

4.2 Results and Discussion

4.2.1 Oxide catalyst layer activation by open-circuit potential (OCP) K+ intercalation

4.2.1.1 Healing effect

After the oxide GDEs, i.e. MnO$_2$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$, were subjected to one hundred potential cycles in a flooded test setup, the effect of GDE rest-time in 6 M KOH at open-circuit potential on the recovery of the ORR and OER electrocatalytic activities was investigated (Figure 4.1 and Figure 4.2). For all degraded samples, improvements in the bifunctional electrocatalytic activities can be observed already after 6 hrs of exposure to 6 M KOH at open-circuit. Moreover, a rest time of six days produced remarkable enhancements in the electrocatalytic activities of the degraded GDEs for both ORR and OER, exceeding even the initial performance of the fresh samples (compare Figure 3.7, Figure 4.1 and Figure 4.2). For MnO$_2$ alone, the ORR current density of fresh GDE (at 680 mV) started at -3 mA cm$^{-2}$, decreasing to -0.9 mA cm$^{-2}$ after one hundred cycles of accelerated degradation tests followed by a significant enhancement to -6 mA cm$^{-2}$ after six-day rest in 6 M KOH (Figure 3.7 and Figure 4.1-A). In the OER region, the current density of fresh MnO$_2$ catalyst at 1600 mV dropped from 1.7 to 1 mA cm$^{-2}$ after extensive potential cycling between ORR and OER regions, reaching 31 mA cm$^{-2}$ after being rested for six days in 6 M KOH at 293 K (Figure 3.7 and Figure 4.1-B). The degraded MnO$_2$-Nd$_3$IrO$_7$ revealed highest ORR performance after the six-day-long rest in 6 M KOH, i.e. possessing about 10 times the ORR current density (at 680 mV) of the degraded sample prior to the treatment (Figure 3.7 and Figure 4.2-C), with MnO$_2$-LaCoO$_3$ showing the biggest enhancement in its ORR performance after the treatment, i.e. possessing 13 times the ORR current density (at 680 mV) of
the degraded sample prior to the treatment (Figure 3.7 and Figure 4.1-C). With regards to OER, the degraded MnO$_2$-LaCoO$_3$ catalyst possessed the highest OER current density of 61 mA cm$^{-2}$ at 1600 mV after six-day-long rest in 6 M KOH, about 67 times that of the degraded sample right after the accelerated degradation test (Figure 3.7 and Figure 4.1-D).
Figure 4.1 The effect of rest-time at open-circuit potential in 6 M KOH at 293 K following accelerated degradation testing in the flooded test setup (i.e. one hundred potential cycles between 633 to 1633 mV in O₂ saturated 6 M KOH at 293 K and Pₐ of 1 atm): A) ORR polarization curve for MnO₂, B) OER polarization curve for MnO₂, C) ORR polarization curve for MnO₂-LaCoO₃ and D) OER polarization curve for MnO₂-LaCoO₃. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1683 mV in O₂ saturated 6 M KOH at 400 rpm, 293 K and Pₒ of 1 atm. Other conditions idem to Figure 3.6.
Figure 4.2 The effect of rest-time at open-circuit potential in 6 M KOH at 293 K following accelerated degradation testing in the flooded test setup (i.e. one hundred potential cycles between 633 to 1633 mV in O₂ saturated 6 M KOH at 293 K and P₀₂ of 1 atm): A) ORR polarization curve for MnO₂-LaNiO₃, B) OER polarization curve for MnO₂-LaNiO₃, C) ORR polarization curve for MnO₂-Nd₃IrO₇ and D) OER polarization curve for MnO₂-Nd₃IrO₇. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1683 mV in O₂ saturated 6 M KOH at 400 rpm, 293 K and P₀₂ of 1 atm. Other conditions idem to Figure 3.6.
Due to the high sensitivity of MnO$_2$-LaCoO$_3$ sample to the OCP activation method discussed here, this mixed-oxide catalyst has been chosen for further in-depth studies to unveil the mechanism behind the remarkable bifunctional activity recovery after the exposure to 6 M KOH at open-circuit. A preliminary structural investigation using XRD and XPS analysis is presented aiming at identifying possible structural changes in the catalyst during extensive potential cycling followed by the six-day-long treatment. Figure 4.3 shows the XRD spectra of MnO$_2$-LaCoO$_3$ GDEs in both initial stage and after being cycled for one hundred cycles (accelerated degradation testing) and rested for six days at open-circuit in 6 M KOH, i.e. black dotted and red solid lines, respectively.

In case of the fresh GDE, the peaks at $2\theta = 18^\circ$, 28.5°, 31.5°, 37.5°, 48.5°, 56.5°, 67.5°, 68.5° and 72° correspond to the PTFE, β-MnO$_2$ (110), LaCoO$_3$ (110), β-MnO$_2$ (101)/α-MnO$_2$ (201), La(OH)$_3$, β-MnO$_2$ (211)/α-MnO$_2$ (221), β-MnO$_2$ (310), α-MnO$_2$ (601) and β-MnO$_2$ (301)/(112), respectively. The major broad peak at $2\theta = 25^\circ$ is mainly due to an overlap of peaks corresponding to LaCoO$_3$ (012), α-MnO$_2$ (110) and graphite (Vulcan XC-72) (100). Moreover, the minor peak at $2\theta = 41^\circ$ represents both LaCoO$_3$ (202)/(006) and β-MnO$_2$ (200).

With regards to the MnO$_2$-LaCoO$_3$ catalyst layer after being cycled for one hundred cycles and rested for six days at open-circuit in 6 M KOH, six new peaks appear at $2\theta = 16.5^\circ$, 24°, 29.5°, 33.5°, 43.5° and 60.5° (labeled as “**” in Figure 4.3) which correspond to MnOOH (010), LaCoO$_3$ (012), Mn$_3$O$_4$ (112), MnOOH (020), MnOOH (410) and both MnOOH (-123)/Mn$_3$O$_4$ (215), respectively.

Looking back at section 1.2.2.1, the γ-MnO$_2$ goes through different reduction and oxidation processes in the ORR and OER potential regions, starting with reduction to MnOOH and then Mn(OH)$_2$ as well as hausmannite (Mn$_3$O$_4$) (unlikely to electrochemically oxidize in the potential
range studied here) in the ORR region followed by conversion to δ-MnO₂ (layered birnessite structure) in the subsequent OER region and final formation of excessive Mn₃O₄ during the following ORR [40, 41, 45, 92, 93]. Poor ORR and OER electrocatalytic activity of Mn₃O₄ in alkaline media has been reported in the literature. 40 μg cm⁻² of Mn₃O₄/C provides about -2.25 mA cm⁻² at -400 mV MOE in O₂ saturated 1 M KOH at 298 K while β-MnO₂/C catalyst exhibits a much better ORR electrocatalytic activity, i.e. over -3.5 mA cm⁻² under similar conditions, Lima et al. reported [45]. Moreover, Ramírez et al. showed that the amorphous MnOₓ (with some content of β-MnO₂) outperforms Mn₃O₄ sample for OER in alkaline media, e.g. 2.3 times the OER current density of the Mn₃O₄ sample (at 1800 mV RHE and 298 K in 1 M KOH) for amorphous manganese oxide [136].

Hence, our XRD results in Figure 4.3 are consistent with the literature confirming MnO₂ converts to MnOOH and inevitably hausmannite (Mn₃O₄) after being severely cycled [40, 41, 93, 228]. Thus, the loss of ORR/OER electrocatalytic activity can be attributed to defective regeneration of active MnO₂ (i.e. γ-MnO₂) from MnOOH and Mn₃O₄ during potential cycling. Regarding the possible degradation of LaCoO₃ in the mixed-oxide catalyst, XRD analysis revealed the formation of LaCoO₃ (012) after accelerated degradation testing, which could have a lower activity compared to the originally present LaCoO₃ (110) (Figure 4.3). Further discussions on the role of perovskites in the performance degradation of mixed-oxide catalysts during long-term durability tests will be given in section 6.2.5.
Figure 4.3 Comparison between the XRD spectrum of the MnO$_2$-LaCoO$_3$ catalyst: 1) Fresh GDE (black dotted line) and 2) After accelerated degradation testing for one hundred cycles in the potential range of 633 to 1633 mV followed by resting for six days at open-circuit in 6 M KOH at 293 K (red solid line) in a flooded test setup.

In order to investigate the reason(s) behind the considerable activity recovery and enhancement of all cycled and rested electrodes for both ORR and OER, XPS analysis has been employed. Figure 4.4 shows the XPS spectra of the MnO$_2$ GDE at its initial stage and after severe potential cycling and resting (for six days) in 6 M KOH at 293 K. The major peak of Mn overlaps with the one corresponding to F at about 690 eV. Fluorine atoms are present in both the catalyst layer (due to the Nafion ionomer and PTFE presence) and substrate (mainly because of
Due to the low signal-to-noise ratio of the XPS spectra arising from the high F:Mn ratio, it was not possible to distinguish between the Mn 3s multiplet peaks and noises of the spectra for further Mn valence studies.

Comparing the XPS spectra for the fresh MnO₂ GDE and after accelerated degradation testing followed by six days of resting at open-circuit in 6 M KOH, a new peak was observed in the latter sample at 380 eV (compare Figure 4.4-A and B). The peak at 380 eV can be specifically assigned to K 2s. Hence, it is proposed that the uptake and intercalation of K⁺ ions in the catalyst layer during extended exposure to 6 M KOH at open-circuit potential could induce a promoter effect for ORR and OER electrocatalysis, being responsible for the recovery (or “healing”) of the electrocatalytic activity of degraded samples.

The reproducibility of “healing” effect by potassium ion intercalation into the structure of degraded mixed-oxide catalysts has been reported in Appendix D. Further experiments investigating whether the initial stage activity (i.e. for the fresh GDEs) could be enhanced by exposure to 6 M KOH and insertion of K⁺ ions at open-circuit potential before use in polarization experiments will be presented in the next section. Moreover, the mechanisms involved with the potassium ion promotion effect on ORR/OER bifunctional electrocatalytic activity of investigated oxide catalysts will be discussed in the next sections.
Figure 4.4 XPS spectra of MnO\textsubscript{2} GDE: A) Fresh, C) After accelerated degradation testing for one hundred cycles in the potential range of 633 to 1633 mV and rested for six days at open-circuit in 6 M KOH at 293 K.
4.2.1.2 Activation of fresh catalysts

Here, the concept of oxide activation by K$^+$ is further advanced by considering the following questions: 1) Is the effect specific to K$^+$ or other alkali-metal ions produce similar effects? and 2) Can also the initial stage bifunctional activity be improved by activation and is this effect durable?

**Bifunctional activation effect of alkali-metal ions**

Figure 4.5 shows the bifunctional polarization curves of MnO$_2$-LaCoO$_3$ recorded after six days of exposure to alkali-metal hydroxide solutions (at 313 K and 400 RPM) with concentrations near their respective ionic conductivity maximum [231]. With respect to ORR (Figure 4.5-A), clearly KOH induced the most significant activity improvement. At a potential of 730 mV, an ORR current density of -12.5 mA cm$^{-2}$ was obtained, whereas in case of exposure to any of the other hydroxides and for the unactivated sample, the current density was at least three times lower, indicating a high level of K$^+$ specificity. These results are corroborated by a different type of investigation, where the ORR on LaMnO$_3$ was comparatively studied in either 0.1 M LiOH, or 0.1 M NaOH or 0.1 M KOH [232]. The ORR current density increased with increasing cation size in the electrolyte. It was proposed that the alkali metal ion may influence the rate determining step by interacting with the O$_2^{2-}$ species formed on the oxide surface. The smaller the cation size the stronger this interaction, inhibiting, therefore, the ORR rate determining step [232]. However, Figure 4.5 shows that in the present case, the performance with six-day exposure or without exposure to LiOH are virtually the same. Thereby, there is no evidence of ORR inhibition by Li$^+$. Furthermore, exposure to Cs$^+$ produces only a minor ORR improvement compared to K$^+$, suggesting that no simple linear correlation can be established based on cation size.

In the OER section of the polarization curve (Figure 4.5-B), extended exposure to all the alkali-metal hydroxides increased the current density compared to the unactivated case. However,
the best results were obtained in the presence of K\textsuperscript{+} and Cs\textsuperscript{+} ions. At a potential of 1450 mV, the OER current density on the MnO\textsubscript{2}-LaCoO\textsubscript{3} electrode was about an order of magnitude higher after the electrode was exposed to either KOH or CsOH. While some degree of non-specific contribution in Figure 4.5-B cannot be completely ruled out, where the longer-term exposure to any alkali-metal hydroxide solution could render the electrode more hydrophilic (e.g. partial PTFE wash-out), hence, a higher fraction of the pores are available for electrolyte penetration and oxygen evolution, Figure 4.5-A and Figure 4.5-B together point to a distinct bifunctional promotion effect mainly by K\textsuperscript{+} and to some extent by Cs\textsuperscript{+}. 
Figure 4.5 Bifunctional activation effect of long-term (i.e. six days) exposure of MnO$_2$-LaCoO$_3$ to alkali-metal hydroxide solutions: LiOH, NaOH, KOH, CsOH. Initial stage IR-corrected polarization curves obtained by potential scanning between 633 to 1483 mV in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Other conditions idem to Figure 3.6.
Accelerated degradation tests on fresh activated mixed-oxide catalysts

Next, the electrocatalytic durability of potassium activated (i.e. six days of exposure to 6 M KOH at 313 K and 400 rpm) MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ electrodes have been investigated under severe potential cycling between 633 to 1483 mV in 6 M KOH at 293 K (Figure 4.6). Extensive cycling drastically diminished the ORR electrocatalytic activity of fresh activated MnO$_2$-LaCoO$_3$ catalyst with ORR current density decreasing from about -21 to -7 mA cm$^{-2}$ (at 680 mV) after one hundred cycles (Figure 4.6). Comparing to the fresh unactivated electrode, the activated MnO$_2$-LaCoO$_3$ catalyst after one hundred cycles possessed 3.5 times the ORR current density (at 680 mV) of the unactivated sample (compare Figure 3.7-A and Figure 4.6-A). With regards to the OER region, the activated MnO$_2$-LaCoO$_3$ showed excellent durability with current density loss of a mere 1 mA cm$^{-2}$ at 1450 mV (i.e. about one tenth of the original OER current density for fresh activated sample) during one hundred cycles of accelerated degradation testing (Figure 4.6-B). For MnO$_2$-Nd$_3$IrO$_7$, the activated sample revealed relatively high ORR and OER performance losses after one hundred cycles of accelerated degradation tests, i.e. about twice the ORR and OER current densities (at 680 and 1450 mV, respectively) of the activated sample at cycle 100 was observed for the fresh activated sample at cycle 1 (Figure 4.6).

Comparing the two K$^+$ activated GDEs, i.e. MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$, looking at the ORR region, the activated MnO$_2$-LaCoO$_3$ performs better in terms of both initial stage activity and durability, e.g. the current density at 680 mV is about -21 mA cm$^{-2}$ compared to -4 mA cm$^{-2}$ for the fresh activated MnO$_2$-Nd$_3$IrO$_7$ (Figure 4.6-A). For OER, the same trend is maintained with the exception that the initial stage electrocatalytic activity of activated MnO$_2$-Nd$_3$IrO$_7$ is superior at potentials higher than 1410 mV (Figure 4.6-A). Thus, one can conclude that the K$^+$ activation
procedure is more effective when MnO₂ is combined with perovskites as opposed to fluorite-type oxides.
Figure 4.6 Electrocatalytic durability testing of fresh activated MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ GDEs: A) ORR polarization curves and B) OER polarization curves. IR-corrected ORR/OER polarization curves obtained by potential scanning between 633 to 1483 mV for one hundred cycles (accelerated degradation testing) in O$_2$ saturated 6 M KOH at 293 K and P$_{O_2}$ of 1 atm. Catalysts were activated by six-day-long exposure to 6 M KOH at 313 K and 400 rpm and open-circuit. Other conditions idem to Figure 3.6.
To gain further insights on the K$^+$ promotion effect as revealed by electrode polarization experiments (Figure 4.5 and Figure 4.6), the XPS spectra of both fresh and K$^+$ activated MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts are presented in Figure 4.7. The Mn and La major peaks overlap with the ones corresponding to F at about 690 and 835 eV, respectively (Figure 4.7-A and B). Fluorine is one of the main constituents of both the carbon cloth substrate (due to teflonation) and catalyst layer (due to Nafion ionomer and PTFE). Furthermore, the Nd major peaks around 980 eV overlap with O (Figure 4.7-C and D).

Comparing the XPS spectrum for fresh and K$^+$ activated catalysts, the latter reveals peaks around 380 eV which correspond to K 2s. Two major spin-orbit splitting peaks appear for K 2p around 290 eV, but these peaks also overlap to a large extent with the ones from C(F) and C 1s due to the carbon material in both substrate and catalyst layer (Figure 4.7). The presence of potassium has been also confirmed by the EDX spectra of the activated catalyst layers (Figure 4.8).
Figure 4.7 XPS spectra of MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ before and after long-term exposure to 6 M KOH: A) MnO$_2$-LaCoO$_3$ fresh electrode, B) MnO$_2$-LaCoO$_3$ activated electrode, C) MnO$_2$-Nd$_3$IrO$_7$ fresh electrode, D) MnO$_2$-Nd$_3$IrO$_7$ electrode. Other conditions idem to Figure 4.6.
Figure 4.8 EDX spectra of the activated catalyst layers after six days of exposure to 6 M KOH: A) MnO$_2$-LaCoO$_3$, B) MnO$_2$-Nd$_3$IrO$_7$. Conditions idem to Figure 4.6.

The intercalation of K$^+$ in MnO$_2$ structure could be understood in terms of the cation vacancy model [233]. During electrode potential cycling between the ORR and OER regions, the fraction of Mn$^{4+}$ and Mn$^{3+}$ ions is changing, as shown also by electron energy loss spectroscopy (EELS) in Figure 4.9. The first charge-transfer process associated with MnO$_2$ can be represented as [90]:

$$ Mn^{4+}_{(s)} + 2O^{2-}_{(s)} + e^- + H_2O \rightarrow Mn^{3+}_{(s)} + O^{2-}_{(s)} + OH^-_{(s)} + OH^-_{(aq)} $$ (35)

Thus, one electron and one proton is inserted per MnO$_2$ leading to the formation of OH$^-_{(s)}$ and Mn$^{3+}_{(s)}$ with lattice expansions [233, 234]. Generally, the composition of partially reduced $\gamma$-MnO$_2$ can be described as:

$$ Mn^{4+}_{1-x-y} . Mn^{3+}_{y} . O^{2-}_{2-4x-y} . V^{\\\...}_{x} . OH^{-}_{4x+y} $$ (36)
where \( x \) is fraction of vacancies, \( y \) is fraction of \( \text{Mn}^{3+} \) ions and \( V^{III} \) represents a cation vacancy in the Schottky notation [90].

