STUDIES OF SOME TECHNOLOGICALLY IMPORTANT INTERFACES

by

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Abstract

This thesis discusses surface and interfacial investigations for two technologically important areas. The first area focuses on surface modification of oxidized high-purity aluminum for improved interfacial bonding with an organosilane, bis-1,2-(triethoxysilyl)ethane (BTSE), for adhesion promotion and corrosion protection. BTSE adsorption onto various pre-treated oxidized aluminum surfaces are compared. Secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to assess the effects of pre-treatment on the direct Al-O-Si covalent bonding and the strength of adhesive bonding. Applying a sulphuric-chromic (FPL – Forest Products Laboratory) pre-treatment to native oxide on high-purity Al generates a compact, well-anchored oxide layer with a surface that is effective for Al–O–Si bonding after BTSE coating. H₂ plasma pre-treatments improve BTSE chemisorption on FPL pre-treated Al surfaces. However, heat pre-treatments can modify a native Al oxide surface for increased adhesion with BTSE.

The second area focuses on the use of transition metal chalcogen thin films and powders in oxygen reduction reaction (ORR) catalysis for proton exchange membrane (PEM) fuel cells. A novel combination of micro-Raman spectroscopy and scanning Auger microscopy (SAM) enabled the identification of different elemental compositions at local regions of a Co-Se thin film which led to a reinterpretation of Raman peaks reported previously. Raman characterization of sputtered Fe-S, Co-S and Ni-S thin film surfaces identified the respective disulfide structures and suggested the presence of polysulfides (Sₙ²⁻) which may contribute to an improved ORR catalytic activity when compared to the corresponding disulfide standard. A sputtered Co-Ni-S thin film containing (Co,Ni)S₂ solid
solution with possible polysulfides showed an enhanced ORR catalytic activity compared with other samples.

A method for synthesizing high-purity, crystalline CoSe₂ powder on high-area carbon support is established; its surface and bulk structures are confirmed by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), micro-Raman spectroscopy, XPS and SAM. CoSe₂ demonstrated significant ORR catalytic activity with an OCP of 0.81 V and higher current density than CoSe. CoSe₂, characterized by combining SAM and backscattered electron (BSE) imaging, was electrochemically modified via cyclic voltammetry to give a Se-rich surface to enhance its ORR catalytic activity.
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<td>γ-APS</td>
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</tr>
<tr>
<td>γ-GPS</td>
<td>γ-glycidoxypropyltrimethoxy silane</td>
</tr>
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<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>AFC</td>
<td>alkaline fuel cell</td>
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<td>Forest Products Laboratory</td>
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<td>FWHM</td>
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<tr>
<td>GC</td>
<td>glassy carbon</td>
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<td>HRTEM</td>
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<td>inelastic mean free path</td>
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<td>molten carbonate fuel cell</td>
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<td>rotating disc electrode</td>
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<tr>
<td>RF</td>
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<td>reversible hydrogen electrode</td>
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<td>secondary electron detector</td>
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<td>surface enhanced Raman spectroscopy</td>
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<td>time-of-flight</td>
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Chapter 1
Introduction

1.1 Surfaces and Interfaces

An interface is formed at the boundary between two separate phases. The term surface is used for a condensed phase in contact with gas. Studying surfaces and interfaces is important for many technological applications, not only because their chemical compositions and states may vary from that of the bulk phase but also because all interactions between the phases occur through their common interface. This gives importance to understanding the processes that occur at interfaces, and their characterizations are increasingly important in solving a wide variety of technological challenges including in such areas as adhesion, corrosion protection, surface coatings, catalysis, microelectronics, new materials, nanotechnology and biomedical applications. The distinctive thermodynamic, physical and chemical properties of surfaces and interfaces are reviewed in a number of standard texts [1-4].

Examining surfaces and interfaces of different materials is a multifaceted practice as chemical composition, chemical structure and topography are just some aspects that are essential for understanding the surface or interface being studied. On the one hand, no single characterization technique can give all such information and hence the gaining of new understanding generally requires use of a combination of different methods; this approach is demonstrated in the research work shown in this thesis. On the other hand, factors such as the nature of the sample and the detection limitations for acquiring the necessary information can be challenging in selecting the appropriate combination of analysis tools.

This thesis highlights investigations on chemical reactivity at surfaces and interfaces for two different technological applications, namely: (i) surface modification of oxidized
high-purity aluminum for improved interfacial bonding with an organosilane, bis-1,2-(triethoxysilyl)ethane (BTSE), for potential applications in adhesion promotion and corrosion protection; and (ii) the synthesis, characterization and evaluation of transition metal chalcogenide materials for potential applications in oxygen reduction reaction (ORR) catalysis for proton exchange membrane (PEM) fuel cells. A common feature for these two themes is that the chemical composition, state and structure of the surfaces and interfaces studied determines the reaction effectiveness. This chapter continues with an introduction to the background for these two areas of research.

1.2 Aluminum and its Treatments

1.2.1 Introduction

Aluminum metal has many properties that contribute to its widespread use in industry. Aluminum, being the second most abundant element in the earth's crust, is extracted from bauxite (a natural ore containing 35-50% alumina or Al₂O₃) through an electrolytic process [5, 6]. Aluminum is light with a density (2.71 g/cm³) only one third that of steel. High purity aluminum has applications that depend on properties such as formability at room temperature, thermal and electrical conductivity, corrosion resistance, neutral taste, non-toxicity, non-magnetic characteristics and good strength for its light weight [5, 6]. Such applications include packaging of foods and drinks; pharmaceuticals; electrical conductors; and nameplates. The addition of selected elements such as Cu, Mn, Si, Mg and Zn to aluminum can produce aluminum alloys with enhanced mechanical strength. Such alloys have applications in the construction of buildings and transportation including the aerospace and automotive industries [5, 6].
Surfaces of aluminum are generally covered with a thin, transparent oxide layer after an exposure to air. Figure 1.1 shows this natural skin (up to 10 nm thick) consisting of two layers – an inner thin and compact barrier layer (~10 Å) as well as a hydrated upper layer (~90 Å). The barrier layer is amorphous and non-porous while the hydrated upper layer is more permeable and porous. The major compositions for the aluminum oxides are Al₂O₃, Al₂O₃·3H₂O (or Al(OH)₃) and Al₂O₃·H₂O (or AlO(OH)). The thermodynamically stable form of Al₂O₃ for the conditions of this study is α-Al₂O₃ with a rhombohedral crystal structure [5-8]. Hydrated aluminum oxides, such as monoclinic gibbsite (Al₂O₃·3H₂O) or orthorhombic boehmite (Al₂O₃·H₂O), have water layers between layers of Al³⁺ ions within the structures; such hydrated porous oxides are not strongly anchored to the Al substrate [5-7] and so do not provide strong links between metal and an adhesive coating. However, at 250°C and above, gibbsite can dehydrate into Al₂O₃ [8]. The native oxide on Al is in general heterogeneous and involves a mixture of these forms. A compact oxide layer on aluminum acts to inhibit the metal from further oxidation and this self-protecting characteristic gives aluminum its high resistance to chemical attack and corrosion in moderate environments. In aggressive environments, breakdown can occur and that emphasizes the need for extra protective coatings on some applications.

Figure 1.2 shows the Pourbaix diagram of Al that illustrates the range of stability for phases in the Al-water system as a plot of electrical potential as a function of pH. The stability range of water in the diagram corresponds to the region between the lines marked (a) and (b). Below line (a), water reduces to form hydrogen via the reaction:

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  \hspace{1cm} (1.1)

Above line (b), water oxidizes to form oxygen via the reaction:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \]  \hspace{1cm} (1.2)
Figure 1.1 Native oxide of aluminum (Based on Ref. [6]).

Figure 1.2 Potential-pH (Pourbaix) diagram for Al-water system at 25°C [6].
As shown in the diagram, aluminum is passivated in the pH range of about 4 to 8.5. Beyond the limits of its passive range, aluminum oxides are soluble in many acidic and basic aqueous solutions, typically yielding $\text{Al}^{3+}$ ions and $\text{AlO}_2^-$ (aluminate) ions respectively.

### 1.2.2 Protective coatings

Protective coatings are often applied to the oxidized surfaces of aluminum and its alloys to give additional corrosion protection in a wide variety of environments and for the promotion of adhesion with further coatings such as paint. Anodization, an electrolytic process that increases the oxide layer thickness (e.g. 2 µm to 25 µm), is one such method but it is too expensive when dealing with large structures and it is not suitable for parts that need further mechanical treatment [5-7]. Other methods include conversion coating, a process where a chemical oxidation-reduction reaction leads to the formation of a protective low-solubility compound (e.g. phosphate or chromate) formed at the aluminum surface. Chromate conversion coatings involve the use of $\text{Cr}^{6+}$ [9, 10], which has received much attention because of its environmental toxicity since it is known to be a cancer-causing agent [11]. Phosphate conversion coatings, which utilize solutions containing phosphoric acid and divalent metal ions such as $\text{Zn}^{2+}$ and $\text{Mn}^{2+}$, are being used but their corrosion resistance is generally less than that for chromate coatings, and they still need supplementing with a chromic acid rinse. Consequently, alternative methods that are more environmentally friendly are being sought and one such method under research and development is the use of organosilane coatings [12-15].

Organofunctional silanes are coupling agents that promote adhesion between organic polymers and substrates through the formation of strong interfacial bonding [14, 16]. Although they have a long history in this context (e.g. bonding organic polymers to glass
fibers [16]), their possible use for corrosion protection is much more recent and is an active area of current research [12-15]. Organosilanes have the general formula $X_3Si(CH_2)_nY$ where $Y$ is an organofunctional group (e.g. amino, epoxy), $X$ is a hydrolysable group (e.g. OCH$_3$, OCH$_2$CH$_3$) and $n$ is typically in the range of 0 to 3. The organofunctional group $Y$ is selected for compatibility and reactivity with the organic coating to be subsequently added. The hydrolysable group allows the formation of silanol groups (SiOH) after hydrolysis which then subsequently permits the formation of direct AlOSi interfacial bonding with hydroxyl groups on the substrate surface, as illustrated in Figure 1.3, after the elimination of water. This mechanism, initially proposed by Plueddemann [16], is now widely accepted as the process by which organosilane coupling agents enhance adhesion between organic polymers and hydrophilic inorganic surfaces [12-14]. Table 1.1 lists some commonly used functional and non-functional organosilanes. Functional organosilanes such as $\gamma$-glycidoxypropyltrimethoxy silane ($\gamma$-GPS) and $\gamma$-aminopropyltriethoxy silane ($\gamma$-APS) have an organofunctional group. Non-functional organosilanes such as bis-1,2-(triethoxysilyl)ethane (BTSE) have, on the other hand, additional hydrolysable groups instead of a $Y$ group and such organosilanes have received considerable research interest for the coating of metal surfaces [12-14].

**Table 1.1 Examples of organosilanes**

<table>
<thead>
<tr>
<th>Non-functional Organosilane</th>
<th>Acronym</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-1,2-(triethoxysilyl)ethane</td>
<td>BTSE</td>
<td>$(H_5C_2O)_3$-Si-CH$_2$-CH$_2$-Si-(OC$_2$H$_5$)$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Functional Organosilanes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$-Glycidoxypropyltrimethoxy silane</td>
<td>$\gamma$-GPS</td>
<td>$\overset{\text{O}}{\text{CH$_2$-CH-CH$_2$-O-(CH$_2$)$_3$-Si-(OCH$_3$)$_3$}}$</td>
</tr>
<tr>
<td>$\gamma$-Aminopropyltriethoxy silane</td>
<td>$\gamma$-APS</td>
<td>$H_2N$-(CH$_2$)$_3$-Si-(OC$_2$H$_5$)$_3$</td>
</tr>
</tbody>
</table>
Figure 1.3 Adsorption of BTSE on aluminum substrate: (a) hydrolysis reaction of BTSE; (b) formation of covalent Al-O-Si bond.
A good quality organosilane film is solidly anchored to the metal by direct Si-O-metal bonding [13], but the organosilane coating process is governed by a number of factors including the pH and the concentration of the organosilane solution. At pH 4, BTSE, for example, hydrolyzes quickly and condenses slowly resulting in a coating solution mainly consisting of monomers that can react completely and form a good quality dense film. Increasing the concentration of an organosilane coating solution increases the thickness of the silane film but with an increase in brittleness and hence a lower quality of organosilane coating [12-14]. After the coating, silanol groups not involved in the interfacial bonding can react to form Si-O-Si bonding according to the condensation reaction: SiOH + SiOH → Si-O-Si + H₂O. The Si-O-Si bonding is resistant to water, acids and solvents [14, 17-21] which helps in retarding the transport of corrosive ions such as chloride towards the metal [14]. Coating a metal surface with a non-functional organosilane such as BTSE, with up six SiOH in its hydrolyzed form, thus has the potential to offer good corrosion protection provided that the coating is well adhered onto the metal.

The availability of up to six SiOH groups in each hydrolyzed BTSE monomer is advantageous for research studies since it may be expected to increase the probability of Al-O-Si bond formation compared with other commonly-used silanes, like γ-GPS or γ-APS [12], which can have no more than three silanol groups per molecule. A second reason to use BTSE, as a model system for exploring the approach to be developed, is that there is no possibility for the alternative “upside down” bonding that can occur, for example, with γ-APS [12]. Third, and most relevant for situations where dual coatings are formed, BTSE is already favored as an initial coating in contact with the substrate. The silanol groups at the other end of the hydrocarbon chain are then available for bonding to a functional organosilane, such as γ-GPS or γ-APS, that may be subsequently layered on top [13].
1.2.3 Surface Pre-treatments

Prior to coating with an organosilane, surfaces of aluminum and its alloys typically require cleaning and some modification in order to enhance the interfacial bonding. Mechanical cleaning such as polishing or sand blasting can be used but such procedures can lead to rough inconsistent surfaces and may additionally remove too much of the protective oxide layer. Chemical pre-treatments, usually involving alkaline and chromic acid pickling treatments, can alternatively etch the oxidized surfaces of metal substrates and form a new compact oxide layer with a cleaner surface and a new surface morphology [7, 12, 14, 22, 23]. The formation of such surfaces helps in the adhesion of organosilane when the metal substrate is subsequently dipped into the freshly hydrolyzed organosilane coating solution [7, 12, 14, 22, 23].

A commonly used pre-treatment involves immersion in a so-called chrome pickle, such as the etching solution containing sodium chromate (or chromic acid) and sulphuric acid, according to the Forest Products Laboratory (FPL) recipe [7, 24]. When an aluminum sample is subjected to a FPL pre-treatment, the native aluminum oxide layer is etched away, and a new and uniform oxide layer is formed when a steady state is reached between the etching and oxidation processes that occur [7]. Matienzo et al. used scanning transmission electron microscopy (STEM) to show that the oxide formed on an A1-2024-T3 surface after the FPL pre-treatment had ‘whisker-like’ protrusions, a morphology that appeared helpful for subsequent adsorption of coatings [24].

Although efforts have been directed at detecting the presence of metal–O–Si interfacial bonding, most studies in this area have been of a more macroscopic nature. For example, trial-and-error testings using the Boeing wedge test, the peel test, the salt fog test or anodic polarization [24-26] have identified pre-treatment conditions for optimizing a
subsequent coating in terms of its adhesive or protective characteristics. Observations from such work have supported the widely-cited recommendation for metal surfaces of using the FPL procedure at 65°C for a 15-30 min duration [7, 24], but they do not give information at the molecular level. Accordingly, a variety of microscopic studies have been made to explore the metal-O-Si interfacial bonding between organosilanes and metal substrates, using such techniques as secondary-ion mass spectrometry (SIMS) [27-30], vibrational spectroscopy [31-33] and X-ray photoelectron spectroscopy (XPS) [34, 35]. Scanning electron microscopy (SEM) has been used for characterizing oxidized aluminum surfaces formed after the recommended FPL pre-treatment times [26, 36], although understanding at the microscopic level for why the conditions identified by the macroscopic studies are optimal is still limited.

Earlier analytical work with XPS has shown that, when applied to oxidized surfaces of metals, the H₂ plasma pre-treatment can enhance the proportion of surface OH groups [37-40], and likewise significant chemical changes have been observed on various Al surfaces after heating [41, 42]. Assessing whether H₂ plasma and heating treatments can modify oxidized Al surfaces in ways that help optimize the adhesive bonding upon coating with BTSE has not been previously investigated. Thus, an objective of this work is to assess how various starting surfaces can be modified either by a H₂ plasma treatment or a heat treatment to enhance the formation of Al-O-Si interfacial bonds.

1.3 Fuel Cell Technology

1.3.1 Introduction

A fuel cell is an electrochemical device that converts chemical energy of fuels directly into usable electrical energy. As illustrated in Figure 1.4, all fuel cells consist of two
Figure 1.4  Operation of a proton exchange membrane fuel cell (PEMFC).

Anode Reaction:  \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \)

Cathode Reaction:  \( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \)
electrodes (i.e. anode and cathode) separated by an electrolyte. Table 1.2 shows a brief summary of the different types of fuel cells, typically classified by the type of electrolytes used along with their respective features and characteristics. By avoiding the combustion process, the fuel cell converts energy more efficiently and cleanly compared with the internal combustion engine [43]. Given the increased global consumption of fossil fuels, its contribution to the greenhouse effect and the noxious pollution of natural resources, alternative power generation systems with greater efficiency and cleaner emission profiles must therefore be developed.

Table 1.2  Comparison of the different types of fuel cells

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Common electrolyte</th>
<th>Conducting ion</th>
<th>Operating temperature</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton exchange membrane (PEMFC)</td>
<td>Solid organic polymer polyperfluorosulfonic acid (typically Nafion)</td>
<td>H⁺</td>
<td>50-100°C</td>
<td>• Solid electrolyte reduces corrosion and electrolyte management problems  • Quick start-up  • Low temperature operation</td>
<td>• Requires expensive catalysts</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>KOH aqueous solution on support</td>
<td>OH⁻</td>
<td>90-100°C</td>
<td>• Fast cathodic reaction</td>
<td>• Requires expensive removal of CO₂ from fuel and air streams</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>Liquid H₃PO₄ on support</td>
<td>H⁺</td>
<td>150-200°C</td>
<td>• High efficiency  • Increased tolerance to impurities</td>
<td>• Large weight/size  • Requires expensive catalysts</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>Molten Li₂CO₃, K₂CO₃ on support</td>
<td>CO₃²⁻</td>
<td>600-700°C</td>
<td>• High efficiency  • Fuel flexibility  • Variety of catalysts can be used.</td>
<td>• High temperature thus more corrosion and degradation of fuel cell components  • Slow start-up</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>Ceramic, typically solid ZrO₂ with small amounts of Y₂O₃</td>
<td>O²⁻</td>
<td>650-1000°C</td>
<td>• High efficiency  • Fuel flexibility  • Variety of catalysts can be used.</td>
<td>• High temperature thus more corrosion and degradation of fuel cell components  • Slow start-up</td>
</tr>
</tbody>
</table>
Fuel cells were first conceived in 1839 by Sir William Robert Grove, though much progress in fuel cell research did not occur until the 1960s when General Electric in the United States first developed the proton exchange membrane fuel cell (PEMFC), also known as polymer electrolyte membrane fuel cell, for use by NASA on their first manned spacecraft, the Gemini space program [43]. Current and potential applications for fuel cells are diverse; all fuel cell types have applications in stationary co-generation plants (i.e. combined heat and power systems) for buildings and distributed power generation. Alkaline fuel cells (AFCs) have been utilized in the Apollo spacecraft and the earlier generations of the space shuttle orbiter [43]. Nevertheless, much of the recent research and development efforts have been on the PEMFC since it has a unique combination of advantageous features including the quick, low temperature start-up and operation (50-100°C); the use of a solid polymer membrane electrolyte (typically Nafion) which reduces potential corrosion problems that liquid electrolytes may otherwise encounter; as well as PEMFC’s ability to generate a higher specific power (Whkg⁻¹) and power density (Whcm⁻²) than other types of fuel cell [43, 44]. Such characteristics make the PEMFC suitable for a wide range of potential commercial applications including automotive and transportation power, utilities as well as mobile consumer electronics. However, much effort is still needed to improve the performance of PEMFCs while reducing the high cost of materials before mass commercialization for such technologies can occur [43, 45, 46].

The PEMFC uses hydrogen (H₂) and oxygen (O₂) to produce electrical current and water (H₂O) via the overall reaction

\[ 2H₂ + O₂ \rightarrow 2H₂O. \]  \hspace{1cm} (1.3)

Reaction 1.3 occurs as long as H₂ and O₂ are respectively continuously supplied to the anode (where electrochemical oxidation occurs) and cathode (where electrochemical reduction...
occurs). In the presence of an acidic electrolyte, the anode oxidizes \( \text{H}_2 \) gas to produce \( \text{H}^+ \) ions (protons) and electrons via reaction

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-.
\]

(1.4)

During fuel cell operation, electrons produced at the anode pass through an external electrical circuit to reach the cathode while \( \text{H}^+ \) ions pass through the ion-conductive electrolyte. At the cathode, the oxygen reduction reaction (ORR) occurs, where \( \text{O}_2 \) gas reacts with the arriving electrons and with \( \text{H}^+ \) ions to form water via the cathodic reaction

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}.
\]

(1.5)

1.3.2 Issues for Cathode Catalysts in PEMFC

The use of expensive platinum-based or other precious metal-based catalysts contributes to the high cost of PEMFCs [47, 48]. Pt-based materials catalyze the ORR at the cathode of the fuel cell. Such catalysts are currently dispersed on high-area carbon supports to maximize the catalytic activity [43, 48]. Although such measures help improve current densities [43], this alone cannot solve the cost issue for PEMFCs. The reduction of the Pt loading in PEMFC applications has been pursued, but this has resulted in reduced lifetimes [48]. Pt-based catalysts are also sensitive to contaminants in the chemical fuel feed system and can be degraded by the production of \( \text{H}_2\text{O}_2 \), a byproduct generated as \( \text{O}_2 \) is being reduced during ORR [48]. Since the commercial potential of PEMFC depends a great deal on reducing the cost of the catalysts, one solution to Pt-based catalysts is to develop new, low-cost, non-precious catalysts capable of ORR catalysis for PEMFC applications [48, 49].

Any cheaper non-precious metal catalyst developed for ORR catalysis for PEMFC applications must be stable in acidic environment and display catalytic activity for oxygen reduction reaction comparable to that of Pt-based catalysts [48, 49]. Various such ORR
catalyst candidates, guided by biological enzymes and based on Co, Fe or Ni centers, have been previously studied, but improving upon their low stabilities (for transition metal oxides) [48, 50] and their low electrochemical activities (transition metal macrocyclic compounds) [48, 51] in acidic environments still remains challenging. In spite of this, the pioneering study dealing with Ru-Mo chalcogenides has been reported to show the unique ability of chalcogenides being highly stable in acidic environments [52]; however, utilizing precious metals such as Ru does not help in reducing the cost of the catalyst. Other studies have reported the ability of chalcogenides to display good stability in an acidic environment, particularly if used in combination with other transition metals [53-55]. In particular, for ORR catalysis applications, chalcogens such as Se have been reported to facilitate electron transfer between oxygen and the metal center [56] as well as to enhance structural stability by protecting the active metal sites from oxide formation and from dissolution [57]. The potential of Co-Se thin films, among other transition metal chalcogenide materials, has been recently demonstrated as a potential low-cost alternative for ORR catalytic activity [58]. Further studies show that Co-Se systems with higher Se content are more stable than Co-Se systems with lower Se content [58, 59]. All these factors bring a motivation to study and develop the supported CoSe2 powders as a potential catalyst for industrial applications.

1.4 Objectives of Research

The first theme of the research described in this thesis is an investigation of some different pre-treatments used to modify oxide surfaces on high-purity Al, and further to investigate their effect on the adsorption with bis-1,2-(triethoxysilyl)ethane (BTSE). The first objective was to develop a methodology to assess the quality of the BTSE adsorption on different oxidized aluminum surfaces using two microscopic measurements of: (i) the
amount of Al-O-Si interfacial bonding between bis-1,2-(triethoxysilyl)ethane (BTSE) and oxidized surfaces of high-purity Al, and (ii) the overall organosilane adhesion on the different pre-treated Al samples. These measurements contrast with the macroscopic tests widely used in industry [24-26]. The development of such a methodology was first systematically established using different oxidized Al surfaces generated by the widely-used Forest Products Laboratory (FPL) pre-treatment process for varying times. The next objective will be to assess, using the established methodology, how modifying the different oxidized Al surfaces with a remote microwave-generated H₂ plasma pre-treatment, and by a separate heat treatment, can affect the overall BTSE adsorption. Finally, the study will conclude with describing which pre-treatments are effective in enhancing the interfacial bonding and the overall adhesion between different oxidized Al surfaces and BTSE coatings.

The second research theme described in this thesis focuses on the synthesis and characterization of transition metal chalcogenide materials for potential applications in ORR catalysis for PEMFCs. The initial objective concentrates on the characterization of thin film model catalysts formed from transition metal chalcogenides prepared by magnetron sputter deposition. Model catalysts in the form of thin films, with known (fixed) surface areas, allow for their respective ORR activities from electrochemical measurements to be compared, and to be related to their surface compositions and structures. However, comparisons of ORR activities for powder catalysts are more challenging. This is attempted in this work, but the thin film model catalysts are used to gain an increase in scientific understanding, and to guide the formation of catalysts in dispersed powder form for use in an actual fuel cell. Raman spectroscopy has been employed to characterize these transition metal chalcogenide materials [60, 61] and is used to complement other analysis methods for characterizing their elemental, chemical, electrochemical and structural characters. Work described will
highlight efforts to assess elemental and chemical information from internal standards to various transition metal chalcogenide thin films (involving varying combinations of Co, Fe, Ni, Se and S) to systematically interpret the Raman peaks observed.

