Driving Chemistry at Photoelectrodes and Electrodes

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Abstract

Photoelectrochemical and electrochemical cells drive redox reactions by electricity with and without light, respectively. Water splitting is a widely-studied electrolytic reaction, where oxygen and hydrogen are produced at the anode and cathode, respectively. This technology, however, is limited by the relatively low value of products. The anodic production of oxygen usually requires a significantly higher electrical potential than the theoretical potential and actually holds very little economic value. The product of cathode reaction, hydrogen, may also be a poor target product because the hydrogen made by water electrolysis costs twice as much as the hydrogen extracted from fossil fuels in most markets. Therefore, a better selection of reactant and target product is required to make a value-added photoelectrochemical or electrochemical reaction.

I show herein that the challenges for anode reaction in a photoelectrochemical cell can be overcomed by two strategies: lowering the amount of electricity required to produce oxygen; or simply driving alternative chemistry that forms products with higher value than oxygen. A bismuth vanadate (BiVO₄) photoanode is used to develop these two strategies. The photoelectrochemical activity of BiVO₄ is improved (i.e. a lower potential is required to drive water oxidation) by exposure to ultraviolet light radiation. I then use this BiVO₄ photoanode to drive alternative anodic reaction, organic oxidation, and generate organic products that are more valuable than oxygen. A variety of organic transformations are demonstrated on BiVO₄ photoanode, including alcohol oxidation, C-H oxidation and lignin decomposition.

I also study an alternative cathode reaction, CO_2 reduction, to replace hydrogen evolution reaction. I demonstrate that pairing cathodic CO_2 reduction with anodic organic oxidation in a single electrochemical cell can make valuable carbon products on both electrodes. I also question a presupposition in many previous CO_2 reduction studies that CO_2 is the best (or even the only) carbon species for cathodic reduction. The direct reductions of bicarbonate and carbonate into CO are demonstrated in an electrochemical flow cell without CO_2 gas feed, which bypasses the energy-intensive step to first thermally extract CO_2 gas in carbon capture and utilization process and suggests bicarbonate/carbonate might be a better cathode reactant than CO_2 .

Lay Summary

Photoelectrochemical and electrochemical water splitting into hydrogen and oxygen offer a promising means of storing electricity into chemical fuels. However, oxygen bears little economic value and is usually vented to the atmosphere rather than utilized as an electrochemical fuel. The common product formed at the cathode is hydrogen, but is more expensive than hydrogen extracted from fossil fuels in most markets. Choosing alternative reactants (other than water) and target products (other than hydrogen and oxygen) can increase the value of this reaction. I show that alternative anode reaction, organic oxidation, can produce higher-value products than oxygen. Oxidations of a variety of organic compounds (alcohol, hydrocarbons, lignin) are driven by photoanodes. Alternative cathode reaction, CO_2 reduction, can be paired with anodic organic oxidation to make valuable products on both electrodes. I also demonstrate that bicarbonate/carbonate could be better reactant for cathode reduction than CO_2 because the direct utilization of bicarbonate/carbonate bypasses the energy-intensive step to first extract CO_2 .

Preface

Portions of Chapters 1 and 2 (sections 1.1, 2.1 and 2.2) have been previously published as a review paper: Lacey M. Reid,* Tengfei Li,* Yang Cao, Curtis P. Berlinguette, "Organic Chemistry at Anodes and Photoanodes". *Sustainable Energy & Fuels*, 2018, 2, 1905-1927 (*Lacey Reid and I contributed equally).¹ Copyright (2018) Royal Society of Chemistry. The portions in the review paper that appear in this thesis were written by me with contributions by Prof. Curtis Berlinguette.

The work in Chapter 3 is reprinted with permission from Tengfei Li, Jingfu He, Bruno Pena, Curtis P. Berlinguette, "Curing BiVO₄ Photoanodes with Ultraviolet Light Enhances Photoelectrocatalysis". *Angew. Chem. Int. Ed.*, 2016, 55, 1769-1772.² Copyright (2016) Wiley-VCH. Prof. Curtis Berlinguette supervised this project. I carried out all the experiments except noted otherwise. Dr. Jingfu He in Berlinguette group performed the XRD and impedance measurements. SEM and AFM images were obtained by Dr. Bruno Pena in Berlinguette group. XPS measurements were carried out by Dr. Ken Wong in UBC Advanced Materials and Process Engineering Laboratory. HRTEM images were obtained by Dr. Ross Bradford in UBC Bioimaging Facility. The manuscript was written by me with contributions by Prof. Curtis Berlinguette.

The work in Chapter 4 is reprinted with permission from Tengfei Li, Takahito Kasahara, Jingfu He, Kevan E. Dettelbach, Glenn M. Sammis, Curtis P. Berlinguette, "Photoelectrochemical Oxidation of Organic Substrates in Organic Media". *Nat. Commun.* 2017, 8, 390, doi:10.1038/s41467-017-00420-y.³ Copyright (2017) Nature Publishing Group. This project was supervised by Prof. Curtis Berlinguette and Prof. Glenn Sammis. I carried out all the experiments except noted otherwise. Dr. Takahito Kasahara in Sammis group performed preliminary organic experiments. Dr. Jingfu He in Berlinguette group performed the electrochemical control experiments. SEM images were obtained by Kevan Dettelbach in Berlinguette group. GC-MS measurements were carried out by me with the help of Dr. Ling Yun in UBC Mass Spectrometry Center. The manuscript was written by me with contributions by Dr. Takahito Kasahara, Prof. Curtis Berlinguette and Prof. Glenn Sammis.