In light of the cation vacancy model and eq. 36, it seems plausible that \( K^+ \) could intercalate into the vacancies, also known as Schottky defects, surrounded by \( \text{OH}^- \) ions. This intercalation may cause lattice distortion since the ionic radius of \( \text{Mn}^{4+} \) ions is much smaller than the one for \( K^+ \), i.e. 53 and 138 pm, respectively [235]. It is then proposed that the lattice distortions induced by \( K^+ \) affect the binding energies of intermediate species involved in ORR and OER such as \( \text{HOO}(\text{ads}) \) and \( \text{HO}(\text{ads}) \), contributing to the enhanced bifunctional activity by breaking away from the universal scaling relationship between their binding energies.

During potential cycling between the ORR and OER regions, diverse \( \text{MnO}_x \) phases are forming with different activity and stability causing an overall complex behavior influencing the electrode durability [4, 39, 45, 67, 90, 98, 113]. An effective way to find the Mn valence would be important to unveil the \( \text{MnO}_x \) associated with different stages of ORR and OER. While XPS analysis can help determine the Mn valence using the Mn 3s peak separation method in the presence of pure \( \text{MnO}_x \) [236-238], EELS is more effective for Mn valence determination when it comes to complex systems such as bifunctional catalyst layers with more than one component [228, 229]. EELS was performed on \( \text{MnO}_2-\text{LaCoO}_3 \) catalyst in three different conditions (Figure 4.9): 1) Fresh catalyst, 2) \( K^+ \) activated catalyst after being cycled for ten cycles between 633 and 1483 mV in \( \text{O}_2 \) saturated 6 M KOH at 293 K and 400 rpm, and 3) \( K^+ \) activated catalyst after being cycled for one hundred cycles under the same conditions (accelerated degradation test).

Figure 4.9 shows the EELS spectra for manganese L edges and oxygen K edges as well as the calculated Mn valences for the \( \text{MnO}_2-\text{LaCoO}_3 \) catalysts during different stages of potential cycling. Figure 4.9-A indicates that not only the shape of Mn(L\(_{2,3}\)) peaks changes during the
accelerated degradation testing but also its position shifts during potential cycling. The Mn(L₃) main peak for MnO₂-LaCoO₃ catalyst shifted from 645.8 to 639.9 eV after one hundred cycles of durability testing (Figure 4.9-A). The O(K) main peak, however, fluctuates around 532 eV for both the fresh sample and the one subjected to one hundred potential cycling. According to the literature, the shifts in the Mn(L₃) and O(K) main peaks could be related to the change of MnOₓ species from MnO₂ to Mn₂O₃ and Mn₃O₄ after being cycled for one hundred cycles [239-241].

The shape of each Mn(L₂,3) and O(K) edges can also represent the type of manganese oxide present in the catalyst layer. The Mn(L₂,3) and O(K) edges of the fresh MnO₂-LaCoO₃ catalyst in EELS spectrum is similar to the ones shown in the literature for MnO₂ [228, 240] (Figure 4.9-A and B). After the K⁺ activation and ten cycles, the EELS spectrum of the MnO₂-LaCoO₃ sample is similar to that of Mn₂O₃ reported in the literature [239-241], especially the Mn(L₃) and O(K) peaks at 644.8 and 532.9 eV, respectively (Figure 4.9-A and B). The Mn (L₂,3) edges of the activated MnO₂-LaCoO₃ after being cycled for ten cycles could be due to MnOOH.

Furthermore, the activated MnO₂-LaCoO₃ catalyst after one hundred cycles shows the typical EELS spectrum of Mn₃O₄, reported in the literature [239, 241], with two Mn(L₃) and one O(K) peaks at 639.9, 641.3 and 531.7 eV, respectively (Figure 4.9-A and B). The Mn₃O₄ doublet peaks could be further deconvoluted to Mn(L₃) edges from MnO to Mn₂O₃ or MnOOH (Figure 4.9-A) [239, 240, 242-244]. It has been reported that the ratio of Mn(L₃) peaks corresponding to Mn³⁺ and Mn²⁺, in the present case 1.1 after one hundred cycles, could indicate the presence of vacancies in the tetrahedral sites of the Mn₃O₄ [245]. These vacancies could also act as sites for K⁺ intercalation.

Figure 4.9-C shows the Mn valence vs. the L₃:L₂ branching ratio defined as:
\[ \frac{L_3: L_2 \text{branching ratio}}{I(L_3) / (I(L_2) + I(L_3))} \]

where \( I(L_3) \) and \( I(L_2) \) are the intensities of Mn(L3) and Mn(L2) edges from the EELS spectrum of each sample.

In order to compare the calculated valences vs. reference values (Figure 4.9-C), the EELS spectra of MnO, Mn2O3 and MnO2 have been extracted from literature and the corresponding L3:L2 branching ratios have been used as reference points [228, 239]. This graph confirms that the Mn valence for the fresh catalyst is about 4, indicating the unreduced MnO2. The Mn valence decreases to 3.1 after ten cycles (i.e. MnOOH and Mn2O3), whereas extensive cycling up to one hundred cycles, lowers the Mn valence to 2.9 and 2.6 for the first and second Mn(L3) edge, respectively (Figure 4.9-C). The latter values indicate the increased formation of Mn^{2+} species such as MnO and Mn(OH)2 leading to hausmannite (Mn3O4) as the final composition. It has been reported that hausmannite, which is believed to appear at about 633 mV during MnO2 reduction, shows poor electrocatalytic activity for both ORR and OER compared to MnO2 alone [4, 40, 45, 246]. There is a debate whether hausmannite can be electrochemically oxidized or not. While some studies have claimed that Mn3O4 is electrochemically inactive and cannot be oxidized to Mn^{4+} oxide species [40, 45, 98, 247], others have identified hausmannite as an ideal candidate for supercapacitor applications and also proposed that it could be transformed to layered birnessite structure (\( \delta \)-MnO2) after severe cycling [113, 248-251]. The present results in Figure 4.9-C show that MnO2 is not regenerated efficiently during potential cycling between 633 to 1483 mV. However, in spite of profound MnO2 structural changes during potential cycling, the electrodes activated by OCP exposure to K+ exhibited superior cycling durability (Figure 4.6). Furthermore,
the activity of degraded electrodes can be regenerated by OCP K\(^+\) treatment, called the “healing effect” (section 4.2.1.1 and Appendix D).

Figure 4.9 EELS analysis of MnO\(_2\)-LaCoO\(_3\): A) EELS spectrum showing Mn (L\(_{2,3}\)) edges, B) EELS spectrum showing O (K) edges, C) L\(_3\):L\(_2\) Branching ratio versus valence state for Mn oxides. The sample was tested under three different conditions: 1) Initial stage, 2) After being activated in KOH for six days (idem to Figure 4.6) and cycled between the ORR and OER regions for ten cycles, 3) After being activated in KOH for six days and cycled between the ORR and OER regions for one hundred cycles (accelerated degradation test idem to Figure 4.6). The (■) and (▲) symbols represent reference data points obtained from literature [228] and the ones calculated directly from EELS spectrum for each sample, respectively. The standard error of the mean associated with Mn valence state, L\(_3\):L\(_2\) branching ratio and energy loss are ± 0.2, ± 0.001 and ± 0.1 eV, respectively.
4.2.2 Oxide catalyst layer activation by potential driven intercalation (PDI) of K$^+$

4.2.2.1 Initial stage electrocatalytic activity of PDI activated mixed-oxide catalysts

In order to accelerate the insertion of K$^+$ into the fresh oxide catalyst layer, an electrophoretic method referred to as potential driven intercalation (PDI), has been developed and investigated. The PDI method includes a constant cathodic current density of -5.4 mA cm$^{-2}$ applied for 30 min. (each round up to seven rounds) to the fresh electrodes in a 0.036 M K$_2$SO$_4$ solution at 343 K and 400 rpm (check section 2.1.5 for more details). Figure 4.10 shows two representative cell potential profiles while performing PDI method on the investigated mixed-oxide catalysts, i.e. MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$. The presence of potassium in the PDI activated samples was confirmed by XPS analysis (Figure 4.11). The XPS spectra of the electrodes activated by the PDI and OCP methods are very similar (compare Figure 4.7 and Figure 4.11). One of the possible differences between the two activation methods could be the 3D distribution of potassium in the catalyst layers, which needs further experimentation in future works.
Figure 4.10 Cell potential profile during potential driven K$^+$ intercalation (PDI) on A) MnO$_2$-LaCoO$_3$ and B) MnO$_2$-Nd$_3$IrO$_7$ as catalyst layers. 5.4 mA cm$^{-2}$ was cathodically applied to each GDE in the RDE setup in a 0.036 M K$_2$SO$_4$ solution for 30 min up to seven times. The rotation speed and temperature were 400 rpm and 343 K, respectively. A platinum mesh was employed as both reference and counter electrode. The figure indicates the cell potential for the third round of PDI in each case.
Figure 4.11 XPS spectra of the potential driven K+ intercalation (PDI) activated catalyst layers: A) MnO$_2$-LaCoO$_3$ electrode after seven rounds of PDI activation, B) MnO$_2$-Nd$_3$IrO$_7$ electrode after six rounds of PDI activation.
Figure 4.12 shows the electrocatalytic activity of MnO$_2$-LaCoO$_3$ and MnO$_2$-Nd$_3$IrO$_7$ catalysts after being activated using the PDI method for up to seven rounds, each activation round lasting 30 min. First it is noted that in the ORR region, for both catalyst layers, a peak current density is reached which is controlled by dissolved O$_2$ mass transfer from the bulk solution to the reaction layer (Figure 4.12-A and C). Next, in case of MnO$_2$-LaCoO$_3$ (Figure 4.12-A), repeating the PDI activation procedure shifted positively the ORR peak potential from 465 mV (1$^{\text{st}}$ round) to 635 mV (6$^{\text{th}}$ round). Further repetition of the PDI activation beyond six rounds did not produce any additional benefits for ORR catalysis. Furthermore, the PDI method (6$^{\text{th}}$ round) increased about ten times the ORR current density at 730 mV compared to the unactivated case (Figure 4.5-A and Figure 4.12-A).

In the case of MnO$_2$-Nd$_3$IrO$_7$ (Figure 4.12-C), the shift of the ORR peak potential was more limited, i.e. from 430 mV (1$^{\text{st}}$ round) to 500 mV (2$^{\text{nd}}$ round and beyond). The ORR current density at 730 mV increased for about two times after the PDI treatment (3$^{\text{rd}}$ round) compared to the unactivated case.

Regarding the OER section of the MnO$_2$-LaCoO$_3$ GDE polarization curve (Figure 4.12-B) and considering 1450 mV as an arbitrary reference potential, PDI activation (after 6$^{\text{th}}$ rounds) generated a current density of 14 mA cm$^{-2}$ while open-circuit K$^+$ activation produced 9.5 mA cm$^{-2}$ (Figure 4.5-B), whereas without any type of K$^+$ activation the current density was only about 0.2 mA cm$^{-2}$ (Figure 4.5-B). Similar improvements were observed in the case of PDI activated MnO$_2$-Nd$_3$IrO$_7$ as well.
Figure 4.12 The effect of potential driven K⁺ intercalation on the initial stage bifunctional polarization of mixed-oxide catalysts: A) ORR on MnO₂-LaCoO₃, B) OER on MnO₂-LaCoO₃, C) ORR on MnO₂-Nd₃IrO₇ and D) OER on MnO₂-Nd₃IrO₇. Other conditions idem to Figure 3.6.

4.2.2.2 Initial stage electrocatalytic activity of PDI activated individual oxides

To better understand the role of potassium intercalation on the bifunctional performance of the mixed-oxide catalysts, five rounds of PDI activation was also applied to individual oxide catalysts, i.e. MnO₂, LaCoO₃ and Nd₃IrO₇ (Figure 4.13). While K⁺ activation enhances the ORR electrocatalytic activity of all individual oxides (compare Figure 3.6-A and Figure 4.13-A), the method is most effective for MnO₂. The OER performance of the individual oxides are also
improved by the PDI activation with MnO₂ surpassing both LaCoO₃ and Nd₃IrO₇ catalysts (Figure 4.13-B). XPS analysis confirmed the presence of potassium (K 2s peak at 380 eV) in all three oxides after PDI activation (Figure 4.14). The individual oxide polarization results presented by Figure 4.13 substantiate the hypothesis that the main mechanism for bifunctional activity enhancement is related to K⁺ intercalation into the vacancies or Schottky defects of MnO₂ surrounded by OH⁻ ions. This promotion effect of intercalated potassium ions on various oxide surfaces can be further explained considering the lattice oxygen vacancy.

Simultaneous reduction of molecular O₂ and its incorporation as solid-state oxygen ions are believed to occur during ORR on oxide surfaces [122, 252-254]. This oxygen incorporation reaction into the lattice vacancies in a solid, coupled with electron transfer, can be described using Kröger-Vink notation as follows [254, 255]:

\[
O_2 + 4e^- + 2V_\text{O} \leftrightarrow 2O_\text{O}^x
\]  

(38)

where \(V_\text{O}\) denotes a lattice oxygen vacancies with double positive charge and \(O_\text{O}^x\) represents an oxygen ion sitting on an oxygen lattice site with neutral charge. These oxygen vacancies can behave as both acceptor and donors, facilitating the charge transfer between adsorbent and adsorbate [122, 253, 254, 256]. Hence, the continuous formation and annihilation of these lattice oxygen vacancies in oxygen-deficient oxides can significantly affect their ORR/OER electrocatalytic activity [122, 253, 254, 256]. Higher concentration of oxygen vacancies is believed to enhance the lattice oxygen mobility, facilitating the adsorption of reactants (such as OH⁻) as well as enhancing the charge transfer, therefore, improving the electrocatalytic activity of deficient oxides for both ORR and OER [122, 256-258].
In consideration of lattice oxygen vacancies, it seems plausible that K$^+$ could intercalate into these vacancies, further facilitating adsorption of OH$^-$ as well as inducing lattice distortions (compare atomic radius of 73 pm for O and ionic radius of 138 pm for K$^+$) which could provide new binding sites for HOO$_{\text{ads}}$ and HO$_{\text{ads}}$ intermediates, help break away from the universal linear scaling relationship and hence, enhance the ORR/OER bifunctional activity of oxides, specially for perovskite and fluorite-type oxides.

Comparing the mixed and individual oxides activated by PDI (Figure 4.12 and Figure 4.13), it is clear that due to the synergy between either MnO$_2$ and LaCoO$_3$ or MnO$_2$ and Nd$_3$IrO$_7$, the mixed-oxide catalysts possess superior bifunctional electrocatalytic activity than any of the oxides individually. This could be due to the two beneficial phenomena occurring at the same time, first, extra binding sites such as additional lattice oxygen vacancies with different HOO$_{\text{ads}}$/HO$_{\text{ads}}$ binding energies, obtained by mixing the individual oxides, and second, the extra induced potassium ions in the structure of activated oxides affecting the intermediates’ binding energies, both help breaking away from the universal linear scaling relationship and hence, improving the bifunctional activity of the catalysts.
Figure 4.13 The effect of potential driven K$^+$ intercalation on the initial stage bifunctional polarization of individual oxides: MnO$_2$, LaCoO$_3$ and Nd$_3$IrO$_7$. A) ORR, B) OER. Other conditions idem to Figure 3.6.
Figure 4.14 XPS spectra of the PDI activated catalyst layers: A) MnO$_2$ after five rounds of K$^+$ PDI activation, B) LaCoO$_3$ after five rounds of K$^+$ PDI activation and C) Nd$_3$IrO$_7$ after five rounds of K$^+$ PDI activation.
4.2.2.3 Galvanostatic long-term durability testing of unactivated and PDI activated mixed-oxide catalysts

In addition to potential cycling experiments, galvanostatic polarization (i.e. chronopotentiometry) was also performed in order to assess the effect of PDI activation on electrocatalytic activity and stability. The oxide loading was the same as in all other experiments, namely, 0.5 mg cm\(^{-2}\) for each of the oxides. For OER, a constant current density (per geometric area) of 5 mA cm\(^{-2}\) (or 5 A g\(^{-1}\) per total catalyst mass) was applied for 2 hrs, whereas for ORR, -2 mA cm\(^{-2}\) (or 2 A g\(^{-1}\) per total catalyst mass) was applied for 30 min (Figure 4.15). The flooded electrode half-cell arrangement used in the present study imposes some limitations with respect to the current densities that can be applied during galvanostatic longer-term experiments. These conditions are different compared to the cell design that would be used in practice, for instance in a rechargeable zinc-air battery. Therefore, the experiments presented by Figure 4.15 provide only a preliminary insight into durability and further studies are required under conditions more relevant to the industrial practice.

The ORR current density was chosen to be sustainable by the availability of dissolved O\(_2\) in the O\(_2\) saturated 6 M KOH electrolyte for a more extended period of time (e.g. 30 min). In practice, a gas diffusion oxygen electrode would be used either air breathing or exposed to a convective air (or oxygen) flow (similar to section 3.2.4). The OER current density of 5 mA cm\(^{-2}\) for 2 hrs, was selected to provide relevant longer-term electrocatalytic stability information, while avoiding the heavy O\(_2\) gas evolution expected at high current densities that could shield and/or damage the electrode surface in the present configuration. Two hours galvanostatic polarization was also proposed as an OER benchmarking criteria by McCrory et al. [131], albeit at a current density of
10 mA cm$^{-2}$ but for an unspecified catalyst loading. Hence, it is difficult to employ identical conditions to the latter study.

Comparing first the unactivated fresh catalysts, the OER behavior of MnO$_2$-LaCoO$_3$ was superior over the 2 hr testing period compared to MnO$_2$-Nd$_3$IrO$_7$ (Figure 4.15-A and B). For the latter catalyst (Figure 4.15-B), the potential increased from 1480 mV (at $t = 1$ min) to 1621 mV (at $t = 2h$), whereas in case of fresh MnO$_2$-LaCoO$_3$ the electrode potential was much more stable, i.e., 1549 mV (at $t = 1$ min) and 1568 mV (at $t = 2h$). PDI activation had a positive influence on both catalysts by reducing the O$_2$ evolution potential by about 110 mV in case of MnO$_2$-LaCoO$_3$ (Figure 4.15-A) and up to 152 mV (at $t = 2$ h) on MnO$_2$-Nd$_3$IrO$_7$ (Figure 4.15-B). Furthermore, the stability of the OER activity for the PDI activated MnO$_2$-Nd$_3$IrO$_7$ catalyst is markedly superior compared to the unactivated case. Thus, for MnO$_2$-Nd$_3$IrO$_7$ the rate of OER potential increase is lowered from 70.5 mV h$^{-1}$ (fresh unactivated catalyst) to 10 mV h$^{-1}$ (PDI activated).