The next set of objectives relate to the development of a CoSe$_2$ catalyst in the form of a supported powder for ORR catalysis applications in PEMFCs. First, a method for synthesizing the high-purity CoSe$_2$ catalyst supported on carbon powders is developed, and second, they are tested for ORR catalytic activity based on their open circuit potential (OCP), their current density as well as their electrochemical stability. Third, a methodology was developed to characterize supported CoSe$_2$ powders, particularly for elemental, chemical or structural changes on the surfaces before and after various electrochemical processes. Fourth, following the synthesis and characterization of the high-purity supported CoSe$_2$ powders, sample surfaces were electrochemically modified in an effort to enhance the ORR catalytic activity. Finally, comparisons are made for supported CoSe$_2$ and CoSe powder catalysts for use in the oxygen reduction reaction.

1.5 Thesis Organization

This thesis is organized as follows. Chapter 2 describes the key techniques used in the research including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), scanning Auger microscopy (SAM), secondary ion mass spectrometry (SIMS), micro-Raman spectroscopy, electrochemical measurements, backscattered electron (BSE) imaging and dual magnetron sputter deposition. Chapter 3 reports investigations for interfaces formed between BTSE and some oxidized Al surfaces after different pre-treatments. Chapter 4 describes the synthesis of transition metal chalcogenide thin films made by magnetron sputtering and their
characterizations using micro-Raman spectroscopy in conjunction with the other surface analysis methods. Chapter 5 discusses surface and interfacial investigations of supported CoSe$_2$ on carbon powder for applications in oxygen reduction reaction (ORR) catalysis with potential applications in proton exchange membrane fuel cells (PEMFCs). Chapter 6 concludes with a summary and suggestions for follow-up research within the two main themes of research described.
Chapter 2
Experimental Methods

2.1 Electron Spectroscopy

2.1.1 Basic Principles

Electron spectroscopy is a method for analyzing the energy distribution of electrons that are emitted from a sample irradiated by an excitation source. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are two techniques commonly used for the surface characterization of solid materials that are stable under vacuum conditions. Such analytical methods can provide qualitative and quantitative information for elements in the surface region of a solid sample. In principle, all elements except for hydrogen and helium can be detected.

More information for the electron spectroscopic techniques discussed in this section is given elsewhere [62-65]. Briefly, XPS is based on the photoelectric effect, discovered by Hertz in 1887 and later explained by Einstein, while its instrumentation was refined by Siegbahn and coworkers which led to the development of the first commercial instruments around 1970. The basic principle for XPS is illustrated in Figure 2.1(a) where kinetic energies ($E_K$) of photoelectrons ejected from a sample surface after irradiation with soft X-rays are given by

$$E_K = h\nu - E_b.$$  \hspace{1cm} (2.1)

In equation 2.1, $h\nu$ is the incident photon energy and $E_b$ is the binding energy of the electron in the sample; the latter is the amount of energy required to remove that particular electron from the solid. Measuring the kinetic energies of the emitted electrons can provide elemental identification since each element has its own characteristic set of electron binding energies.
Figure 2.1  Schematics of (a) photoelectron emission; (b) Auger electron emission; (c) X-ray emission.

Figure 2.2  Dependence of mean free path on electron energy [66].
Additionally, high-resolution XPS measurements can provide chemical state information since the same atom can have small variations in the $E_b$ values due to variations in chemical environment and bonding state.

The emission of Auger electrons can also occur upon irradiation of X-rays onto a sample surface and this process is illustrated in Figure 2.1(b). The Auger electron emission process starts with an initial core vacancy followed by a two-electron process in which one electron fills the vacancy from a higher-energy orbital and a second electron is ejected from the atom. The Auger electron in Figure 2.1(b) is designated as a KL$_1$L$_{2,3}$ electron and its kinetic energy can be expressed as

$$E_{KL_1L_{2,3}} = E_K - E_{L_1} - E_{L_{2,3}},$$

although a correction is strictly needed since the process starts with a singly charged ion and finishes with one that is doubly charged [62-65]. Equation 2.2 indicates that Auger kinetic energies are characteristic of the sample and that allows elemental identification. Changes in the chemical state of an atom may also lead to changes in high-resolution Auger spectra. The initial vacancy may also be created by an incident electron beam of sufficient energy, as in scanning Auger microscopy (SAM), where a finely focused electron beam allows the detection of Auger electrons from specific local regions of a sample surface.

Figure 2.1(c) illustrates that X-ray fluorescence is another possible process that can occur from an initial excitation with X-rays or electrons. X-ray fluorescence provides the basis of another technique called energy dispersive X-ray spectroscopy (EDX) which will be described later. The Auger electron emission process competes with the X-ray emission process. However, the Auger emission process dominates if the binding energy of the initial vacancy is less than around 2 keV [62-65]. This is generally the case for lighter atoms but X-ray emission dominates when the initial vacancy is in an inner level of a heavier atom.
The surface analysis capabilities of XPS and AES depend on the electrons emitted from solid samples having kinetic energies of less than about 2 keV. Such electrons have a high probability to experience inelastic scattering. The inelastic mean free path (IMFP), $\lambda$, is the parameter representing the average distance traveled by an electron before losing energy due to inelastic collisions. Figure 2.2 shows empirical $\lambda$ values in the form of a "universal curve" for different elements as a function of electron kinetic energy, and illustrates that $\lambda$ values are typically around 10 Å for electrons with kinetic energies ranging from about 20 eV to 2,000 eV [66]. This ensures that electrons detected in sharp peaks in XPS and AES spectra originate from the surface region of the sample (say within $\sim 3\lambda$ [62]). Strong inelastic scattering for electrons inside a solid with kinetic energies less than about 2 keV therefore ensures the surface sensitivity for the XPS and AES techniques.

2.1.2 Qualitative Analyses of XPS and AES Spectra

Figure 2.3(a) shows a XPS survey spectrum of Al coated with BTSE that is displayed in a plot of intensity (number of counts) versus binding energy. This survey spectrum, covering a wide energy range (e.g. up to 1,200 eV), was acquired using a Mg Kα excitation source under low energy resolution. Peaks from XPS survey spectra can be identified with the aid of tabulated binding energy values given in reference handbooks [67], and those in Figure 2.3(a) are identified and labeled by the regular atomic orbital nomenclature such as Al 2s, Al 2p, Si 2s, Si 2p, C 1s and O 1s. X-ray induced Auger electron emissions were also detected for the O KLL and C KLL transitions. A high-energy background, which corresponds to the emission of inelastically scattered electrons, accompanies the sharp distinct features in XPS spectra.
Figure 2.3  XPS spectra from high-purity Al: (a) survey scan after coating with 1% BTSE; (b) high resolution Al 2p spectrum after FPL pre-treatment for 60 min with Shirley approach to non-linear background subtraction; and (c) spectrum in (b) fitted to oxide and metallic components.
Higher resolution spectra are measured over a restricted energy range (e.g. 10-50 eV) for the element of interest. Figure 2.3(b) shows an example of an XPS narrow scan spectrum for the Al 2p peak from a high-purity Al sample. Two Al 2p peaks are observed due to two different chemical environments for Al. The peaks at binding energies 72.7 eV and 75.5 eV are attributed to metallic Al and Al oxide respectively. This difference in binding energy positions gives information on the chemical environment and the valence state of the Al atoms. The loss of valence charge density shows up as an increase in the binding energy of the core electrons [62, 63]. For heavier atoms, extra spectral structure due to spin-orbit coupling can occur [68].

The nomenclature for Auger peaks is based on conventional atomic orbital labeling. However, since the Auger process involves three energy levels, Auger transitions are identified based on the K, L, M notation (respectively denoting n = 1, 2, 3, etc.) [62-64]. Each level is further identified by subscripts; for example, L₁ for 2s₁/₂, L₂ for 2p₁/₂, L₃ for 2p₃/₂ and V for valence band. Figure 2.4 shows a survey scan for a Co-Se thin film where the Auger transitions of Co LMM and Se LMM are indicated. Auger peak positions and shapes can also give information on the chemical environment of the element. Higher resolution Co LMM spectra for metallic Co and for the Co-Se thin film are compared in Figure 2.5 where an additional Auger transition at 754.5 eV is observed for the Co-Se thin film; this is an indication of Co-Se bonding (with the absence of an Auger O KLL transition at around 512.0 eV according to the survey scan in Figure 2.4). This example shows that Auger spectra can also be used to identify chemical differences in elemental bonding albeit such analysis is more complex for AES than for XPS since three energy levels are involved.
Figure 2.4 Auger survey scan of a Co-Se thin film.

Figure 2.5 Co LMM Auger spectra from metallic Co and compared with a Co-Se thin film.
2.1.3 Quantitative Analysis

Quantitative information can be obtained from analysis of measured peak intensities from XPS and AES spectra. The intensity contribution for electrons exiting the sample from an infinitesimal thickness dx at depth x is

\[ dl = n \sigma A T \exp(-x/\lambda) \, dx, \]  

(2.3)

where \( n \) is the number of appropriate atoms per unit volume of the sample, \( f \) is the incident beam flux, \( \sigma \) is the scattering cross-section, \( A \) is the area of a sample from which electrons are detected, \( T \) is the instrumental transmission function and \( \lambda \) is the inelastic mean free path. Simple integration for a semi-infinite homogeneous sample gives

\[ I = n f \sigma A T, \]  

(2.4)

where the contributions \( f, \sigma, A \) and \( T \) can be grouped into an instrumental atomic sensitivity factor \( S \) for given instrumental conditions and for a given peak. In principle, the atomic ratio for two elements in the sample \((n_1/n_2)\) can be determined using the equation:

\[ \frac{n_1}{n_2} = \left[ \frac{I_1}{S_1} \right] / \left[ \frac{I_2}{S_2} \right] \left[ \frac{\lambda_2}{\lambda_1} \right] \]  

(2.5)

when tabulated values of \( \lambda_1 \) and \( \lambda_2 \) are used for the appropriate electron kinetic energies [66]. For semi-quantitative work, the \( \lambda_2/\lambda_1 \) ratio is commonly taken as a constant and equal to unity. The elemental composition ratio \( n_1/n_2 \) for the two elements within the depth probed can then be determined directly from measured peak intensities and the ratio of sensitivity factors. This relationship can be further applied to give atomic percentages for a multi-element analysis, for example:

\[ C_i = \frac{n_i}{\sum n_i} = \left[ \frac{(I_i/S_i)}{(\sum I_i/S_i)} \right] \times 100 \]  

(2.6)
where \( i \) is summed over the various constituents in the sample.

In practice, measured spectral peaks have to be corrected for background prior to a quantification analysis. The non-linear background subtraction method introduced by Shirley [69] has been used for this purpose and is discussed with the spectrum shown in Figure 2.3(b). Briefly, assumptions for this method include that the number of inelastically scattered electrons at any point in a spectrum is proportional to the number of elastically scattered electrons at higher kinetic energies. Correcting for the inelastic contribution over an energy range of \( E_1 \) to \( E_2 \) (chosen by the operator), the following iterative algorithm is used:

\[
N'_{K+1}(E) = N(E) - N(E_2) - C \int_{E_1}^{E_2} N'_K(E) dE
\]

(2.7)

where \( N(E) \) is the measured count rate and \( N'_K(E) \) is the background corrected count rate (the index \( K \) indicates the \( K \)-th iteration). The reference background level is provided by \( N(E_2) \) and the constant \( C \) is fixed by the requirement that \( N'_K(E_1) = 0 \). The process starts with \( N'_0(E) = 0 \) and continues until \( N'_{K+1} \sim N'_K \); four iterations are typically required for convergence.

After background subtraction, a curve fitting process is commonly used to assess the different chemical species that are present in a sample and an example is shown in Figure 2.3(c) where the Al 2p spectrum of high-purity aluminum was curve fitted to the metallic Al and Al oxide components. This approach requires some chemical knowledge of the system to realistically estimate the number of different chemical species that may be present for the element of interest. Each such species is represented by a mixed Gaussian-Lorentzian function which represents an approximation to the Voigt function (convolution of Lorentzian and Gaussian) [62] incorporating variations in peak position, peak height and peak width expressed as full width at half maximum (FWHM):
where $E_0$ is the energy for the maximum of the individual component (i.e. the peak centre position); $\beta$ is nearly 0.5 of the FWHM; $M$ is the ratio of Gaussian and Lorentzian contributions to the peak component shape where it can take any value between 0 (for a pure Gaussian peak shape) to 1 (for a pure Lorentzian peak shape) inclusive [62].

All the curve fitted components are represented by a set of functions (each like that in equation 2.8) and they are iterated to optimize the fit between the measured spectrum and the simulated spectrum. At each stage in the optimization, the quality of the fit obtained can be evaluated by using the least-square function ($\chi$):

$$\chi = \left( \frac{1}{N_{\text{free}}} \sum_i \left( \frac{Y_{\text{mea},i} - Y_{\text{fit},i}}{Y_{\text{mea},i}} \right)^2 \right)^{1/2}$$

where $i$ is the number of data points (1 to $N$), $Y_{\text{mea},i}$ is the measured count rate at the $i$-th data point, $Y_{\text{fit},i}$ is the corresponding value of the simulated function; $N$ is the number of data points and $N_{\text{free}}$ equals $N - N_{\text{fit}}$, where $N_{\text{fit}}$ is the number of parameters to be fitted. The smaller the $\chi$ value, the better the quality of the fit between the sum of all the curve fitted components and the measured spectrum. Visual comparison is always useful to ensure that the curve fitting procedure does not introduce any artifacts of a non-chemical nature.

2.2 Leybold MAX 200

The Leybold MAX200 spectrometer was used for XPS measurements presented in this thesis. This instrument operates in an ultrahigh vacuum (UHV) environment ($10^{-9} - 10^{-11}$ Torr) and it is equipped with a dual-anode X-ray source, a hemispherical energy analyzer, an ion gun for sample cleaning as well as magnetic coupling transfer rods for sample transfer
and movement between the four interlinked chambers shown schematically in Figure 2.6. A sample can be moved under vacuum between the transfer chamber (for sample entry), the analysis chamber, the metal deposition chamber as well as the plasma chamber. UHV conditions are achieved by a combination of ion and turbomolecular pumps; each turbomolecular pump is backed by a rotary pump. An auxiliary titanium sublimation pump is also available if required. UHV conditions are needed for operating the spectrometer for several reasons. First, that environment can enable a high proportion of electrons emitted from the sample to reach the energy analyzer without being scattered by residual gas molecules. Second, such low pressure environments are necessary to keep the surface in its initial state and relatively free from unwanted adsorption and contamination from background gases. Third, low pressure conditions are required for effective operation of the X-ray source and other analysis components.

2.2.1 X-ray Source

Bombarding an anode with electrons (from a heated filament) that have been accelerated to 10 – 15 kV generates X-rays. The MAX 200 is equipped with a dual anode X-ray source that has Al and Mg deposited on different faces of the anode block; a simple switch allows the selection of the desired anode to be used. A deionized water system cools the anode to prevent failure due to overheating during operation. The Kα lines of Al and Mg with energies of 1486.6 eV and 1253.6 eV respectively can be produced from the dual anode X-ray source. The line widths for the Al and Mg sources are 0.85 eV and 0.70 eV respectively. The Al Kα source is frequently used since its higher energy allows a wider energy range spectrum to be acquired, but the Mg Kα source has the advantage of better energy resolution. A 2 μm thick Al foil window is positioned between the anode and the
Figure 2.6  Schematic of pumping system for MAX 200.
sample in order to prevent stray electrons and contamination from the anode region reaching
the sample. This Al foil window is thick enough to help reduce the intensity of additional X-
ray lines (such as Kβ) that can add satellite structure in an XPS spectrum but is thin enough
such that the X-ray flux reaching the sample is not significantly attenuated [62].

2.2.2 Electron Energy Analyzer

The function of an electron energy analyzer is to disperse the electrons emitted from
the sample according to their energies [62, 64, 70]. The energy analyzer of the MAX 200
illustrated in Figure 2.7 is briefly described here; it consists basically of a collection lens
system, a concentric hemispherical analyzer (CHA), and a multichannel plate (MCP)
detector. The collection lens system functions in two stages: the first stage controls the
analysis area (spot size) and collection angle for the electrons coming from the sample
surface, while the second stage retards the electrons to a particular pass energy value and
controls the angle at which they enter the analyzer.

The analyzer has two hemispheres (with inner radius R₁ and outer radius R₂), with a
potential difference, ΔV, applied between them. The lens assembly retards the initial kinetic
energy of the incoming electrons and focuses them onto the entrance region of the analyzer.
The entrance slit (width ω₁) and exit slit (width ω₂) are centered on the mean radius, R₀
\[ R₀ = \frac{(R₁ + R₂)}{2}, \]  

(2.10)
The trajectory of an electron in the analyzer depends on its kinetic energy and the applied
potential difference across the hemispheres. The condition for an electron of kinetic energy
E₀ to pass through the analyzer is given by:
Figure 2.7  Schematic of the lens system and the concentric hemispherical analyzer (CHA) in the MAX 200 (modified from Ref. [64]).
For a given potential difference, $\Delta V$, only electrons with kinetic energy $E_0$ (pass energy) follow a trajectory that will bring them to the entrance slit of the detector where they can be counted [71]. The detector is constructed from two channel plates in a chevron array to give 18 discrete microchannels that act as individual electron multipliers. The voltage across the plate is set to allow count rates at above $10^7$ s$^{-1}$.

The relative resolution of the analyzer ($\Delta E_{\text{spec}}$) is given by

$$
\frac{\Delta E_{\text{spec}}}{E_0} = \left( \frac{(\omega_1 + \omega_2)}{4R_o} \right) + \left( \frac{\alpha^2}{4} \right),
$$

where $\alpha$ is half the entrance angle to the analyzer. Since $\omega_1$, $\omega_2$, $R_o$ and $\alpha$ are fixed by the physical construction of the spectrometer, the resolution can be varied only by changing the pass energy $E_0$. Equation 2.12 shows that as $E_0$ reduces, the resolution becomes better. However, a lower pass energy results in a drop in the signal intensity, and thus a balance is needed between a high analyzer resolution and a high signal intensity. XPS measurements in this thesis utilized pass energies 192 eV for survey scans and 48 eV for high-resolution narrow scans.

The energy resolution for a measured photoelectron peak is expressed by its FWHM, and that depends on broadening from the X-ray source ($\Delta E_{\text{source}}$), from the electron energy analyzer ($\Delta E_{\text{spec}}$) as well as from the natural width of the core level ($\Delta E_{\text{line}}$) according to

$$
\Delta E_{\text{total}} = (\Delta E_{\text{source}}^2 + \Delta E_{\text{spec}}^2 + \Delta E_{\text{line}}^2)^{1/2},
$$

assuming that all contributions have the Gaussian form [63].

The kinetic energy of a photoelectron measured in the spectrometer ($E_{k^{'}}$) is referenced to the spectrometer’s vacuum level, while the binding energy of the electron
inside the sample (Eb) is referenced to the Fermi energy of the sample. When a conducting sample is in electrical contact with the spectrometer, the Fermi energies of the sample and spectrometer are equal and thus the measured binding energy can be expressed as [72]

\[ hv = E_b + E_k' + W_{sp}, \]  

(2.14)

where \( W_{sp} \) is the work function of the spectrometer. In practice, \( W_{sp} \) is determined by a calibration with a standard gold sample to ensure that the Au 4f\(_{7/2}\) line has a binding energy of 84.0 eV [62]. This line is chosen due to its high intensity and accurately known position. Additionally, gold is an inert metal and thus its binding energy should not be influenced by chemical shifts or charging effects. When measuring insulating samples, positive charge can build up on the surface and hence the energy referencing needs some modification. For such situations in this thesis, the C 1s peak associated with adventitious hydrocarbon contamination is set at a binding energy of 285.0 eV.

2.3 Thermo Electron Microlab 350

2.3.1 Auger Analysis

All Auger spectra, some SEM micrographs and all BSE images presented in this thesis were acquired using the Thermo Electron Microlab 350 system, which is primarily designed for scanning Auger microscopy (SAM). Figure 2.8 shows a schematic of the equipment, and more detailed information can be found in the Microlab 350 Operating Manual [73]. The Microlab 350 is equipped with a Schottky field emission electron source, a transfer chamber for sample entry, a preparation chamber for sample treatment, an analysis chamber for sample analysis as well as a CHA and six-parallel-connected channeltrons for Auger electron measurements. Sample transfer between the chambers is done with wobble sticks and a rack-pinion transfer rod. The analysis chamber operates under UHV conditions.
Figure 2.8  Schematic of pumping system for Microlab 350.
with a base pressure of $1.5 \times 10^{-9}$ Torr and Figure 2.8 additionally shows the pumping arrangements for the whole system.

Figure 2.9 is a schematic diagram for the field emission electron gun (used at 10 keV for much of the work presented in this thesis). Emission occurs from a tip made of a single crystal tungsten wire (radius <1 µm) that is coated with zirconium and welded onto the tungsten filament used to resistively heat the tip (~1,800 K). For its use, a potential is applied to create an electric field (~$10^7$ Vcm$^{-1}$) at the tip that causes the emission of electrons. To avoid contamination and to maintain stable operation of the electron beam, the electron source must be differentially pumped by an ion pump (as shown in Figure 2.8). Electrons extracted from the field emission tip are focused (≤10 nm) by a system of electromagnetic lenses and apertures (Figure 2.9). The field emission source provides high brightness ($5 \times 10^8$ A/cm$^2$ steradian), low energy spread of 0.3 eV and long life time (~5,000 h) when operated under low-pressure conditions.

The basic principle of a CHA was outlined for the MAX200 (Section 2.2.2), but the Microlab 350 is operated in the constant retarding ratio (CRR) mode for Auger measurements in contrast to the constant analyzer energy (CAE) mode used in XPS. In the CRR mode, the pass energy is varied to maintain a constant $\Delta E_{\text{spec}}/E_0$ ratio. The advantage of using the CRR mode is that it offers good resolution at the lower kinetic energies where many Auger transitions of interest occur. Although the resolution in the CRR mode reduces as energy increases, this is less serious for Auger measurements whose peaks tend to be broader than photoelectron peaks. The analyzer can be set to detect either a particular element of interest or programmed for the sequential detection of several elements. In the spectra, Auger electrons form distinguishable peaks on the slowly-varying background of the
Figure 2.9  Illumination system in Microlab 350 [73].
inelastically scattered electrons. The incident electron beam can be focused to a single spot on the sample surface as seen from a scanning electron microscopy (SEM) image (discussed in Section 2.3.2) for Auger point analysis, and this method was utilized for work done in Chapters 4 and 5. The Microlab 350 is also capable of using AES, in conjunction with sputtering with Ar ions from an ion gun, to acquire depth profiles to analyze the depth composition of a thin film; an example, featured later in Chapter 4, is shown in Figure 2.10 after normalization with elemental sensitivity factors.

2.3.2 Scanning Electron Microscopy (SEM)

The Microlab 350 is equipped with a secondary electron detector (SED) to detect secondary electrons (i.e. kinetic energies <50 eV) to enable the formation of images in scanning electron microscopy (SEM). These micrographs give visual topographical information (three-dimensional appearance) of the sample surface as the secondary electrons emitted from the sample surface are collected in the photomultiplier detector while the incident electron beam is rastered across the surface. Brightness of the signal at any point depends on the local nature of the surface and atomic number of the elements involved. In the absence of surface charging, steeper surfaces tend to show brighter image than flat surfaces. Also, elements of higher atomic number tend to have a greater yield of secondary electrons than those of low atomic number. SEM images are useful for Auger point analysis, with the process initiated by using the focused electron beam to obtain a SEM image for an area on the sample surface. Then the incident electron beam is focused on the particular local regions of interest and Auger measurements are obtained using the CHA. Before the Microlab 350 became available, some SEM micrographs (in Chapter 3) were acquired with the Hitachi S4100 in the Advanced Materials and Process Engineering Laboratory building.
Figure 2.10  Auger depth profile of a Co-Se thin film.

Figure 2.11  Schematic of backscattered electron (BSE) and secondary electron pathways to the BSE detector (BSD) and the secondary electron detector (SED) respectively upon electron beam irradiation (modified from Ref. [74]).
(Professor T. Tiedje's laboratory). The Hitachi S4100 SEM, operated under a vacuum of $10^{-6}$ Torr, is equipped with a field emission source that operates at room temperature.