Regarding the galvanostatic ORR response (at -2 mA cm$^{-2}$), the electrode potential on fresh MnO$_2$-Nd$_3$IrO$_7$ was about 43 mV (at $t = 30$ min) higher than on MnO$_2$-LaCoO$_3$. PDI activation increased the ORR electrode potential of the latter catalyst by about 75 mV (at $t = 30$ min) (Figure 4.15-A), whereas it had a lesser influence on MnO$_2$-Nd$_3$IrO$_7$ (15 mV higher potential). These findings corroborate the cycling polarization experiments on the two catalyst formulations presented by Figure 4.12. The rate of ORR potential degradation was also dropped from -30 mV h$^{-1}$ to -24 mV h$^{-1}$ for MnO$_2$-LaCoO$_3$ and from -38 mV h$^{-1}$ to -14 mV h$^{-1}$ for MnO$_2$-Nd$_3$IrO$_7$ after PDI activation.
Figure 4.15 Galvanostatic polarization of mixed-oxide catalysts without and with potential driven K$^+$ intercalation activation: A) MnO$_2$-LaCoO$_3$ and B) MnO$_2$-Nd$_3$IrO$_7$. Tests started with 5 mA cm$^{-2}$ anodically applied to each GDE for 2 hrs followed by -2 mA cm$^{-2}$ applied cathodically for 30 min in O$_2$ saturated 6 M KOH using a flooded test setup. The rotation speed and temperature were 400 rpm and 293 K, respectively. $P_{O_2}$ was 1 atm. The oxide loadings were 0.5 mg cm$^{-2}$ each.
4.2.3 Comparison of Bifunctional ORR/OER Activities: present work vs. literature

It is inherently difficult to compare catalysts from various literature sources because the apparent performance is dependent not only on the intrinsic electrocatalytic activity but also on other interacting factors such as the catalyst loading and dispersion, catalyst layer structure and composition (e.g. presence or absence of support and/or ionomer and/or PTFE) and electrode manufacturing conditions. In spite of the above-mentioned shortcomings, the author believes a comparison with literature results is warranted to place in a broader context the results obtained here with respect to representative precious and non-precious metal catalysts reported in the literature.

Figure 4.16 presents a comprehensive comparison of the ORR and OER overpotentials (at -2 and 2 mA cm\(^{-2}\), respectively) for the individual and mixed-oxide catalysts investigated here, and relevant catalyst examples from literature. The overpotentials at 2 and -2 mA cm\(^{-2}\) were chosen for comparison because of the available literature data in the latter current density range for diverse catalysts and catalyst loadings. Catalysts with the best and worst bifunctional activity are in the lower bottom-left and top-right corner of Figure 4.16, respectively.

The K\(^+\) activated oxide catalysts (i.e. MnO\(_2\), MnO\(_2\)-LaCoO\(_3\) and MnO\(_2\)-Nd\(_3\)IrO\(_7\), with indices between 21 and 25, Figure 4.16) are all situated in the lower half of the diagram due to their low OER overpotential at 2 mA cm\(^{-2}\). The latter is between 100 to 150 mV lower than the reported OER overpotentials for catalysts such as: 20 wt% Ir/C (#13) [69], 20 wt% Ru/C (#12) [67, 69], Pt/IrO\(_2\) (#6) [259], Pt/Ir-IrO\(_2\) (#7) [259] and Pt/Ir\(_3\)(IrO\(_2\))\(_7\) (#8) [260]. Compared to the unactivated MnO\(_2\), MnO\(_2\)-LaCoO\(_3\) and MnO\(_2\)-Nd\(_3\)IrO\(_7\) catalysts (indices 17, 19 and 20, respectively), K\(^+\) activation lowered the OER overpotentials by up to 175 mV.
With respect to ORR, catalysts such as nano sized Ag (#16) [75], 20 wt% Pt/C (#11) [67], Pt/Ir-IrO$_2$ (#7) [259] and Pt/Ir$_3$(IrO$_2$)$_7$ (#8) [260] generated more positive overpotentials than those reported in the present work. However, other non-precious metal catalysts such as nanostructured Mn oxide thin film (#5) [69] and Core-Corona Structured Bifunctional Catalyst (CCBC) (#10) [76] showed lower ORR electrocatalytic activity with far more negative overpotentials compared to the oxide catalysts investigated here (Figure 4.16).
Figure 4.16 Comparison between the ORR and OER overpotential values of the catalyst materials investigated here (shown as (▲)) with those reported in the literature for other bifunctional electrodes (shown as (♦)) [4, 64, 67, 69, 71, 72, 74, 76, 121, 259, 260]. For the catalyst investigated here: a) Fresh catalyst without activation. b) Activation by K⁺ insertion at open-circuit potential (OCP), c) Activation by K⁺ insertion using five rounds of potential driven intercalation (PDI), d) Activation by K⁺ insertion using six rounds of potential driven intercalation (PDI), e) Activation by K⁺ insertion using three rounds of PDI. The max error associated with overpotential values is ±5 mV.
4.3 Conclusion

The effect of alkali-metal ions insertion on the ORR/OER electrocatalytic activity and durability of fresh and degraded oxide catalysts was investigated using in-depth structural and electrochemical analysis. It has been shown that the degradation in the ORR/OER electrocatalytic activity of fresh oxide catalysts, i.e. MnO₂, MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇, after accelerated degradation tests can be fully restored by resting the electrodes in 6 M KOH at open-circuit potential, called the “healing” effect. It was observed that the performance recovery of the degraded electrodes improved with exposure to 6 M KOH from six hours to six days, with six-day-long activated electrodes exceeding the bifunctional activity of the fresh samples.

In addition, the role of K⁺ insertion in the catalyst structure of fresh oxides was investigated by two methods: A) Longer-term exposure of the catalysts to 6 M KOH and B) Potential driven (electrophoretic) intercalation. Both methods are effective for enhancing the bifunctional activity and durability of the mixed-oxide catalysts. At a constant current density of 5 mA cm⁻² (or 5 A g⁻¹) applied for 2 hrs, the OER overpotential is lowered by 110 mV and 152 mV due to potential driven potassium ion intercalation on MnO₂-LaCoO₃ and MnO₂-Nd₃IrO₇, respectively. Furthermore, the rate of OER potential increase, a measure of electrocatalytic activity degradation, is diminished by the application of the potential driven potassium intercalation from 70.5 mV h⁻¹ (for fresh unactivated MnO₂-Nd₃IrO₇) to 10 mV h⁻¹.

In the case of ORR, the potential driven intercalation of potassium was also effective lowering the electrode potential on MnO₂-LaCoO₃ by 75 mV at a constant current density of -2 mA cm⁻² (or -2 A g⁻¹). The rate of ORR potential degradation was also improved from -30 mV h⁻¹ to -24 mV h⁻¹ for MnO₂-LaCoO₃ and from -38 mV h⁻¹ to -14 mV h⁻¹ for MnO₂-Nd₃IrO₇ after K⁺ potential driven intercalation activation.
It is proposed that the reason for the enhanced ORR/OER performances of the activated catalysts is the uptake of $\text{K}^+$ into the catalyst layer (mostly in the vacancies and defects of the oxide crystal structures such as Schottky and lattice oxygen vacancies), acting as a promoter for both ORR and OER. The $\text{K}^+$ uptake was demonstrated by both XPS and EDX analysis. It is proposed that the insertion of potassium ions in the aforementioned vacancies provides new binding sites with distinct binding energies for $\text{HO}_2(\text{ads})$ and $\text{HO}(\text{ads})$ intermediates, help breaking away from the universal scaling relationship and thus, enhancing the ORR/OER bifunctional activity of the investigated catalysts.
Chapter 5: Surfactant-assisted electrodeposition of Mn oxides as promising ORR/OER bifunctional non-PGM electrocatalysts: Factorial design study of the electrodeposition factors ****

5.1 Introduction

A systematic study has been performed in this chapter to find an active nanostructured manganese oxide for both oxygen reduction and evolution reactions via surfactant-assisted anodic electrodeposition method. The main and interaction effects of key electrodeposition factors that significantly influence the electrosynthesis of manganese oxides, i.e. Mn$^{2+}$ concentration (C), applied anodic potential (E), temperature (T), surfactant concentration (S), on the bifunctional activity of MnO$_x$ has been studied using a two-level half-fraction factorial design. Sodium dodecyl sulfate (SDS) as anionic, hexadecyl-trimethyl-ammonium bromide (CTAB) as cationic and Triton X-100 as non-ionic surfactants were used in this study to electro-synthesize the nanostructured MnO$_x$. Triton X-100 samples provide the best performing nano-sized structures with promising ORR and OER performances comparing to both noble and non-precious metals and their oxides, i.e. between 50 to 150 mV more positive ORR overpotential (at -2 mA cm$^{-2}$) comparing to CoMn$_2$O$_4$ and Core-Corona Structured Bifunctional Catalyst (CCBC) and min. 100 mV lower OER overpotential (at 2 mA cm$^{-2}$) comparing to Ir, Ru and IrO$_2$. Galvanostatic polarizations of Triton-run no. 9 sample at 5 mA cm$^{-2}$ showed low OER potentials of 1446 mV (at t=2 hrs), about

**** A version of this chapter is in preparation for publication. Parts of this chapter were filed as United States and Canadian patent applications:
- P. Hosseini-Benhangi, A. Alfantazi, E. Gyenge, “Surfactant-assisted electrodeposition of Mn oxides as promising ORR/OER bifunctional non-PGM electrocatalysts: Factorial design study of the electrodeposition factors”, to be submitted.
40 mV lower than the commercial MnOₙ, and degradation rate of 43 mV h⁻¹, about 10 mV h⁻¹ lower than its commercial counterpart. The surface modifications of MnOₓ via surfactant-assisted electrodeposition can help destabilizing the HOO(ads) and HO(ads) intermediates, breaking away from the linear scaling relationship between their binding energies as a major contributor to the ORR and OER overpotentials, enhancing the ORR and OER electrocatalytic activity of electrodeposited manganese oxides. The formation of hydrogen-bonded complexes, i.e. HOO(ads)...H-OH, with specially configured water molecules called “activated water”, can further explain the enhancements in the ORR electrocatalytic activity of the catalysts.

5.2 Results and discussion

5.2.1 Anodic electrodeposition behavior of Mn oxides with and without surfactants

Linear sweep voltammetry (LSV) tests have been used to investigate the anodic electrodeposition behavior of manganese oxides on carbon cloth in presence of diverse types and different concentrations of surfactants, seeking to identify suitable potential range for MnOₓ electrodeposition while avoiding OER (Figure 5.1). As shown in Figure 5.1, the anodic peak, corresponding to the electrodeposition of MnOₓ on the pre-treated carbon cloth with no surfactant available, starts at around 450 mV_MOE, reaches its max. current density of 1.2 mA cm⁻² at 1365 mV_MOE and is then joined by the OER at around 2000 mV_MOE. The decrease in the anodic current density of the Mn²⁺ oxidation peak has been attributed to the formation of insulating MnOOH layer (eq. 33) (Figure 5.1). The addition of surfactants, i.e. Triton X-100, SDS and CTAB, with different concentrations, i.e. 5 and 10 vol%, to the 0.2 M Mn(CH₃COO)₂ and 0.1 M Na₂SO₄ solution seems to shift the anodic peak of MnOₓ deposition along with the OER onset potential to more negative potentials (Figure 5.1). While the Mn²⁺ oxidation peak stays between 1000 to 1200 mV_MOE for all types of surfactants at the concentration levels studied here (Figure 5.1), the
OER onset potential, determined at the first increase in the current density after the Mn$^{2+}$ oxidation peak, reaches its min. at around 1350 mV$_{MOE}$ for the solution with 5 vol% of Triton X-100 (Figure 5.1-A). This decrease in the OER onset potentials with introduction of surfactant has been reported in the literature for water electrolysis on carbon electrodes in acidic media and in the presence of a cationic surfactant [261]. In order to avoid the OER, the potential range was fixed to 800 to 1200 mV$_{MOE}$ with a center-point at 1000 mV$_{MOE}$ for all conditions.
Figure 5.1 IR-corrected linear sweep voltammograms of nitric acid pre-treated 40 wt% PTFE treated carbon cloth starting from 0 to 2500 mV_{MOE} in presence of: A) 5 vol% and B) 10 vol% of Triton X-100, SDS and CTAB. The solution was made of 0.2 M Mn(CH₃COO)₂ and 0.1 M Na₂SO₄ at 293 K. The scan rate and rotation speed were 5 mV s⁻¹ and 400 rpm, respectively.
5.2.2 Characterization of the electrodeposited samples

XPS spectra were used to identify the Mn valence of electrodeposited manganese oxides. Three representative XPS spectra for T1, T9 and T10 samples are shown in Figure 5.2. The electrodeposition factors for each sample are as follows: T1 (C: 0.3 M, T: 295 K, S: Triton, 10 vol%, E: 800 mVMOE), T9 (C: 0.1 M, T: 343 K, S: Triton, 10 vol%, E: 800 mVMOE), T10 (C: 0.3 M, T: 295 K, S: Triton, 0 vol%, E: 1600 mVMOE). Table 5.1 summarizes the deconvoluted data for Mn 2p, O 1s and Mn 3s regions of these samples. The determination of Mn valence based on the location of Mn 2p peaks is usually associated with high uncertainties mainly due to the differential charging imposed by ejection of photoelectrons from inadequate conductivity of the material’s surface, leading to broadening or shifting of the peaks [237, 262]. However, a combined analysis of Mn 3s doublet peak splitting and O 1s constituents can provide a meaningful understanding of Mn valence in the manganese oxides [236-238, 262]. The Mn 3s peak separation is caused by the electron exchange interaction in the 3s-3d level of Mn upon photoelectron ejection [237]. Several Mn 3s doublet peak separation values have been reported in the literature including 4.5, 5.2, 5.4 and 5.8 for MnO₂ (Mn⁴⁺), Mn₂O₃ (Mn³⁺), Mn₃O₄ (Mn²⁺,³⁺) and MnO (Mn²⁺), respectively [237, 262, 263]. As demonstrated in Figure 5.2 and Table 5.1, the Mn 3s doublet peak separation values are consistent with the literature showing Mn valence of 2, 4 and mixture of 3 and 4 for T1, T9 and T10 samples, respectively. Further, O 1s can be deconvoluted to three oxygen containing chemical bonds including Mn-O-Mn (oxide), Mn-O-H (hydroxide) and H-O-H (water molecule) [237, 262]. Relatively high content of hydroxide oxygen was detected on the surface of T1 and T9 samples, suggesting the co-existence of Mn³⁺/Mn²⁺ species for T1 and Mn⁴⁺/Mn³⁺ species for T9 (Figure 5.2 and Table 5.1).
Figure 5.2 XPS spectra of three representative electrodeposited MnOₓ samples at Mn 2p, Mn 3s and O 1s regions. The electrodeposition factors for each sample are as follows: T1 (C: 0.3 M, T: 295 K, S: Triton, 10 vol%, E: 800 mVₘₒₑ), T9 (C: 0.1 M, T: 343 K, S: Triton, 10 vol%, E: 800 mVₘₒₑ), T10 (C: 0.3 M, T: 295 K, S: Triton, 0 vol%, E: 1600 mVₘₒₑ).
Table 5.1 XPS peak analysis of electrodeposited MnO$_x$ samples (T1, T9 and T10). The deconvoluted data for Mn 2p, Mn 3s and O 1s is presented. The error associated with binding energy of peak position is ±0.1 eV. Other conditions idem to Figure 5.2.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mn 2p</th>
<th>Mn 3s</th>
<th>O 1s</th>
</tr>
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<tr>
<td></td>
<td>3/2 (eV)</td>
<td>1/2 (eV)</td>
<td>Eb1 (eV)</td>
</tr>
<tr>
<td>T1</td>
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<td>654.4</td>
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</tr>
<tr>
<td>T9</td>
<td>642.3</td>
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<tr>
<td>T10</td>
<td>642.9</td>
<td>654.3</td>
<td>84.5</td>
</tr>
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</table>
Several methods have been reported in the literature for surfactant removal from the electrodeposited samples including heat treatment, UV/ozone treatment and acetone/IPA washing methods [147, 264, 265]. IPA washing for 15 min at 343 K and 400 rpm rotation was chosen as a fast effective method without losing active material and damaging the crystal structure of electrodeposited MnO$_x$. FT-IR analysis was utilized to examine the effectiveness of the IPA washing method for surfactant removal from the manganese oxides deposited in solutions with highest surfactant concentration, i.e. 10 vol%. Figure 5.3 shows FTIR spectra for the electrodeposited MnO$_x$ samples under various electrodeposition conditions. The black dotted line (graph I), which represents FTIR spectrum of 40 wt% PTFE treated carbon cloth after nitric acid pre-treatment, shows two characteristic peaks between 1100-1200 cm$^{-1}$ that disappear after the completion of electrodeposition process (Figure 5.3). This could be an indication for deposition of materials on the substrate in all cases. In the case of electrodeposited MnO$_x$ in SDS containing solution, two major peaks for SDS at 1200 and 1460 cm$^{-1}$ overlaps with peaks associated with MnO$_2$ stretching and O-H bending vibrations of water, respectively [150, 266]. Similar interferences happen for both CTAB and Triton samples where same peaks overlap with major peaks for CTAB at 1486 cm$^{-1}$ and Triton X-100 at 1113 and 1512 cm$^{-1}$ [150, 266]. This makes it impossible to employ those peaks for evaluating the effectiveness of surfactant removal procedure. Since all of the surfactants used in this study contain a hydrocarbon chain composed of C and H, e.g. SDS (NaC$_{12}$H$_{25}$SO$_4$), CTAB (C$_{19}$H$_{42}$BrN) and Triton X-100 (C$_{14}$H$_{22}$O(C$_2$H$_4$O)$_n$(n=9-10)), traces of each surfactant on the electrodeposited MnO$_x$ can be detected using C-H stretching and C-H deformation vibrations of these hydrocarbon chains between 2700 to 3100 cm$^{-1}$ and approximately 1490 cm$^{-1}$, respectively [147]. As shown in Figure 5.3, the absence of such major peaks between
2700 and 3100 cm⁻¹ for all of the samples indicates the efficiency of IPA washing method as a fast effective surfactant removal technique for the cases studied here.

Figure 5.3 FT-IR spectra of MnOₓ samples (after IPA washing) electrodeposited on the pre-treated carbon cloth as substrate in presence of Triton X-100, SDS and CTAB. The electrodeposition factors for each sample are as follows: Carbon cloth (no electrodeposited material), Triton (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV MOE), SDS (C: 0.3 M, T: 295 K, S: 10 vol%, E: 800 mV MOE), CTAB (C: 0.3 M, T: 343 K, S: 10 vol%, E: 1600 mV MOE).

5.2.3 Factorial design experiments

A 2ⁿ half-fraction factorial design of four factors (Table 2.1) with three center-points (2ⁿ⁻¹+3) was constructed for each surfactant type, i.e. anionic, cationic and non-ionic, using JMP 11
statistical software compiling to a total of 33 random runs for the entire screening design experiments. With the defining relation of $I=CTSE$ in $2^{4-1}$ design, no main effect is aliased with any other main effect or any two-factor interaction. However, two-factor interactions are aliased with each other. The four main factors plus the three two-factor interaction alias pairs account for the seven degrees of freedom for the design. Pareto plots with estimates of factors and aliases were used to find the most important two-factor interaction in each alias pair based on the Ockham’s razor principle (check Appendix E). A single replicate factorial design is used to minimize the number of experimental runs. The single replicate strategy is a very common approach in variable screening experiments due to large number of factors under consideration [267]. In order to remedy for the random error, a wide range for factor levels as well as three center-points were introduced for each set of the experiments. Three different responses were introduced to better assess the ORR/OER bifunctional performances of the surfactant-assisted electrodeposited catalysts: 1) ORR mass activity at 656 mV, 2) OER mass activity at 1556 mV and 3) ORR/OER potential window (the absolute difference between the ORR onset potential at -2 mA cm$^{-2}$ and OER onset potential at 2 mA cm$^{-2}$). The catalyst loading was calculated using Fraday’s law via integration of the chronoamperometry graphs assuming the current efficiency for the main MnO$_2$ anodic electrodeposition reaction is 100% (eq. 28). Since the catalyst loadings were different for each run due to various factors involved (Table 2.1), the mass activity values, defined as the ORR or OER current densities at 656 and 1556 mV, respectively, divided by calculated loadings, were employed as responses in the factorial design. The standard error for the mean value of each response, calculated based on the three center-point tests, has been assumed to be the max. error involved in all of the measurements for each surfactant type.
5.2.3.1 Triton X-100 surfactant-assisted electrodeposition

Table 5.2 shows the design matrix and each response value for factorial runs in presence of Triton X-100 in a random order. Highest ORR and OER mass activities of -1359±202 and 20076±2098 mA g⁻¹, respectively, are obtained at high Mn concentration, low temperature, high surfactant concentration and low applied potential, i.e. run no. 1 (Table 2.1). However, the lowest ORR/OER potential window of 600±20 mV is achieved under opposite conditions of low Mn concentration and high temperature for run no. 9 (Table 2.1). It is worth mentioning that the MnOₓ electrodeposited at run no. 9 possesses the second best ORR and OER mass activity of -334±50 and 8417±879 mA g⁻¹, respectively.
Table 5.2 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of Triton X-100. Other conditions idem to Table 2.1.

<table>
<thead>
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<th>ORR mass activity (mA g(^{-1}))</th>
<th>OER mass activity (mA g(^{-1}))</th>
<th>ORR/OER potential window (mV)</th>
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\(a\) The Mn valence calculated based on the XPS results. The bold value corresponds to higher content of that specific Mn valence in the electrodeposited manganese oxide.

* Average factorial design response with standard error of the mean value calculated based on the center-point (0000) tests (The percentage of relative error is specified in parenthesis):

\(b\) 20.6±0.7 (3\%) mg cm\(^{-2}\), \(c\) -322±48 (15\%) mA g\(^{-1}\), \(d\) 4742±495 (10\%) mA g\(^{-1}\), \(e\) 625±21 (3\%) mV

Figure 5.4 shows the surface plots of three different responses studied here for the electrodeposited manganese oxides in presence of Triton X-100, correlating them to the most important factors and two-factor interactions based on the Pareto plots of estimates (Appendix E). The Pareto plot analysis of the estimates for factors has shown that the Mn concentration effect on the performance of electrodeposited MnO\(_x\) is not significant (Appendix E). The highest ORR mass activity can be achieved at high surfactant concentration and low temperature (Figure 5.4-A).
Moreover, low applied anodic potential is found to further improve the ORR mass activity of the electrodeposited samples. Same trend is observed for the highest OER mass activity since it appears at high surfactant concentration, low temperature and low applied anodic potential (Figure 5.4-B). The lowest ORR/OER potential window can be obtained at high surfactant concentration, low applied anodic potential but high temperature (Figure 5.4-C). The temperature seems to be a defining factor for the optimum bifunctional characteristics of electrodeposited manganese oxides with high temperatures providing low ORR/OER potential window while low temperatures lead to high ORR/OER mass activities (Figure 5.4). Other than the temperature, high surfactant concentration together with low applied anodic potential bring best bifunctional performances for the electrodeposited oxides in presence of Triton X-100.

The Rsquare for the responses, i.e. ORR mass activity, OER mass activity and ORR/OER potential window, is 0.987, 0.994 and 0.778, respectively, indicating negligible curvature effect for the first two responses (Rsquare close to 1) while a degree of non-linearity is observed in the behavior of the factors on the third response, i.e. ORR/OER potential window (check Appendix E).
Figure 5.4 Surface plots for $2^4 + 3$ factorial design in presence of Triton X-100 including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm$^{-2}$, respectively. Details of each run has been given in Table 5.2. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively.
5.2.3.2 **SDS surfactant-assisted electrodeposition**

In the presence of SDS, -988±45 and 31426±2481 mA g\(^{-1}\) are obtained as highest ORR and OER mass activities, respectively, for run no. 1 at high Mn concentration, low temperature, high surfactant concentration and low applied anodic potential (Table 5.3). While the lowest ORR/OER potential window of 620±7 mV is achieved for run no. 9 at the same conditions but low Mn concentration and low surfactant concentration (i.e. 0%), run no. 1 seems to be a better choice considering its high ORR and OER mass activities as well as second-lowest ORR/OER potential window, i.e. 658±8 mV (Table 5.3).
Table 5.3 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of SDS. Other conditions idem to Table 2.1.

<table>
<thead>
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<th>T</th>
<th>S</th>
<th>E</th>
<th>Mn valence&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Calculated loadings (mg cm&lt;sup&gt;-2&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ORR mass activity (mA g&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>OER mass activity (mA g&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>ORR/OER potential window (mV)&lt;sup&gt;e&lt;/sup&gt;</th>
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<sup>a</sup> The Mn valence calculated based on the XPS results. The bold value corresponds to higher content of that specific Mn valence in the electrodeposited manganese oxide.

* Average factorial design response with standard error of the mean value calculated based on the center-point (0000) tests (The percentage of relative error is specified in parenthesis):

<sup>b</sup> 13.9±1.9 (14%) mg cm<sup>-2</sup>, <sup>c</sup>-395±18 (5%) mA g<sup>-1</sup>, <sup>d</sup> 4742±953 (8%) mA g<sup>-1</sup>, <sup>e</sup> 684±8 (1%) mV

Figure 5.5 shows the surface plots representing the relationship between the most important two-factor interactions with different responses for the electrodeposited manganese oxides in presence of SDS as surfactant. The Pareto plot analysis of estimates for factors revealed that the applied anodic potential is the least significant factor contributing to each of the responses for electrodeposited MnOx in this case. LSV graphs in presence of SDS shown in Figure 5.1 further confirm the insignificancy of applied anodic potential in the investigated regime, i.e. 800 to
1600 mV$_{\text{MOE}}$, since they all contribute about the same current density for deposition of manganese oxides on nitric acid pre-treated 40% PTFE treated carbon cloth. As shown in Figure 5.5-A, the highest ORR mass activity of about 600 mA g$^{-1}$ can be achieved at high surfactant concentration and high Mn concentration. Moreover, low temperature enhances the ORR mass activity of the electrodeposited MnO$_x$. OER mass activity of about 35000 mA g$^{-1}$ can be obtained at similar conditions of high surfactant concentration and low temperature but low Mn concentration (Figure 5.5-B). The lowest ORR/OER potential window of about 600 mV is achieved at high surfactant concentration, high Mn concentration and low temperature (Figure 5.5-C). One can conclude that the optimum bifunctional responses of deposited manganese oxides are sensitive to the Mn concentration with high Mn concentration leading to highest ORR mass activity and lowest ORR/OER potential window while low Mn concentration provides samples with highest OER mass activity. Overall, high surfactant concentration and low temperature lead to electrodeposited manganese oxides with preferable bifunctional properties.

Moreover, the Rsquare for the responses, i.e. ORR mass activity, OER mass activity and ORR/OER potential window, is 0.997, 0.924 and 0.833, respectively, showing negligible curvature effect for the first two responses (Rsquare close to 1) while a degree of non-linearity is observed in the behavior of the factors on the third response, i.e. ORR/OER potential window (check Appendix E ).
Figure 5.5 Surface plots for $2^{4+1}+3$ factorial design in presence of SDS including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm$^{-2}$, respectively. Details of each run has been given in Table 5.3. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively.
5.2.3.3 CTAB surfactant-assisted electrodeposition

Looking at Table 5.4, CTAB-assisted electrodeposition of MnO₅ for run no. 8 generates -774±32 and 49237±2220 mA g⁻¹ as highest ORR and OER mass activities, respectively, at high Mn concentration, low temperature, high surfactant concentration and low applied anodic potential. However, the lowest ORR/OER potential window of about 730 mV is obtained for run no. 5 and 6 at high surfactant concentration but different other electrodeposition factors such as high temperature (Table 5.4). Overall, run no. 6 provides the best compromise between the two types of responses for the bifunctional electrocatalytic activity of the electrodeposited MnO₅ with the second best ORR/OER mass activities and ORR/OER potential window among the other runs (Table 5.4).
Table 5.4 Design matrix (in random order), Mn valence, calculated loadings and responses for the factorial design experiments in presence of CTAB. Other conditions idem to Table 2.1.

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<th>S</th>
<th>E</th>
<th>Mn valence(^a)</th>
<th>Calculated loadings (mg cm(^{-2}))(^b)</th>
<th>ORR mass activity (mA g(^{-1}))(^c)</th>
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<td>-144</td>
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\(^a\) The Mn valence calculated based on the XPS results. The bold value corresponds to higher content of that specific Mn valence in the electrodeposited manganese oxide.

\(^b\) 8.3±0.7 (6%) mg cm\(^{-2}\), \(^c\) -231±10 (4%) mA g\(^{-1}\), \(^d\) 4847±219 (5%) mA g\(^{-1}\), \(^e\) 857±40 (5%) mV

Figure 5.6 represents surface plots depicting effect of most important two-factor interactions on the three responses during CTAB-assisted electrodeposition of MnO\(_x\). The estimate analysis of factors using Pareto plots revealed that applied anodic potential in the investigated range has lesser effect on the responses comparing to the other three electrodeposition factors. In presence of CTAB, LSV graphs have also shown almost a constant current density through the whole potential range investigated here, i.e. 800 to 1600 mV\(_{\text{MOE}}\), confirming that the applied anodic potential is
not a major factor affecting the sample responses during surfactant-assisted electrodeposition of MnO$_x$ (Figure 5.1). According to the factorial design analysis showcased as surface plots in Figure 5.6, the highest ORR mass activity of about 450 mA g$^{-1}$ can be obtained at high Mn concentration and low temperature. High surfactant concentration can further enhance the ORR mass activity of the electrodeposited MnO$_x$. The highest OER mass activity of almost 30000 mA g$^{-1}$ is achieved at similar conditions of high surfactant concentration, low temperature and high Mn concentration (Figure 5.6-B). When it comes to the ORR/OER potential window, values as low as 800 mV can be reached at high surfactant concentration but low Mn concentration and high temperature, unlike the mass activity cases (Figure 5.6-C). The optimum level of electrodeposition factors for the best ORR/OER bifunctional performance of MnO$_x$ samples depends on the definition of each response. While the ORR/OER potential window reflects on the catalyst performance at low current densities neglecting the effect of loading, ORR and OER mass activities provide better insight on the high current density responses of electrodeposited MnO$_x$, normalized based on the calculated catalyst loading. Both responses are valuable as the latter reflects on more practical version of the ORR/OER catalyst performance covering the implications of mass transport limitations due to the loading differences whereas the former looks at the intrinsic bifunctional activity of the electrodeposited MnO$_x$ with different morphologies and crystal structures.

In the case of CTAB as surfactant, the Rsquare is 0.906, 0.955 and 0.848 for the ORR mass activity, the OER mass activity and the ORR/OER potential window, respectively. While a degree of non-linearity is observed in the behavior of the factors, i.e. C, T, S and E, on the ORR mass activity as well as the ORR/OER potential window, negligible curvature effect (Rsquare close to 1) is shown for the OER mass activity (check Appendix E).
Figure 5.6 Surface plots for $2^{4+3}$ factorial design in presence of CTAB including factorial responses with the most important factors and two-factor interactions based on the Pareto plots of estimates: A) ORR mass activity at 656 mV, B) OER mass activity at 1556 mV and C) ORR/OER potential window at -2 and 2 mA cm$^{-2}$, respectively. Details of each run has been given in Table 5.4. Red and green colors in the surface plots correspond to highest and lowest values of each response, respectively.
5.2.4 ORR/OER performance comparison

Figure 5.7 shows a comparison between the ORR and OER performances of the most active electrodeposited MnOₓ from each surfactant category. XPS studies have shown a mixture of Mn³⁺ and Mn⁴⁺ with higher contents of Mn³⁺ species including MnOOH for these samples (Table 5.2, Table 5.3 and Table 5.4). However, it is not possible to determine the exact content of each Mn species in different samples or identify the crystal structure of MnOₓ by only employing XPS analysis. Further structural analysis is needed to find the crystallographic forms of these electrodeposited Mn oxides.

In the ORR region, the electrodeposited MnOₓ labeled as Triton run no. 9 reveals the highest ORR electrocatalytic activity with 1.4, 2.2 and 64 times the ORR current densities (at 406 mV) of the SDS run no. 1, CTAB run no. 6 and carbon cloth substrate samples, respectively. The characteristic cathodic peaks observed for Triton run no. 9 at about 706 and 406 mV resemble the performance of β-MnO₂ (pyrolusite) in alkaline media with the first peak mainly due to the reduction of adsorbed oxygen on the unreduced active Mn⁴⁺ sites and the latter due to the reduction of dissolved oxygen on Mn³⁺/Mn⁴⁺ surfaces based on the mechanism discussed in eqs. 17-19 [45, 90, 98, 110, 268]. Pyrolusite has been known to possess largest oxygen sensitive specific area comparing to the other crystallographic forms of MnO₂, adsorbing high contents of O₂ and reducing it at more positive ORR potentials in alkaline media [90]. The reduction peak corresponding to adsorbed oxygen is reported to disappear at high rotation speeds when the mass transport limitations for the reduction of bulk dissolved oxygen (second cathodic peak) are lifted, or in the case of crystal structures with low ability of oxygen adsorption such as electrodeposited MnOₓ at SDS no. 1 and CTAB no. 6 [90]. One can also refer the enhanced ORR activity of electrodeposited oxide in Triton run no. 9 to its nano-sized petal-like microstructure of nano sheets.
with high porosity, as shown in Figure 5.8-A and B. This unique microstructure can also provide high surface area, further improving the ORR activity of the sample (Figure 5.7-A, Figure 5.8-A and B). The lowest ORR performance obtained by the CTAB sample could be explained by its micron-sized petal-shape microstructure with needle-like fibers (having high length to thickness ratio) (Figure 5.7-A, Figure 5.8-C and D) comparing to SDS run no. 1 exhibiting nano-sized sphere-shape protrusions (between 200-400 nm in diameter) (Figure 5.8-E and F).

In the OER region, electrodeposited MnOₓ for Triton run no. 9 shows the lowest onset potential and highest OER current densities while being followed by the other two manganese oxides with virtually the same OER activity, e.g. OER onset potential of 1435 mV at 10 mA cm⁻² for Triton run no. 9, about 30 mV lower than the SDS and CTAB samples and over 400 mV lower than the carbon substrate (Figure 5.7-B). Su et al. showed both experimentally and theoretically via DFT calculations that the β-MnO₂ is one of the most active forms of MnOₓ for OER in alkaline media [121]. This, with the unique nano-sized porous petal-shape microstructure could be the main reasons behind enhanced OER electrocatalytic activity of electrodeposited manganese oxide at Triton run no. 9 sample (Figure 5.7-B, Figure 5.8-A and B). One can conclude that the surface modification of MnOₓ via surfactant-assisted electrodeposition can help destabilizing the HOO_ads and HO_ads intermediates by introducing more binding sites such as lattice oxygen vacancies, breaking away from the linear scaling relationship between their binding energies, enhancing the ORR and OER electrocatalytic activity of electrodeposited manganese oxides. While Su et al. proposed that low number of adsorbed water molecules enhances the ORR activity based on the DFT calculations, Staszak-Jirkovský et al. argue that it could be more complicated than that since sensitive interaction between covalently bonded OH_ads and water molecules can form hydrogen-bonded complexes, i.e. HO_ads…H-OH, with specially configured water molecules called...
“activated water”, acting as a promoter for ORR [121, 269]. This can further enhance the ORR activity of the catalyst by facile transfer of protons to weakly adsorbed \( \text{HOO}_{\text{ads}}/\text{O}_{\text{ads}} \) intermediates and breaking away from the linear universal scaling relationship between binding energies of \( \text{HOO}_{\text{ads}} \) and \( \text{HO}_{\text{ads}} \) [121, 269]. The surface coverage of \( \text{OH}_{\text{ads}} \) has a defining role on the electrocatalytic activity of the catalyst since an optimum coverage is needed to provide sites for formation of \( \text{HO}_{\text{ads}} \)…H-OH complexes (promoter effect) as well as having bare catalyst sites necessary for formation of other reaction intermediates such as \( \text{HOO}_{\text{ads}} \) and \( \text{O}_{\text{ads}} \) (spectator effect) [269].

The comparison between ORR and OER overpotentials (at -2 and 2 mA cm\(^{-2}\), respectively) for the electrodeposited manganese oxides investigated here with relevant catalyst materials from the literature, reveals modest ORR activity but superior electrocatalytic activity towards OER, i.e. ORR overpotential of -366 mV (at -2 mA cm\(^{-2}\)) for the Triton run no. 9, between 50 to 150 mV more positive comparing to other non-precious metal catalysts such as Mn\(_2\)O\(_3\) [67], CoMn\(_2\)O\(_4\) [71], nanostructured Mn oxide thin film [69] and Core-Corona Structured Bifunctional Catalyst (CCBC) [76] as well as OER overpotential of 234 mV (at 2 mA cm\(^{-2}\)) for the Triton run no. 9, min. 100 mV lower than 20 wt% Ir/C and 20 wt% Ru/C [67, 69] (Figure 4.16 and Figure 5.7).
Figure 5.7 IR-corrected bifunctional performance comparison of electrodeposited MnOx in presence of different surfactants, i.e. Triton X-100, SDS and CTAB: A) ORR, B) OER. The electrodeposition factors for each sample are as follows: Carbon cloth substrate (no electrodeposited material), CTAB-Run no. 6 (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV MOE), SDS-Run no. 1 (C: 0.3 M, T: 295 K, S: 10 vol%, E: 800 mV MOE), Triton-Run no. 9 (C: 0.1 M, T: 343 K, S: 10 vol%, E: 800 mV MOE). Electrolyte: O2 saturated 6 M KOH at 293 K and P02 of 1 atm. Rotating electrode speed and potential scan rate were 400 rpm and 5 mV s^{-1}, respectively. Cycle number five is reported in all cases.
Figure 5.8 SEM micrographs of best performing electrodeposited MnOₓ oxides on nitric acid pre-treated carbon cloth: A and B) Triton run no. 9, C and D) SDS run no. 1, E and F) CTAB run no. 6. The electrodeposition factors are stated in Figure 5.7.
5.2.5 **Galvanostatic long-term durability testing of deposited MnO\textsubscript{x}**

Figure 5.9 presents the galvanostatic polarization comparison of the best performing electrodeposited MnO\textsubscript{x}, i.e. Triton run no. 9, and commercial manganese oxides. These galvanostatic polarization tests provide only a preliminary insight into durability of catalysts since the applied current density and test duration were chosen to avoid limitations associated with the employed flooded electrode half-cell design such as limited dissolved oxygen, needed during ORR, and heavy oxygen gas evolution, shielding the electrode surface during OER. In practice, air/oxygen breathing gas diffusion electrodes and electrolyte circulation would be employed as solutions to avoid dissolved oxygen limitations during ORR and O\textsubscript{2} gas evolution during OER, respectively.