2.3.3 Backscattering Electron (BSE) Imaging

Along with the concentric hemispherical analyzer (CHA) and secondary electron detector (SED), the Microlab 350 is also equipped with a backscattered electron detector (BSD). Measurements to be discussed in Chapter 5 utilized the backscattered electron (BSE) imaging capability of the Microlab 350. Backscattered electrons have high kinetic energies that are comparable with the incident beam energy (i.e. with relatively small losses in energy after undergoing a few scattering events) [72, 74, 75]. For a given situation, the number of generated backscattered electrons also varies with atomic number contrast and surface topography. Figure 2.11 illustrates that backscattered electrons travel basically in straight lines (high velocity) to the four quadrants of the solid-state silicon-based detectors placed above the sample. Signals collected at BSD quadrant pairs A and B can be independently processed to generate different modes of BSE imaging including the A+B mode (i.e. adding all signals collected from quadrant pairs A and B) as well as the A-B mode (i.e. signals from quadrant pair B are subtracted from the signals collected from quadrant pair A). In the A+B mode (also referred to as the COMPO mode), signals from all quadrants of the BSD are summed together to generate a BSE image based on the atomic number contrast for the elements present in the analyzed sample area; higher atomic numbered elements appear significantly brighter in such a BSE image. The A-B mode (also referred to as the TOPO mode) after amplification generates a BSE image based on the topographic contrast of the analyzed sample area where contoured features are better revealed.
2.4 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray (EDX) spectroscopy measures photons emitted according to the process illustrated in Figure 2.1(c) after a sample is irradiated with a high energy electron beam. Since each atom type has its own set of core energy levels, different photon energies can be measured to identify the elements in a tested sample. EDX is used in Chapter 4 of this thesis to assess the elemental composition at different local regions of various transition metal chalcogenide thin films. All EDX measurements utilized a Hitachi S3000N SEM instrument (in the Department of Materials Engineering at the University of British Columbia); it has a tungsten hairpin source that produces electrons by thermionic emission, and is equipped with an AP3 ultra-thin polymer X-ray window (Moxtek Inc.) [76] which (unlike the conventional Be window) allows for transmission of photons from lighter elements. An EDX spectrum is shown in Figure 2.12 for a Co-Se thin film where a plot of counts per second as a function of energy (keV) is displayed. The peak energies in an EDX spectrum are identified and labeled by comparison with an X-ray emission database available in the system.

Using EDX for quantitative analysis depends on measuring peak areas after applying non-linear background corrections. The amount of element i present in a sample (C_i) can be expressed concisely as

\[ C_i = k_i \frac{I_i}{I_{(0)}} \]

(2.15)

where \( I_{(0)} \) is the corrected peak area from the standard composed of element i, \( I_i \) is the area measured from the specimen under analysis and \( k_i \) is a factor (referred to as the ZAF factor [74]) that corrects for the effects of atomic number, self-absorption and fluorescence probabilities for the different elements. The detection limit for EDX is at the 0.1 wt% level.

Since energetic electrons (e.g. 20 keV) are used to excite the process and photons produced
Figure 2.12  EDX spectrum of a Co-Se thin film.
have long mean free paths when compared to electrons, EDX gives elemental composition from depths of several \( \mu \text{m} \). Compared with XPS and SAM, EDX must therefore be considered to be a bulk analysis technique.

2.5 Secondary Ion Mass Spectrometry (SIMS)

2.5.1 Introduction

Secondary ion mass spectrometry (SIMS) involves the measurement of the sputtered ions after bombarding a sample surface with a primary ion beam (e.g. 0.5 to 10 keV). Figure 2.13 is a schematic of the sputtering process where, during this bombardment, energy is passed to target atoms via momentum transfer in a cascade of collisions and this results in secondary ions (along with neutral secondary species) being sputtered off \([63, 64]\). The secondary ions are detected by a mass spectrometer and such SIMS measurements are plotted as a spectrum of intensity as a function of the mass-to-charge (m/z) ratio. Figure 2.14 shows a SIMS spectrum measured with a quadrupole mass spectrometer from a high-purity Al sample that had been coated with BTSE. In that example, secondary ions with m/z values of 27, 28, 70 and 71 are identified and that sets the scene for work described in Chapter 3.

SIMS measurements can be conducted in three analysis modes, namely static, dynamic and imaging SIMS. The difference between static SIMS and dynamic SIMS is in the ion dose of the primary beam \([77-79]\). Static SIMS involves using sufficiently low primary ion doses (e.g. \(10^{12}\) ions \(\text{cm}^{-2}\) or less) so that sample measurements can be made without significant modification to the surface. In practice, the ultimate static SIMS measurements are made with a time-of-flight SIMS (TOF-SIMS), where the TOF analyzer enables parallel detection of secondary ions with a high mass resolution and high
Figure 2.13  Sputtering process in SIMS (modified from Ref. [63]).

Figure 2.14  SIMS positive ion spectrum from a high-purity Al sample acid etched for 10 min and then coated with 1% BTSE.
transmission after a pulsed primary ion beam sputters the top-most surface of the sample [80, 81]. Imaging SIMS represents an extension whereby the primary beam is rastered across the surface to allow measurement of the distribution of sputtered ion species from different regions of the surface. Dynamic SIMS involves the use of much higher primary ion doses (e.g. 10^{14} \text{ ions cm}^{-2} \text{ or more}) so that surface layers can be sputtered off the sample over time to give information on depth distribution associated with the secondary ions of interest (i.e. this mode generates depth profiles). The work presented in Chapter 3 uses a quadrupole mass analyzer operated in an intermediate situation (ion dose ~10^{13} \text{ ions cm}^{-2}) to cover both static and dynamic capabilities (see Section 2.5.2 for details).

Converting secondary ion signals to concentrations within the sample can represent a significant challenge in SIMS analysis since the secondary ion yield can vary markedly with the chemical state of the element being analyzed [63, 79, 82]. For example, the positive ion yield for Al, increases by a factor of 10^2 after oxidation [83]. Accordingly matrix effects must be taken into account when semi-quantitative SIMS analyses are attempted.

2.5.2 VG MM12-12S

Figure 2.15(a) shows a schematic of the VG Scientific MM12-12S instrument used for the SIMS work in Chapter 3. A gate valve separates the analysis chamber and the transfer chamber. For SIMS measurements, a sample is first loaded into the transfer chamber. After the transfer chamber is pumped down to 10^{-8} \text{ Torr}, the gate valve is opened and the sample is then transferred into the analysis chamber using a wobble stick while the sample position can be adjusted through a manipulator in the analysis chamber. Figures 2.15(b) shows the pumping system of the VG MM12-12S. Base pressures for the analysis chamber, transfer
Figure 2.15  VG quadrupole SIMS system: (a) analysis chamber with facilities available; (b) schematic of pumping system.
chamber and the duoplasmatron ion source are $5 \times 10^{10}$, $7 \times 10^{-9}$ and $2 \times 10^{-7}$ Torr respectively.

This instrument is equipped with three ion sources: the duoplasmatron ion source (DP5B), the gallium liquid ion source (MIG100) as well as the argon ion source (AG61). The duoplasmatron source (with 90% Ar gas, 10% $O_2$ gas) was used for the work presented in Chapter 3. Such an ion source produces primary ions by plasma arc discharge (300-600 V applied between the cathode and anode); an opening in the anode allows primary ions to be extracted and then accelerated to 5 kV [84, 85]. The primary ion beam is transmitted through a Wien filter in order to remove unwanted ion masses. The beam diameter can range from 1 to 100 μm.

Figure 2.16 shows a schematic diagram for the MM12-12S quadrupole mass analyzer that contains three major components: the ion energy filter, the mass filter and the ion detector. The ion energy filter prevents high energy ions from entering the mass filter. The quadrupole mass analyzer, which acts as a mass filter in the range of 1 to 800 amu, has two pairs of molybdenum rods (diameter 12 mm) where opposite pairs of rods are connected electrically; the sinusoidal potentials applied to each set of rods are equivalent, but with opposite sign:

$$\phi(t) = U + V \cdot \cos(2\pi ft)$$  \hspace{1cm} (2.16)

$$\phi(t) = U - V \cdot \cos(2\pi ft)$$  \hspace{1cm} (2.17)

For a given set of voltages $U$ and $V$, only ions with a particular mass-to-charge ratio can pass through the mass analyzer for detection, while other ions strike the rods and are neutralized [63, 86]. Mass scanning is achieved by keeping both the $V/U$ ratio and $f$ (e.g. 2 MHz) constant while varying $U$ and $V$ (in typical ranges to 100 V and 1500 V respectively). Ions exiting the mass filter are detected by a single channeltron multiplier which can give a gain.
Figure 2.16  Schematics of (a) the major components found within the SIMS MM12-12S quadrupole mass analyzer; (b) the quadrupole mass filter.
of up to $10^8$ over the input signal.

2.6 Micro-Raman Spectroscopy

2.6.1 Introduction

Detailed information on the Raman process can be found in standard references [87-91]. Briefly, Raman scattering occurs when the electric field of incident light distorts the electron cloud of a molecule creating an induced electrical dipole that can lead to the exchange of energy with molecular vibrations and the emission of light of different wavelength. Lasers are the ideal excitation source for Raman spectroscopy as they emit intense, monochromatic light and can provide spatial resolution down to 1 μm for analyses of small micro-regions on samples. The electric field strength ($E_f$) of the laser radiation fluctuates with time (t) as

$$E_f = E_o \cos(2\pi v_0 t),$$

(2.18)

where $E_o$ is the amplitude and $v_0$ the frequency of the light. The irradiation induces an electric dipole moment $P$ in the molecule

$$P = \alpha E_f = \alpha E_o \cos(2\pi v_0 t),$$

(2.19)

where $\alpha$ is the polarizability (i.e. a measure of the ease with which the electron cloud around the molecule can be distorted). If the molecule is vibrating with a frequency $v_{vib}$, the nuclear displacement $q$ is written as

$$q = q_o \cos(2\pi v_{vib} t),$$

(2.20)

where $q_o$ is the vibrational amplitude. The polarizability of electrons in the molecule will be modulated by the molecular vibration so that

$$\alpha = \alpha_o + \left( \frac{\partial \alpha}{\partial q} \right)_o q_o + ..., $$

(2.21)
where $\alpha_0$ is the polarizability at the equilibrium position, and $(\partial \alpha / \partial q)_0$ is the rate of change of $\alpha$ with respect to the change in $q$, evaluated at the equilibrium position. Combining equations 2.19, 2.20 and 2.21, the following expression can be obtained

$$P = \alpha_o E_o \cos 2\pi \nu_o t + \frac{1}{2} \frac{\partial \alpha}{\partial q}_o q_o E_o \{ \cos \{2\pi(\nu_0 + \nu_{\text{vib}})t\} + \cos \{2\pi(\nu_0 - \nu_{\text{vib}})t\} \}. $$

(2.22)

The first term in Equation 2.22 represents Rayleigh scattering where an oscillating dipole radiates at frequency $\nu_0$; the second term corresponds to the anti-Stokes Raman scattering at frequency $(\nu_0 + \nu_{\text{vib}})$ and Stokes Raman scattering at frequency $(\nu_0 - \nu_{\text{vib}})$. Based on Equation 2.22, a vibration is Raman-active only if

$$\left( \frac{\partial \alpha}{\partial q}_o \right) \neq 0.$$  

(2.23)

Equation 2.23 is the basis of the primary selection rule for Raman scattering where a vibration is Raman-active if the polarizability changes during the vibration. This is in contrast to infrared spectroscopy where a vibration is infrared-active if the dipole moment is changed during the vibration. In general, molecular vibrations symmetric with regard to the center of symmetry are Raman-active but not infrared-active, whereas molecular vibrations that are antisymmetric with regard to the center of symmetry are infrared-active but not Raman-active; this is known as the mutual exclusion principle [89-91]. Qualitatively, Raman scattering is stronger for moieties where the electrons are less tightly held and weaker for molecules with lower polarizabilities.

Figure 2.17 illustrates Rayleigh and Raman scattering in terms of an energy level diagram showing just two vibrational energy levels ($g0$ and $g1$) for the ground electronic state. In Raman spectroscopy, the laser energy ($\nu_0$) needs to be less than the energy of the
Figure 2.17 Schematics for light scattering processes: (a) Rayleigh scattering, (b) Stokes Raman scattering and (c) anti-Stokes Raman scattering.
first excited electronic state. The virtual state shown in Figure 2.17 is not a true quantum state of the molecule, but it represents a short-lived distortion (excitation) of the electron cloud caused by the oscillating electric field of the incident photon.

Following laser impact, most photons (>99.999%) undergo elastic Rayleigh scattering (Figure 2.17(a)), where the scattered photons retain the incident frequency as the system relaxes from the virtual state to the ground electronic state. In contrast, some photons (<0.001%) undergo inelastic Raman scattering resulting in scattered photons with different frequencies. In Stokes scattering (Figure 2.17(b)), the photons have the energy

\[ E = h\nu_o - \Delta E = h(\nu_o - \nu_{\text{vib}}), \]  

(2.24)

while in anti-Stokes scattering (Figure 2.17(c)) the scattered photons have energy

\[ E = h\nu_o + \Delta E = h(\nu_o + \nu_{\text{vib}}). \]  

(2.25)

In Raman spectroscopy, the vibrational frequency (\(\nu_{\text{vib}}\)) is measured as a shift from the incident beam frequency (\(\nu_o\)). Figure 2.18(a) shows a Raman spectrum measured for a silicon wafer using a HeNe laser source where intensity of scattered light is plotted as a function of the Raman shift in both positive and negative directions. The Raman shift is conventionally expressed in wavenumber units (\(\tilde{\nu}, \text{cm}^{-1}\)) and is obtained from \(\nu_{\text{vib}}\) (units s\(^{-1}\)) using

\[ \tilde{\nu} = \frac{\nu_{\text{vib}}}{c}, \]  

(2.26)

where \(c\) is the velocity of light (3 x 10\(^{10}\) cm s\(^{-1}\)). Peaks from Raman spectra due to the Stokes and anti-Stokes Raman scattering along with (reduced) Rayleigh scattering can be observed. However, since both types of Raman scattering give the same type of information (i.e. the magnitude of the Raman shift) and Stokes scattering is typically stronger than anti-Stokes
Figure 2.18 Raman spectra of Si using helium-neon (HeNe) excitation laser source (632.8 nm) showing (a) Rayleigh and Raman scattering; (b) standard practice of only measuring Stokes Raman scattering.
scattering, work in this thesis follows the standard practice of measuring the Stokes side of a spectrum as shown in Figure 2.18(b).

By comparing peaks from fingerprint Raman spectra with literature databases and internal standards, the identity of a material can be determined. However, care must be taken in acquiring and interpreting Raman spectra since factors such as laser power setting and acquisition time can influence the quality of the resulting Raman spectra (e.g. charring with high-intensity sources, leading to spectra that are not representative of the original sample state). In a solid crystalline lattice, the large number of vibrations oscillating in phase can result in sharp peaks being observed in a Raman spectrum. However, with amorphous, defect and nano-crystalline structures, the Raman spectra generally show broader and less well-defined peaks [89-91].

Advances in instrumentation have allowed Raman spectroscopy to play an increasingly useful role in the characterization of surfaces [88-92]. One established example, beyond the context of this thesis, is surface enhanced Raman spectroscopy (SERS) where Raman signals can be increased by factors as large as \(10^6\) for adsorption on colloids or on rough surfaces formed by silver or gold. Examples in Chapter 4 will demonstrate applications of micro-Raman spectroscopy to the characterization of some transition metal chalcogen surfaces.

### 2.6.2 Renishaw inVia Raman Microscope

The Renishaw inVia Raman Microscope is used for acquiring Raman spectra of various samples discussed in Chapters 4 and 5. Detailed information for the instrument can be found in the inVia User's Guide [87]. Briefly, Figure 2.19 shows a schematic of the instrument and its major components including the laser excitation source; focusing and
Figure 2.19  Schematic of optical pathway in the Renishaw inVia Raman Microscope (based on Refs [87, 91]).
collection optics; sample stage; spectrometer as well as the detection system. The inVia Raman microscope is equipped with a helium-neon (HeNe) laser source (632.8 nm) and an argon ion (Ar⁺) laser source (514.5 nm).

Before obtaining a Raman spectrum, an optical image (obtained from a built-in video camera and the microscope objective lens) of the analyzed sample area is first viewed on the computer monitor. Such optical images (which can be stored for later viewing) are used to help guide movement of the motorized xyz stage so that the desired micro-region on the sample can be studied for point analysis. The laser is focused on the micro-region of interest by selecting the appropriate microscope objective lens, adjusting the working distance between sample and the objective lens as well as adjusting the laser power intensity. Figure 2.19 shows the optical pathway for the incident and scattered light; the latter passes through the holographic notch filter where much of the Rayleigh scattered light is filtered out while allowing transmission of the Raman contribution. This scattered light enters the spectrograph and is dispersed with a diffraction grating onto a charge-coupled detector (CCD) which converts photons to electrical signals that are processed by the computer to plot a Raman spectrum. Much of the work presented in this thesis utilizes the HeNe laser source (one reason being the CCD detector in the inVia Raman Microscope is optimized to the HeNe laser [87, 91]) although some comparisons are made in Chapter 4 with the Ar⁺ laser source, which in earlier research was used more often.

2.7 Magnetron Sputter Deposition

Sputter deposition is one particular method within the physical vapour deposition (PVD) techniques which involves sputtering a target source (typically using Ar⁺ from plasma) in order to deposit a thin film on a substrate in vacuum. More information on sputter
deposition can be found in standard texts [93-96]. Briefly, the plasma glow discharge is formed from electron-atom collisions in the presence of Ar when a high potential is applied between the electrodes. The sputtered species are primarily atoms but can also include atom clusters, molecular fragments, ions and secondary electrons. The secondary electrons emitted from the target surface enable the plasma glow discharge to be sustained in the region adjacent to the target. Magnetron sputter deposition refers to sputter deposition methods that use a magnetron gun. Figure 2.20 shows a cross-sectional schematic of a magnetron gun which consists of a magnet in electrical contact with the target that is used for the deposition. The magnetron gun utilizes magnetic and electric fields to confine the secondary electrons for collisions with Ar gas atoms near and around the target to maintain an effective glow discharge. This gives magnetron sputtering advantages for film deposition including high film deposition rates, large deposition areas, reduced substrate heating, and an ability to use various target source materials for synthesizing films of varying compositions. Generally magnetron sputter deposition gives good film adhesion as well as lower working chamber pressures when compared to the other PVD methods. All these advantages make magnetron sputter deposition the appropriate method with which to prepare thin films with different transition metal chalcogenide compositions in the work in Chapter 4.

Figure 2.21 shows a schematic of the Corona Vacuum Coaters Model V3T, a dual magnetron sputter deposition chamber developed by Professor R.R. Parsons (Department of Physics and Astronomy, the University of British Columbia); this system was used to prepare the various transition metal chalcogen thin films discussed in this thesis. The V3T sputter coater consists of a glove box (for sample introduction), a deposition chamber, sample substrate holders, two magnetron guns (targets) and power supplies operated by home-designed software. The targets for the magnetron guns were obtained either from a
Figure 2.20  Schematic cross-section of magnetron gun showing pathways of secondary electrons generated from the target.

Figure 2.21  Schematic of Corona Vacuum Coaters Model V3T dual magnetron sputter deposition chamber.
commercial supplier or were home-made by cold pressing (pressure 35 MPa) mixtures of appropriate commercial powders. Both elemental and compound targets were used (see Chapter 4 for details). All targets were cylindrical in shape (5 cm diameter, 0.6 cm thick) and were bonded to Cu back plates prior to introduction into the sputter coater. After installation of the magnetron guns, a glassy carbon (GC) substrate was introduced into the deposition chamber through the glove box, and then the sputter coater was turbomolecular pumped to a base pressure of $3.5 \times 10^{-6}$ Torr. The magnetron guns were water-cooled before, during and after applying power to the targets. A direct current (DC) potential is generally used for sputtering metal targets, while a radio-frequency (RF) potential is applied for sputtering non-conducting target materials. The RF potential is operated at frequency 13.56 MHz (allocated by the Federal Communications Commission for industrial-scientific-medical purposes) to prevent significant ion charge accumulation by oscillating the electron cloud through the sea of ions [93-96].

The targets were pre-sputtered for 10 min as the plasma discharge initiates at around $3.5 \times 10^{-3}$ Torr with a continuous throttled flow of argon gas (99.9%). Following pre-sputtering, the deposition began as the substrate was moved into the deposition zone with the target-to-substrate distance set at 10 cm. A negative bias was applied to the substrate (-180 V for the first minute, -75 V for the remaining deposition time) to help promote film adhesion. After the film deposition (e.g. 30 min for a 40 μm thick film), the vacuum pumps were turned off and isolated; the sputter coater was then vented with $N_2$ gas to atmospheric pressure to allow removal of the thin-film sample.
2.8 Electrochemical Measurements

2.8.1 Introduction

This section will briefly discuss some electrochemical background relevant to the work in this thesis; further information on electrochemistry can be found in standard references [97-99]. Electrochemical processes like the oxygen reduction reaction (ORR, Equation 1.3) involves charge transfer at an electrode/electrolyte interface. The rate of electron transfer from the electrode in ORR can be conveniently expressed as

\[ v = \frac{I}{nF} \]  

(2.27)

where \( v \) is the rate of charge transfer, \( I \) is the measured current, \( n \) is the number of moles of electrons transferred, \( F \) is Faraday’s constant and \( A \) is the electrode area exposed to electrolyte. Thus, the measured current (\( I \)) directly gauges ORR catalytic activity for the thin film and powder catalysts studied in this work. Strictly to compare different systems on an equal footing, the current density (\( i = I/A \)) is used (i.e. current per unit surface area).

Electron transfer in ORR involves surmounting an activation barrier that varies with the applied potential. An expression for the relationship between current density (\( i \)) and applied potential was derived by Butler and Volmer [97-99]

\[ i = i_0 \left( \frac{[R]_o}{[R]_{bulk}} \exp \left( \frac{(1 - \alpha)F\eta}{RT} \right) - \frac{[O]_o}{[O]_{bulk}} \exp \left( \frac{-\alpha F\eta}{RT} \right) \right). \]  

(2.28)

In equation 2.28, \( i_0 \) is the exchange current density at equilibrium (i.e. anodic current is equal to the cathodic current); \( \alpha \) is the transfer coefficient which lies in the range of 0 to 1 and depends on how the applied potential modifies the energy of the transition state; and \( \eta \) is the overpotential, characterized as the difference between the applied and the equilibrium potential (\( E - E_{eq} \)) set by the Nernst equation. The Butler-Volmer equation distinguishes the
concentrations of the reduced and oxidized species at the electrode surface ([R]₀ and [O]₀) from those in the bulk ([R]_{bulk} and [O]_{bulk}) electrolyte. An extension to Equation 2.28 is when the electrolyte is well stirred, so that concentrations of reactants at the electrode surface remain equal to their concentrations in the bulk (i.e. [R]₀ = [R]_{bulk} and [O]₀ = [O]_{bulk}) and thus Equation 2.28 simplifies to

\[ i = i_0 \left( \exp\left(\frac{(1-\alpha)F\eta}{RT}\right) - \exp\left(-\alpha F \eta \right) \right). \tag{2.29} \]

Equation 2.29 allows tests of how potential influences the current density in the absence of concentration effects. The overpotential is affected by kinetic processes and the potential in a practical situation that exactly balances the anodic and cathodic currents is defined as the open circuit potential (OCP) [97-99]. For ORR, the Nernst equation gives \( E_{eq} = 1.23 \text{ V} \) but the highest value obtainable in practice with polycrystalline Pt as a catalyst is 1.05 V [100]. For work in this thesis, where other catalysts are considered, a higher OCP is desirable since the ORR catalytic reaction can then occur over a larger potential range, although values less than 1.05 V are always obtained.

For applied negative potentials (where reduction dominates in the case of ORR), Equation 2.29 effectively becomes

\[ \ln i = \ln i_0 - \frac{\alpha F \eta}{RT}. \tag{2.30} \]

Equation 2.30 represents a Tafel equation and this is the basis of a Tafel plot; \( \alpha F/RT \) is known as the Tafel slope. Tafel plots can be displayed as a plot of potential vs. log current density \( i \) (or sometimes vs. log current \( I \) if the relevant surface area \( A \) is unknown). Such plots can be experimentally acquired using the three-electrode setup briefly described in the next section.
2.8.2 Experimental Set-up and Measurements

Figure 2.22 shows the type of three-electrode system that is used in this thesis to conduct all electrochemical measurements in acidic aqueous electrolyte. This system consists of a counter electrode (a Pt coil), a reference electrode (reversible hydrogen electrode, RHE) as well as the working electrode (which may consist of one of the thin films prepared as described in Section 2.7 or a powder sample described later in Chapter 5). In the three-electrode system, current is measured between the working and counter electrodes while the potentiostat ensures that no current or only a negligibly small current flows between the working and reference electrodes as the potential applied to the working electrode is varied. All electrode potentials mentioned subsequently are referenced to the RHE.