In the OER region, electrodeposited MnO\textsubscript{x} sample in presence of Triton X-100 shows the highest OER electrocatalytic activity comparing to commercial manganese oxides, i.e. OER potentials of 1446, 1489 and 1694 mV (at 5 mA cm\textsuperscript{-2} and t=2 hrs) for the Triton run no. 9, commercial MnO\textsubscript{x} and γ-MnO\textsubscript{2} samples, respectively (Figure 5.9). The rate of OER potential increase for the Triton run no. 9 sample is the second low, i.e. 43 mV h\textsuperscript{-1}, for the total 2 hrs of testing comparing to 51 and 14 mV h\textsuperscript{-1} for commercial MnO\textsubscript{x} and γ-MnO\textsubscript{2}, respectively. However, the electrodeposited manganese oxide provides the lowest OER degradation rate of 5 mV h\textsuperscript{-1} for the second half of the OER testing compared to others tested here (Figure 5.9).

For the ORR part, commercial MnO\textsubscript{x} delivers the highest ORR electrocatalytic activity compared to others, i.e. electrode potentials of 856, 840 and 754 mV (at -2 mA cm\textsuperscript{-2} and t=2 hrs) for commercial MnO\textsubscript{x}, γ-MnO\textsubscript{2} and the Triton run no. 9 samples, respectively (Figure 5.9). In terms of stability, however, γ-MnO\textsubscript{2} sample possesses the lowest ORR potential degradation, i.e.
-2.4 mV h\(^{-1}\) comparing to -173 and -29 mV h\(^{-1}\) for the Triton run no. 9 and commercial MnO\(_x\) samples, respectively (Figure 5.9).

![Galvanostatic polarization comparison](image)

**Figure 5.9** Galvanostatic polarization comparison of in-house made and commercial manganese oxide GDEs: I) Manganese oxide/C GDE from Gaskatel GmbH (20 mg cm\(^{-2}\)), II) γ-MnO\(_2\)/C from Sigma Aldrich (loading 5.6 mg cm\(^{-2}\)) and III) Triton run no. 9 (C: 0.1 M, T: 343 K, S: 10 vol\%, E: 800 mV\(_{\text{MOE}}\)) (calculated loading 17.5 mg cm\(^{-2}\)). The galvanostatic polarization started at 5 mA cm\(^{-2}\) anodically applied to each GDE for 2 hrs followed by -2 mA cm\(^{-2}\) applied cathodically for 30 min in O\(_2\) saturated 6 M KOH. The rotation speed and temperature were 400 rpm and 293 K, respectively. P\(_{\text{O}_2}\) was 1 atm.

### 5.3 Conclusion

A comprehensive study was performed via \(2^n\) half-fraction factorial design to investigate the effects of main factors, such as Mn\(^{2+}\) concentration, applied potential, temperature, surfactant
concentration, as well as their two-factor interactions on the ORR and OER electrocatalytic activity of anodically electrodeposited manganese oxides. Triton X-100 as non-ionic, Sodium dodecyl sulfate (SDS) as anionic and hexadecyl-trimethyl-ammonium bromide (CTAB) as cationic surfactants were employed in this chapter to electro-synthesize nanostructured MnOₓ while several surface characterization methods were used to analyze morphology and Mn valence of the synthesized catalysts. In the Triton X-100 cases, high surfactant concentration together with low applied anodic potential are believed to bring the best ORR/OER bifunctional performances for the electrodeposited Mn oxides. Mn concentration was found to be an insignificant player. Temperature, on the other hand, is believed to have different effect depending on its level with high temperature providing low ORR/OER potential window while low temperature leads to high ORR/OER mass activities. In the SDS category, the ORR/OER bifunctional responses of the deposited manganese oxides were sensitive to the Mn concentration with high Mn concentration leading to highest ORR mass activity and lowest ORR/OER potential window, while low Mn concentration provides samples with highest OER mass activity. Overall, high surfactant concentration and low temperature were found to lead to preferable bifunctional activities. For the CTAB samples, the highest ORR and OER mass activities were found to achieve at high surfactant concentration, low temperature and high Mn concentration. When it comes to the ORR/OER potential window, high temperature and low Mn concentration were more favorable. The effect of anodic applied potential on the ORR and OER activities of the electrodeposited samples was found to be negligible in the case of SDS and CTAB surfactants.

The surface modifications of MnOₓ via surfactant-assisted electrodeposition can significantly alter the morphology and Mn valence in the deposited material, provide new binding sites for the HOO\(_{(\text{ads})}\) and HO\(_{(\text{ads})}\) intermediates, help break away from the linear scaling relationship between
their binding energies as a major contributor to the ORR and OER overpotentials and hence, enhance the ORR and OER electrocatalytic activity of electrodeposited manganese oxides. The formation of hydrogen-bonded complexes, i.e. \( \text{H}_2\text{O}^{(\text{ads})} \cdots \text{H-OH} \), with specially configured water molecules called “activated water”, can further enhance the ORR activity of the catalyst by facile transfer of protons to weakly adsorbed \( \text{HOO}^{(\text{ads})}/\text{O}^{(\text{ads})} \) intermediates and break away from the linear universal scaling relationship. This, however, depends on the surface coverage of \( \text{OH}^{(\text{ads})} \) which provides binding sites for formation of \( \text{HO}^{(\text{ads})} \cdots \text{H-OH} \) complexes (promoter effect).

The electrodeposited MnO\(_x\) for Triton run no. 9 was found to show the best ORR and OER electrocatalytic activities among other deposited manganese oxides investigated here, mainly due to a possible crystal structure of \( \beta\)-MnO\(_2\) and a nano-sized petal-like microstructure of nano sheets with high porosity. Comparing to wide range of noble metals and their oxides such as Ir, Ru and IrO\(_2\), the electrodeposited manganese oxide for Triton run no. 9 showed lower OER overpotential (min. 100 mV) at 2 mA cm\(^{-2}\). For the ORR, it provides between 50 to 150 mV more positive overpotential at -2 mA cm\(^{-2}\) compared to the other non-precious metal compounds such as CoMn\(_2\)O\(_4\) and Core-Corona Structured Bifunctional Catalyst (CCBC). The galvanostatic polarization tests further confirmed the promising OER activity for the Triton run no. 9 sample with potentials as low as 1446 mV (at 5 mA cm\(^{-2}\) and t=2 hrs), about 40 mV lower than the commercial MnO\(_x\), and a degradation rate of 43 mV h\(^{-1}\), about 10 mV h\(^{-1}\) lower than its commercial counterparts.
Chapter 6: Carbon support effect on ORR/OER bifunctional activity and durability of non-PGM mixed-oxide catalyst: Graphene vs. commercial carbon materials ††††

6.1 Introduction

This chapter aims at investigating the electrocatalytic activity and long-term durability of different carbonaceous materials, i.e. Vulcan XC-72, multi-walled carbon nanotubes (MWCNT), graphene and N-doped graphene, either as a support for a highly active ORR/OER bifunctional non-PGM catalyst, i.e. MnO$_2$-LaCoO$_3$, or an oxygen electrocatalyst itself in alkaline media. RRDE measurements were performed to give an insight on the mechanism involved on each carbonaceous material during ORR. Cyclic voltammetry tests on the carbons further revealed Vulcan XC-72 to be the most active bifunctional catalyst for both ORR and OER among other carbons investigated here. The carbonaceous materials employed as supports for MnO$_2$-LaCoO$_3$ were found to contribute differently to each part of oxygen electrocatalysis on the non-PGM catalyst. For ORR, the order of electrocatalytic activity for the samples containing MnO$_2$-LaCoO$_3$ vs. Pt is as follows: MWCNT-Graphene > Vulcan XC-72 > Pt > MWCNT-N-doped graphene > MWCNT > Graphene > N-doped graphene. However, the OER electrocatalytic activity of oxides containing carbons vs. Pt follows a different trend: MWCNT-Graphene > MWCNT-N-doped graphene > MWCNT >

†††† A version of this chapter is in preparation for publication. Parts of this chapter were filed as United States and Canadian patent applications:
- P. Hosseini-Benhangi, M. A. Garcia-Contreras, A. Alfantazi, E. Gyenge, “Carbon support effect on ORR/OER bifunctional activity and durability of non-PGM mixed-oxide catalyst: Graphene vs. commercial carbon materials”, to be submitted.
Vulcan XC-72 > Pt > Graphene > N-doped graphene. The ORR/OER bifunctional durability performances of GDEs containing MnO$_2$-LaCoO$_3$ supported on MWCNT-Graphene and Vulcan XC-72 were tested using an accelerated degradation testing protocol. Overall, MnO$_2$-LaCoO$_3$-MWCNT-Graphene GDE showed better durability than the Vulcan XC-72 containing sample. The main factors affecting the performance degradation of mixed-oxide GDEs during ORR and OER were discussed. The role of lanthanum cobalt oxide in the performance loss of the mixed-oxide catalyst during accelerated degradation test was concluded to be insignificant. A wide range of characterization techniques including SEM and TEM studies were employed to investigate the microstructure-property relations as well.

6.2 Results and discussion

6.2.1 Microstructural studies of catalyst and support materials

Figure 6.1 presents the TEM images of carbonaceous materials as well as non-PGM oxides, i.e. MnO$_2$ and LaCoO$_3$, used as support and catalyst material in this study. The microstructure of graphene consists of crumpled and randomly oriented large-area graphene sheets together with small number of flakes with an average length of 200 nm (Figure 6.1-A). Low-magnification TEM images show the tendency of graphene sheets to agglomerate even after hours of sonication in IPA. For N-doped graphene sample, the morphology is almost the same as graphene with less flakes and more ultrathin graphene sheets (Figure 6.1-B). The material’s tendency to agglomerate even after prolonged sonication in IPA is observed. Figure 6.1-C shows the nano-sized carbonaceous particles of Vulcan XC-72 that range from 20 to 30 nm in size. Excellent particle distribution is observed in low-magnification TEM images for Vulcan XC-72 dispersed in IPA. As for MWCNT, TEM micrographs show tangled tubes with outer diameter of 8-18 nm and length of 0.5-5 µm with modest distribution in IPA (Figure 6.1-D). The MnO$_2$ particles vary in shape from pillars with
various length-to-width ratios to smooth spheres (Figure 6.1-E). For pillar-shaped particles, the length-to-width ratio changes from 3 to 7.5 with the lengths as small as 30 nm to max. 450 nm (Figure 6.1-E). The size of sphere-like MnO₂ particles goes from 70 to 100 nm in diameter (Figure 6.1-E). LaCoO₃ particle size extends between 50-100 nm (Figure 6.1-F).
Figure 6.1 TEM images of materials investigated in this chapter as oxygen catalyst or catalyst support: A) Graphene, B) N-doped graphene, C) Vulcan XC-72, D) MWCNT, E) MnO$_2$ and F) LaCoO$_3$. 
6.2.2  RRDE studies of carbonaceous materials for ORR

As mentioned in section 1.2.2.2, the ORR in alkaline media is composed of series of complex electrochemical reactions with two proposed pathways: a) Four-electron pathway or b) Two-electron pathway (Table 1.2).

In order to better understand the ORR pathway on carbonaceous materials, RRDE experiments were performed (Appendix B and Figure 6.2). A closer look at the shape of O₂ electro-reduction voltammograms on different catalysts reveals a noticeable downward peak between 670 and 750 mV for all carbonaceous materials (Figure 6.2-A). This reduction peak becomes less visible after increasing the rotation speed from 400 to 2500 rpm (Figure 6.2-A). The data for other rotation speeds are not presented in the Figure 6.2-A for the sake of clarity. The presence of this peak at low rotation speeds is attributed to the electro-reduction of adsorbed oxygen on the catalyst layer [270-272]. Increasing the rotation speed leads to higher diffusion-controlled ORR currents for the oxygen in bulk electrolyte, gradually masking the peak current from adsorbed O₂. The absence of adsorbed O₂ peak during the ORR on N-doped graphene could be related to its flat morphology of flakes and ultrathin graphene sheets (Figure 6.1-B) which limits the presence of adsorbed oxygen in different layers of catalyst material. As shown in Figure 6.2-A, Vulcan XC-72 possesses the highest electrocatalytic activity for ORR, i.e. lowest ORR onset potential of 781 mV at -0.2 mA cm⁻² and highest ORR limiting current density of -0.248 mA cm⁻² at 600 mV, followed by MWCNT, graphene and N-doped graphene, respectively. The carbonaceous materials that showed a peak in the early stages of ORR, possess distinguishable peaks in the same potential region for calculated hydrogen peroxide ion content (Figure 6.2-B) and the number of electrons involved in the ORR (Figure 6.2-C). This means that the adsorbed oxygen is going through a different ORR pathway comparing to the oxygen from bulk electrolyte. As an example,
Vulcan XC-72 shows HO$_2^-$ content of 58% at 725 mV which corresponds to 2.8e$^-$ while it moves between 90% to 100% for HO$_2^-$ ions below 660 mV, showing 2e$^-$ transfer during the ORR for oxygen from bulk electrolyte (Figure 6.2-B and C). This further reveals that the ORR is going through two competitive 2e$^-$ and 4e$^-$ pathways near the peak for the electro-reduction of adsorbed O$_2$. It is most likely that the adsorbed oxygen coordinates parallel to the catalyst surface, showing direct 4e$^-$ pathway (eqs. 12, 15 and 16) while the ORR for the O$_2$ in the bulk electrolyte follows a 2e$^-$ pathway leading to hydrogen peroxide ions (eqs. 12, 13 and 14). For both MWCNT and graphene, the competition between the 2e$^-$ and 4e$^-$ pathways in the potential region of adsorbed oxygen reduction continues with about 60% HO$_2^-$ content and 2.8 e$^-$ (Figure 6.2-B and C). Out of this region, MWCNT favors 2e$^-$ pathway more while graphene shows lower HO$_2^-$ content, moving toward 4e$^-$ pathway (Figure 6.2-B and C). N-doped graphene, however, depicts lowest content of hydrogen peroxide ions below 710 mV, meaning it favors 4e$^-$ pathway even though the 2e$^-$ pathway is dominant at some sites (Figure 6.2). While it is generally believed that the 4e$^-$ ORR pathway is dominant on metals and their oxides (both noble and transition metals) and the 2e$^-$ pathway primarily prevails on the surface of carbonaceous materials [2, 10, 17, 45, 90, 98, 110], many studies reported a mixture of 2e$^-$ and 4e$^-$ pathways for MWCNT, graphene and N-doped graphene with the nitrogen-doped graphene showing close-to-four values for the electrons involved in ORR per each mole of oxygen [10, 100, 199, 206, 273]. Lower ORR performances of graphene and N-doped graphene, despite the higher number of electrons involved comparing to Vulcan XC-72, could be related to the flat morphology of graphene-based materials, blocking the pores necessary for the electrolyte to reach the active sites and hence, reducing their ECSA for the same loadings of Vulcan XC-72 (Figure 6.2).
Figure 6.2 Rotating ring disk electrode results for ORR on Graphene (I), N-doped Graphene (II), MWCNT (III) and Vulcan XC-72 (IV): A) $O_2$ reduction current densities obtained from disk electrode ($i_d$) when polarized from 1170 to 500 mV (bottom) and the corresponding oxidation current densities on the ring at 1353 mV ($i_r$) as a function of disc potentials (top). B) Calculated percentage of hydrogen peroxide ions produced during ORR (%$HO_2^-$). C) Calculated number of electrons transferred per molecule of oxygen during ORR ($n$). Carbon loadings of 0.5 mg cm$^{-2}$ each. $O_2$ saturated 6 M KOH. 5 mV s$^{-1}$. 293 K. $P_{O_2}$ of 1 atm.
6.2.3 ORR/OER bifunctional electrocatalytic activity measurements: Carbonaceous materials as oxygen catalysts

Figure 6.3 shows the ORR/OER electrocatalytic activity of the investigated carbonaceous materials at their initial stage. Higher ORR peak current densities for the carbonaceous materials, comparing to the ones from RRDE experiments on the same carbons, are mainly due to the employed testing protocol for assessing the ORR/OER bifunctional performance of these materials where the samples were anodically polarized first, forming both adsorbed and bulk oxygen at the active sites during OER. The resulting oxygen layer is easily accessible to be reduced during the subsequent cathodic polarization, enhancing the ORR current densities on the carbonaceous materials (compare Figure 6.2-A and Figure 6.3-A). While Vulcan XC-72 demonstrates the highest ORR peak current density of -0.9 mA cm\(^{-2}\) at around 760 mV, MWCNT containing catalyst layers, i.e. MWCNT, MWCNT-N-doped graphene and MWCNT-graphene, possess the lowest ORR overpotentials of about 305 mV at -0.2 mA cm\(^{-2}\) (Figure 6.3-A). Small synergistic effect after 593 mV is observed when MWCNT is mixed with N-doped graphene (Figure 6.3-A). Similar to the RRDE experiments, N-doped graphene shows the poorest ORR electrocatalytic activity when used as lone oxygen catalyst (Figure 6.2-A and Figure 6.3-A). As explained earlier, this is mainly due to the flat morphology of N-doped graphene with high content of ultra-thin sheets that tend to agglomerate and lie on top of each other (Figure 6.1-B), effectively reducing the ECSA of the N-doped graphene, leading to its poor ORR performance even though high ORR electrocatalytic activity for N-doped carbon-based materials is reported in the literature [10, 100, 199, 206, 273].