Cyclic voltammetry (CV) is one type of electrochemical measurement that involves measuring current as a function of potential on the working electrode that is linearly swept at a constant rate forward and then backward between two fixed potential values as time progresses. In Chapter 5, CV is used to monitor (a) electrochemical stability of supported CoSe$_2$ powders, and (b) modification to these powders supported on electrodes. Examples of the two different types of cycles used in CV measurements are illustrated in Figures 2.23 and 2.24. For the example in Figure 2.23, (a) shows the waveform for a CV cycle which is swept linearly from OCP (0.81 V), to 0.0 V and back to OCP (0.81 V) as a function of time; (b) shows how the measured current varies as a function of potential. For the other example in Figure 2.24, (a) shows the waveform of a CV cycle which is swept linearly from 0.5 V to 1.2 V to 0.0 V and finally back to 0.5 V as a function of time, while (b) shows the resulting measurements of current.
Figure 2.22  Rotating disc electrode (RDE) system for electrochemical measurements.
Figure 2.23  (a) Plot of potential versus time in a linear step sweep waveform progressing from OCP (Point A) to 0.0 V vs. RHE (Point B) back to OCP (Point C) for a cyclic voltammetry (CV) cycle in an electrochemical stability test for a supported CoSe₂ powder sample in an O₂-saturated H₂SO₄ solution; (b) measurement of a CV cycle progressing from Points A to B to C as in (a).
Figure 2.24  (a) Plot of potential versus time in a linear step sweep waveform progressing from 0.5 V (Point A) to 1.2 V (Point B) to 0.0 V (Point C) and back to 0.5 vs. RHE (Point A) for a cyclic voltammetry (CV) cycle in an electrochemical modification for a supported CoSe$_2$ powder surfaces in an O$_2$-saturated H$_2$SO$_4$ solution; (b) Measurement of a CV cycle progressing from points A to B to C and back to A as in (a).
In dynamic cathodic polarization measurements (Figure 2.25), current \( I \) is measured as a function of potential on the RDE (rotating at a constant rate, e.g. 2,000 rpm) as it is swept linearly from OCP to zero potential (vs. RHE) as in (a), while (b) shows a resulting measurement. Dynamic cathodic polarization measurements are useful in this work to highlight the OCP for different materials, and to demonstrate whether a material has the capability for ORR catalytic activity (i.e. the material must demonstrate higher currents in \( O_2 \)-saturated electrolyte than in \( N_2 \)-saturated electrolyte).

Measurements were made with the electrochemical cell holding 0.5 M \( H_2SO_4 \) (in Chapter 5) or 0.1 M \( HCIO_4 \) (in Chapter 4) maintained at 30°C; depending on the experiment, the electrolyte is either out-gassed, via bubbling, with \( N_2 \) to remove \( O_2 \) for background measurements or with \( O_2 \) gas for experiments on the ORR process. The working electrode, in the form of a glassy carbon (GC) disc with a sputtered deposited thin film model catalyst (Chapter 4) or a powder catalyst (Chapter 5) prepared on its surface, is centrally embedded within a larger cylindrical Teflon holder and is in electrical contact with the central metal cylinder of the rotating disc electrode (RDE). The RDE allows the working electrode to be rotated at a constant speed to enable a continuous supply of fresh electrolyte to be supplied to the electrode interface. The reversible hydrogen electrode (RHE), initially formed by bubbling \( H_2 \) over a large-area Pt electrode and operating under standard conditions (\( P(H_2) = 1 \) atm, reversible with respect to [\( H^+ \)]), has its potential conventionally set to zero. The RHE is placed in the reference electrode compartment of a Luggin capillary tube while the counter electrode is held in a separate compartment separated by a frit; both compartments are filled with the electrolyte.
Figure 2.25  (a) Plot of potential versus time in a linear step sweep waveform progressing from OCP of 0.81 V to 0.0 V vs. RHE for a dynamic cathodic polarization measurement for a supported CoSe$_2$ powder sample in an O$_2$-saturated H$_2$SO$_4$ solution; (b) Tafel plot of an actual dynamic cathodic polarization measurement based on (a).
Chapter 3

Surface Modification of Oxidized Aluminum for Improved Interfacial Bonding with Bis-1,2-(triethoxysilyl)ethane (BTSE)

3.1 Introduction

Organosilanes have potential applications to protect metals against corrosion and to promote adhesion with organic polymers as discussed in Chapter 1, with BTSE (Table 1.1) of particular interest. Modifying the surfaces of aluminum and its alloys is required to aid the adhesion with organosilanes. The sulphuric-chromic acid (FPL – Forest Products Laboratory) surface pre-treatment has been widely used in industry to prepare such surfaces and it is believed that such pre-treatments first etch away the looser native oxide layer then oxidize the aluminum surface to form a more compact oxide layer [7, 24]. Hydroxyl groups (Al-OH) on this new aluminum oxide layer, in principle, can react with silanol groups (Si-OH) from hydrolyzed silane to form Al-O-Si interfacial bonds via a condensation process [13, 16]. The FPL pre-treatment produces an oxide morphology that consists of a “whisker” like structure, roughly 400 Å in diameter and 400 Å high, which is believed to enhance the silane adhesion by an interlocking mechanism [24, 36].

A widely-cited recommendation to optimize conditions for the adhesion of an organosilane to a metal surface is to use the FPL pre-treatment at 65°C for 15-30 min as proven by macroscopic tests mentioned in Chapter 1 [7, 24]. However, understanding at the microscopic level is still limited for why the conditions identified by the macroscopic studies are favorable for FPL pre-treated samples. In principle, the optimal coating conditions may

\* The content in this chapter pertaining to the Forest Products Laboratory (FPL) pre-treatments, done in collaboration with J. Kim, has been published as M. Teo, J. Kim, P.C. Wong, K.C. Wong, K.A.R. Mitchell, Investigations of interfaces formed between bis-1,2-(triethoxysilyl)ethane (BTSE) and aluminum after different Forest Product Laboratory pre-treatment times, Appl. Surf. Sci. 221 (2004) 340. The material involving H₂ plasma and heat pre-treatments had been published as M. Teo, J. Kim, P.C. Wong, K.C. Wong, K.A.R. Mitchell, Pre-treatments applied to oxidized aluminum surfaces to modify the interfacial bonding with bis-1,2-(triethoxysilyl)ethane (BTSE) Part I. High-purity Al with native oxide, Appl. Surf. Sci. 252 (2005) 1293.
vary with the underlying microstructure and it should be useful to have a methodology (utilizing several surface analytical techniques) for choosing an appropriate pre-treatment according to the nature of the particular surface at hand. The work described in this Chapter is an exploration to meet this objective. Ultimately, such information should help refine the design of improved coating procedures including the tailoring of procedures for different surfaces. Such information will help to assess how other pre-treatments, specifically exposure to a remote microwave-generated H\textsubscript{2} plasma and separately to heating, can modify different oxidized surfaces of aluminum (generated by different FPL pre-treatment times) to enhance adhesion with BTSE coatings.

High-purity Al sample was chosen for this work in order to gain understanding of the factors that affect the BTSE coating process without complications of chemical heterogeneity at an alloy surface. BTSE also has the advantages of being non-functional with up to six silanol groups per molecule after hydrolysis, and this increases the probability of Al-O-Si bond formation when compared to organofunctional silanes such as γ-APS and γ-GPS. Additionally, use of a non-functional silane simplifies the coating process due to the absence of “upside down” bonding that may occur with organofunctional groups [12]. The final objective is to identify pre-treatment conditions that help maximize the adhesive bonding of BTSE for high purity Al surfaces. Key characterization techniques used in this work are secondary-ion mass spectrometry (SIMS) to assess the Al–O–Si bonding, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to analyze chemical and topographical changes to the surfaces, as well as an ultrasonic rinsing test used to compare strengths of BTSE adhesion on aluminum.
3.2 Experimental

3.2.1 FPL Pre-treated Samples

Aluminum samples (Puratronic, 99.997%) of 0.1 mm thickness were cut into 1 cm$^2$ square panels, and cleaned ultrasonically (in consecutive order) in acetone (30 min), methanol (5 min) and distilled water (5 min). The acid pre-treatment involved immersing the samples in an agitated FPL solution at 65°C for a range of designated times (0-90 min). The FPL solution was made by slowly mixing 17 vol% concentrated H$_2$SO$_4$ (Fisher Scientific) with 83 vol% distilled water, and this was followed by the addition of sodium dichromate (Aldrich Chemical Co., 99.5%, 60 g added for 1 L of solution). Following immersion in this acid solution, samples were rinsed in distilled water (5 min) before undergoing the various coating and test procedures.

The BTSE coating solution was prepared by mixing 1 vol% BTSE (Aldrich, 96% purity) with 6 vol% distilled water and 93 vol% methanol (Fischer Scientific, HPLC grade). This solution was stirred for 5 h at 25°C to ensure complete hydrolysis of the BTSE and to maintain its monomeric form. The prepared BTSE solution maintained a clear, colourless appearance at the pH of 4.0. Following the described pre-treatments, each Al sample that was coated was immersed into the 1% BTSE solution for 2 h immediately after the solution was prepared. With the exception of samples undergoing SIMS analysis, where coated samples were immediately rinsed in distilled water for 5 min to minimize BTSE polymerization, other coated samples were dried without a rinse and subjected to XPS analysis.

SIMS measurements were performed with a VG MM12-12S quadrupole mass spectrometer fitted with a duoplasmatron ion gun for producing an Ar$^+$ primary beam (5 keV, current density $1.3 \times 10^{13}$ ions cm$^{-2}$). XPS spectra were measured from a 4 x 7 mm$^2$
sample area using the Mg Kα source (1253.6 eV) on a Leybold MAX200 spectrometer. The source was operated at 10 kV, 20 mA with pressure in the analytical chamber at 1.5 x 10⁻⁹ Torr. Survey spectra were measured with the analyzer pass energy set at 192 eV with the binding energies referenced to C 1s associated with adventitious hydrocarbon contamination at 285.0 eV. Higher-resolution Al 2p and O 1s spectra were measured from various uncoated samples with a pass energy of 48 eV and the binding energies were referenced to the metallic Al 2p peak at 72.7 eV in order to protect against effects due to charging. SEM micrographs were measured at 10k magnification using a Hitachi Model S4100 field emission scanning electron microscope, with the primary electron beam set at 10 kV for a 10 mA beam current.

In order to examine how well a coated BTSE film adhered to the pre-treated aluminum surface, a combination of XPS and ultrasonic rinsing test in water was conducted. FPL pre-treated samples after being coated with BTSE first underwent XPS analysis. After the XPS analysis, the samples were then subjected to the rinsing test where samples were exposed for 30 min in distilled water in a sonication bath (Solid State/Ultrasonic T14B, L&R Manufacturing). Each sample was then dried in nitrogen prior to undergoing its second XPS measurement, which immediately identified the degree of de-adhesion as a result of the sonication test. Comparing XPS measurements before and after the sonication showed the degree of silane retention, and in practice two groups of adhesive ability were identified. Those with "low or poor" retention showed decreases in the Si 2p/Al 2p ratio of more than 70%, whereas those with "high or good" retention showed decreases of less than 10%.
3.2.2 H₂ Plasma and Heat Pre-treated Samples

In order to study the different starting oxidized Al surfaces prior to the H₂ plasma and heat pre-treatments (discussed later in Section 3.3.1), separate high-purity Al samples were immersed in the agitated FPL solution at 65°C for times of 0, 15 and 60 min. Following immersion in the FPL solution, Al samples were rinsed in distilled water (5 min) before undergoing further pre-treatment and coating processes (summarized in Figure 3.1 and Table 3.1).

The H₂ plasma pre-treatment involved placing a sample in a hydrogen stream (1.5 Torr) excited by an electrodeless discharge (microwave generator at 2.45 GHz, total power 60 W), with the sample 30 cm from the front end of the luminous zone. The operating pressure was monitored by a Pirani gauge positioned 50 cm downstream from the sample. After 60 min of hydrogen plasma exposure, the reaction chamber was taken back to atmospheric pressure under dry N₂, and the samples were promptly given the subsequent preparation and coating procedures (Figure 3.1). The heat pre-treatments were done on a heating plate in air (250°C, 60 min), with a chromel-alumel thermocouple attached to the sample surface for temperature measurement. These samples were cooled and held under vacuum (10⁻² Torr) at room temperature before carrying out the further treatment and analyses procedures. Experimental parameters for SIMS, XPS and the ultrasonic rinsing test were previously described in Section 3.2.1. SEM micrographs were measured at 5,000x magnification using a Thermo VG Scientific Microlab 350 scanning Auger microscope with a 10 kV, 10 nA primary beam and with the samples tilted at 45°.
Figure 3.1: Flowchart to give an overview of the different sample treatments used.
Table 3.1: Sample preparation procedures

<table>
<thead>
<tr>
<th>Designation</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>Al samples pre-treated in FPL solution* as in Section 3.2.1, followed by distilled water rinse (5 min), air dried.</td>
</tr>
<tr>
<td>A1</td>
<td>Samples A0 dipped in 1% BTSE solution (2 h), water rinsed (5 min), air dried (used for SIMS).</td>
</tr>
<tr>
<td>A2</td>
<td>Samples A0 dipped in 1% BTSE solution (2 h), air dried.</td>
</tr>
<tr>
<td>A3</td>
<td>Samples A2 ultrasonically rinsed (30 min), air dried.</td>
</tr>
<tr>
<td>B0</td>
<td>Samples A0 exposed to H\textsubscript{2} plasma (1 h).</td>
</tr>
<tr>
<td>B1</td>
<td>Samples B0 dipped in 1% BTSE solution (2 h), water rinsed (5 min), air dried (used for SIMS).</td>
</tr>
<tr>
<td>B2</td>
<td>Samples B0 dipped in 1% BTSE solution (2 h), air dried.</td>
</tr>
<tr>
<td>B3</td>
<td>Samples B2 ultrasonically rinsed (30 min), air dried.</td>
</tr>
<tr>
<td>C0</td>
<td>Samples A0 heated to 250°C (1 h).</td>
</tr>
<tr>
<td>C1</td>
<td>Samples C0 dipped in 1% BTSE solution (2 h), water rinsed (5 min), air dried (used for SIMS).</td>
</tr>
<tr>
<td>C2</td>
<td>Samples C0 dipped in 1% BTSE solution (2 h), air dried.</td>
</tr>
<tr>
<td>C3</td>
<td>Samples C2 ultrasonically rinsed (30 min), air dried.</td>
</tr>
</tbody>
</table>

* Each preparation is associated with a specific time of FPL pre-treatment (0, 15 or 60 min) as specified in the text.

3.3 Results and Discussion

3.3.1 Studies of FPL Pre-treated Samples

3.3.1.1 SIMS Analyses

Although a range of studies have been undertaken to probe the nature of Al surfaces after various pre-treatments (both alkaline and acidic) [22, 101-103], the emphasis in this work is more empirical in that it aims to assess with SIMS the conditions for a subsequent favorable bonding of BTSE. In this chapter, the test for direct Al–O–Si bonding is the presence of AlOSi\textsuperscript{+} at nominal mass 71 amu in the positive SIMS spectrum. However, this point needs elaboration since a recent report of work with the time-of-flight SIMS (TOF-SIMS) technique, by Abel et al., has legitimately pointed out that the nominal mass of 71 amu can arise from other sources, including ion fragments from hydrocarbon contamination,
residual chemicals from the sample preparation process, or from the polymerized organosilane coating itself [104]. Nevertheless, the same study also reported that after the outermost layers of the sample had been sputtered off the main contribution to the peak at 71 amu was indeed mainly attributable to the AlOSi\(^+\) ion. An additional TOF-SIMS study by Bexell et al. also confirmed that the 71 amu peak was predominantly AlOSi\(^+\) at the aluminum-silane interface [105]. Taking this information together, the philosophy taken in this work is that it is reasonable to assign the peak at 71 amu to AlOSi\(^+\), even in our lower-resolution measurements, provided the analysis applies to the actual aluminum-silane interface. Guidance to this was assessed by measuring the I\(_{71}/I_{70}\) ratio, from peak intensities at 71 amu and 70 amu. Thus after the samples had been coated with BTSE, they were rinsed immediately with distilled water to avoid formation of a thick BTSE polymer layer on the surface, and care was taken to gently sputter the outer layer with Ar\(^+\) to avoid ion fragments from hydrocarbon contamination. The AlOSi\(^+\) signal was monitored as a ratio of peak intensities at 71 and 70 amu, where the latter intensity is interpreted by an analogous argument to correspond to the species Al\(_2\)O\(^+\), which is in turn assumed to arise from the oxidized surface.

Investigations of the BTSE coated surface began by performing a gentle depth profile for each sample, measuring the [AlOSi]\(^+\)/[Al\(_2\)O]\(^+\) (I\(_{71}/I_{70}\)) ratio against sputtering time [104-106]. Figure 3.2 shows an example of such a depth profile for a rough oxide surface (e.g. whisker-like structure) that is covered by a thin BTSE coating. Adventitious contamination and polymerized silane are first gently sputtered off. Upon detection of the [AlOSi]\(^+\) and [Al\(_2\)O]\(^+\) secondary ions, the I\(_{71}/I_{70}\) ratio increases as more Al-O-Si chemisorption is probed, but with prolonged sputtering the ratio falls to zero. The maximum in the I\(_{71}/I_{70}\) ratio is taken to indicate the interface between the Al oxide and the BTSE coating [104-106].
Figure 3.2: SIMS depth profile from a high-purity Al sample coated with BTSE after FPL pre-treatment for 60 min.

Figure 3.3: Maximal values of $I_{71}/I_{70}$ from peaks in curves like that in Figure 3.2 plotted against FPL pre-treatment time for high-purity Al samples after coating with BTSE.
All depth profiles for other pre-treatment times show the same tendency as in Figure 3.2, namely that each plot of the $I_{71}/I_{70}$ ratio goes through a maximum, and the time associated with the maximum ratio is taken to indicate the depth where the number of OH bonding sites when immersed in the coating solution was maximized for the original aluminum oxide surface (thus leading to the maximum amount of Al-O-Si bonding for that interface). Figure 3.3 plots the maximum $I_{71}/I_{70}$ ratio values for the differently FPL pre-treated samples and independent measurements from different areas of particular samples suggest that the uncertainty in the ratio of about 0.03. A trend is observed where the $I_{71}/I_{70}$ ratio is low when the BTSE was applied for short FPL pre-treatment times (<5 min) and the ratio increases for times 5-10 min [106]. The ratio then peaks at pre-treatment times in the 10-25 min range and steadily decreases back to its initial value over longer times (25-90 min). The optimal chemisorption between the BTSE coating and high-purity Al (i.e. direct Al-O-Si bonding) therefore is indicated to occur for the FPL pre-treatment time range of 10-25 min; accordingly, the untreated native oxide of Al (0 min FPL pre-treatment time) has less active OH sites than the treated oxide surfaces. The FPL treatment time of 10-25 minutes that was used to obtain increased amounts of chemisorption among tested samples, according to this microscopic analysis, is in close correspondence with the normal FPL recipe that has been identified by performance in macroscopic tests [7, 24].

3.3.1.2 XPS and SEM Analyses

XPS was used in combination with the ultrasonic rinsing test to assess the strength of BTSE adsorption on FPL pre-treated surfaces. Figure 3.4 compares survey XPS spectra of BTSE-coated samples after different periods for the FPL pre-treatment before and after the ultrasonic rinsing test. Prominent peaks in the spectra in Figure 3.4 include Si 2s (binding
Figure 3.4: XPS survey spectra from high-purity Al samples coated with BTSE before and after the ultrasonic rinsing test. Prior to coating, samples were FPL pretreated for: (a) 1 min, (b) 10 min.
energy 154.0 eV), Si 2p (102.5 eV), Al 2s (119.0 eV) and Al 2p (74.6 eV). Figure 3.4(a), corresponding to a FPL pre-treatment for 1 min, is representative of samples that had been FPL pre-treated for short times (0-5 min). Although substantial silane adsorption occurs on such surfaces, it is clear that much of that layer is poorly adhered to the substrate since the Si peak intensity in XPS is reduced after the ultrasonic rinsing test (and correspondingly the Al structure becomes more prominent); thus such samples fail the ultrasonic rinsing test since much of the BTSE coating is lost. Figure 3.4(b), corresponding to a FPL pre-treatment for 10 min, is representative of samples that had been pre-treated for longer times (10-60 min). For such samples, a much higher proportion of the silane coating remains strongly bound after the ultrasonic rinsing test as Si signals in XPS do not by themselves show any significant change. These BTSE coatings adhered more strongly on such pre-treated surfaces and thus passed the ultrasonic rinsing test [106].

SEM and XPS analyses of uncoated samples can be used to offer insights into why samples FPL pre-treated for shorter times failed the ultrasonic rinsing test in comparison to those samples pre-treated for longer times. Figure 3.5 shows some relevant SEM micrographs of native oxide and FPL pre-treated surfaces. The unetched Al surface (Figure 3.5(a)) shows a scarred, flaky surface of native-born oxide. After 1 min FPL pre-treatment, the image in Figure 3.5(b) suggests that the scarring is still present; the surface now appears flatter, even if the changes are still fairly small. A 5 min pre-treatment gives a somewhat similar image to that in Figure 3.5(b), although small circular structures start to appear on the surface. These structures have previously been described as having a scallop form [22]. The micrograph in Figure 3.5(c), corresponding to a FPL treatment for 10 min, shows that the scallops are now well established, and these circular regions increase in size as the FPL treatment time increases from 10 to 60 min (the micrograph for 25 min is shown in Figure
Representative SEM micrographs of uncoated high-purity Al surfaces that were FPL pre-treated for: (a) 0 min, (b) 1 min, (c) 10 min, and (d) 25 min.

Figure 3.5: Representative SEM micrographs of uncoated high-purity Al surfaces that were FPL pre-treated for: (a) 0 min, (b) 1 min, (c) 10 min, and (d) 25 min.
3.5(d)). These scallop structures are believed to result from the new oxide on the Al metal due to the FPL treatment. The presence of the scallop-like structures on FPL pre-treated surfaces corresponds to samples that survive the ultrasonic rinsing tests; such topography may play a helping role in the adsorption process. Others have reported the scallop structure, on aluminum alloys after the FPL treatment, as being favorable for subsequent adhesion applications, as judged by peel tests and salt fog tests [24, 26, 36, 107]. A common view is that the surface morphology may influence mechanical interlocking within the adsorbed layer [6, 36, 108-111].

Figure 3.6 shows typical examples of Al 2p spectra from high-purity Al samples that have been FPL pre-treated for 0, 15 and 60 min; peaks at binding energies of 72.7 eV and 75.5 eV refer to the metallic Al and Al oxide components respectively. Some changes are apparent in Al 2p spectra measured for the FPL pre-treated (uncoated) samples, specifically in relation to the relative proportions of the oxide and metallic components. For the natural sample that had not been pre-treated, approximately 86% of the Al 2p signal corresponds to the oxide form (and 14% as metallic form), but as the pre-treatment process was applied the proportions changed, with the metallic form becoming proportionately larger. For example, after 1 min pre-treatment the relative amounts were 79% oxide, 21% metallic; at 5 min 66% oxide, 34% metallic; and by 25 min the proportions had leveled out at 56% oxide, 44% metallic. For times longer than 25 min, the proportions did not change. These results show etching of the oxide is dominant for the shorter pre-treatment times while the etching and oxidation processes reach equilibrium after around 25 min of the pre-treatment. The strong etching that occurred for the initial FPL pre-treatment can be seen to remove contamination as well as the less firmly anchored parts of the sample substrate. Thus, the combination of observations where flaky surfaces were seen for shorter times of FPL pre-treatment (SEM)
Figure 3.6: Al 2p spectra curve fitted for the Al oxide (Al$_{ox}$) and metallic Al (Al$_{met}$) components for the oxidized Al surfaces: (a) native oxide (i.e. no FPL pre-treatments), (b) after 15 min FPL pre-treatment, (c) after 60 min FPL pre-treatment.
and significant etching was also occurring for the same time range (XPS Al 2p) suggests that the samples that were FPL pre-treated for short times failed the ultrasonic rinsing test due to loosely-held BTSE, poor oxide adhesion or both.

3.3.2 H₂ Plasma and Heat Pre-treatments

3.3.2.1 Trends for BTSE Adsorption

Section 3.3.1 established a methodology using microscopic analytical methods to assess the quality of the overall adhesion of the BTSE coating on different FPL pre-treated Al surfaces, as well as the importance of both the amount of Al-O-Si interfacial bonding and the presence of a well-anchored oxide layer for good BTSE adsorption. This section progresses into using alternative pre-treatments, namely H₂ plasma and heating, to modify the different surfaces of oxidized aluminum (generated by different FPL pre-treatment times) in an effort to enhance the quality of adhesion with BTSE. A series of different samples have been treated in this work and their preparations are summarized in Table 3.1 and the flowchart in Figure 3.1. Briefly, three main groups of samples were used, referred to as set A (whose pre-treatment just involved the FPL pre-treatment applied for 0, 15 or 60 min), set B which received the FPL pre-treatments for the same different times each followed by the H₂ plasma pre-treatment, and set C which received the FPL treatments followed by heating. Within sample set A, the samples A0 (for FPL treatments of 0, 15 or 60 min) were used for SEM and XPS analyses prior to BTSE coating. The samples A1 and A2 were coated; the first being water-rinsed prior to measuring the \( \frac{I_{71}}{I_{70}} \) ratio with SIMS, while the second set were not rinsed and were characterized by XPS to determine the amount of BTSE that can be coated. Sample A3 was used to determine how much of the BTSE was retained after exposure to the ultrasonic rinse. The numerical part of the labeling for the sample sets B and
C followed analogously to that just given to set A (Figure 3.1). Table 3.2 summarizes the measurements made by SIMS and XPS for the BTSE-coated samples.