For the OER, Vulcan XC-72 reveals the highest electrocatalytic activity up to 1650 mV with the lowest OER overpotential of 211 mV at 0.2 mA cm\(^{-2}\) (Figure 6.3-B). A significant synergistic effect is observed when either graphene or N-doped graphene is mixed with MWCNT, showing
13 and 150 times, respectively, the OER current densities (at 1600 mV) of the individual graphene-based materials (Figure 6.3-B). Moreover, the MWCNT-graphene surpasses the OER electrocatalytic activity of Vulcan XC-72 after 1650 mV, further confirming the synergistic effect of mixed carbons (Figure 6.3-B). This synergistic effect can be attributed to the unflattened morphology of the carbonaceous mixture, i.e. MWCNT with either graphene or N-doped graphene. This morphology provides a porous structure with increased ECSA for ORR as well as necessary pore density for oxygen bubble evolution and release, which itself enhances OER performance of the mixture significantly [5, 226].
Figure 6.3 Bifunctional ORR/OER performance of carbonaceous materials, i.e. Graphene, N-doped graphene, MWCNT, Vulcan XC-72, MWCNT-Graphene and MWCNT-N-doped graphene: A) ORR, B) OER. Initial stage IR-corrected polarization curves obtained by potential scanning between 475 to 1673 mV, starting with anodic polarization. Carbon loadings are fixed at 0.5 mg cm\(^{-2}\), each. In cases where two materials were mixed, a weight ratio of 1:1 was used. Cycle number five is reported in all cases. \(O_2\) saturated 6 M KOH. 293 K. 400 rpm. 5 mV s\(^{-1}\). \(P_o\) of 1 atm.
The ORR Tafel plots further confirms the enhanced ORR electrocatalytic activity of MWCNT containing carbonaceous catalyst materials, i.e. MWCNT, MWCNT-graphene and MWCNT-N-doped graphene, comparing to each of the individual graphene-based materials as well as Vulcan XC-72 (Figure 6.4-A). The best performing ORR catalyst material, i.e. MWCNT-graphene reveals small synergistic effect comparing to each of its constituents at overpotentials more negative than -280 mV with Tafel slope and exchange current density values of -41mV dec\(^{-1}\) and 7.7×10\(^{-6}\) µA cm\(^{-2}\), respectively (Figure 6.4-A and Table 6.1). For the OER, the superior electrocatalytic activity of Vulcan XC-72 is easily observable as shown in Figure 6.4-B. However, almost all of the carbonaceous materials (excluding N-doped graphene) show abnormal Tafel slopes (i.e. 223 to 444 mV dec\(^{-1}\)) and orders of magnitude higher OER exchange current densities comparing to the ORR part (Figure 6.4-B and Table 6.1). This could be related to the fact that the OER is not the main reaction occurring on the surface of carbonaceous materials at anodic potentials in alkaline media [204, 205]. Ross et al. reported that part of the overall anodic current obtained from acetylene black surface in the OER region is due to the corrosion of carbon, which is a function of both potential and temperature [204, 205]. According to their study, the carbon corrosion at room temperature mainly comes from two distinctive processes: 1) Dissolution to carbonate ion (CO\(_3^{2-}\)) and 2) Carbon gasification to carbon monoxide [204, 205]. While the rate of these processes are different for carbons made under different treatments or catalyzed with diverse catalysts [203-205, 274], their occurrence decreases the current efficiency of OER which leads to unusual values for the calculated OER kinetic parameters such as Tafel slope and exchange current density (Figure 6.4-B and Table 6.1). It is important to note that the current efficiency of the oxygen evolution reaction on both catalyzed and un-catalyzed carbons is reported to increase at high anodic potentials, going over 75% at about 1600 mV in concentrated KOH solutions [204].
Figure 6.4 IR-corrected bifunctional ORR/OER Tafel-lines of investigated carbonaceous catalyst materials: A) ORR, B) OER. The numbers associated with each line represent the respective apparent Tafel slopes. Cycle number five is reported in all cases. The N₂-baseline is subtracted from the ORR part for all samples. For the OER part, capacitive background current at open circuit potential is removed from each corresponding voltammogram. Other conditions idem to Figure 6.3.
Table 6.1 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated carbonaceous catalyst materials in Figure 6.3. The exchange current densities are expressed per geometric area. The apparent Tafel slope and exchange current density values are obtained over a potential range of min. 50 mV on six replicates. Other conditions idem to Figure 6.3.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$b_{\text{ORR}}$ (mV dec$^{-1}$)</th>
<th>$i_{0,\text{ORR}}$ (µA cm$^{-2}$)</th>
<th>$b_{\text{OER}}$ (mV dec$^{-1}$)</th>
<th>$i_{0,\text{OER}}$ (µA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>-46 ±1</td>
<td>4.6×10$^{-5}$ ±0.09×10$^{-5}$</td>
<td>263 ±5</td>
<td>1.3 ±0.03</td>
</tr>
<tr>
<td>N-doped graphene</td>
<td>-122 ±2</td>
<td>6.3×10$^{-2}$ ±0.1×10$^{-2}$</td>
<td>37 ±1</td>
<td>9.3×10$^{-12}$ ±0.2×10$^{-12}$</td>
</tr>
<tr>
<td>MWCNT</td>
<td>-55 ±1</td>
<td>4.7×10$^{-4}$ ±0.09×10$^{-4}$</td>
<td>299 ±6</td>
<td>15 ±0.3</td>
</tr>
<tr>
<td>Vulcan XC-72</td>
<td>-83 ±2</td>
<td>2.0×10$^{-2}$ ±0.04×10$^{-2}$</td>
<td>444 ±9</td>
<td>101 ±2</td>
</tr>
<tr>
<td>MWCNT-Graphene</td>
<td>-41 ±1</td>
<td>7.7×10$^{-6}$ ±0.2×10$^{-6}$</td>
<td>223 ±4</td>
<td>7.4 ±0.1</td>
</tr>
<tr>
<td>MWCNT-N-doped graphene</td>
<td>-51 ±1</td>
<td>2.3×10$^{-4}$ ±0.05×10$^{-4}$</td>
<td>249 ±5</td>
<td>12 ±0.2</td>
</tr>
</tbody>
</table>
6.2.4 ORR/OER bifunctional electrocatalytic activity measurements of non-PGM oxide oxygen catalyst: MnO$_2$-LaCoO$_3$ supported on carbonaceous materials

Figure 6.5 shows the initial stage cyclic voltammograms of mixed-oxide catalyst, i.e. MnO$_2$-LaCoO$_3$ (1:1 weight ratio), supported on different investigated carbonaceous materials in O$_2$ saturated 6 M KOH. The cyclic voltammogram of 50 wt% Pt/Graphitized carbon has been added as a baseline for comparison. The Pt voltammogram reveals two distinctive oxidation and reduction peaks at 861 and 756 mV which are associated with adsorption of hydroxyl ion (OH$^-$), also known as formation of PtOH layer, and reduction of the oxide layer (PtOH), respectively (Figure 6.5) [275, 276]. The addition of a MnO$_2$-LaCoO$_3$ catalyst to the carbons significantly enhances the ORR/OER bifunctional performance of the carbonaceous materials (compare Figure 6.3 and Figure 6.5). Compared to Pt, the activity of MnO$_2$-LaCoO$_3$-N-doped graphene toward oxygen reduction and evolution reactions is virtually absent mainly due to its flattened morphology of ultra-thin sheets (Figure 6.5-A and Figure 6.1-B). A considerable synergistic effect is observed when MWCNT is being physically mixed with either N-doped graphene or graphene as a support for MnO$_2$-LaCoO$_3$ (Figure 6.5). The overall best performing catalyst layer was found to be the MnO$_2$-LaCoO$_3$-MWCNT-Graphene with visually enhanced ORR and OER waves, e.g. ORR and OER mass activities of -6.694 A g$^{-1}$ at 850 mV and 15.536 A g$^{-1}$ at 1650 mV (Figure 6.3 and Figure 6.5). This enhanced ORR/OER bifunctional electrocatalytic activity can be better presented in comparison to the benchmark used in this study, i.e. 50 wt% Pt/graphitized carbon performance. The Pt sample possesses ORR mass activity of -3.828 A g$^{-1}$ (at 850 mV) and OER mass activity of 7.992 A g$^{-1}$ (at 1650 mV), about 43% and 48%, respectively, lower than the ones associated with the MnO$_2$-LaCoO$_3$-MWCNT-Graphene catalyst layer (Figure 6.5-C).
Figure 6.5 Bifunctional ORR/OER performance of MnO$_2$-LaCoO$_3$ catalyst supported on various carbonaceous materials: A) Graphene and N-doped graphene, B) MWCNT and Vulcan XC-72, C) MWCNT-Graphene and MWCNT-N-doped graphene. The 50 wt% Pt/Graphitized carbon is being shown as the baseline for comparison (Pt loading of 0.25 mg cm$^{-2}$). The oxide and carbon loadings were 0.5 mg cm$^{-2}$ each. A weight ratio of 1:1:1:1 for MnO$_2$:LaCoO$_3$:Carbon1:Carbon2 (if available) was used. Cycle number five is reported in all cases. Other conditions idem to Figure 6.3.
As discussed in section 1.2.2.4, a major contributor to ORR and OER overpotentials is found to be the difference in the binding energy levels of HOO\textsubscript{(ads)} and HO\textsubscript{(ads)} intermediates, known as the universal scaling relationship [121, 124, 133]. Breaking away from this confining linear scaling relationship is only attainable by modifications applied to catalyst surfaces and not blindly browsing other possible elements active for both ORR and OER. These modifications can include, but not limited to, manipulating the crystal structure of catalyst materials with introduction of dopants, defects or magnetic fields as well as changing the nature of catalyst/support interactions at their interfaces [122]. Now, this could explain the different ORR/OER electrocatalytic activity shown for mixed-oxide catalyst, i.e. MnO\textsubscript{2}-LaCoO\textsubscript{3}, supported on the wide range of carbonaceous materials studied here (Figure 6.5). To explain the synergistic effect of MWCNT mixed with either graphene or N-doped graphene, the combination could have provided near-the-ideal configuration/distribution of the materials for the electron transfer during both ORR and OER on mixed oxides, help destabilizing the HOO\textsubscript{(ads)} and HO\textsubscript{(ads)} intermediates with the new available binding sites and radically breaking away from the linear scaling relationship between their binding energies, thus enhancing the ORR and OER activity of the catalyst layer compared to other investigated oxygen catalysts here (Figure 6.5-C).

Turning the attention to the OER performance of studied MnO\textsubscript{2}-LaCoO\textsubscript{3}-Carbons catalyst layers, there are two other factors that can partially interfere with the anodic currents obtained in the OER region: 1) Carbon corrosion, 2) MnO\textsubscript{2} electro-corrosion (eq. 39).

\[
\text{MnO}_2 + 4OH^- \rightarrow \text{MnO}_4^- + 2H_2O + 3e^- \quad (E_{298K}^0 = 0.595 \text{ V}_{SHE})
\] (39)
As discussed in section 6.2.3, it has been shown that the rate of carbon corrosion processes on catalyzed or un-catalyzed carbons in concentrated alkaline solutions decreases dramatically at certain anodic potentials (about 1600 mV in 30 wt% KOH at 318 K) [204]. Different mechanisms have been proposed for this behavior with the most plausible theory based on limited wet area when gas bubble formation and entrapment in the microporous sublayer pushes out the electrolyte and dries the interior layer, effectively lowering the ECSA and hindering the electro-oxidation reactions to occur [205, 277]. This, however, fails to explain the experimentally-backed data showing an increase in the OER rate of catalyzed carbon at high anodic potentials where carbon corrosion rate drops dramatically, Staud and Ross argued [205]. With this in mind and the fact that the anodic current densities (at 1650 mV) for catalyzed MWCNT-N-doped graphene and MWCNT-Graphene samples are 7 and 17 times the ones for un-catalyzed samples, respectively, one can conclude that the carbon corrosion effect is likely to be negligible here, specially at high anodic potentials (Figure 6.3 and Figure 6.5-C).

While thermodynamics indicates the second possible corrosion factor in the OER region, i.e. MnO₂ electro-corrosion to MnO₄⁻ (eq. 39), should take place at above 1690 mV, it kinetically depends on the nature of the electrolyte and the available ions [230]. Gao et al. studied the effects of alkali-metal cations on electro-corrosion of MnOₓ using atomic absorption spectroscopy, showing that small electro-corrosion currents diminish at a certain anodic potential (about 1900 mV in 0.5 M KOH) to almost zero [230]. They argue that it could be due to the formation of a passivating oxide layer without much effect on the catalyst’s electrocatalytic activity for OER [230]. Hence, it can be inferred that the major portion of anodic currents in the potential range studied here is associated with the OER catalyzed by MnO₂-LaCoO₃-Carbon(s) catalyst layers (Figure 6.5).
Next, the Tafel plots associated with the MnO$_2$-LaCoO$_3$ catalyst supported on wide range of carbons are shown in Figure 6.6, with the Tafel slopes and exchange current densities summarized in Table 6.2. With respect to ORR, the Tafel slope for different samples ranges from -52 to -86 mV dec$^{-1}$, all within the kinetic control region limits (Figure 6.6). MWCNT-Graphene sample possesses the highest electrocatalytic activity with Tafel slope and exchange current density of -84 mV dec$^{-1}$ and 2.1 $\mu$A cm$^{-2}$, respectively, followed by Vulcan XC-72 and Pt (Figure 6.6-A and Table 6.2). For the OER part, Tafel slope values extend from 83 to 127 mV dec$^{-1}$, still within the kinetic controlled region but near the max. limit, i.e. 120 mV dec$^{-1}$ (Figure 6.6). This is expected since other parasitic reactions can influence the anodic currents in the OER region as discussed earlier. MWCNT-Graphene still shows the highest electrocatalytic activity followed by MWCNT-N-doped graphene and Pt, obtaining a Tafel slope and exchange current density of 123 mV dec$^{-1}$ and 2.1 $\mu$A cm$^{-2}$, respectively (Figure 6.6-B and Table 6.2). Similar exchange current densities calculated from the ORR and OER parts of the voltammograms in the presence of mixed oxides corroborate the discussion earlier on high current efficiencies for both ORR and OER in respective potential regions, especially in high anodic potentials where parasitic reactions are probable (Table 6.2). The synergistic effect of mixing MWCNT with either graphene or N-doped graphene is further confirmed with order of magnitude higher exchange current densities for the mixture comparing to each lone support, e.g. the exchange current densities for MWCNT:Graphene and MWCNT:N-doped graphene supported catalyst layers are 16 and 1000 times, respectively, the ones for the samples with the respective individual graphene-based material as catalyst support (Table 6.2).
Figure 6.6 IR-corrected bifunctional ORR/OER Tafel-lines of investigated MnO$_2$-LaCoO$_3$ catalyst supported on various carbonaceous materials studied in Figure 6.5 (50 wt% Pt/Graphitized carbon as the baseline): A) ORR, B) OER. The numbers associated with each line represent the respective apparent Tafel slopes. Cycle number five is reported in all cases. The N$_2$-baseline is subtracted from the ORR part for all samples. For the OER part, capacitive background current at open circuit potential is removed from each corresponding voltammogram. Other conditions idem to Figure 6.5.
Table 6.2 The apparent exchange current densities and Tafel slopes for the initial stage ORR and OER activities of the investigated catalyst materials in Figure 6.5. The exchange current densities are expressed per geometric area. The apparent Tafel slope and exchange current density values are obtained over a potential range of min. 50 mV on six replicates. Other conditions idem to Figure 6.5.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>b_{ORR} (mV dec^{-1})</th>
<th>b_{OER} (mV dec^{-1})</th>
<th>i_0 (µA cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO_2-LaCoO_3-Graphene</td>
<td>-86 ±2</td>
<td>127 ±3</td>
<td>0.13 ±0.003</td>
</tr>
<tr>
<td>MnO_2-LaCoO_3-N-doped graphene</td>
<td>-52 ±1</td>
<td>83 ±2</td>
<td>3.4×10^{-4} ±0.07×10^{-4}</td>
</tr>
<tr>
<td>MnO_2-LaCoO_3-MWCNT</td>
<td>-82 ±2</td>
<td>120 ±2</td>
<td>0.62 ±0.01</td>
</tr>
<tr>
<td>MnO_2-LaCoO_3-Vulcan XC-72</td>
<td>-72 ±1</td>
<td>125 ±3</td>
<td>0.61 ±0.01</td>
</tr>
<tr>
<td>MnO_2-LaCoO_3-MWCNT:Graphene</td>
<td>-84 ±2</td>
<td>123 ±2</td>
<td>2.1 ±0.04</td>
</tr>
<tr>
<td>MnO_2-LaCoO_3-MWCNT-N-doped graphene</td>
<td>-73 ±1</td>
<td>106 ±2</td>
<td>0.33 ±0.007</td>
</tr>
<tr>
<td>50 wt% Pt/Graphitized carbon</td>
<td>-67 ±1</td>
<td>127 ±3</td>
<td>0.28 ±0.006</td>
</tr>
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</table>
6.2.5 Bifunctional accelerated degradation testing: MnO$_2$-LaCoO$_3$ supported on MWCNT-Graphene or Vulcan XC-72

Figure 6.7 shows the ORR/OER bifunctional durability performance of GDEs with MnO$_2$-LaCoO$_3$ and two carbonaceous materials studied here, i.e. MWCNT-Graphene and Vulcan XC-72, during one hundred continuous potential cycling. MWCNT-Graphene containing catalyst layer was chosen as the best performing ORR/OER bifunctional catalyst investigated here while the Vulcan XC-72 was chosen as the baseline, mainly due to being the conventional support for oxygen catalysts. MWCNT-Graphene GDE provided superior ORR and OER electrocatalytic activity comparing to Vulcan XC-72 throughout the whole potential cycling tests. The ORR and OER performance losses of MWCNT-Graphene GDE was found to be about half of what Vulcan XC-72 GDE revealed during the first fifty cycles of accelerated degradation tests (Figure 6.7). Overall, MnO$_2$-LaCoO$_3$-MWCNT-Graphene GDE seems to provide better ORR/OER durability compared to Vulcan XC-72 supported GDE.

It is well known in the literature that the MnO$_2$ witnesses extensive changes in its Mn valence and crystallographic structure during potential cycling between ORR and OER regions, resulting in diverse Mn containing phases with different activity and durability for both ORR and OER [4, 5, 39, 45, 46, 67, 90, 98, 113, 227]. In section 4.2.1.2, we have shown using EELS analysis that the MnO$_2$ in MnO$_2$-LaCoO$_3$-Vulcan XC-72 GDE was not regenerated efficiently in the same conditions as here during extensive potential cycling between ORR and OER regions, forming MnO, Mn(OH)$_2$ and mostly Mn$_3$O$_4$ after one hundred cycles with low electrocatalytic activity for both ORR and OER comparing to the original manganese oxide [4, 5, 40, 45, 246]. Hence, one can argue that the loss in the ORR and OER performance of both GDEs is partly associated with the phase changes in the manganese oxide content of the catalyst layer to less active forms of
MnO$_x$ for both ORR and OER. Moreover, other phenomena such as carbon corrosion and MnO$_2$ electro-corrosion (eq. 39) in high anodic potentials (as discussed in section 6.2.4) as well as catalyst layer detachment from the carbon substrate, no matter how small, could have a significant impact on the long-term bifunctional performance of these GDEs by affecting the surface interactions between the different components of the catalyst (specially catalyst and support), including lattice oxygen vacancy concentrations and HOO$_{\text{ads}}$/HO$_{\text{ads}}$ binding energies as major contributors to ORR/OER overpotentials of oxide surfaces.