Table 3.2: Observations by SIMS and XPS for BTSE-coated samples after different pre-treatments

<table>
<thead>
<tr>
<th>Starting Surface</th>
<th>No FPL Pre-treatment (Native Al oxide)</th>
<th>15 min FPL</th>
<th>60 min FPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample set*</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>SIMS I_{71}/I_{70} ratio</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Retention of BTSE after sonication test</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

* Sets B and C for the H\textsubscript{2} plasma and heat pre-treated samples respectively (Table 3.1); those designated A just have the FPL pre-treatment (that for 0 min gives a reference sample with no pre-treatment prior to the BTSE adsorption).

The three samples designated as A0, which correspond to FPL pre-treatments of 0, 15 and 60 min, have been discussed previously in Section 3.3.1 in relation to the adsorption of BTSE [106], and the SIMS and XPS sonication results (Table 3.2) are just noted here briefly in order to provide a reference point for assessing the effects of the further pre-treatments. The coated sample with the native oxide (A1, 0 min FPL) has a SIMS ratio (I_{71}/I_{70}) of 0.6 which is indicative of a relatively low level of direct Al–O–Si interfacial bonding, and the sonication test shows poor adhesion. Parts of the native oxide layer are only weakly anchored to the Al substrate, as discussed more broadly by Kozma et al. [7], and accordingly that does not provide a basis for strong adhesive bonding by BTSE [106]. When the H\textsubscript{2} plasma is applied in the pre-treatment, the I_{71}/I_{70} ratio is increased to 0.9 for the BTSE-coated sample (B1, 0 min), an observation which indicates more direct Al–O–Si bonding. That suggests that the H\textsubscript{2} plasma pre-treatment affects the chemistry of the
(uncoated) oxide layers, but since the sonication test still shows poor adhesion, it is concluded that the oxide layers basically maintain their original physical character. By contrast, the heat pre-treatment does lead to better adhesion, as well as to an amount of direct Al–O–Si bonding comparable to that given by the H₂ plasma pre-treatment (in both cases the I₇₁/I₇₀ ratio is 0.9). This suggests that some physical transformation has occurred through the oxide layers. However, the heating used in the pre-treatment is not sufficient to improve the surface for BTSE bonding to the level achieved by the FPL pre-treatment applied for 15 min.

When the initial surfaces have received the FPL pre-treatments for 15 min or 60 min, the BTSE adsorption shows good adhesion (Table 3.2), and that is maintained when either of these initial surfaces is exposed to the H₂ plasma or is heated. For both starting surfaces, the H₂ plasma pre-treatment leads to a larger I₇₁/I₇₀ ratio (1.4 for 15 min FPL, and 1.1 for 60 min FPL). It is particularly interesting that the plasma pre-treatment applied to the surface that had previously received the optimal (15 min) FPL pre-treatment, after the application of BTSE, still appears to increase the amount of direct Al–O–Si interfacial bonding. However, that is not the case with the heat pre-treatment. When the latter is applied after the 15 min FPL process, the I₇₁/I₇₀ ratio reduces from 1.2 to 0.9, while following the 60 min FPL pre-treatment, heating does not change the I₇₁/I₇₀ ratio from the value of 0.6.

Certain trends can be noted at this point. First, application of the H₂ plasma pre-treatment is seen to result in an increase in the direct Al–O–Si bonding. As a working hypothesis, the plasma pre-treatment may be expected to increase the number of OH groups on the surface [37-40], and that should help favor the coupling reaction when dipped in the BTSE solution. However, that is not sufficient to ensure strong BTSE adhesion, which also depends on the nature of the Al oxide layer; in that regard, the native oxide is unfavorable. The optimal FPL pre-treatment (e.g. 15 min) certainly results in the formation of a compact
oxide that is well-adhered to the substrate, and alternatively heating the native oxide sample may help to anchor the oxide to some degree. By contrast, the H₂ plasma pre-treatment seems mainly to chemically modify the oxide layer insofar as it appears unable to change the physical character of the different oxides tested, from the perspective of the overall adhesive binding.

3.3.2.2 Nature of Pre-treated Surfaces

Observations were made with SEM for each of the samples designated A (i.e. which required FPL treatments of 0, 15 or 60 min) along with their respective H₂ plasma pre-treated (sample set B) and heat pre-treated (sample set C) counterparts; tests from different regions showed that each SEM micrograph in Figure 3.7 is representative of the whole surface after application of the specific pre-treatment. Figure 3.7(a) shows that the topography of the starting native oxide surface (i.e. A0, 0 min FPL) is scarred and flaky as reported previously [106], and no appreciable change is observed when it is H₂ plasma pre-treated or heated. The native oxide surfaces that received the 15 min FPL pre-treatment had the scallop structure (Figure 3.7(a)) identified previously with well-adhered oxide [24, 26, 36, 106, 107], and no significant change in the SEM image is seen after subjecting it to the H₂ plasma pre-treatment. By contrast, the heat treatment gives a bumpier, less even topography (Figure 3.7(b)). The initial surfaces that were FPL pre-treated for 60 min had the larger scallop structures identified previously, and there was no significant change according to SEM after the H₂ plasma pre-treatment (both as Figure 3.7(c)). Nevertheless, the heat treatment gives a topography with larger scallops (Figure 3.7(d)). Although SEM observations can only give part of a view of what is happening in these different situations, it is nevertheless clear that substantially different behaviors are indicated. For example, when
Figure 3.7: Representative SEM micrographs of oxidized Al surfaces: (a) after 15 min FPL pre-treatment; (b) sample in (a) after heating at 250°C; (c) after 60 min FPL pre-treatment; (d) sample in (c) after heating at 250°C.
the H₂ plasma pre-treatment is applied to each of the initial surfaces (FPL pre-treatments: 0, 15 or 60 min) no significant change occurs in the surface topographies, at the level seen in Figures 3.5 and 3.7. Also, while FPL and heating pre-treatments can lead to substantial rearranging of the surfaces, that is not the case with the H₂ plasma pre-treatment, which does not lead to changes visible by SEM.

The differently pre-treated surfaces were all coated with BTSE solution under the same conditions, and differences in their adsorption behavior should therefore relate back to the nature of the surfaces prior to the BTSE exposure. XPS was used to give an initial assessment of the pre-treated surfaces, and the Al 2p and O 1s spectra measured prior to the BTSE coating are shown in Figures 3.8 and 3.9 respectively. The interpretation for the Al 2p spectra is straightforward and involves identifying the varying proportions for the metallic and oxide components (at 72.7 eV and around 75.5 eV respectively); the relative proportions measured are quoted in Table 3.3. The interpretation for O 1s spectra can be more challenging [112-127], but systematic trends are observed in relation to fitting to two components which are referred to here as O1 (lower binding energy) and O2 (higher binding energy). There are indications in the literature that these components are 1.1 to 1.5 eV apart [121-127], and consistently with published experience the curve fitting used in this work has O1 and O2 constrained within the ranges 532.1±0.1 eV and 533.3±0.2 eV respectively [123-125]. O1 is believed to be due to oxide (i.e. O²⁻ species), and its full-width-at-half-maximum (FWHM) height was fixed at 2.0 eV [124, 125, 127]. It has been suggested that the other component, O2, includes OH, H₂O and O bonded within hydrocarbon contamination (referred to as C(O)) [117-122], and the curve fitting done in this work showed the need for broader components in that case. The results included in Table 3.3 show larger values for the FWHM of O2 (2.3-2.6 eV), compared with O1 (2.0 eV), and that is fully consistent with the
Figure 3.8: Al 2p spectra curve-fitted for the oxide (Al\textsubscript{ox}) and metallic (Al\textsubscript{met}) components for oxidized Al surfaces: (a) native oxide (i.e. no FPL pre-treatment); (b) after 15 min FPL pre-treatment; (c) after 60 min FPL pre-treatment; (d) sample in (a) after H\textsubscript{2} plasma pre-treatment; (e) sample in (b) after H\textsubscript{2} plasma pre-treatment; (f) sample in (c) after H\textsubscript{2} plasma pre-treatment; (g) sample in (a) after heat pre-treatment; (h) sample in (b) after heat pre-treatment; (i) sample in (c) after heat pre-treatment.
Figure 3.9: O 1s spectra curve fitted for the components O1 (O²⁻) and O2 (OH, H₂O, C(O)) for oxidized Al surfaces: (a) native oxide (i.e. no FPL pre-treatment); (b) after 15 min FPL pre-treatment; (c) after 60 min FPL pre-treatment; (d) sample in (a) after H₂ plasma pre-treatment; (e) sample in (b) after H₂ plasma pre-treatment; (f) sample in (c) after H₂ plasma pre-treatment; (g) sample in (a) after heat pre-treatment; (h) sample in (b) after heat pre-treatment; (i) sample in (c) after heat pre-treatment.
former structures having several overlapping components. Incidentally, there is no evidence for significant charging effects (e.g. the FWHM and binding energy for the Al 2p oxide component remain essentially fixed for the different samples).

Table 3.3: Observations by XPS for oxidized high-purity Al surfaces after different pre-treatments

<table>
<thead>
<tr>
<th>Sample set*</th>
<th>No FPL Pre-treatment</th>
<th>Starting Surface</th>
<th>15 min FPL</th>
<th>60 min FPL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A0</td>
<td>B0</td>
<td>C0</td>
<td>A0</td>
</tr>
<tr>
<td>Components in O1s Relative areas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>0.20</td>
<td>0.40</td>
<td>0.63</td>
<td>0.12</td>
</tr>
<tr>
<td>O2</td>
<td>0.80</td>
<td>0.60</td>
<td>0.37</td>
<td>0.88</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>O2</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Peak positions (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>532.2</td>
<td>532.2</td>
<td>532.2</td>
<td>532.0</td>
</tr>
<tr>
<td>O2</td>
<td>533.5</td>
<td>533.5</td>
<td>533.5</td>
<td>533.1</td>
</tr>
<tr>
<td>Components in Al 2p Relative area (Alox)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>0.88</td>
<td>0.87</td>
<td>0.59</td>
</tr>
</tbody>
</table>

*See Table 3.1; the surface designated B0 have been H2 plasma pre-treated while the surfaces C0 have been heated to 250°C.

The nature of the starting surfaces is well-established from other work: the native oxide has a scary, flaky structure that is poorly adhered on to the Al substrate and allows incorporation by water and other species [7]. The FPL process gives etching and oxidation, and the balance seems optimized by the pre-treatment applied for 15 min [7, 106]. This allows an etching away of the native oxide as well as subsequent oxidation to form a new compact oxide. The 60 min FPL pre-treated sample appears to have less surface OH for participation in BTSE bonding at a level comparable with when the native Al oxide is treated in BTSE solution but with a well-adhered oxide surface.
Certain broad trends in the overall nature of the pre-treated surfaces can be identified from the data in Table 3.3. Of the initial surfaces, the native oxide is thickest and has a porous structure with water incorporation [7]; that is consistent with the observation that a broader O2 component is needed for interpreting O 1s spectra from the surfaces derived from the native form (i.e. A0, B0 and C0). In addition, these surfaces show an O2 component at 533.5 eV binding energy, some 0.3-0.4 eV less than for surfaces derived from a FPL pre-treatment. It is widely believed that the FPL pre-treatment removes much of the native oxide and replace with a more compact oxide [7, 24, 26, 36, 106, 107]. The consistently smaller FWHM found for the O2 components after a FPL treatment could result from less water being incorporated into the newly formed oxide.

XPS detects an increase in the oxide component after both the H2 plasma and the heat pre-treatments. Since both these pre-treatments help remove adventitious contamination [41, 128], it is necessary to compare the relative sizes of the components within both Al 2p and O 1s spectra. The trend of increasing oxide thickness after both the H2 plasma and the heat pre-treatments is shown most directly in the Al 2p spectra for the FPL pre-treated surfaces. Also, these two pre-treatments both show increased O1 components, compared with O2, in the O 1s spectra, and that suggests the resulting surfaces assume a more Al2O3-like character (although decreases in O2 may include some unknown contributions from removal of contamination). Although the cold-cathode H2 plasma can help remove adventitious contamination, water desorption from the walls of the chamber at 10^-2 Torr also occurs resulting in some increase in the thickness of the Al oxide.

All evidence presented in this work appears to show that the H2 plasma pre-treatment cannot physically modify the foundations of the oxide but it can chemically modify it. For all three starting surfaces, this modification acts to increase the potential for chemical
bonding with BTSE according to SIMS observations. In contrast, the heat pre-treatment acts favorably for the BTSE adhesive bonding only with the native oxide. It appears that dehydration occurs, for example by driving \(H_2O\) molecules from the surface and from within the oxide layer. This apparently helps the oxide become more compact and more adhering, while enhancing the amount of surface OH groups for subsequent bonding once dipped into the BTSE coating solution.

3.4 Concluding Remarks

The various pre-treatment processes carried out prior to bonding with the organosilane BTSE to a high-purity Al surface was assessed by characterizing the nature of the coatings formed by using a combination of SIMS, XPS, SEM and ultrasonic rinsing tests. The different techniques give complementary information, but central to the approach are two key aspects to effective adhesive bonding: first, the amount of Al-O-Si bonding formed at the BTSE-aluminum oxide interface as measured by the \(I_{71}/I_{70}\) ratio obtained by SIMS; and second, the overall morphology of the oxide Al layer prior to silane coating. Different pre-treatments can modify the various oxidized Al surfaces and this consequently influences the amount of direct Al-O-Si bonding after such Al samples are coated with BTSE. Pre-treatments are needed not only for the formation of surface OH groups once Al samples are in the coating solution, but also for the formation of a well-anchored oxide layer prior to coating for effective adhesive bonding by BTSE. Such a well-anchored oxide layer can be formed by the FPL pre-treatment and the FPL process is used in this work primarily to provide different Al oxide surfaces prior to BTSE coating rather than for studying the FPL process itself. For industrial practice, such processes ultimately need to be replaced by other approaches that avoid the used of \(Cr^{6+}\).
Work in this chapter has demonstrated that a 15 min FPL pre-treatment applied to native oxide on a high-purity Al sample is effective for generating a compact, well-anchored oxide layer as well as for forming increased Al–O–Si bonding after BTSE coating compared with all other times for the FPL pre-treatment. This FPL pre-treatment time is consistent with the widely-cited recipe that the FPL pre-treatment should be carried out for 15 to 30 min. This program of study has additionally demonstrated the ability of H$_2$ plasma and heat pre-treatments to modify surfaces of native oxide and of different oxides (generated by different FPL pre-treatment times) on high-purity Al samples to enhance adhesion with BTSE coatings. Specifically, heat pre-treatments can help modify a native oxide surface on high-purity Al to aid a subsequent adhesive bonding to BTSE. H$_2$ plasma pre-treatments help improve BTSE chemisorption on oxidized Al surfaces that had been FPL pre-treated for 15 or 60 min.
Chapter 4

Raman Spectroscopy for Characterization of Transition Metal Chalcogen Thin Films

4.1 Introduction

Work in this Chapter is part of a broader project to study transition metal chalcogen thin films prepared by magnetron sputtering in relationship to potential applications for PEM fuel cells. Transition metal chalcogens have other established technological applications ranging from solar cells to tribological friction films [129-133]. Such diverse applications give interest to the fabrication and characterization of transition metal chalcogenide materials, in the form of both thin films for academic interest and powders for industrial applications. Raman spectroscopy has an important role for characterizing these materials [60, 61].

The theme of this Chapter is to show how Raman spectroscopy can help to characterize thin film model catalysts of varying composition prepared by magnetron sputter deposition; such characterizations will be used along with scanning Auger microscopy (SAM) to interpret new Raman peaks, as well as with X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to interpret some results from electrochemical measurements. This chapter has three parts with an objective for each. The first objective is to demonstrate the combination of micro-Raman spectroscopy and SAM as an analytical approach for characterizing a Co-Se thin film, including identifying elemental composition at local regions of the material. A second objective is to use Raman spectroscopy for identifying chemical composition between a well-characterized FeS₂-like thin film and a

natural FeS$_2$ mineral pyrite to assess differences between their XPS and electrochemical measurements. A third objective is to demonstrate how micro-Raman spectroscopy can be used with XRD to help identify the structures present in Co-S, Ni-S and Co-Ni-S thin films to help explain their relationships with ORR catalytic activity.

4.2 Experimental

4.2.1 General Preparation and Characterization of Thin Films

All thin film samples discussed here were deposited on a glassy carbon (GC) substrate (Tokai Carbon). For the Co-Se thin film, the GC substrate was machined into a 1 cm x 2 cm rectangular shape; all other thin films had GC substrates machined in a "top hat" shape with a working surface area of 1.23 cm$^2$ (as shown in Figure 4.1). The top surfaces of the GC substrates were initially polished using SiC paper (P4000 Microcut, Buehler) followed by successive polishings with 6 μm and 1 μm diamond suspension (Leco) sprayed onto a polishing microcloth (Buehler). GC substrates were ultrasonicated in deionized water for 2 min between polishing stages and for 2 min in acetone (HPLC grade, Fisher Scientific) after the final polish. All thin film samples were deposited onto the polished GC substrates using the magnetron sputter deposition chamber described in Section 2.7; further experimental details for specific samples will be discussed in the appropriate sections below.

Auger spectra and scanning electron micrographs were obtained using a Microlab 350 system (Thermo Electron Corp) equipped with a field emission source (10 keV, 3.5 nA) and hemispherical energy analyzer. For Auger depth profiles, an Ar ion beam (3 kV, 1 μA cm$^{-2}$) was used to sputter an 1 x 1 mm$^2$ area of the thin film sample. EDX spectra were measured with a Hitachi S3000N spectrometer (20 keV incident electron beam). A Leybold MAX200 spectrometer (base pressure 2 x 10$^{-9}$ Torr) with Mg Kα source (hν = 1253.6 eV)
Figure 4.1: Rotating disc electrode (RDE) designed to accommodate a top-hat shaped glassy-carbon (GC) substrate with a sputtered thin film to allow convenient transfer between different methods of characterization.
operated at 15 kV and 20 mA was used to measure XPS survey scans and high resolution spectra with pass energies of 192 eV and 48 eV respectively. Binding energies were referenced to the Au 4f\textsubscript{7/2} peak at 84.0 eV, but the C 1s peak at 285.0 eV from adventitious hydrocarbon contamination was used as an alternative reference for calibration when charging occurred. Finally, Raman spectra were acquired with the Renishaw inVia Raman Microscope; before each measurement, the instrument was calibrated with a standard Si sample (520 cm\textsuperscript{-1}). Specific details on experimental parameters of the micro-Raman and other characterization tools are discussed in their respective sections to follow.

4.2.2 Co-Se Thin Film

The sputtering of the Co-Se thin film was accomplished with DC power (80 W) applied to a Co target (99.95% purity, Kurt Lesker) and RF power (35 W) applied to a Se target (99.9% purity, Angstrom Sciences). High-purity thin-film standards for both elemental Se and Co were prepared in the same coating system using the individual targets at 35 and 50 W respectively. The Co-Se thin film primarily discussed here had a thickness of 0.4 μm, as measured with a Tencor Alfa Step profilometer, and a bulk composition 84 at.% Se, 16 at.% Co, as determined by energy-dispersive X-ray (EDX) spectroscopy.

A cobalt oxide standard was needed for the Raman measurements and that was prepared by oxidizing a Co thin film in a Pyrex glass tube by flushing with O\textsubscript{2} gas for 1 h at 150°C; the product was Co\textsubscript{3}O\textsubscript{4} as characterized by XPS.

Raman spectra were acquired separately using the 514.5 nm line of the argon ion (Ar\textsuperscript{+}) laser and the 632.8 nm line of the helium-neon (HeNe) laser. The microscope was equipped with a 50x objective (numerical aperture of 0.75). To avoid excessive heating during measurement of Raman spectra, the output power of both lasers was <0.5 mW on the
sample surface. Nevertheless, a sample is described in Section 4.3.2 where part of the surface was modified by operating the Ar\(^+\) laser at a higher power. For the Raman measurements, each spectrum was acquired using 10\% of the maximum laser power and co-adding 20 scans of 50 s exposure.

4.2.3 Fe-S Materials

A Fe-S thin film was deposited onto a polished GC substrate using a pyrite target (FeS\(_2\) purity 99.9\%, Super Conductor Materials, Inc.) connected to a RF power supply operated at 38 W. A separate natural pyrite sample (Zacatecas, Mexico) was cleaved in air, and the fresh surface exposed to air for 1 h prior to introduction into the UHV chamber for surface analysis. This was done to make it comparable to the sputtered thin films which were exposed to air before and after electrochemical analysis.

Glancing angle X-ray diffraction (XRD) measurements were performed using a Bruker D8 advanced diffractometer with Cu K\(\alpha\) source (\(\lambda = 1.5418\) Å), and intensities were recorded as the diffraction angle, 2\(\theta\), varied from 5 to 90° at 0.02° s\(^{-1}\). Raman spectra were acquired using the 632.8 nm line of the HeNe laser with a 20x objective (numerical aperture of 0.40); each spectrum was acquired using 10\% of the maximum laser power (<0.5 mW on the sample surface), and co-adding individual scans for a total exposure of 500 s.

The ORR catalytic activities of the sputtered Fe-S thin film and the Zacatecas FeS\(_2\) mineral pyrite (Mexico) of high purity were monitored with dynamic cathodic polarization measurements; such measurements were acquired in a O\(_2\)-saturated 0.1 M HClO\(_4\) electrolyte using an Eco-Chimie PG30 (Autolab) potentiostat in a standard three-electrode electrochemical setup (Section 2.8) where each sample, acting as the working electrode, was rotated at 2,000 rpm at a sweep rate of 10 mVs\(^{-1}\); all potential measurements were referenced
to the reversible hydrogen electrode (RHE). The rotating disc electrode (RDE) holder was designed (Figure 4.1) to accommodate the GC substrate (top-hat shape) with the sputtered thin film and to allow sample transfer between the electrochemical and surface analysis characterization systems. The OCP measured from the thin film electrode was compared to that from the natural pyrite, whose electrode was prepared by placing a small piece of Zacatecas pyrite into a glass tube filled with epoxy (Buehler). Electrical contact was made using Cu wire, and upon drying (24 h) the surface of the mineral electrode was polished (with a surface area of 0.30 cm$^2$) until a mirror shine was obtained using the same procedure as for the GC substrates. Solution cleanliness was regularly assessed by measuring the voltammogram for an analytical Pt RDE (diameter 3 mm, Ω Metrohm), and checking that it closely matched literature reports [134].

4.2.4 Co-S, Ni-S and Co-Ni-S Materials

Co-S, Ni-S and Co-Ni-S thin films were deposited on GC substrates using targets connected to a RF power supply which varied between 35 to 40 W during the sputtering process. The targets used for preparing the Co-S and Ni-S thin films were commercial CoS$_2$ and NiS$_2$ samples, in each case with a small amount of S cold pressed together. The targets used for preparing Co-Ni-S thin films were composite targets prepared by cold pressing equal weights of CoS$_2$ and NiS$_2$ (99.5%, Alfa Aesar) with S powder (99.98%, Sigma Aldrich) as a binder.

Electrochemical measurements of the sputtered thin films utilized the same set-up as mentioned in Section 4.2.3. Glancing angle XRD measurements were made with a high-resolution Philips X'Pert X-ray diffractometer equipped with a Cu Kα1 source; diffraction data were collected over a 2θ range of 0.4-90° with a scanning rate of 0.02° s$^{-1}$. Micro-
Raman spectra were acquired using the 632.8 nm line of the HeNe laser and a 50x objective (numerical aperture of 0.75). Each Raman spectrum was acquired using 10% of the maximum output laser power (<0.5 mW on the sample surface), at total exposure times ranging from 100 to 1000 s.

4.3 Results and Discussion for the Co-Se Thin Film

4.3.1 Auger Characterization of As-Prepared Film

Auger electron spectra of the as-prepared thin film surface (Figure 4.2(a)) showed the presence of structure associated with the C KLL, Co LMM and Se LMM transitions. After 120 s of Ar ion sputtering, the C KLL peak is no longer detected and only the Co and Se Auger lines are seen (Figure 4.2). This indicates that the C is just found on the topmost surface, and is primarily from air-borne contamination. The Auger depth profiling analysis (Figure 4.2(b)) is also consistent with the Co and Se being mixed uniformly to a good approximation with depth into the film, while maintaining the 84 at.% Se composition. No other elements were detected within the main part of the film, and this is consistent with the EDX measurements.

Higher-resolution Auger spectra provide clues to the environment in which the Co and Se atoms exist in this material. Figure 4.3(a) shows that the Se LMM structure from high-purity Se has its most intense peak at 1306.9 eV, while the Co-Se thin film has a corresponding peak at 1308.4 eV. The shift of 1.5 eV compared with high-purity Se does not appear to be an artifact since some other Se LMM peaks remain unchanged, but this shift is taken to indicate a Co-Se interaction throughout the film. Figure 4.3(b) shows Co LMM spectra for the thin film and for the Co standard; the former shows a peak at 754.5 eV which appears as another signature of Co-Se bonding.
Figure 4.2: Auger measurements for the Co–Se thin film: (a) (i) before Ar ion sputtering, (ii) after 120 s sputtering; (b) depth profile over 300 s sputtering.
Figure 4.3: Comparison of Auger spectra from Co-Se thin film with high-purity elemental standards: (a) Se LMM spectra; (b) Co LMM spectra.
4.3.2 Co-Se Thin Film After Exposure to Full Power Ar\(^+\) Laser

A serendipitous exposure of the Co-Se thin film to the Ar\(^+\) laser at full power (i.e. 5 mW generated on the surface for 50 s) damaged the sample, as shown by the structural blemish seen in both the SEM and optical images (Figure 4.4). Using Auger point analysis, five specific regions from the structural blemish and its surrounding regions were analyzed for elemental composition; these regions are labeled in the SEM micrograph (Figure 4.4(a)) as the center hole, the matrix, the trench, the ridge region I (close to the center hole) and ridge region II (further from the center hole). Auger analysis indicated three distinct regions of composition (Figure 4.5): the trench region consists of Se (Figure 4.5(a)), the matrix and ridge region II contains Co and Se (Figure 4.5(b)), while the center hole and the ridge region I are composed of Co, Se and O (Figure 4.5(c)). This matrix region corresponds to the original Co-Se thin-film surface, except there is less C contamination than for the spectrum shown in Figure 4.2(a), part (i). It is argued below that these differences in composition at and near the structural blemish can help interpret Raman spectra from the local regions.

4.3.3 Raman Spectra from Thin Film Samples

Using both the Ar\(^+\) and HeNe laser sources at low power (<0.5 mW on the sample surface), Raman spectra were obtained from each of the regions previously characterized by Auger electron spectroscopy (Figure 4.6). Figure 4.6(a) shows the transmission curve for each notch filter used; that for the Ar\(^+\) laser source cuts in around 165 cm\(^{-1}\), while that for the HeNe source cuts in around 130 cm\(^{-1}\). These values define the minimum wavenumber that can be measured with each excitation source.
Figure 4.4: Structural blemish on Co–Se thin film generated by the Ar$^+$ laser at high power: (a) SEM micrograph measured with Auger spectrometer identifying different regions studied; (b) optical image measured with Raman microscope.
Figure 4.5: Auger spectra from different regions of structural blemish on Co-Se thin film: (a) trench region containing Se; (b) matrix region containing Co and Se; (c) center hole region containing Co, Se and O.
Figure 4.6: Raman spectra from Ar\(^+\) and HeNe laser sources: (a) transmission curves for notch filters; (b) high-purity Se standard; (c) oxidized Co standard; (d) matrix region of Co–Se thin film showing Co and Se; (e) center hole region of Co-Se thin film showing presence of Co, Se and O.
Metallic Co has no Raman features [135], but Raman spectra for the high-purity Se thin film show a broad feature between 165 to 290 cm\(^{-1}\) for the Ar\(^+\) laser excitation, and between 130 to 290 cm\(^{-1}\) for the HeNe laser excitation (Figure 4.6(b)). The minimum wavenumber reported in each case is due to the characteristics of the notch filter used. Previous studies for Se have indicated that distinctive Raman peaks at 251-253 cm\(^{-1}\) can be attributed to rings (Se\(_8\)) and at 141, 233-234 cm\(^{-1}\) for chains (Se\(_n\)) [135-142] within the various crystal forms while the presence of polyselenides (Se\(_n^2\)) at 269 cm\(^{-1}\) is also possible [143]. The feature in Figure 4.6(b) resembles a sum of spectra associated with the different molecular arrangements, which suggests that the high-purity Se film prepared by magnetron sputtering encompasses a mixture of both the ring and chain structures.

Figure 4.6(c) shows Raman spectra measured for oxidized Co using both laser sources. The Ar\(^+\) laser spectrum contains weak peaks at 197 and 619 cm\(^{-1}\), medium-intensity peaks at 481 and 523 cm\(^{-1}\), and a strong peak at 693 cm\(^{-1}\). The corresponding spectrum measured with the HeNe laser retained the five characteristic peaks but at slightly modified wavenumbers (i.e. 198, 484, 523, 622 and 693 cm\(^{-1}\)), and with some differences in the relative peak intensities. These spectra are consistent with literature reports for using the Ar\(^+\) and HeNe excitations [144, 145] insofar as the relative intensities are similar and the peak positions agree to within 3 cm\(^{-1}\).

The Raman spectrum measured from the trench region of the modified Co-Se film is similar to that in Figure 4.6(b), thereby showing consistency with the Auger analysis that this region is composed of high-purity Se. Figure 4.6(d) shows Raman spectra from the matrix region, but they are also representative of measurements from the ridge region II. The spectrum measured with the Ar\(^+\) source has broad features in our measurable range between
165 to 280 \text{ cm}^{-1}$, while for the HeNe source the observed range is 130 to 280 \text{ cm}^{-1}. These features were previously attributed to structures formed by Se, but the distinctive peak at 181 \text{ cm}^{-1} from both laser sources is separate. Auger electron spectra show these regions contain Co and Se. When compared to the broad Raman spectrum from the trench region which contains only Se, the peak at 181 \text{ cm}^{-1} stands out. The difference between the matrix and trench regions is the presence of Co which strongly suggests that this new peak involves Co bonding to Se in a Se-rich environment. This conclusion is supported by evidence from Auger electron spectroscopy (Section 4.3.1) for the presence of direct Co-Se interactions.

The Raman spectra measured with the two laser sources from the center hole (Figure 4.6(e)) are similar to the corresponding measurements from the ridge region I; each spectrum has six peaks, but depending on the laser used there is a slight difference in wavenumber. Specifically, excitation with the Ar$^+$ laser produced peaks at 168, 189, 484 and 520 \text{ cm}^{-1}, a weak peak at 619 \text{ cm}^{-1} and a strong one at 691 \text{ cm}^{-1}; in addition there is broad structure between 165 and 280 \text{ cm}^{-1}, which is attributed to the Se environment. Use of the HeNe laser gave a Raman spectrum consisting of six distinct peaks at 175, 195, 480, 520, 619 and 688 \text{ cm}^{-1}, as well as a broad feature in the 130-280 \text{ cm}^{-1} range associated with Se. The five peaks located around 189, 484, 520, 619 and 691 \text{ cm}^{-1} using the Ar$^+$ laser excitation, along with peaks at 195, 480, 520, 619 and 688 \text{ cm}^{-1} from the HeNe laser, are attributed to cobalt oxide. The measured positions and relative intensities are close to measurements made for the standard formed by oxidized Co, as well as to those from published reports for this material [144, 145].

The remaining peak at 168-175 \text{ cm}^{-1} (depending on the excitation source) is interesting. It was previously attributed to Co-Se bonding by Campos et al. [135, 136], but the Auger analysis in the present investigation shows that the center hole region and the
ridge region I both contain significant amounts of O in addition to Co and Se. By contrast, the matrix region and ridge region II show only Co and Se are present, and both are accompanied by a Raman peak positioned at 181 cm\(^{-1}\). The oxidized Co spectra did not contain any Raman peaks below 189 cm\(^{-1}\), and therefore the peak at 168-175 cm\(^{-1}\) cannot be attributed to cobalt oxide. Similarly, the spectra from high-purity Se did not show any sharp distinctive peaks in this spectral region, and therefore the peak at 168-175 cm\(^{-1}\) is not solely due to Se. As no structure was found at 181 cm\(^{-1}\) from the O-containing areas on the thin film, it is concluded that the peak at 168-175 cm\(^{-1}\) results from O bonding in a CoSe complex. Incidentally, Campos et al. in their measurements used powder samples for which EDX analysis showed the presence of O [135, 136]; hence it appears most likely that the peaks they observed at 166-175 cm\(^{-1}\) resulted from an oxygenated Co-Se species, although no knowledge is available currently for the actual structure. From this discussion, the new conclusion from the present work is that the Raman structure at 181 cm\(^{-1}\) is indicative of Co-Se bonding in a Se-rich environment.

Figure 4.6 shows clearly that the spectra measured with the HeNe laser source in general have better resolution and better signal-to-noise characteristics to those measured with the Ar\(^+\) source. However, the latter measurements are included in this report since that source was used in previous Raman measurements made for the Co-Se system. It is assumed that the HeNe source is associated with more favorable scattering cross sections and better detection efficiency [91].
4.4 Results and Discussion for Fe-S Materials

4.4.1 Electrochemical Characterization

Figure 4.7 shows dynamic cathodic polarization electrochemical measurements for mineral pyrite FeS$_2$ and for the magnetron sputtered Fe-S thin film in both O$_2$-free and O$_2$-saturated 0.1 M HClO$_4$ electrolyte. This work was done in collaboration with Dr. L. Zhu. Larger currents are observed for both samples in the O$_2$-saturated electrolyte indicating that these samples have significant ORR catalytic activity. However, the OCP of the sputtered Fe-S thin film is 0.77 V and much higher than the OCP of 0.62 V measured for the Zacatecas natural pyrite. The latter is consistent with other measurements for mineral FeS$_2$ samples in the literature [146-149]. Additionally, Figure 4.8 shows that at each potential in O$_2$-saturated solution, the current density observed from the Fe-S thin film is larger than that from mineral FeS$_2$ pyrite by around one order of magnitude. These differences in electrochemical measurements for the two samples must relate to the different natures of the starting surfaces.

4.4.2 XRD Characterization

Figure 4.9 compares diffractograms measured from the sputtered Fe-S thin film and from the ground pyrite mineral (Zacatecas). The thin film pattern is dominated by broad peaks at 2$\theta$ = 25.8°, 42.8°, 52.3° and 78.5° from the glassy carbon substrate, while the narrow peaks at 2$\theta$ = 28.3°, 33.2°, 36.9°, 40.7° and 56.2° match those from natural pyrite as well as from expectation from the XRD database for FeS$_2$ [150]. The most intense signal from the thin film is at 2$\theta$ = 33.2°, associated with scattering from the (200) planes of crystalline FeS$_2$, whereas for natural pyrite that at 2$\theta$ = 56.2°, associated with scattering from the (311) plane, is strongest. This difference may result from a preferred orientation for the
Figure 4.7: Dynamic cathodic polarization measurements in O₂-free and O₂-saturated 0.1 M HClO₄ with sweep rate 10 mV per second: (a) Zacatecas FeS₂ pyrite, and (b) sputtered Fe-S thin film.
Figure 4.8: Dynamic cathodic polarization measurements of Zacatecas FeS$_2$ pyrite and sputtered Fe-S thin film in O$_2$-saturated HClO$_4$. 
Figure 4.9: X-ray diffractograms measured for sputtered Fe-S thin film and Zacatecas FeS$_2$ mineral pyrite.
thin film as previously observed in other samples prepared by magnetron sputtering [151].
There is no evidence in the diffraction pattern from the Fe-S thin film for the presence of
pyrrhotite (Fe$_{1-x}$S), marcasite (orthorhombic FeS$_2$) or oxide phases.

4.4.3 Raman Characterization

Figure 4.10 compares Raman spectra measured from the natural Zacatecas pyrite and
the sputtered thin film. The spectrum from natural pyrite, with peaks at 343, 379 and 430
cm$^{-1}$, agrees with previous findings [60, 61, 152-155]; the peak at 379 cm$^{-1}$ is the most
intense peak followed by the peaks at 343 and 430 cm$^{-1}$. Raman scattering from the Fe-S
thin film is consistent with that from the natural pyrite but with several notable differences.
When compared to the FeS$_2$ mineral pyrite, differences in the Raman spectrum for the Fe-S
thin film include: (1) the peak widths are larger; (2) the intensity of the peak at 340 cm$^{-1}$ is
greater than that of 378 cm$^{-1}$; (3) the Raman peak intensity at 425 cm$^{-1}$ has decreased; as well
as (4) the appearance of a new shoulder peak at ca. 460-470 cm$^{-1}$ is observed which is
believed to be indicative of the presence of polysulfides [152, 156-160]. The first three
differences can be attributed to the nano-crystalline nature of the film when prepared by
magnetron sputtering as previously reported [161, 162], and due to the preferred film
orientation (as suggested from XRD) as well as other defects possibly present in the thin
film sample which was not annealed. Polysulfides, with a Raman fingerprint transition at
460-470 cm$^{-1}$ [152, 156-160], are believed to be intrinsic to the thin film formed by
magnetron sputtering. For example, short-chain polysulfides have been reported to form
when S vapor is exposed to an electrical discharge [163]. Similar conditions exist during the
sputtering process since S vaporization occurs as Ar$^+$ bombardment heats the target to
Figure 4.10: Raman spectra measured (using HeNe laser) from (a) Zacatecas FeS$_2$ mineral pyrite and (b) sputtered Fe-S thin film.
around 60-80°C. Additionally, sputtered S dimers may interact on the substrate to form polysulfides during the film growth.

Raman fingerprint spectra of solid elemental sulfur (i.e. $S_n$ where $n$ can be 6 or more) consist of several vibrations within the wavenumber region of 400-500 cm$^{-1}$ and multiple intense Raman peaks below 300 cm$^{-1}$ [159]. For example, among the more well-established sulfur allotropes are $S_8$ with major Raman peaks at 151, 221 and 474 cm$^{-1}$, as well as $S_6$ with strong Raman vibrations at 202, 262, 448 and 471 cm$^{-1}$ [159, 164]. However, Figure 4.10 did not show evidence for significant peaks below 300 cm$^{-1}$, and hence a substantial presence of elemental S must be excluded from this sample. In this way, and for the possible recognition of polysulfides [152, 156-160], Raman spectroscopy has a useful role for probing the origin of the different ORR catalytic activities between $FeS_2$ mineral pyrite and the Fe-S thin film.

### 4.4.4 XPS Characterization

Figure 4.11 shows Fe 2p spectra measured from natural pyrite and the sputtered Fe-S thin film. The spectra are similar with the Fe 2p$_{3/2}$ peaks located at binding energies 707.2 eV and 707.4 eV respectively. That is consistent with Fe$^{2+}$ bonded to disulfide (i.e. S$_2^{2-}$) rather than to monosulfide (S$^2^-$) [152, 165-167]. Also, the spin-orbit splitting between Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ from both spectra is 12.8 eV, a value that is smaller than those measured for metallic Fe or Fe oxides [113].

Figure 4.12(a) shows that the shape of the normalized S 2p spectrum measured from the cleaved Zacatecas pyrite differs from that of the as-prepared thin film, and this again indicates that the surface of the sputtered film is not identical to that of the natural sample. The Zacatecas mineral FeS$_2$ pyrite is used as a reference for assessing the extra components required for the thin film sample, as outlined in the following. This work was done in
Figure 4.11: Fe 2p spectra of Zacatecas FeS$_2$ mineral pyrite and sputtered Fe-S thin film.
Figure 4.12: S 2p spectra: (a) comparison of normalized spectra for Zacatecas FeS$_2$ mineral pyrite and Fe-S thin film; (b) curve fitting for Zacatecas FeS$_2$ mineral pyrite with components for bulk S$_2^{2-}$ and energy loss peak as noted in the main text; (c) curve fitting for Fe-S thin film with two components in (b) plus those for surface S$_2^{2-}$ and polysulfides.
collaboration with Dr. D. Susac. Figure 4.12(b) shows the S 2p spectrum from natural pyrite fitted with a 2p<sub>3/2</sub> and 2p<sub>1/2</sub> doublet (binding energies 162.6 eV and 163.8 eV respectively), consistently with expectation for S<sup>2-</sup> dimers being fully coordinated by iron [152, 165-171], and a broad component at 165.6 eV associated with energy loss processes [167, 169]. Although the sample was exposed to air after cleavage, no sulfate species could be detected at around 168 eV. This spectral shape was then used to fit the S 2p spectrum from the sputtered film, a step that required two additional components at 161.8 eV and 163.6 eV (Figure 4.12(c)). Previous reports have interpreted the first component to arise from surface S<sup>2-</sup> dimers with less than the full Fe coordination [167, 169]; while that at 163.6 eV is consistent with the presence of short-chain polysulfides S<sub>n</sub><sup>2-</sup> (2 < n < 8) [169], an observation consistent with Raman observations of polysulfides on the sputtered Fe-S thin film sample. Elemental sulfur was not detected with Raman spectroscopy and thus was not fitted as a S 2p component. Overall, the Raman spectrum of the sputtered thin film is able to help interpret its S 2p spectrum with the presence of the FeS<sub>2</sub>-like structure, polysulfides and defects stemming from surface S<sup>2-</sup> with less than the full Fe coordination. The latter two features are believed to be enhanced in the thin film compared with the Zacatecas FeS<sub>2</sub> mineral pyrite, and thus are suggestive of factors that contribute to the different ORR activities measured electrochemically.

4.5 Results and Discussion for Co-S, Ni-S and Co-Ni-S Materials

4.5.1 Electrochemical Characterization

Figure 4.13 shows electrochemical data acquired for Co-S, Ni-S and Co-Ni-S thin films in collaboration with Dr. L. Zhu. The Co-S thin film has a significant catalytic activity for ORR with an OCP of 0.82 V in O<sub>2</sub>-saturated solution when compared to the OCP of 0.74
Figure 4.13: Dynamic cathodic polarization measurements of Co-S, Ni-S and Co-Ni-S thin films in O₂-free and O₂-saturated 0.1 M HClO₄ electrolyte.
V in O₂-free 0.1 M HClO₄ electrolyte. Similarly, the Ni-S thin film has OCPs of 0.80 V and 0.60 V in O₂-saturated and O₂-free electrolyte respectively demonstrating its capability for ORR catalysis. However, at the same potentials, the Ni-S thin film has lower current values when compared to its Co-S counterpart and thus has less ORR catalytic activity than the Co-S thin film. The ORR catalytic activities for Co-S and Ni-S thin films are significantly higher than those of CoS₂ and NiS₂ reported in the literature [172, 173], thereby suggesting differences at their surfaces.

The Co-Ni-S thin film has OCPs of 0.89 V and 0.76 V in O₂-saturated and O₂-free electrolytes. At a common constant potential (e.g. 0.5 V), the Co-Ni-S thin film in O₂-saturated solution gives a larger cathodic current (-2.0 x 10⁻³ Amperes) than the Co-S (-1.5 x 10⁻³ Amperes) or Ni-S (-0.2 x 10⁻³ Amperes) thin films. All these comparisons show an increased activity for ORR by the Co-Ni-S film, compared with the other two, and therefore further characterizations of these films are required. The OCP for the Co-Ni-S film appears as the largest found for a sulfide material, although it is still short of the values measured for thin films of Pt (0.95-1.02 V).

4.5.2 XRD Characterization

Figure 4.14 shows characteristic XRD peaks located at 2θ = 36.2° from the Co-S thin film and at 2θ = 35.2° from the Ni-S thin film pattern; both diffraction patterns are in good agreement with the (210) peaks of standard CoS₂ [174] and NiS₂ [175] samples from literature reports and internal standard measurements. The appearance of a unique peak for both Co-S and Ni-S thin films indicates that both thin films have a preferred orientation. The XRD pattern obtained from the Co-Ni-S thin film exhibits two small peaks located separately at 2θ = 34.8° and 36.0° and this coincides with the fingerprint region between 2θ
Figure 4.14: X-ray diffractograms of Co-S, Ni-S and Co-Ni-S thin film catalysts.
= 32.0° and 40.0° for (Co,Ni)S₂ solid solution alloys [176, 177]. The XRD peak shifts from 2θ = 35.2° to 34.8° (for Ni-S to Co-Ni-S) and from 2θ = 36.2° to 36.0° (for Co-S to Co-Ni-S) may be indicative of a solid solution. That cannot be definitive on this evidence, although the possibility is suggested by the Co-Ni-S phase diagram [178].

XRD patterns for all three thin films show broad peaks at 2θ = 25.8°, 42.8°, 52.3° and 78.5° from the glassy carbon substrate as well as a shoulder at 2θ = ca. 22.0°. After searching for all the Co, Ni and S related diffraction patterns available in the International Center for Diffraction Database, the peak at 2θ = ca. 22.0° coincides with the most intense peak of S₈ [179], Ga₁.₆₆CrS₄ [180] and BaVS₃ [181] structures as well as with the lesser intense peaks of S₁₁ [182], S₁₈ [183] and S₂₀ [184]. While the elements Ga, Cr, Ba and V are certainly not present in the thin films, it cannot be ruled out that one or more anionic S species may be present. Raman spectroscopy will be used to further characterize the surfaces of these films.

4.5.3 Raman Characterization

Commercial CoS₂ and NiS₂ samples (purity > 99.5%, Alfa Aesar) were used as internal standards for Raman measurements on the Co-S, Ni-S and Co-Ni-S thin films, and Figure 4.15 reports spectra measured from these samples. The Raman spectrum of the commercial CoS₂ powder shows characteristic peaks at 287 and 389 cm⁻¹ along with a shoulder at around 410 cm⁻¹; this is in close agreement with literature reports for CoS₂ single crystals [60, 61]. For comparison, the Raman spectrum for the Co-S thin film is broadened but resembles that of the internal standard CoS₂ insofar as it has peaks at 289 and 391 cm⁻¹ along with a shoulder centered at 410 cm⁻¹; however, there is also a shallow shoulder.
Figure 4.15: Raman spectra measured with HeNe laser from CoS\textsubscript{2} and NiS\textsubscript{2} powder standards as well as from Co-S, Ni-S and Co-Ni-S thin films.
stretching from 440 to 510 cm\(^{-1}\). The latter spectral feature is attributed to polysulfides as they are known to exhibit a characteristic Raman peak at ca. 460-470 cm\(^{-1}\) [152, 156-160], and this is similar to the situation for the Fe-S thin film analyzed in Section 4.4.3.

The Raman spectrum from commercial NiS\(_2\) has peaks at 273, 477 and 488 cm\(^{-1}\), which are in close agreement with literature values for a NiS\(_2\) single crystal [60, 61, 185]. The Raman spectrum from the Ni-S thin film is again broadened, but there is consistency with bulk NiS\(_2\) since there is an asymmetric peak at 475 cm\(^{-1}\), a narrow shoulder around 484 cm\(^{-1}\), and a bump centered at 277 cm\(^{-1}\). However, the asymmetric shoulder stretching below 475 cm\(^{-1}\) is new and overlaps the region where polysulfides are expected. Although this is not definitive, it at least keeps open the possibility that the Ni-S thin film (like those of Co-S and Fe-S types) also contains polysulfides.

Figure 4.15 shows that the Co-Ni-S thin film has a Raman spectrum different from either CoS\(_2\) or NiS\(_2\); the ternary film has a broad asymmetric peak centered at 290 cm\(^{-1}\) and another stretching between 360-472 cm\(^{-1}\) (with a peak maximum at 409 cm\(^{-1}\)). The Raman peak centered at 409 cm\(^{-1}\) from the Co-Ni-S thin film is different from and in between those of the Co-S (391 cm\(^{-1}\)) and Ni-S (477 cm\(^{-1}\)) thin films, although part of the broad peak centered at 409 cm\(^{-1}\) could overlap a small contribution from the former. However, the Raman peak attributed to NiS\(_2\) at 475-477 cm\(^{-1}\) is definitely absent in the Co-Ni-S thin film, and this spectrum has a notable similarity to the Raman spectrum of the alloy Co\(_{0.9}\)Ni\(_{0.1}\)S\(_2\) [60, 61]. The broad shoulder of the peak at 409 cm\(^{-1}\) also overlaps the region (460-470 cm\(^{-1}\)) where polysulfides are expected. Extra broadening seen in the Raman spectrum of Co-Ni-S, compared with the other thin films, could be a signature for the formation of a solid solution [90, 91, 186].
As mentioned in Section 4.4.3, Raman fingerprint spectra of the different allotropes of solid elemental S typically have intense Raman peaks within the wavenumber region of 400-500 cm$^{-1}$ and multiple intense Raman peaks below 300 cm$^{-1}$ [159]. Among the more established Raman spectra of solid S allotropes are S$_8$ with major Raman fingerprint peaks at 151, 221 and 474 cm$^{-1}$ as well as S$_6$ with strong Raman vibrations at 202, 262, 448 and 471 cm$^{-1}$ [159, 164]. However, Figure 4.15 does not show evidence of the Raman fingerprint features expected for the different solid elemental S allotropes. This is especially emphasized by the absence of multiple intense peaks below 300 cm$^{-1}$ [159], aside from the peaks at 289 cm$^{-1}$ for the Co-S thin film, at 277 cm$^{-1}$ for the Ni-S thin film, and at 290 cm$^{-1}$ for the Co-Ni-S thin film which were all attributed earlier to expected Raman features for the basic disulfides. Overall, the Raman analysis suggests that solid elemental S is not present significantly on any of the thin films studied in this section, as for the Fe-S thin film.

Evidence from both XRD and Raman suggests that the Co-Ni-S thin film is composed of a (Co,Ni)$_2$S$_2$ solid solution, with some polysulfides likely present. There is no evidence for elemental S, and therefore the improved ORR catalytic activity for these materials apparently relates to the possible presence of the polysulfides.

4.6 Concluding Remarks

Work in this Chapter has demonstrated how micro-Raman spectroscopy can be used to help characterize various transition metal chalcogen thin film model catalysts. The first part of this work involved developing a methodology of combining the imaging and point analysis capabilities of scanning Auger microscopy and micro-Raman spectroscopy to characterize a Co-Se thin film that had a visible structural blemish created by a high-powered Ar$^+$ laser. This approach allowed a reinterpretation of previous analyses in the
literature. It is established here that (1) the Raman peak at 181 cm\(^{-1}\) is associated with bonding between Co and Se in a Se-rich environment and (2) the vibrational structure between 168 and 175 cm\(^{-1}\) is associated with an oxygenated species involving the three elements Co, Se and O.