The role of lanthanum cobalt oxide in the performance loss of the mixed-oxide catalyst during accelerated degradation test is more complex than manganese oxide (Figure 6.7). The reason behind this is mainly due to the diversity of proposed reaction mechanisms for oxygen electrocatalysis on perovskite surfaces with no reliable method to experimentally detect the reaction intermediates and confirm what exactly is happening on these surfaces during ORR and OER [122, 123]. In the OER potential region, La-based perovskites, such as LaMnO$_3$ and LaCoO$_3$, are reported to be structurally stable during severe potential cycling according to a study using High-Resolution TEM and Fast Fourier Transform analysis by May et al. [257]. Moreover, the sluggish ORR performance of LaCoO$_3$, comparing to manganese oxides, was previously reported in this work and the literature [4, 5, 123, 220]. Hence, one can conclude that the LaCoO$_3$ itself has a low impact on the performance loss of mixed-oxide GDEs (e.g. MnO$_2$-LaCoO$_3$) during accelerated degradation tests. The real question here goes back to the surface interactions of LaCoO$_3$ with other components of the catalyst layer, such as MnO$_2$ and carbons, during severe potential cycling. Slight changes to these shared surfaces by either carbon corrosion or formation of passivating oxide layers during electro-corrosion of MnO$_x$ could have a drastic impact on the electrical conductivity of LaCoO$_3$:Carbon or MnO$_2$:LaCoO$_3$ shared interfaces, effectively
insulating the electron paths of perovskite's particles or manipulating the $\text{HOO}_{\text{ads}}/\text{HO}_{\text{ads}}$ binding energies and therefore, lowering the overall ORR/OER electrocatalytic activity of the catalyzed GDEs. Further in-situ characterization is needed to examine the nature of each catalyst/support interfaces during ORR and OER to be able to fully understand the mechanism behind the performance losses of GDEs during the applied accelerated degradation tests.

Figure 6.7 Electrocatalytic durability testing: ORR (bottom) and OER (top) current densities at 800 mV and 1750 mV, respectively, during one hundred successive potential cycling between 673 to 1873 mV on $\text{MnO}_2$-$\text{LaCoO}_3$-MWCNT-Graphene (weight ratio 1:1:1:1) and $\text{MnO}_2$-$\text{LaCoO}_3$-Vulcan XC-72 (weight ratio 1:1:1) GDEs in flooded test setup. The oxide and carbon loadings were kept at 0.5 mg cm$^{-2}$, each, spayed on a 40 wt% PTFE treated carbon cloth as porous substrate. The error associated with ORR and OER current densities was found to be between 2% and 10%. Other conditions idem to Figure 6.3.
6.3 Conclusion

A systematic study has been performed to comparatively investigate the electrocatalytic activity and long-term durability of six different carbonaceous materials, i.e. Vulcan XC-72, multi-walled carbon nanotubes (MWCNT), graphene, N-doped graphene, MWCNT mixed with graphene or N-doped graphene, either as a support for a highly active ORR/OER bifunctional non-PGM oxide catalyst, i.e. MnO₂-LaCoO₃, or a lone oxygen electrocatalyst in alkaline media.

The RRDE experiments on the carbonaceous materials revealed a distinguished reduction peak at low rotation speeds (below 1000 rpm) and between 670-750 mV, mainly due to the electro-reduction of adsorbed oxygen on the catalyst surfaces, following a 4e⁻ pathway. Vulcan XC-72 possessed the lowest ORR onset potential and highest ORR limiting current density followed by MWCNT, graphene and lastly, N-doped graphene. While Vulcan mostly catalyzed the bulk oxygen reduction through a 2e⁻ pathway leading to hydrogen peroxide ions (except for the potential region around adsorbed oxygen reduction peak), MWCNT and graphene went through 2.8e⁻ and 3e⁻, respectively, for the reduction of bulk oxygen indicating a competition between the 2e⁻ and 4e⁻ pathways. N-doped graphene, however, favors 4e⁻ pathway with lowest ORR performance due to the flat morphology and small ECSA for the same loadings of Vulcan XC-72.

Next, the initial-stage bifunctional electrocatalytic activities of the carbons for both ORR and OER were investigated. Overall, Vulcan XC-72 showed highest current densities for both ORR and OER (up to 1650 mV). Significant synergistic effect was observed in the OER region when either graphene or N-doped graphene was mixed with MWCNT. This synergistic effect could be attributed to the unflattened morphology of the carbonaceous mixture by the introduction of MWCNT to it. Unusual values for kinetic parameters such as high OER Tafel slopes and orders
of magnitude higher OER exchange current densities compared to the ORR ones were attributed mainly to the carbon corrosion, interfering with the OER currents at high anodic potentials.

The performance of carbonaceous materials as catalyst support for MnO$_2$-LaCoO$_3$ (weight ratio 1:1), was also investigated and compared to a 50 wt% Pt supported on graphitized carbon. The addition of MnO$_2$-LaCoO$_3$ to the carbons significantly increased their ORR and OER electrocatalytic activity. With regards to the ORR, the order of electrocatalytic activity for carbon(s) supported mixed-oxide catalysts vs. Pt is as follow: MWCNT-Graphene > Vulcan XC-72 > Pt > MWCNT-N-doped graphene > MWCNT > Graphene > N-doped graphene.

The OER electrocatalytic activity of oxide containing samples decreases in a different sequence: MWCNT-Graphene > MWCNT-N-doped graphene > MWCNT > Vulcan XC-72 > Pt > Graphene > N-doped graphene. Highest ORR and OER mass activities of -6.694 A g$^{-1}$ at 850 mV and 15.536 A g$^{-1}$ at 1650 mV were achieved for MnO$_2$-LaCoO$_3$-MWCNT-Graphene compared to Pt sample.

Diverse ORR/OER electrocatalytic activities shown for mixed-oxide catalyst supported on wide range of carbonaceous materials studied here were explained by the difference in surface characteristics of each type of carbons. These surface characteristics such as morphology, active sites, defects, etc., can affect the nature of catalyst/support interactions at their interfaces. This provides various binding sites for the HOO$_{\text{(ads)}}$ and HO$_{\text{(ads)}}$ intermediates, leading to wide range of ORR and OER electrocatalytic activity for each combination.

The effects of carbon corrosion and electro-reduction of MnO$_x$ on the OER electrocatalytic activity of MnO$_2$-LaCoO$_3$-Carbon(s) catalyst layers were also discussed. It was concluded that the currents associated with the two aforementioned processes were negligible comparing to OER in the potential range studied here.
The main factors affecting the ORR/OER durability of mixed-oxide GDEs were found to be: A) MnO$_x$ phase changes during ORR and OER, B) Carbon corrosion, C) MnO$_x$ electro-corrosion, and D) Catalyst layer detachment from the carbon substrate. The role of lanthanum cobalt oxide in the overall performance loss of the mixed-oxide catalyst during accelerated degradation test was concluded to be insignificant due to its structural stability in the OER region and lack of activity in the ORR region.
Chapter 7: Conclusions and recommendations for future work

7.1 Conclusions

The primary goal of this study is to design electrochemically active and durable ORR/OER bifunctional non-PGM MnO_x-based catalysts. To accomplish such a task, several steps including physical incorporation of active non-PGM co-catalysts, i.e. perovskite and fluorite-type oxides, microstructural modifications, i.e. surfactant-assisted electrodeposition of nanostructured manganese oxides, surface modification methods, i.e. alkali-metal ion insertion into the oxide structure and addition of carbon contents to the oxide catalyst layer were taken. In-depth structural characterizations and electrochemical measurements coupled with theoretical studies were further employed to carefully investigate the mechanisms by which the aforementioned methods affect the bifunctional electrocatalytic activity and durability of “designed” catalysts.

7.1.1 ORR/OER electrocatalytic activity and durability of individual and mixed-oxide catalysts

A positive synergistic effect on the ORR/OER electrocatalytic activity of the physically-mixed oxide catalysts, i.e. MnO_2-LaCoO_3, MnO_2-LaNiO_3 and MnO_2-Nd_3IrO_7, was found. This was shown by either a decrease in the apparent Tafel slope or an increase in the apparent exchange current density for the mixed-oxide formulations compared to the respective individual oxide catalysts.

The mechanism for the mixed oxides’ synergistic electrocatalytic effect could be rationalized in terms of the scaling relationship between HOO_{(ads)} and HO_{(ads)} binding energies. The structurally diverse oxide combinations provide different binding energies for the key intermediates, thus, “breaking” away from the linear scaling relationship.
The MnO$_2$-Nd$_3$IrO$_7$ GDE revealed the highest ORR activity and long-term stability followed by MnO$_2$-LaCoO$_3$ as the second best, both outperforming the commercial Pt and commercial MnO$_x$ GDEs with up to 100 mV (air) and 150 mV (oxygen) more positive ORR overpotentials during 24 hrs of galvanostatic polarizations in 11.7 M KOH at 323 K and $P_{\text{gas}}$ of 1 atm. The structural analysis on the MnO$_2$-based GDEs during ORR galvanostatic polarization tests showed that the gradual transformation of MnO$_2$ to less active forms of manganese species (i.e. Mn$^{3+}$/Mn$^{2+}$) during ORR could attribute to the ORR performance degradation of mixed-oxide catalysts.

### 7.1.2 Oxide catalyst activation by alkali-metal ion intercalation

Potassium ion insertion in the catalyst structure of fresh oxides, i.e. MnO$_2$, LaCoO$_3$, Nd$_3$IrO$_7$, MnO$_2$-LaCoO$_3$, MnO$_2$-LaNiO$_3$ and MnO$_2$-Nd$_3$IrO$_7$, by A) Longer-term exposure to 6 M KOH and B) Potential driven (electrophoretic) intercalation of potassium, was found to be effective for enhancing the bifunctional activity and durability of the oxide catalysts, e.g. OER (at 5 mA cm$^{-2}$ or 5 A g$_{\text{catalyst}}^{-1}$) and ORR (at -2 mA cm$^{-2}$ or -2 A g$_{\text{catalyst}}^{-1}$) overpotentials are enhanced by 110 and 75 mV, respectively, for MnO$_2$-LaCoO$_3$ subjected to potential driven potassium ion intercalation or the rates of OER and ORR potential increase, a measure of electrocatalytic activity degradation, under similar conditions are diminished by 60.5 and 24 mV h$^{-1}$, respectively, for MnO$_2$-Nd$_3$IrO$_7$ after K$^+$ potential driven intercalation activation.

It is proposed that the reason for the enhanced ORR/OER performances of the activated catalysts is the uptake of K$^+$ into the catalyst layer (mostly in the vacancies and defects of the oxide crystal structures such as Schottky and lattice oxygen vacancies), acting as a promoter for both ORR and OER and providing new binding sites with distinct binding energies for HOO$_{\text{ads}}$ and
HO$_{\text{ads}}$ intermediates, help breaking away from the universal scaling relationship and thus, enhancing the ORR/OER bifunctional activity of the investigated catalysts.

### 7.1.3 Surfactant-assisted electrodeposition of Mn oxides: Factorial design study of the electrodeposition factors

For all surfactant cases studied here for the anodic electrodeposition of manganese oxides, high concentration of surfactants provided samples with the best ORR/OER bifunctional performances, based on all three specified responses of the factorial design study. Moreover, low temperature was reported to lead to high ORR/OER mass activities for all surfactant choices. While the effect of applied anodic potential on the ORR and OER activities of electrodeposited MnO$_x$ was found to be negligible in the case of SDS and CTAB surfactants, Mn concentration seemed to be an insignificant player for the Triton X-100 samples.

The electrodeposited MnO$_x$ for Triton run no. 9 was found to show the best ORR and OER electrocatalytic activities among other electrodeposited manganese oxides investigated here. Compared to Ir, Ru and IrO$_2$, it showed lower OER overpotential (min. 100 mV) at 2 mA cm$^{-2}$. For the ORR, the manganese oxide electrodeposited during Triton run no. 9 provided between 50 and 150 mV more positive overpotential (at -2 mA cm$^{-2}$) compared to the other non-precious metal compounds such as CoMn$_2$O$_4$ and Core-Corona Structured Bifunctional Catalyst (CCBC). The galvanostatic polarization tests further confirmed the promising OER activity for the Triton run no. 9 sample with potentials as low as 1446 mV (at 5 mA cm$^{-2}$ and t=2 hrs), about 40 mV lower than the commercial MnO$_x$, and a degradation rate of 43 mV h$^{-1}$, about 10 mV h$^{-1}$ lower than its commercial counterparts.

The surface modifications of MnO$_x$ via surfactant-assisted electrodeposition can significantly alter the morphology and Mn valence in the deposited materials, provide new binding sites for the
HOO\(_{\text{ads}}\) and HO\(_{\text{ads}}\) intermediates, help break away from the linear scaling relationship between their binding energies as a major contributor to the ORR and OER overpotentials and hence, enhance the ORR and OER electrocatalytic activity of electrodeposited manganese oxides.

The formation of hydrogen-bonded complexes, i.e. HO\(_{\text{ads}}\)…H-OH, with specially configured water molecules called “activated water”, can further explain the enhancement in the ORR activity of the catalysts, mainly by facile transfer of protons to weakly adsorbed HOO\(_{\text{ads}}\)/O\(_{\text{ads}}\) intermediates. This, however, depends on the surface coverage of OH\(_{\text{ads}}\) which provides binding sites for formation of HO\(_{\text{ads}}\)…H-OH complexes (promoter effect).

### 7.1.4 The effect of carbon supports: Graphene vs. commercial carbon materials

The RRDE experiments on the carbonaceous materials revealed that Vulcan mostly catalyzes the bulk oxygen reduction through a 2e\(^-\) pathway leading to hydrogen peroxide ions while MWCNT and graphene goes through 2.8e\(^-\) and 3e\(^-\), respectively, indicating a competition between the 2e\(^-\) and 4e\(^-\) pathways. N-doped graphene, however, favors 4e\(^-\) pathway.

Unusual values for kinetic parameters such as high OER Tafel slopes and orders of magnitude higher OER exchange current densities compared to the ORR ones were attributed mainly to the carbon corrosion, interfering with the OER currents at high anodic potentials.

Significant synergistic effect was observed in the ORR and OER region when either graphene or N-doped graphene was mixed with MWCNT. This synergistic effect could be attributed to the unflattened morphology of the carbonaceous mixture by the introduction of MWCNT to it, providing new binding sites for the HOO\(_{\text{ads}}\)/HO\(_{\text{ads}}\) intermediates.

The orders of ORR and OER electrocatalytic activities for carbon(s) supported mixed-oxide catalysts vs. Pt are as follows:
**ORR:** MWCNT-Graphene > Vulcan XC-72 > Pt > MWCNT-N-doped graphene > MWCNT > Graphene > N-doped graphene.

**OER:** MWCNT-Graphene > MWCNT-N-doped graphene > MWCNT > Vulcan XC-72 > Pt > Graphene > N-doped graphene.

Diverse ORR/OER electrocatalytic activities shown for the mixed-oxide catalyst supported on the carbonaceous materials studied were explained by the difference in surface characteristics of each type of carbon. These surface characteristics such as morphology, active sites, defects, etc., can affect the nature of catalyst/support interactions at their interfaces. This provides various binding sites for the HOO\(_{\text{(ads)}}\) and HO\(_{\text{(ads)}}\) intermediates, leading to wide range of ORR and OER electrocatalytic activity for each combination.

The main factors affecting the ORR/OER durability of mixed-oxide GDEs were found to be: A) MnO\(_x\) phase changes during ORR and OER, B) Carbon corrosion, C) MnO\(_x\) electro-corrosion, and D) Catalyst layer detachment from the carbon substrate. The role of lanthanum cobalt oxide in the overall performance loss of the mixed-oxide catalyst during accelerated degradation test was concluded to be insignificant due to its structural stability in the OER region and lack of activity in the ORR region.

### 7.2 Contributions to knowledge

Major novelties and contributions to science for this study are mentioned as follows:

1) The synergistic effect for incorporation of perovskite and fluorite-type oxides to manganese dioxide on the MnO\(_x\) activity for oxygen electrocatalysis has been reported for the first time. The study paves the way toward fundamental understanding of oxide-oxide interactions in catalyst layers which could significantly help “design” an active and durable non-PGM bi-
material catalyst for both ORR and OER to be used in wide range of energy generation and storage applications such as alkaline fuel cells and rechargeable metal-air batteries.

2) The effect of alkali-metal ions, i.e. Li⁺, Na⁺, K⁺ and Cs⁺, on the bifunctional performance of individual and mixed-oxide catalysts has been investigated and announced for the first time in this work. Novel potassium insertion methods such as open-circuit potential (OCP) and potential driven intercalation (PDI) were first introduced here which can “heal” the bifunctional performance of degraded catalysts or significantly enhance both initial stage activity and long-term durability of fresh oxide catalysts. The potassium activation methods, specially PDI, present a time-and-cost-effective way to enhance the activity and life-time durability of non-PGM oxide catalysts to replace the precious metal catalysts currently being used in industrial applications.

3) The comprehensive investigation on surfactant-assisted electrodeposition of MnOₓ using factorial design analysis provided a unique and comprehensive study on main electrodeposition factors affecting the final bifunctional activity of deposited manganese oxides. The study helps understand the important role of two-factor interactions during the electrodeposition process, something that is usually neglected in the literature. The most active manganese oxide electrodeposited in presence of Triton X-100 provided one of the lowest OER overpotentials and highest OER stability ever reported for MnOₓ in the literature. This opens a new path for manganese oxides as active OER electrocatalysts in applications like water electrolyzers.

4) The systematic study on the carbon support/catalyst interactions for a non-PGM catalyst, i.e. MnO₂-LaCoO₃, provides better insights on the mechanisms by which the catalyst layer is degraded during extensive potential cycling and helped find optimum catalyst composition for better and more durable non-PGM ORR/OER bifunctional catalyst.
5) The novel utilization of EELS structural characterization method on the non-PGM catalyst layer during extensive potential cycling between ORR and OER regions provided an excellent experimental evidence for structural changes associated with manganese dioxide as well as corresponding Mn valence at each stage. This is specially helpful to understand the limits of developed MnO$_x$-based catalyst and “design” them accordingly for commercial applications.

7.3 Recommendation for future work

The following recommendations are proposed for future work based on the findings of this study:

1) Experimental evidence corroborated possibly by theoretical calculations of the binding energies of ORR and OER intermediate species on MnO$_2$, LaCoO$_3$ and Nd$_5$IrO$_7$ with and without lattice distortions is required to validate the proposed hypothesis for enhanced bifunctional activity of oxides with induced potassium ions.

2) DFT calculations seems necessary to calculate the formation energy as well as concentration of lattice oxygen vacancies on the investigated catalysts.

3) Further experimentations and 3D distribution modeling is needed to better understand the possible differences between the potassium intercalation in each of two activation methods.

4) A study on the effect of alkali-ion insertion on surfactant-assisted deposited MnO$_x$ could translate to further enhancement in the ORR/OER electrocatalytic activity and durability of deposited manganese oxides. Simultaneous electrodeposition of Mn oxides and potassium activation should be considered to simplify the process.

5) Large-scale performance testing of catalyst materials in commercial scenarios for tandem ORR and OER should be performed.
6) The application of investigated catalysts and developed activation methods in aqueous solutions needs to be further studied in non-aqueous battery electrolytes such as metal induced room temperature ionic liquids (RTIL), e.g. [C$_{2}$mim][dca]+Zn(dca)$_{2}$ or gel-like [P$_{6,6,6,14}$][Cl].2(MgCl$_{2}$).37H$_{2}$O, to seek the possibility of an active and durable rechargeable non-aqueous metal-air battery catalyzed by MnO$_{x}$-based cathode catalyst. Room temperature ionic liquids have gained much attention lately to be used as the battery electrolyte due to their safety (non-volatile), high conductivity and support of some metals’ electrochemistry such as Zn and Mg [278].
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225


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Appendices

Appendix A: Introduction to the Butler-Erdey-Grúz-Volmer (BE-GV) equation

In 1905, J. Tafel proposed, based on experimental studies, that the current density increases exponentially with the overpotential [279]. However, the fundamental equation of electrode kinetics was developed later in the late 1920s and 1930s mainly by T. Erdey-Grúz and M. Volmer with independent contribution from J. Butler [218, 219, 280-284]. The BE-GV equation expresses the net current density as a function of surface overpotential for a single reaction at a single electrode (eq. 40) (Figure A.1) [103, 218, 219]:

\[ i = i_0 \left[ \exp\left( \frac{\alpha_a F}{RT} \eta \right) - \exp\left( -\frac{\alpha_c F}{RT} \eta \right) \right] \tag{40} \]

\[ \eta = E - E_e \tag{41} \]

\[ \alpha_a = (1 - \beta) \cdot n \tag{42} \]

\[ \alpha_c = \beta \cdot n \tag{43} \]

where \( i_0 \) is the exchange current density [A m\(^{-2}\)], \( \alpha_a \) is the anodic transfer coefficient, \( F \) is the Faraday constant [C mol\(^{-1}\)], \( \eta \) is the surface overpotential [V], \( R \) is the gas constant [J mol\(^{-1}\) K\(^{-1}\)], \( T \) is the temperature [K], \( \alpha_c \) is the cathodic transfer coefficient, \( E \) is the operating electrode potential [V\(_{\text{SHE}}\)], \( E_e \) is the equilibrium electrode potential [V\(_{\text{SHE}}\)], \( \beta \) is the symmetry factor and \( n \) is the number of electron exchanged in the rate determining step of the reaction.

The exchange current density is a measure of the electrocatalytic properties of the electrode surface. Considering multiple species that affect the rate of a reaction, the exchange current density can be written as [218, 219]:
\[ i_0 = nFk^0 \prod_j a_j^{m_j} \]  

where \( k^0 \) is the standard heterogeneous rate constant of the electrochemical reaction [mol m\(^{-2}\) s\(^{-1}\)], \( a_j \) is the activities of species \( j \) and \( m_j \) is a power expressing the concentration/pressure dependence of the activity for species \( j \). The exchange current density \( (i_0) \) is a function of the catalytic properties of the electrode (via heterogeneous rate constant), temperature, activities of species and reaction mechanism. Typically, the exchange current density values over 1 A m\(^{-2}\) correspond to “fast” electrode kinetics [219].

For practical calculations, when the absolute value of overpotential exceeds 0.1 V (|\( \eta \)| > 0.1 V), either the anodic or cathodic partial current density is significant and the eq. 40 can be simplified to Tafel equation [103, 218, 219]:

\[
|\eta| = b \log|i| + a \quad (45)
\]

\[
b = \frac{2.303RT}{\alpha F} \quad (46)
\]

\[
a = -\frac{2.303RT}{\alpha F} \log i_0 = -b \log i_0 \quad (47)
\]

where \( a \) and \( b \) [V decade\(^{-1}\)] are Tafel parameters, Tafel intercept and Tafel slope, respectively, and \( \alpha \) is the transfer coefficient. Both Tafel parameters are temperature and composition dependent constants containing the electrode reaction parameters. The experimentally measured Tafel slopes are typically between 30 to 300 mV decade\(^{-1}\) with high apparent Tafel slope values (i.e. over...
120 mV decade$^{-1}$) indicating other polarization effects such as adsorption, mass transfer, etc. interfere with “pure” intrinsic kinetic measurement [218, 219].

![Figure A.1](image-url)  

**Figure A.1** Effect of the symmetry factor ($\beta$) on the symmetry of the current-overpotential curve described by the BE-GV equation (eq. 40).
Appendix B : Introduction to the rotating disk and ring disk electrode (RDE and RRDE)

The rotating disk and ring-disk electrodes provide a hydro-dynamically well-characterized, laminar-forced convective flow to the smooth electrode surface, up to rotation speeds of about 5000 rpm (rotation per minute). Generally, the polarization curve measured under these conditions has a sigmoid shape with three distinct regions (Figure B.1) [218]:

1) Pure electrode kinetic (or charge transfer) control region, where the convective mass transfer has no effect on the polarization curve.
2) Mixed control region, where both electrode kinetic and mass transfer influence the polarization curve.
3) Pure mass transfer control region, generating a limiting current density ($i_L$).

Figure B.1 Typical cathodic polarization curves obtained by a RDE as a function of angular velocity ($\omega$). $\omega_1 < \omega_2 < \omega_3$. 

231
In the mass transfer control region, the limiting current density \((i_L)\) for the oxidation or reduction of an electroactive species \(j\) can be expressed using [218, 219]:

\[
\begin{align*}
    i_L &= \frac{n \cdot F}{s_j} \cdot \frac{D_j}{\delta} \cdot C_j = \frac{n \cdot F}{s_j} \cdot K_{m,j} \cdot C_j \\
    \delta &= 1.61 \cdot D_j^{\frac{1}{3}} \cdot \nu^{\frac{1}{6}} \cdot \frac{1}{\sqrt{\omega}} \quad (laminar \ flow, 10^2 \leq Re \leq 10^4)
\end{align*}
\]

where \(s_j\) is the stoichiometric coefficient of species \(j\), \(D_j\) is the diffusion coefficient of the electroactive species \(j\) \([m^2 s^{-1}]\), \(C_j\) is the bulk reactant concentration of species \(j\) \([kmol m^{-3}]\), \(K_{m,j}\) is the mass transfer coefficient of species \(j\) \([m s^{-1}]\), \(\delta\) is the diffusion layer thickness \([m]\), \(\nu\) is the kinematic viscosity of the electrolyte \([m^2 s^{-1}]\) and \(\omega\) is the angular velocity \([\text{rad} s^{-1}]\).

The RDE measurement is a commonly employed technique to determine number of exchanged electrons as well as kinetic parameters, i.e. Tafel slope and exchange current density, for an electrochemical reaction like ORR which uses Levich equation as follows [218, 219]:

\[
i_{L,j} = 0.62 \cdot \frac{n \cdot F}{s_j} \cdot D_j^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2} \cdot C_j = B_{L,j} \cdot \omega^{1/2}
\]

The Levich equation shows that \(i_{L,j}\) increases linearly with \(\omega^{1/2}\). Hence, the number of electrons involved \((n)\) or the diffusion coefficient of species \(j\) \((D_j)\) can be calculated from the slope of experimentally observed limiting current density \((i_L)\) versus the square root of angular velocity \((\omega^{1/2})\), i.e. Levich slope \((B_{L,j})\).
Kinetic parameters, e.g. Tafel slope and exchange current density, can be further extracted from the polarization curves by employing the reciprocal equation for the mixed control region (kinetic and mass transfer control) and substituting Levich equation in it [218, 219]:

\[
\frac{1}{i_j} = \frac{1}{i_{k,j}} + \frac{1}{i_{L,j}} = \frac{1}{i_{k,j}} + \frac{1}{i_{L,j} \cdot \omega^{1/2}}
\]  

(51)

where \(i_j\) is the measured current density of species \(j\) [A m\(^{-2}\)] and \(i_{k,j}\) is the pure electrode kinetic current density of species \(j\) [A m\(^{-2}\)].

With the collection of a series of experimental data points from the polarization curves, i.e. \(i_j\) at different potentials in the mixed control region for various rotation speeds, \(\frac{1}{i_j}\) vs. \(\omega^{-1/2}\) (Koutecky-Levich plot) can be plotted at different potentials in the mixed control region. The slope and intercept of the linear Koutecky-Levich plot allows the calculation of number of electrons (\(n\)) and the purely electrode kinetic current density (\(i_{k,j}\)), respectively, at various potentials.

An alternative way for understanding the ORR pathway on different catalysts is the rotating ring disk electrode (RRDE) tests [218]. The relative formation rate of hydrogen peroxide ions (eq. 9) and hydroxyl ions (eq. 2) can lead to the number of electrons involved in the ORR on each catalyst surface [218, 285, 286]. This rate can be quantitatively determined by setting an oxidative potential (about 1353 mV) at the ring where the oxidation of the \(\text{HO}_2^-\), formed by \(\text{O}_2\) reduction on the disk electrode in the first place, is diffusion limited [218, 285, 286]. The selectivity of catalyst toward hydrogen peroxide ion formation (%\(\text{HO}_2^-\)) is calculated by:
\[
\% H O_2^- = \frac{2}{1 + \left(\frac{I_d}{I_r} \times N\right)} \times 100
\]  

(52)

where \(I_d\), \(I_r\) and \(N\) refer to the disk current (A), ring current (A) and collection efficiency of the ring, respectively [285-287]. Then, the number of electrons transferred during ORR (n) can be calculated by:

\[
n = \frac{4}{1 + \left(\frac{I_r}{I_d \times N}\right)}
\]  

(53)
Appendix C: Break-in protocol test results for GDE flow-by cell

As mentioned in section 2.3, the ORR performance and stability of oxide catalysts developed here were tested in commercial scenarios using a galvanostatic test protocol (i.e. chronopotentiometry) in a flow-by test cell with air (CO₂ removed) or oxygen flowing through the gas chamber. Prior to the reported electrocatalytic performance tests (Figure 3.8), each fresh electrode was subjected to a break-in polarization protocol composed of 24 hrs of galvanostatic polarization at constant cathodic current densities, i.e. -33 mA cm⁻² in air and -67 mA cm⁻² in oxygen. Figure C.1 shows the performance of each fresh GDE during the twenty-four-hour-long break-in protocol with air or oxygen flowing through the flow-by cell.
Figure C.1 Long-term ORR durability testing of fresh GDEs containing Pt, MnO₂, MnO₂-LaCoO₃, MnO₂-LaNiO₃ and MnO₂-Nd₃IrO₇ catalysts compared with commercial MnOₓ GDE from Gaskatel GmbH: A) With air at -33 mA cm⁻² and B) With oxygen at -67 mA cm⁻². IR-corrected galvanostatic polarization curves obtained in 11.7 M (45 wt%) KOH at 323 K for 24 hrs with either air (CO₂ removed) or oxygen flowing through the gas chamber of a flow-by cell from Gaskatel GmbH as twenty-four-hour-long break-in protocol. The absolute gas pressure and flow rate were fixed at 1 atm and 1.51×10⁻³ SLPM. The catalyst(s) loadings were 2 mg cm⁻² each (except for Pt with 0.5 mg cm⁻²) with final weight ratio of 1:1:2:0.6:0.6 for MnO₂ or Pt:co-catalyst (if present):Vulcan XC-72:Nafion:PTFE in the catalyst layer. The catalyst loading for the commercial MnOₓ from Gaskatel was 20 mg cm⁻². The standard error of the mean calculated based on min. two replicates is indicated for each data point.
Appendix D : The effect of inter-stage OCP activation

In order to further investigate the “healing effect”, i.e. ORR and OER performance recovery of degraded mixed-oxide catalysts by potassium ion intercalation, a fresh MnO₂-LaCoO₃ exposed to 6 M KOH for six days at 313 K and 400 rpm, was subjected to three hundred potential cycles between 633 to 1483 mV with twelve-hour intervals after each one hundred cycles while resting at open-circuit in 6 M KOH solution at 293 K and 400 rpm. The ORR and OER electrocatalytic activities of K⁺ activated MnO₂-LaCoO₃ electrode after durability tests followed by inter-stage activation are shown in Figure D.1. As mentioned in 4.2.1.2, the ORR electrocatalytic activity of K⁺ activated MnO₂-LaCoO₃ drops drastically after being extensively cycled for one hundred cycles, i.e. almost 65% of loss in the ORR current density (at 683 mV) after one hundred potential cycles (Figure D.1-A). The so-called inter-stage OCP activation process, i.e. 12 hrs of rest time at open-circuit in 6 M KOH at 293 K and 400 rpm, significantly enhances the ORR performance of the degraded MnO₂-LaCoO₃ sample by increasing the ORR current density for 126% from -7.2 to -16.8 mA cm⁻² at 683 mV (Figure D.1-A). This recovers the ORR electrocatalytic activity of degraded MnO₂-LaCoO₃ catalyst to some extend and bring its polarization curve close to that of K⁺ activated MnO₂-LaCoO₃ electrode at cycle one, i.e. almost identical current densities up to 783 mV (Figure D.1-A). Although the second round of durability test for one hundred cycles severely decreases the ORR electrocatalytic activity of the healed MnO₂-LaCoO₃ electrode, i.e. almost 60% drop in the ORR current density from -16.8 mA cm⁻² (cycle 100) to -6.6 mA cm⁻² (cycle 200) at 683 mV, the second twelve-hour-long inter-stage OCP activation, enhances the ORR current density of MnO₂-LaCoO₃ electrode at cycle one hundred by 120% from -6.6 to -14.6 mA cm⁻² (at 683 mV) (Figure D.1-A). The same trend is also observed for the third round of durability test followed by inter-stage OCP activation process: First, decreasing the ORR current density of
MnO$_2$-LaCoO$_3$ electrode by almost 62% from -14.6 mA cm$^{-2}$ (cycle two hundred) to -5.6 mA cm$^{-2}$ (cycle three hundred) at 683 mV, and second, increasing the current density of MnO$_2$-LaCoO$_3$ electrode at cycle three hundred to -12.3 mA cm$^{-2}$ at 683 mV, i.e. 120% increase in the ORR performance after third round of inter-stage OCP activation (Figure D.1-A). The total loss in the ORR current density of the K$^+$ activated mixed-oxide catalyst after three hundred cycles of durability tests and subsequent inter-stage OCP activation process is found to be about 41% at 683 mV (Figure D.1-A).

In the OER region, unlike ORR, the K$^+$ activated MnO$_2$-LaCoO$_3$ catalyst exhibits more stable OER performance during three hundred cycles of durability testing and three rounds of inter-stage OCP activation. The most drastic drop in OER electrocatalytic activity of K$^+$ activated MnO$_2$-LaCoO$_3$ catalyst during the three durability stages corresponds to the third round of durability testing (Figure D.1-B), i.e. almost 20% drop in the OER current density from 16.5 mA cm$^{-2}$ (cycle two hundred) to 13.1 mA cm$^{-2}$ (cycle three hundred) at 1483 mV. The total OER performance drop for the K$^+$ activated MnO$_2$-LaCoO$_3$ catalyst after three hundred cycles of durability tests and three rounds of inter-stage OCP activation is maximized at 27% (at 1483 mV).

The results here further confirm the reproducibility of “healing effect” by K$^+$ activation of degraded mixed-oxide catalysts. This could be explained by constant formation of Schottky defects and lattice oxygen vacancies during ORR on the oxides’ surfaces which provides the ideal sites for potassium ions to intercalate. The intercalated potassium ions could introduce new binding sites for oxygen catalysis intermediates such as HOO$_{(ads)}$ and HO$_{(ads)}$ and hence, manipulating the ORR/OER electrocatalytic activities of degraded catalysts.
Figure D.1 The effect of inter-stage OCP activation: ORR and OER polarization curves of the activated MnO$_2$-LaCoO$_3$ electrodes tested for three hundred cycles with OCP activation in between, A) ORR polarization curves, B) OER polarization curves. The samples are kept at OCP in 6 M KOH solution for 12 hrs at 293 K and a rotation speed of 400 rpm after each one hundred cycles of durability testing. Other conditions are same as Figure 3.6.
Appendix E : Factorial design study

Pareto plots of estimates

The JMP software employs Pareto plot of estimates to demonstrate the main and interaction effects of various factors on the responses that are being investigated in a factorial design study. In the factorial design investigations of the current work, i.e. $2^{4+1}+3$ half-fraction $2^n$ factorial design studies in presence of various surfactants, these plots are powerful tools for judging the significance of the effect that each factor or two-factor interaction can have on the final responses, hence help remove the insignificant two-factor interaction in each aliased pair as explained earlier in the section 5.2.3. To calculate the main ($X_i$) or two-factor interaction ($X_iX_j$) effects in each surfactant category, the following equations have been employed:

\[
\text{Main effect of } X_i = \frac{\sum (\text{Response at high } X_i) - \sum (\text{Response at low } X_i)}{(\text{Half the number of factorial runs})} \quad (54)
\]

\[
\text{Interaction effect of } X_iX_j = \frac{\sum (\text{Response at high } X_iX_j) - \sum (\text{Response at low } X_iX_j)}{(\text{Half the number of factorial runs})} \quad (55)
\]

The levels of two-factor interactions ($X_iX_j$) for each factorial run in eq. 55 are determined based on the levels of each individual factor, i.e. $X_i$ and $X_j$. For example, high level of factor $X_i$ ("+") and low level of factor $X_j$ ("-" ) lead to low level of their two-factor interaction $X_iX_j$ ("-"").

Figure E.1 shows the estimates of effects that each main factor and aliased two-factor interaction pair have on the ORR mass activity of the electrodeposited MnO$_x$ in presence of Triton X-100 as a response for the factorial design study. The graph shows clearly that between the four main factors (see Table 2.1), surfactant concentration (S), Temperature (T) and applied anodic
potential (E) have the most significant effect on the response while Mn concentration (C) is the most insignificant factor in this case for the defined response (Figure E.1). Employing the Ockham’s razor principle, one can assume the most significant two-factor interactions are $S \times T$, $S \times E$ and $E \times T$ among the $C \times E + S \times T$, $C \times T + S \times E$ and $C \times S + E \times T$ aliased pairs, respectively, since Mn concentration is shown to have the least effect on the ORR mass activity of the electrodeposited manganese oxides. Hence, the surface plots can be easily constructed using the most significant three main factors and three two-factor interactions. This is similar to the case that Mn concentration is discarded from the beginning and a $2^3 + 3$ full factorial design with three factors and three center-points leading to 11 runs in total is being constructed for the Triton X-100 samples.
Figure E.1 Pareto plot of estimates for the effects of four main factors (i.e. surfactant concentration (S), temperature (T), Mn concentration (C) and applied anodic potential (E)) and three aliased two-factor interactions on the ORR mass activity in the $2^{4-1}+3$ factorial design study on the anodic electrodeposition of MnO$_x$ in presence of Triton X-100.

**Curvature effect**

Traditionally, the curvature effect is estimated as the difference between the average of the center-point responses and the average of the factorial points. A strong curvature effect is then a reflection of a non-linear system behavior. JMP demonstrates the curvature effect in terms of “RSquare” when center-points are added to the factorial design study. RSquare estimates the proportion of variation in the response that can be attributed to the model rather than to random error. RSquare (also called the coefficient of multiple determination in the JMP software) is calculated as:
\begin{equation}
R^2 = \frac{\text{Sum of squares (C. total)} - \text{Sum of squares (Error)}}{\text{Sum of squares (C. total)}}
\end{equation}

where “sum of squares (C. total)” is the sum of the squared differences between the response values and the sample mean (representing the total variation in the response values) and “sum of squares (Error)” is the sum of the squared differences between the fitted values and the actual values (representing the variability that remains unexplained by the fitted model). A R^2 closer to 1 indicates a better fit to the data than does a R^2 closer to 0, meaning the curvature effect is negligible. A R^2 near 0 indicates that the model is not a much better predictor of the response than is the response mean, meaning a degree of non-linearity in the behavior of variables.