The second part of the work in this Chapter utilizes micro-Raman spectroscopy to distinguish different types of sulfur species on various transition metal sulfide thin films and to make an initial correlation with ORR catalytic activity. Specifically, micro-Raman spectroscopy, in conjunction with the other characterization techniques, helps confirm for all sputtered transition metal sulfide thin films (i.e. Fe-S, Co-S, Ni-S, Co-Ni-S) the presence of disulfide structures, and suggests that the excess sulfur occurs as polysulfides rather than the elemental form. The nature of these surfaces appears to depend on the use of magnetron sputtering in their preparation. So far there is no mechanistic information to relate these structures to the ORR activities. The improved ORR activity for the Co-Ni-S thin film, compared with those of Co-S and Ni-S types, suggests the need to investigate ternary and even quaternary thin films formed by sputtered transition metal chalcogenides.
Chapter 5
Preparation and Characterization of CoSe$_2$ Supported on High-Area Carbon

5.1 Introduction

Research undertaken in this chapter forms part of a broad program, funded by Ballard Power Systems, a world leading company in fuel cell development, and the United States Department of Energy, to develop new catalysts for proton exchange membrane fuel cell (PEMFC) applications. Before PEMFC technology can be implemented for commercial applications, such as to the mass automobile market, there are challenges to overcome, including use of costly Pt-based catalysts and the slow kinetics of the oxygen reduction reaction (ORR) on Pt. Hence, there is a need to develop alternative catalysts [48, 49], and this work is directed toward alternatives based on non-precious metals. The broad objective of this program is to investigate the performance for ORR of transition metal chalcogen combinations with an initial emphasis to study model catalysts in the form of thin films grown in controlled ways via sputter deposition. Performances of these materials are being assessed through a range of electrochemical, surface and materials characterization methods in order to identify relationships between catalytic performance and their underlying structure and composition. As promising combinations and compositions of transition metal chalcogens are identified from the thin film work, parallel studies are needed for the corresponding supported powder catalysts to allow use in actual fuel cells.

From this research program, Co-Se thin films of varying overall composition have demonstrated promise as ORR catalysts [58, 59], and CoSe in powder form was prepared on a high-area carbon support [58]. The work in this Chapter has the first objective of

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1 The work in this Chapter is currently being prepared for publication.
establishing a synthesis for high-purity CoSe₂ supported on carbon powders used for a PEMFC, while a second objective is to evaluate the ORR activity of such materials based on the open circuit potential (OCP), current density and electrochemical stability. A third objective is to compare the electrochemical performances of the supported CoSe₂ and CoSe powder catalysts. A final objective is to investigate whether the CoSe₂ surfaces can be electrochemically modified to increase the surface Se and the ORR activity, as suggested by previous studies on Co-Se thin films with chalcogen rich surfaces [58, 59]. Central to these electrochemical measurements was the development of a methodology to analyze the changes induced on the powder surface before and after the various electrochemical processes. These changes are assessed using surface and bulk characterization techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), micro-Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning Auger microscopy (SAM), scanning electron microscopy (SEM) and backscattered electron (BSE) imaging as outlined in Figure 5.1.

5.2 Experimental

5.2.1 Synthesis of Powder CoSe₂

Initial research presented here describes work directed at producing high-purity CoSe₂ supported on high-area carbon. No synthesis for this system had been reported. In previous work on this whole program, an approach was developed by Dr. S.A. Campbell (Ballard Power Systems) for preparing CoSe powder supported on high-area carbon [58]. That approach was extended here for CoSe₂, and the following gives the synthesis details established in this work.
As-prepared supported CoSe$_2$ powder

Surface & bulk analyses: XRD, TEM, Raman, XPS, SAM

Electrochemical stability test (ECST)

Acid immersion (Al)

Electrochemical ORR test (EC1)

Raman, XPS, SAM

Electrochemical surface modification (EC2)

Raman, XPS, SAM

Electrochemical ORR test (EC3)

Raman, XPS, SAM, BSE

Figure 5.1 Flowchart outlining the experimental methodology used to characterize CoSe$_2$ supported on carbon powders using surface, bulk and electrochemical techniques.
1 g of high-area carbon powder (XC72R powder from Cabot) was dispersed into 1 L of deionized water (NCCLS Type 1, ultra-pure, 18.2 MΩcm); 50 mL of isopropanol (Fisher Scientific) was introduced to aid wetting, followed by 10.2 g of CoSO$_4$·7H$_2$O (Sigma, 99% purity) and 8.2 g of SeO$_2$ (Aldrich, 99.9% purity). After 1 h of stirring, 500 mL of 0.2 M NaBH$_4$ (Sigma-Aldrich, 99% purity) was slowly added to the solution. The addition of NaBH$_4$ was followed by another 1 h of stirring. The precipitated powder was filtered, washed twice with deionized water, and then dried for 4 h at 600°C in a tube furnace (Model 79300, Thermolyne) with an Ar atmosphere.

X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were used to assess whether the powder prepared by the recipe in the previous paragraph really corresponds to crystalline CoSe$_2$ on high-area carbon. The XRD measurements were performed using a Bruker D8 advanced diffractometer with a Cu Kα radiation source (wavelength 1.5418 Å) and varying 2θ from 5° to 90° at a scan rate of 0.02° per second. Figure 5.2(a) shows a diffractogram of a product sample that was obtained after heating the precipitate at 600°C for 4 h as described above. The good fit to the diffractogram of a highly crystallized bulk structure of cubic CoSe$_2$ (Figure 5.2(b)) [187] confirms that a successful synthesis of CoSe$_2$ powder has been accomplished. Supported CoSe$_2$ on carbon powder does not show strong carbon peaks from the XRD diffraction pattern and this is because (1) the carbon powder is well covered with CoSe$_2$, and (2) some of the carbon peaks [188, 189] overlapped with the CoSe$_2$ peaks as shown in Figure 5.2(c). Overall, XRD showed that a CoSe$_2$ powder was formed with high crystallinity. Samples that were not heated long enough, or to a high enough temperature, do not show well-defined XRD patterns.
Figure 5.2  X-ray diffractograms: (a) measured for CoSe$_2$ supported on carbon powder; (b) peak positions and intensities for cubic CoSe$_2$ from Ref. [187]; and (c) part of (a) magnified to show an overlapping carbon peak [188, 189].
The HRTEM sample analysis was done by Professor F. Ernst (Department of Materials Science and Engineering, Case Western Reserve University) [190]. Synthesized powder was ultrasonically dispersed in ethanol, dried and placed on a Cu grid for study in a Tecnai F30 TEM. Figure 5.3 shows a TEM micrograph of the CoSe$_2$ powder sample. According to selective area elemental mapping (SAEM, i.e. local EDX examination), the darkest powder particles in Figure 5.3 have Se/Co ratios of 2.0, and thus were assigned to be CoSe$_2$, while lightly shaded particles were attributed to XC72R (high-area carbon powder support from Cabot). From TEM imaging, CoSe$_2$ particles appear to be agglomerated on XC72R and this confirms that CoSe$_2$ was obtained on high-area carbon powder. The material from the above synthesis is referred to subsequently as an as-prepared supported CoSe$_2$ powder.

5.2.2 Electrochemical Analysis

All electrochemical measurements used a three-electrode electrochemical setup as described in Section 2.8, and all potentials are quoted with respect to the reversible hydrogen electrode (RHE). The working electrode consists of CoSe$_2$ catalyst supported on high-area carbon powder adhering onto a glassy carbon (GC) substrate (similar to that of Figure 4.1). The preparation of the working electrode is performed as follows: 20 mg of the supported CoSe$_2$ powder was ultrasonically dispersed in glacial ethanoic acid (2 mL), and 5 $\mu$L of that dispersion (corresponding to 50 $\mu$g of powder) was pipetted onto the polished GC substrate (Section 4.2.1) and dried using hot air. For the purposes of this Chapter, depositing 50 $\mu$g of powder onto the working electrode is referred to as a single catalyst loading.

The working electrode is assembled onto the rotating disc electrode (RDE) similar in design with Figure 4.1. The RDE holder was specially designed in this lab to accommodate
Figure 5.3: Transmission electron microscopy (TEM) image of CoSe$_2$ powder on high-area carbon support (XC72R), courtesy of Ref. [190].
the top-hat-shaped GC substrate to allow convenient transfer between the electrochemical and surface characterization systems after rinsing the working electrode with double deionized water, drying in Ar, and then storing the sample under Ar prior to analysis. All electrochemical measurements were performed in 0.5 M H₂SO₄ electrolyte at 30°C using a PAR 263A potentiostat and the cleanliness of the electrolyte was assessed routinely by measuring the voltammogram for an analytic Pt RDE (diameter 3 mm, Ω Metrohm), verifying that it closely matched literature reports [134].

Figure 5.1 outlines the overall measurement procedure which includes four separate electrochemical measurements (denoted EC1, EC2, EC3 and ECST) as well as one control measurement (denoted Al).

EC1 examines the ORR catalytic activity of supported CoSe₂ powder by comparing its electrochemical dynamic cathodic polarization measurements (as described in Section 2.8.2) in N₂-saturated and O₂-saturated electrolyte at a sweep rate of 5 mVs⁻¹ with a RDE rotation speed of 2,000 rpm. This measurement was compared with separate electrochemical measurements of a blank GC substrate disc as well as Johnson Matthey HiSpec 4000 powder (i.e. 40 wt% of Pt on high-area carbon XC72R powder support) in O₂-saturated electrolyte under the same conditions.

The control sample AI consists of the as-prepared supported CoSe₂ powder immersed in O₂-saturated electrolyte for 30 min. This was to determine whether detectable compositional changes in powder surface after EC1 were due to powder dissolution in acidic media or to electrochemistry; AI was used to help interpret results obtained from XPS, SAM and micro-Raman spectroscopy.

EC2 involves electrochemically modifying the surface of the CoSe₂ powder in an effort to improve its ORR catalytic ability. This was accomplished via cyclic voltammetry
(CV) where the working electrode underwent four successive cycles in O₂-saturated electrolyte (with the potential varied linearly with time from 0.5 V to 1.2 V to 0.0 V to 0.5 V for each cycle as described in Section 2.8.2); the sweep rate and RDE rotation speed were 100 mVs⁻¹ and 2,000 rpm respectively.

EC3 examined the change in the ORR catalytic activity of the supported CoSe₂ powder after surface modification. This involved measuring the dynamic cathodic polarization curve for the working electrode after EC2 in O₂-saturated electrolyte at a sweep rate of 5 mVs⁻¹ with a RDE rotation speed of 2,000 rpm. This allowed comparisons for ORR catalytic activity for the supported CoSe₂ powder before (EC1) and after the electrochemical surface modification (EC3).

ECST is an electrochemical stability test of the as-prepared supported CoSe₂ powder to investigate its stability under ORR conditions as the potential of the working electrode is linearly swept while immersed in O₂-saturated acidic electrolyte. This was performed using ten successive CV cycles without rotating the RDE. Each cycle starts from the OCP value 0.81 V and is varied to 0.0 V back to OCP (Section 2.8.2) at a sweep rate of 10 mVs⁻¹.

5.2.3 Further Characterization of Powder CoSe₂

The flowchart in Figure 5.1 that summarizes the experimental methodology for characterizing the synthesized CoSe₂ powder also shows use for the XPS, SAM, Raman and BSE techniques. The procedures for these methods are defined as follows. Raman spectra of the powder sample were acquired using the 632.8 nm line of a helium-neon (HeNe) laser (Renishaw inVia Raman Microscope) and a 20x objective (Numerical Aperture = 0.40). Each Raman spectrum was acquired using 10% of the maximum output laser power (<0.5 mW on the sample surface) co-adding a relatively short exposure time of 100 s to limit any
possible heating. Before each measurement, the instrument was calibrated with a standard Si sample (520 cm$^{-1}$). XPS measurements were obtained with the Leybold MAX200 spectrometer operated with the Al Kα source (1486.6 eV) at 10 kV, 20 mA with the analytical chamber at 2 x 10$^{-9}$ mbar; the survey and higher-resolution narrow scans were acquired using pass energies of 192 eV and 48 eV respectively, and binding energies were referenced to the C 1s peak associated with adventitious contamination at 285.0 eV. The Microlab 350 system (Thermo Electron Corp) equipped with a field emission source (10 keV, 3.5 nA) and hemispherical energy analyzer was used to obtain Auger spectra as well as scanning electron micrographs (SEM) and backscattered electron (BSE) images from local regions of the powder surface. A unique analytical approach to combining BSE with Auger point analysis is demonstrated in Section 5.3.9.

5.3 Results and Discussion

5.3.1 Further Compositional Characterization for the As-Prepared CoSe$_2$ Powder

Figure 5.4 shows the Raman spectrum measured from the as-prepared CoSe$_2$ powder sample with a characteristic peak at 188 cm$^{-1}$, in full agreement with early measurements by Anastassakis for CoSe$_2$ [60, 61]. The peaks at 1331 and 1593 cm$^{-1}$ agree with Raman measurements for the high-area carbon powder support, where values at 1330 and 1591 cm$^{-1}$ are found both in internal standard measurements and in the literature [191]. Such measurements substantiate the view that the as-prepared sample corresponds to CoSe$_2$ supported on carbon powder.

Figure 5.5 shows that the Co 2p$_{3/2}$ photoelectron peak from the CoSe$_2$ powder surface is located at binding energy 779.0 eV, which is in good agreement with a literature report [192], and hence is higher than that of elemental Co which is expected at 777.9 eV [67].
Figure 5.4 Raman spectra measured for high-area XC72R carbon as well as for CoSe$_2$ powder on this carbon support: as-prepared, after acid immersion (AI), and after the electrochemical treatments EC1, EC2 and EC3.
Figure 5.5  Co 2p, Se 3d and Se 3p spectra for supported CoSe$_2$ powders in the as-prepared form, after acid immersion (AI) and after EC1.
Strong broad spectral features to the higher binding energy regions of the Co 2p$_{1/2}$ and 2p$_{3/2}$ photoelectron peaks, at 796.0 - 807.0 eV and 780.0 - 790.0 eV respectively, are almost as intense as the characteristic Co 2p photoelectron peaks, suggesting the presence of a second component. These features largely disappear after acid immersion (AI) and this coincides with a significant reduction in the O 1s photoelectron peak. It is concluded that the broad spectral features are due to Co-O interactions in the surface region while the characteristic Co 2p$_{3/2}$ photoelectron peak at 779.0 eV is attributed to CoSe$_2$.

Figure 5.5 also shows that the Se 3d photoelectron peak centered at 55.7 eV is maintained after acid immersion (AI), a value that agrees closely with expectation for the Se$_2^{2-}$ ion at binding energy 55.6 eV [193]. There is no evidence for Se$^{2-}$, where peaks would be expected at a lower binding energy position (e.g. 53.4 eV [67], 54.1 eV [62]), but the additional peak at 59.9 eV is attributed to Co 3p [67]. The Se 3p spectra also show that the 3p$_{3/2}$ peak at 161.7 eV [62, 67], and its shape, are retained after AI, so further supporting the concept that the chemical state of Se is maintained at the topmost surface. Overall, XPS spectra can only indicate the possibility of CoSe$_2$ and Co-O existing on the sample surface, with no evidence of Se$^{2-}$ from CoSe. The Se/Co ratio of the CoSe$_2$ powder surface after AI is 2:1, in close correspondence with the stoichiometry for CoSe$_2$.

Figure 5.6 shows a SEM micrograph of the supported CoSe$_2$ powder, and the constituent particles have spherical shape with diameters ranging from ca. 100 nm to 800 nm. Figure 5.7 displays Auger survey spectra from the supported CoSe$_2$ powder. The expected Co LMM and Se LMM Auger transitions are seen along with adventitious C KLL and O KLL transitions. Figure 5.8 highlights Co LMM Auger spectra from high-purity Co and the supported CoSe$_2$ powder; the latter shows an additional transition at 754.5 eV which is indicative of the presence of Co-Se bonding interactions. Although the possibility of Co-O
Figure 5.6  SEM micrograph of CoSe$_2$ powder supported on glassy carbon (GC) substrate.

Figure 5.7  Auger survey spectra of supported CoSe$_2$ powder in the as-prepared form, after acid immersion (AI), after EC1 and after EC2.
Figure 5.8  Co LMM Auger spectra from high-purity Co and supported CoSe$_2$ powder.
interaction causing the Auger transition at 754.5 eV in Figure 5.8 cannot be totally ruled out, Figure 5.7 shows that the peak associated with the O KLL Auger transition is not detected after AI and the transition at 754.5 eV in the Co LMM Auger spectrum seen in Figure 5.8 is still maintained.

Figure 5.9 draws attention to a peak shift of 2.2 eV for the strongest Se LMM Auger transition for the CoSe₂ powder sample (1309.1 eV) compared with 1306.9 eV for high-purity Se. This is believed to be a true peak shift since the positions of other Se LMM Auger transitions (e.g. at 1350.0 eV) did not shift. This peak shift also appears to likely result from the strong Co-Se bonding in the CoSe₂ structure; its magnitude here is larger than values found in earlier studies of CoSe thin films, where the shifts were in the 1.2 to 1.5 eV range [58, 194]. This indicates that the Se interactions in the CoSe₂ powder sample are different from those in CoSe, as is expected from their different crystal structures.

Combined together, observations from XRD, HRTEM, micro-Raman spectroscopy, XPS and Auger electron spectroscopy are fully consistent with the predominant chemical state for Se in the CoSe₂ powder bulk and surface being Se²⁻, with the as-prepared samples corresponding to CoSe₂ on the high-area carbon support.

5.3.2 Methodology to Estimate Surface Areas for Different Catalysts

The purpose of this section is to explain the methodology used to estimate the actual ORR catalytic activity of the CoSe₂ catalyst itself from a single loading of powder on the working electrode. There are two main factors required in this methodology:

(1) The current (\( I_{\text{Measured}} \), Amperes) from dynamic cathodic polarization measurements needs to be converted to current density (\( i \), Amperes-m⁻²), so that different catalysts (e.g. CoSe₂, CoSe and Pt) can be compared on a common basis.
Figure 5.9  Se LMM Auger spectra from high-purity Se and from supported CoSe$_2$ powder in both the as-prepared form and after EC1.
All electrochemical activities stemming from the supported background (i.e. from the GC substrate and from the XC72R support) need to be subtracted from the dynamic cathodic polarization measurements in order to get a true ORR catalytic activity for each catalyst considered.

The methodology to be described below is also applicable to single loadings of supported CoSe powder [58] and the HiSpec 4000 (40 wt% Pt on high-area XC72R carbon powder support) on separate working electrodes.

For factor (1), knowledge is needed for the surface area of each catalyst (i.e. powder excluding the high-area XC72R carbon support). For the HiSpec 4000 powder with 40 wt% of Pt on high-area carbon, the manufacturer’s value of ca. 24 m$^2$/g [195] is used. However, the total surface areas of CoSe$_2$ and CoSe, being home-made, are unknown and need to be calculated following steps in the flowchart illustrated in Figure 5.10. This analysis is based on the following assumptions:

- The entire catalyst surface is active for ORR, excluding contributions from the XC72R support.

- The catalyst particles can be modeled as spherical in shape with a uniform size distribution fixed by the average diameter.

The following summarizes steps 1 to 8 in Figure 5.10. For this work, all current densities are calculated for a 50 µg loading of powder on the working electrode:

1. **Determine the weight percent of catalyst on high-area carbon powder support (XC72R):** Assuming that all of the starting CoSO$_4$·7H$_2$O is used for synthesizing CoSe$_2$ or CoSe, the weight of catalyst ($W_{\text{Catalyst}}$) supported on 1 g of high-area carbon ($W_{\text{XC72R}}$) is determined as a weight percent ($W_{\text{Percent}}$).
**Step 1**

\[ W_{\text{Percent}} = \frac{W_{\text{Catalyst}}}{W_{\text{Catalyst}} + W_{\text{XC72R}}} \]

**Step 2**

\[ M_{\text{Catalyst}} = W_{\text{Percent}} \times M_{\text{Powder}} \]

**Step 3**

\[ V_{\text{Total}} = \frac{M_{\text{Catalyst}}}{D_{\text{Catalyst}}} \]

**Step 4**

Diameter of catalyst particle calculated using XRD Scherrer equation (Equation 5.1).

Then, the following is determined:

\[ SA_{\text{Particle}} = 4\pi r^2 \quad V_{\text{Particle}} = \frac{4}{3}\pi r^3 \]

**Step 5**

\[ N_{\text{Particles}} = \frac{V_{\text{Total}}}{V_{\text{Particle}}} \]

**Step 6**

\[ SA_{\text{Total}} = N_{\text{Particles}} \times SA_{\text{Particle}} \]

**Step 7**

\[ I_{\text{Catalyst}} = I_{\text{Measured}} - I_{\text{Background}} \]

**Step 8**

\[ i = \frac{I_{\text{Catalyst}}}{SA_{\text{Total}}} \]

---

**LEGEND**

- \( W_{\text{Percent}} \): Weight percent of catalyst in powder
- \( W_{\text{Catalyst}} \): Weight of catalyst
- \( W_{\text{XC72R}} \): Weight of XC72R
- \( M_{\text{Catalyst}} \): Mass of catalyst (per loading)
- \( M_{\text{Powder}} \): Mass of catalyst + XC72R (per loading)
- \( V_{\text{Total}} \): Total volume of catalyst (per loading)
- \( D_{\text{Catalyst}} \): Density of catalyst
- \( SA_{\text{Particle}} \): Surface area per catalyst particle
- \( V_{\text{Particle}} \): Volume per catalyst particle
- \( N_{\text{Particles}} \): Number of particles (per loading)
- \( SA_{\text{Total}} \): Total surface area
- \( I_{\text{Catalyst}} \): Current from catalyst (Amperes)
- \( I_{\text{Measured}} \): Current measured from working electrode (Amperes)
- \( I_{\text{Background}} \): Current from background (Amperes)
- \( i \): Current density (Amperes\( \cdot \)m\(^{-2} \))

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**Figure 5.10** Flowchart for calculating current densities from surface areas for CoSe\(_2\) and CoSe powder catalysts on the working electrode. The calculation is done for a 50 \( \mu \)g loading in each case.
2. Determine the mass of catalyst in each loading: The working electrode has 50 μg of powder (i.e. \( M_{\text{Powder}} = 50 \) μg), and the mass of catalyst is determined (\( M_{\text{Catalyst}} = W_{\text{Percent}} \times M_{\text{Powder}} \)) excluding the mass of the high-area carbon support.

3. Determine the total volume occupied by catalyst in each loading: From the known densities (\( D_{\text{Catalyst}} \)) of CoSe\(_2\) (7.22 g/mL) and CoSe (7.65 g/mL), as well as from the calculated masses of catalyst (\( M_{\text{Catalyst}} \) from step 2), the total volume (\( V_{\text{Total}} \)) of each catalyst can be calculated.

4. Determine the surface area and volume in each ‘spherical’ particle: The average catalyst particle size can be determined from the peak width in XRD using the Scherrer equation [196]

\[
D = 0.9\lambda/(\beta\cos\theta),
\]

(5.1)

where \( D \) is the average particle diameter; \( \lambda \) is the wavelength used (1.5418 Å for monochromatic Cu K\( \alpha \) radiation); \( \theta \) is the angle between the diffracted X-ray and the crystal plane under consideration for an intense, well-defined diffraction peak; and \( \beta \) is the full width at half maximum (FWHM) for the peak. From the average diameter, the surface area (\( S_{\text{Particle}} = 4\pi r^2 \)) and volume (\( V_{\text{Particle}} = \frac{4}{3}\pi r^3 \)) for each average spherical particle can be determined.

5. Determine the total number of catalyst particles: Dividing the total catalyst volume (\( V_{\text{Total}} \) from step 3) by the volume of each particle (\( V_{\text{Particle}} \) from step 4) gives the total number of spherical catalyst particles (\( N_{\text{Particles}} \)).

6. Determine the total surface area of catalyst used: Multiplying the surface area per particle (\( S_{\text{Particle}} \) from step 4) and the total number of spheres (\( N_{\text{Particles}} \) from step 5) gives the total surface areas (\( S_{\text{Total}} \)) of the catalyst used. The determined total
surface areas are quoted in Table 5.1 for the CoSe₂, CoSe and Pt catalyst samples tested.

7. **Determine the current from catalyst:** The background current ($I_{\text{Background}}$) measured from the GC substrate and high-area XC72R carbon powder support is subtracted from the current measured for each catalyst ($I_{\text{Measured}}$) so allowing the current from the catalyst itself ($I_{\text{Catalyst}}$) to be determined.

8. **Determine the current density from catalyst:** The current from the catalyst ($I_{\text{Catalyst}}$ from step 7) is divided by the total surface area of the catalyst ($SA_{\text{Total}}$ from step 6) for conversion to current density ($i$).

### Table 5.1: Calculated surface areas for different catalyst powder samples

<table>
<thead>
<tr>
<th></th>
<th>CoSe₂</th>
<th>CoSe</th>
<th>Pt from HiSpec 4000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²</td>
<td>$5.6 \times 10^{-4}$</td>
<td>$3.8 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*Catalyst area per 50 µg loading

5.3.3 **Electrochemical Evaluation of Supported CoSe₂ Powder (EC1)**

EC1 involves evaluating and comparing the ORR catalytic activity of CoSe₂ with those of CoSe, Pt from Johnson Matthey HiSpec 4000 powder and the GC substrate from electrochemical dynamic cathodic polarization measurements in 0.5 M H₂SO₄. Figure 5.11 shows supported CoSe₂ powder with an OCP of 0.81 V in O₂-saturated H₂SO₄ solution which is higher than the OCP of 0.74 V in N₂-saturated electrolyte. Figure 5.11 additionally shows that in the potential window of 0.1 V – 0.4 V, supported CoSe₂ powder can conduct about 40 times more current in O₂-saturated solution than in N₂-saturated solution. This demonstrates an ability for supported CoSe₂ powder to catalyze the reduction of O₂.
Figure 5.11 Dynamic cathodic polarization measurements for supported CoSe$_2$ powder in O$_2$-saturated 0.5 M H$_2$SO$_4$ and compared against the measurement in N$_2$-saturated solution.
From the current densities \((i)\) calculated using the method illustrated in Figure 5.10, Figure 5.12 reports Tafel plots showing that for a given common potential, CoSe\(_2\) has a higher current density than the blank GC substrate (which has a fixed surface area of 1.23 cm\(^2\)), as well as a higher OCP value (0.81 V) than that of GC (0.70 V), although the former is still less than that for Pt from the Johnson Matthey HiSpec 4000 powder sample (0.97 V). Interestingly though, the current density of CoSe\(_2\) is within one order of magnitude than that of Pt. Figure 5.13 shows the comparison between CoSe (with an OCP of 0.72 V) and CoSe\(_2\); on the grounds of both higher OCP and current density, it is clear that CoSe\(_2\) has a better ORR catalytic activity than CoSe.

### 5.3.4 Characterization of Supported CoSe\(_2\) Powder after EC1

The CoSe\(_2\) powder after EC1 was characterized with micro-Raman spectroscopy, XPS and SAM to determine if the CoSe\(_2\) structure is preserved. Figure 5.4 shows a Raman spectrum measured for the supported CoSe\(_2\) powder after EC1, and it is clear that the peak at 188 cm\(^{-1}\) characteristic of CoSe\(_2\) [60, 61] is retained. Figure 5.5 displays the Co 2p\(_{3/2}\) photoelectron peak being maintained at 779.0 eV and is very similar to that of the supported CoSe\(_2\) powder surface after acid immersion (AI). This similarity in spectra implies that exposure to acidic electrolyte during electrochemistry dissolves only oxide on the surface. Evidence for the dissolution of oxide is also indicated by a significant decrease in the O 1s photoelectron peak, as well as by the absence of the O KLL transition in the Auger survey spectrum after EC1 (Figure 5.7). Figure 5.5 shows that the Se 3d and 3p photoelectron peaks maintain their respective peak shapes and positions after EC1. The Se/Co ratio is maintained at 2.0 according to XPS. The Co LMM Auger spectrum remains similar to that in Figure 5.8, while Figure 5.9 shows that the strongest Se LMM Auger transition at 1309.1 eV and its
Figure 5.12  Tafel plots measured in O₂-saturated 0.5 M H₂SO₄ for blank GC substrate disc, CoSe₂ powder (EC1) and Pt (Johnson Matthey HiSpec 4000).

Figure 5.13  Tafel plots measured in O₂-saturated 0.5 M H₂SO₄ for CoSe₂ (EC1) and CoSe powders.
peak shape are retained after EC1. Overall, these characterizations demonstrate that the CoSe$_2$ chemical structure is maintained on the powder surface during EC1, thereby indicating its relative stability.

### 5.3.5 Stability Test for Supported CoSe$_2$ Powder (ECST)

ECST is an independent electrochemical stability test which examines the stability of the as-prepared supported CoSe$_2$ powder under ORR conditions as the potential of the working electrode is linearly swept while immersed in O$_2$-saturated electrolyte. Figure 5.14 shows cyclic voltammograms for the first, second and tenth cycles for the supported CoSe$_2$ powder as part of this stability test (ECST). The first cycle shows an OCP of 0.81 V; this value drops to 0.79 V for the second cycle, but is maintained through to the tenth cycle. Additionally, the electrochemical plot shape did not substantially change between the second and tenth cycle. A decrease in the current between the first and second cycle was attributed to some poorly adhered powder detaching from the working electrode. Furthermore, two minima were observed at ca. 0.55 V and ca. 0.77 V in the first cycle of the stability test. The reduction peak at ca. 0.77 V only appears in the first cycle and is likely attributed to Co oxide [197]; the absence of this peak beyond the first cycle suggests that Co oxide is not present after the first cycle and hence coincides with earlier observations that any Co-O interactions originally on the as-prepared CoSe$_2$ powder surface is removed in the acidic electrolyte independent of electrochemistry. The other minima peak at ca. 0.55 V is observed in all ten cycles and this is assigned to the quinone-hydroquinone redox couple [198] that exists on surfaces of high-area XC72R carbon powder [100]. Overall, based on maintaining its OCP at 0.80±0.01 V under tested conditions, the CoSe$_2$ powder demonstrated its electrochemical stability.
Figure 5.14 Cyclic voltammetry (CV) plots measured for 1st, 2nd and 10th cycles for supported CoSe$_2$ powder in O$_2$-saturated 0.5 M H$_2$SO$_4$ undergoing electrochemical stability test (ECST); stationary electrode, scanning rate 10 mVs$^{-1}$. 
5.3.6 Electrochemical Modification of CoSe\textsubscript{2} Powder (EC2)

In a previous study within this broad program, a Co-Se thin film, which underwent ORR catalysis, was studied by high-resolution TEM and XRD; the surface structure was shown to be consistent with non-stoichiometric CoSe nanoparticles embedded into a Se matrix [59]. This section describes an effort to modify surfaces of supported CoSe\textsubscript{2} by cyclic voltammetry to see whether the nature of the surface can be changed in order to enhance the ORR catalytic activity beyond that observed at the EC1 stage. This process, denoted EC2 (Section 5.2.2), involved a relatively fast cycling (sweep rate of 100 mV s\textsuperscript{-1}) on the working electrode between the potentials of 0.0 V and 1.2 V (with each cycle starting from 0.5 V up to 1.2 V down to 0.0 V and back to 0.5 V). The aim is to increase elemental Se content on the powder sample to make it more like the situation for the thin film sample mentioned above [59].

Figure 5.15 shows the resulting CVs from the first and fourth cycles from EC2. The curves have similar shapes. Between 0.0 V and 0.81 V, the CV curves overlap implying that the powders are stable in that potential range as expected from observations from EC1 and ECST. Thus as the potential is increased from 0.5 V to 0.81 V in the first cycle, the CoSe\textsubscript{2} structure is expected to be maintained. However, as the potential is increased above 0.81 V to 1.2 V, both CV curves begin to show a rapid increase of current. This is consistent with oxidation of the Se\textsubscript{2}\textsuperscript{2-} component, especially with the formation of Se\textsuperscript{4+} (in the potential range of 0.74 V to 1.15 V) and of Se\textsuperscript{6+} (at 1.15 V and above) [199, 200]. These species in solution are likely to be in the form of H\textsubscript{2}SeO\textsubscript{3} and H\textsubscript{2}SeO\textsubscript{4} respectively in accordance with the Pourbaix diagram. When cycling back from 1.2 V down to 0.5 V, a rapid decrease in
Figure 5.15  Cyclic voltammetry (CV) plots measured for the 1st and 4th cycles for supported CoSe$_2$ powder in the electrochemical modification (EC2).
current is observed and this suggests that the oxidized Se species undergo reduction via the following reactions

\[
\begin{align*}
H_2SeO_3 + 4H^+ + 4e^- &= Se^0 + 3H_2O, \quad (5.2) \\
H_2SeO_4 + 6H^+ + 6e^- &= Se^0 + 4H_2O. \quad (5.3)
\end{align*}
\]

According to the Pourbaix diagram, Se\(^0\) is the most stable Se species in the potential range of 0.0-0.74 V [199, 200].

This entire cycling process is continued until the end of the fourth cycle, though any Se\(^0\) existing on the sample surface from an earlier stage of EC2 can be subsequently oxidized and reduced back to Se\(^0\) in a later CV cycle. The origin of the slight decrease in the oxidation current between the first and fourth cycles is not yet clear. Throughout EC2, Co remains as Co\(^{2+}\) but with some dissolution as the Se\(^{2-}\) oxidizes.

### 5.3.7 Characterization of Modified CoSe\(_2\) Powder after EC2

The powder after EC2 is characterized by micro-Raman spectroscopy, XPS and SAM to observe if the surface of CoSe\(_2\) has been modified from the EC2 process. Figure 5.4 is the Raman spectrum of the modified powder with the characteristic peak at 188 cm\(^{-1}\) attributed to CoSe\(_2\) along with another peak at 231 cm\(^{-1}\) which is in close agreement to that of trigonal Se typically found at 233-234 cm\(^{-1}\) [137-142]; thus, EC2 appears to have formed Se\(^0\) on CoSe\(_2\). The peak position of Co 2p, Se 3d and Se 3p from XPS measurements are maintained (i.e. similar to that of Figure 5.5 after EC1) with no evidence of Co oxide; however, the Se/Co ratio of the supported CoSe\(_2\) powder surface on the working electrode increased to 2.3 after EC2. Figure 5.7 shows Auger transitions due to Co LMM and Se LMM are still detected from the modified CoSe\(_2\) powder while their respective high resolution Auger spectra (similar to Figures 5.8 and 5.9 respectively) resembles that of EC1.
The above observations suggest that although the CoSe$_2$ structure is preserved, some changes of the sample surface do occur due to the formation of Se$^0$ (as expected from electrochemistry in EC2) and this resulted in a higher Se/Co ratio. Overall, the EC2 process appears to have modified the CoSe$_2$ powder by forming some Se$^0$ on its surface while retaining much of its original CoSe$_2$ structure.

5.3.8 Electrochemical Evaluation of Modified CoSe$_2$ Powder (EC3)

EC3 involves evaluating the ORR catalytic activity of the CoSe$_2$ powder modified by the EC2 process. Figure 5.16 compares Tafel plots for the CoSe$_2$ sample at the EC1 stage (i.e. before the modification in EC2) and for the sample at EC3 (i.e. after the EC2 modification). Both samples have almost the same OCP (0.80±0.01 V), but the current densities at a given potential can vary. In the potential range of OCP to 0.60 V, Figure 5.16 shows that EC3 always has a lower current density than EC1 at a particular potential. However, in the potential range of 0.0 V to 0.60 V, this situation is reversed with the modified surface (EC3) having higher current densities. This comparison shows that the EC2 modification process has an effect on the electrochemistry of the sample, but further characterizations are needed to improve understanding. However, it is noted that the decrease of the current densities in EC3 as the potential drops from 0.60 V to 0.0 V must depend in part on the two samples converging to a common diffusion controlled current density [97-99].

5.3.9 Characterization of Modified CoSe$_2$ Powder after EC3

The CoSe$_2$ powder after EC3 was characterized with micro-Raman spectroscopy, XPS, SAM and BSE imaging to determine its chemical composition and structure. The
Figure 5.16  Tafel plots for supported CoSe$_2$ in O$_2$-saturated 0.5 M H$_2$SO$_4$ before (EC1) and after electrochemical surface modification (EC3).
Se/Co ratio from XPS for the modified CoSe$_2$ powder after both EC2 and EC3 equal 2.3, showing an increase in Se content compared with the stoichiometric compound. The Raman spectrum in Figure 5.4 also indicates similar compositions after EC2 and EC3, particularly with regard to the elemental Se peak at 231 cm$^{-1}$. Further characterizations for the powder CoSe$_2$ samples after EC3 involved the combination of BSE imaging and Auger point analysis.

Although most of the CoSe$_2$ electrode surface looks like that in Figure 5.6, the analysis here focuses on a selected region shown in Figure 5.17(a). This illustrates a SEM micrograph of an isolated region of supported CoSe$_2$ powder on the working electrode, and shows the spherical nature of the individual powder particles along with some agglomeration. Upon utilization of BSE imaging from the same region with the detector set in the COMPO mode, Figure 5.17(b) shows that brighter regions of the image mainly overlap with areas associated with the supported CoSe$_2$ powder particles while the darker regions represent bare areas of the exposed GC substrate. Figure 5.18 confirms that the brightest areas of the BSE image seen in Figure 5.17(b) has Co LMM, Se LMM and C KLL Auger transitions coming directly from the supported CoSe$_2$ powder particles.

In addition, Figure 5.17(b) shows semi-bright regions surrounding the supported CoSe$_2$ powder particles, and such regions are designated as ‘off-particle regions’ for the Auger electron spectroscopic study in Figure 5.18. The off-particle regions show Se LMM and C KLL Auger transitions, but no Co LMM Auger transitions are observed. This suggests that the elemental Se may be formed onto the off-particle region by the electrochemical processes. Figure 5.17(c) is a BSE image of the same sample area taken with the detector in the TOPO mode and shows that the elevated sphere-like regions correspond to the round CoSe$_2$ powder particles seen in the SEM image (Figure 5.17(a)). However, areas
Figure 5.17  Micrographs of supported CoSe$_2$ powder after EC3: (a) SEM; and BSE with the detector set to the (b) COMPO mode; (c) TOPO mode; (d) COMPO mode with computer-generated artificial colouring.

Figure 5.18  Auger survey spectra from supported CoSe$_2$ powders for on-particle and off-particle regions after EC3.
corresponding to the off-particle regions are also flat and correspond to the GC substrate. Figure 5.17(d) shows an BSE image based on Figure 5.17(b) with artificial, computer-generated colour-coding to better observe contrasts between regions with higher atomic number elements (i.e. Se and Co), which are more red, compared with regions with low atomic number elements (i.e. C), which are more blue. Although the overall CoSe$_2$ structure is maintained throughout the series of electrochemical treatments, Se$^0$ is detected on the sample after the surface modification EC2, and that is maintained after EC3.

5.4 Concluding Remarks

A new method for synthesizing high-purity CoSe$_2$ on high-area carbon powder support has been established, with supporting evidence from characterizations by XRD, high-resolution TEM, micro-Raman spectroscopy, XPS, SAM and BSE imaging. This form of CoSe$_2$ has a significant ORR catalytic activity with an increased OCP (of 0.81 V) and higher magnitudes of current density when compared the equivalent supported CoSe catalyst. Characterizations from micro-Raman spectroscopy, XPS and SAM showed that the CoSe$_2$ surface composition and structure of the powder catalyst is maintained even after electrochemical measurements. Furthermore, the supported CoSe$_2$ powder demonstrated that it can maintain its OCP of 0.80±0.01 V in an electrochemical stability test.

In an effort to enhance the ORR catalytic activity of the CoSe$_2$ catalyst, its surface was modified by a cyclic voltammetry procedure to form some Se$^0$ on its surface while retaining much of its original CoSe$_2$ structure as confirmed by micro-Raman spectroscopy, XPS, SAM and BSE imaging. The resulting electrochemical measurements of the modified CoSe$_2$ powder showed that the OCP was still maintained at 0.80±0.01 V although higher current densities were observed within the potential window of 0.0 to 0.60 V.
Despite the fact that the OCP of the supported CoSe$_2$ powder at 0.81 V is not as high as the OCP of the HiSpec 4000 Pt powder standard at 0.97 V, the current density of CoSe$_2$ can be within one order of magnitude of that of Pt. Additionally, the OCP of the supported CoSe$_2$ powder is higher than that of the best Co-Se thin film (at 0.74 V vs. RHE) previously studied [58]. This suggests that there may be benefits in extending this work to investigate the use of supported powder CoSe$_2$ as the cathodic ORR catalyst in an actual PEM fuel cell.
Chapter 6
Concluding Remarks

6.1 New Results

The first research theme presented in this thesis was to increase understanding, at the microscopic (molecular) level, on how the natures of different starting oxidized Al surfaces can lead to different BTSE coating outcomes. In particular, these BTSE coatings were shown to be affected by both the Al-O-Si chemisorption bonding at the interface as well as by the morphology of the starting oxide surface. Different pre-treatments can modify the various oxidized Al surfaces and this consequently influences the amount of direct Al-O-Si bonding after these samples are coated with BTSE. Pre-treatments are needed not only to form surface OH groups once Al samples are in the coating solution, but also to establish a well-anchored oxide layer. The Forest Products Laboratory (FPL) pre-treatment applied for 15 min to the native oxide on a high-purity Al sample was shown by SIMS to be effective for maximizing the chemisorption bonding, compared with the other FPL pre-treatment times tested, while SEM showed that this pre-treatment gave a scallop-like morphology that also appeared to facilitate the formation of a well-adhered BTSE coating. This pre-treatment time was consistent with a standard recipe that the FPL pre-treatment should be carried out for 15-30 min, a recommendation that comes almost entirely from the performance in empirical tests at the macroscopic level. Further tests were done to demonstrate that H₂ plasma and heat pre-treatments are capable of modifying surfaces of native oxide and of different oxides (generated by different FPL pre-treatment times) on high-purity Al samples to enhance adhesion with BTSE. Specifically, a native oxide surface on high-purity Al can be modified by heating to improve the subsequent adhesive bonding to BTSE. However, if an oxidized
Al surface has been FPL pre-treated for 15 or 60 min, its chemisorption with BTSE can still be further improved with H₂ plasma pre-treatments.

Figure 6.1 schematically summarizes models for the different oxidized layers formed after the different pre-treatments of FPL, exposure to H₂ plasma and heating as suggested by the observations reported in Chapter 3. Figure 6.1(a) for the native Al oxide indicates a flaky topography, and a hydrated form that is not well-anchored to the Al sample. Figure 6.1(b) illustrates that after 15 min of FPL pre-treatment, the native oxide is etched away while oxidation of the metal gives a thinner, better anchored Al₂O₃ layer with a topography of circular scallops and an increased amount of surface OH. However, Figure 6.1(c) covers the extension of the FPL pre-treatment to 60 min, when there is an Al₂O₃ layer with larger circular scallops albeit with fewer surface OH groups.

Figures 6.1(d), (e) and (f) draw attention to the ability of a H₂ plasma exposure to increase the available surface OH groups while preserving the original physical characteristics of the native, 15 min and 60 min FPL pre-treated oxides respectively. Figure 6.1(g) highlights the fact that the native oxide can be dehydrated by heating, so allowing the formation of a better anchored, Al₂O₃-like layer with more surface OH groups. Figures 6.1(h) and (i) summarize the observations that heating can produce an oxide topography with bumpier and larger circular scallops on the 15 min and 60 min FPL pre-treated Al oxides respectively with increased oxide thickness; however, the surface OH are not enhanced.

The second research theme presented in this thesis was part of a larger program which aims to develop transition metal chalcogen materials as potential alternatives to Pt-based catalysts for the oxygen reduction reaction (ORR) in applications to the proton exchange membrane (PEM) fuel cell. Two projects were running in parallel – the first involves synthesizing transition metal chalcogen materials in the form of model thin film
Figure 6.1: Model illustrations of oxidized Al surfaces (micron level) after the different pre-treatments: (a) native oxide; (b) after 15 min FPL; (c) after 60 min FPL; (d) sample in (a) after H₂ plasma; (e) sample in (b) after H₂ plasma; (f) sample in (c) after H₂ plasma; (g) sample in (a) after heating; (h) sample in (b) after heating; (i) sample in (c) after heating.
catalysts, prepared by magnetron sputter deposition, while the second focuses on synthesizing and characterizing CoSe₂ in powder form on a high-area carbon support. A number of different methodologies were investigated for the characterization of their surfaces, including before and after various electrochemical measurements. It is hoped that this work can ultimately help understand how the nature of the surfaces involved affect their ORR catalytic activities.

Central to the characterization of transition metal chalcogen materials is the use of micro-Raman spectroscopy and this is the basis of the first fuel cell project. A methodology of combining the imaging and point analysis capabilities of micro-Raman spectroscopy and SAM was developed to help identify the chemical composition at local regions around a structural blemish on a Co-Se thin film sample formed by a chance use of an Ar⁺ laser at high power. This allowed a re-interpretation for Raman active vibrations of the Co-Se system, compared with previous reports in the literature. The most significant is that the Raman peak at 181 cm⁻¹ should be associated with bonding between Co and Se in a Se-rich environment, while the Raman peak at 168-175 cm⁻¹ is associated with an oxygenated species.

Micro-Raman spectroscopy was also used in conjunction with other analytical techniques to characterize model thin film structures formed by magnetron sputtering for Fe-S, Co-S, Ni-S and Co-Ni-S systems. These materials had improved ORR catalytic activity compared with standard FeS₂, CoS₂ and NiS₂ compounds according to electrochemical measurements performed in O₂-saturated acidic electrolyte. Raman spectroscopy and XRD confirmed the presence of disulfide structures in the thin films, but also the possibility of the presence of some polysulfides, which are not detected in the standard materials. These
observations suggest that the polysulfides may facilitate the conduction and the transfer of electrons during ORR catalysis, although no mechanistic understanding is yet available.

The sputtered Co-Ni-S thin film demonstrated the best ORR catalytic activity of all chalcogen-based thin films studied to date. This is based on the highest OCP (at 0.89 V) and highest current density for the non-precious metal thin films tested in this work. A new broadened, asymmetric Raman band at 404 cm\(^{-1}\) from the Co-Ni-S thin film surface appears characteristic of a (Co,Ni)S\(_2\) solid solution. This band overlaps the region 460-470 cm\(^{-1}\), and so the possibility of polysulfides being present cannot be ruled out at present. The ternary alloy nature of this film must contribute to its enhanced ORR activity although its OCP remains less than that of Pt (0.95-1.02 V) and its current density is at least one order of magnitude less than for Pt.

In the second project, a new method of synthesizing high-purity CoSe\(_2\) on high-area carbon powder support has been established. The combination of XRD, HRTEM, micro-Raman spectroscopy, XPS and SAM characterization techniques shows that the synthesis described produces a powder consisting of high-purity, crystalline CoSe\(_2\) supported on high-area carbon. CoSe\(_2\) has a significant ORR activity in acidic electrolyte; compared with CoSe, synthesized previously, this sample of CoSe\(_2\) has a higher OCP (0.81 V) and a higher current density. The latter is demonstrated to be within an order of magnitude of that for a standard Pt powder sample.

Additional investigation on the supported CoSe\(_2\) powder showed that its basic structure is maintained through the various electrochemical measurements; further its OCP is maintained through an electrochemical stability test. An endeavor to modify the CoSe\(_2\) catalyst to form some Se\(^0\) on its surface via cyclic voltammetry was performed in an effort to enhance the catalytic activity. The surface modification was characterized by XPS, SAM,
micro-Raman spectroscopy and BSE imaging. The electrochemical measurements showed that the OCP remained essentially constant, but higher current densities were demonstrated within the potential window of 0.0 to 0.60 V.

6.2 Future Directions

The research results presented in Chapter 3 show how different pre-treatments can modify Al oxide surfaces to enhance chemisorption and adhesion with BTSE. Further studies of the different crystal structures in the oxide layers with glancing angle XRD should help give a better understanding of whether the adhesion to organosilanes is strongly affected by the specific oxide structure. Additional insights on how the BTSE coating solution can modify the various pre-treated Al oxide surfaces at the solid-liquid interfaces (e.g. via protonation reactions which may form more available surface OH groups) and how they subsequently affect the overall chemisorption with BTSE may be indicated by correlating the SIMS I_{71}/I_{70} ratio as a function of parameters for the organosilane coating solution (e.g. dipping time, pH) on a standardized oxidized Al sample. Ultimately there is a need for in-situ probing of surface OH groups undergoing the condensation reaction with the BTSE coating solution to form the direct Al-O-Si linkages. Methods based on sum-frequency generation [201] may in time be developed sufficiently to do that.

More research for metal surfaces of industrial interest is needed for investigating pre-treatments that do not involve applications of Cr(VI). The use of H₂ plasma and heat treatments for preparing the different microstructural regions of Al and Mg alloys should be examined, particularly with a focus on the adsorption of a range of organosilanes, including γ-GPS and γ-APS. Studying the interfaces of such systems would require TOF-SIMS to help delineate the interfacial bonding species at the different local regions [202]. Another
direction is for research into higher-end micro-scale electronic components and devices [203, 204] requiring organosilane adsorption onto Al surfaces. In that context, the use of H₂ plasma pre-treatments may avoid the undesirable contamination and waste that can occur with conventional chemical pre-treatments. The use of pre-treatments involving laser heating for local regions of oxidized Al surfaces on such electronic components can also be studied.

Work presented in this thesis showed that transition metal chalcogen thin films are capable for significant ORR catalytic activity and, based on this foundation, further progress can be made to target OCPs approaching 1.0 V in the realm of non-precious metal catalysts. Fundamental work on investigating mechanisms for electron transfer in ORR catalysis in such materials is required to further the scientific understanding. TOF-SIMS appears as a very important probe for the surface structures of transition metal sulfide thin film catalysts, particularly for investigating the presence of polysulfides. As here, such studies should be made in conjunction with electrochemical measurements and characterizations by XPS, SAM, micro-Raman spectroscopy, XRD and HRTEM. Other model catalysts based on ternary and quaternary systems should be investigated; for example, in Chapter 4, the OCP of 0.82 V for the Co-S thin film increased to 0.89 V with the addition of Ni. This increase is large, and suggests that by considering a wider range of materials, there is likely to be scope for further increases to approach the OCP of Pt. In parallel with the work on thin film (model) systems, there is a need for further investigation on related supported powder catalysts of comparable composition, following the type of approach used in Chapter 5. In extension, with a sufficient scientific basis developed by the approaches considered here, these powder catalysts need testing in real PEM fuel cell operation.
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