The work in Chapter 5 is based on a manuscript: Tengfei Li, Jia Yi Mo, David M. Weekes, Kevan E. Dettelbach, Glenn M. Sammis, Curtis P. Berlinguette, "Lignin decomposition at a Photoanode", which has been submitted for publication. This project was supervised by Prof. Curtis Berlinguette and Prof. Glenn Sammis. I carried out all the experiments except noted otherwise. Jia Yi Mo in Sammis group synthesized the lignin substrates and performed NMR measurements. SEM images were obtained by Kevan Dettelbach in Berlinguette group. GC-MS measurements were carried out by me with the help of Dr. Ling Yun in UBC Mass Spectrometry Center. The manuscript was written by me with contributions by Dr. David Weekes in Berlinguette group, Prof. Curtis Berlinguette and Prof. Glenn Sammis.

The work in Chapter 6 is reprinted with permission from Tengfei Li, Yang Cao, Jingfu He, Curtis P. Berlinguette, "Electrolytic CO₂ Reduction in Tandem with Oxidative Organic Chemistry". *ACS Cent. Sci.* 2017, 3, 778–783.⁴ Copyright (2017) American Chemical Society. This project was supervised by Prof. Curtis Berlinguette. I carried out all the experiments except noted otherwise. NMR experiments were carried out by me and Dr. Yang Cao in Berlinguette group. Dr. Jingfu He in Berlinguette group performed XRD measurements and prepared the cathode catalyst. The manuscript was written by me with contributions by Dr. Yang Cao and Prof. Curtis Berlinguette.

The work in Chapter 7 is based on a manuscript: Tengfei Li, Danielle A Salvatore, David M. Weekes, Curtis P. Berlinguette, "Electrolytic Conversion of Bicarbonate and Carbonate into CO in a Flow Cell", which has been submitted for publication. This project was supervised by Prof. Curtis Berlinguette. I carried out all the experiments except noted otherwise. Danielle Salvatore in Berlinguette group prepared cathode catalyst and designed the flow cell assembly. The manuscript was written by me with contributions by Dr. David Weekes in Berlinguette group and Prof. Curtis Berlinguette.

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List of Symbols and Abbreviations

$\eta_{ m STE}$	solar-to-electricity efficiency
λ	wavelength
А	amp
ACP	acetophenone
AEM	anion exchange membrane
AM	air mass
AFM	atomic force microscopy
ATR-IR	attenuated total reflectance infrared spectroscopy
Ag	silver
AgCl	silver chloride
Ar	argon
Au	gold
Bi	bismuth
BiVO ₄	bismuth vanadate
BPM	bipolar membrane
^t BuOOH	tert-butyl hydroperoxide
СВ	conduction band
CCS	carbon capture and storage
CCU	carbon capture and utilization
CH ₃ OH	methanol
CH ₄	methane
C_2H_4	ethylene
C ₂ H ₅ OH	ethanol
Cl ₄ NHPI	tetrachloro-N-hydroxyphthalimide

cm	centimetre
Co	cobalt
СО	carbon monoxide
Co-Pi	cobalt oxy/hydroxide phosphate catalyst
CO_2	carbon dioxide
CO ₂ RR	carbon dioxide reduction reaction
CO ₃ ²⁻	carbonate
Cu	copper
CV	cyclic voltammetry
Ε	potential
E°	standard redox potential
e	electron
E_F	Fermi level
$E_{F,n}$	quasi Fermi level of electron
$E_{F,p}$	quasi Fermi level of hole
EC	electrochemical
ECSA	electrochemical surface area
EIS	electrochemical impedance spectrum
FDCA	2,5-furandicarboxylic acid
Fe	iron
F.E.	Faradaic efficiency
FID	flame ionization detector
FTIR	Fourier transform infrared spectroscopy
FTO	fluorine tin oxide
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry

h	hour
h^+	hole
H^+	proton
H ₂	hydrogen
H ₂ O	water
H_2O_2	hydrogen peroxide
ΔH_{CO}	CO adsorption enthalpy
НСООН	formic acid
HCO ₂ -	formate
HCO ₃ ⁻	bicarbonate
HER	hydrogen evolution reaction
HMF	5-hydroxymethylfurfural
(HR)TEM	(high-resolution) transmission electron microscopy
i	current
In	indium
J	current density
$J_{ m total}$	total current density
K _{hydration}	hydration constant
KHCO ₃	potassium bicarbonate
K_2CO_3	potassium carbonate
КОН	potassium hydroxide
LiClO ₄	lithium perchlorate
LSV	linear sweep voltammetry
М	molar
mA	milliamp
MEA	membrane electrode assembly

MeCN	acetonitrile
mF	milliFarads
min	minute
mM	millimolar
mm	millimeter
MO_x	metal oxide
mV	millivolt
N ₂	nitrogen
NaHCO ₃	sodium bicarbonate
NHPI	N-hydroxyphthalimide
NHS	N-hydroxysuccinimide
Ni	nickel
NIRDD	near-infrared driven decomposition
nm	nanometers
NMR	nuclear magnetic resonance
O_2	oxygen
OER	oxygen evolution reaction
Pd	palladium
1-PEA	1-phenylethanol
PEC	photoelectrochemical
PINO	phthalimido-N-oxyl
Pt	platinum
PV	photovoltaic
RHE	reversible hydrogen electrode
rpm	revolutions per minute
S	second

SEM	scanning electron microscopy
Sn	tin
TCD	thermal conductivity detector
ТЕМРО	2,2,6,6-tetramethylpiperidine-1-oxyl
Ti	titanium
UV	ultraviolet
UVDD	ultraviolet driven decomposition
UV-vis	ultraviolet-visible
V	volt
V _{app}	voltage applied
V_{ph}	photovoltage
V_2O_5	vanadium oxide
VB	valance band
w/w%	weight percent
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

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献给我的妻子和父母

Chapter 1: Introduction

1.1. Motivation for work

The high gravimetric energy density of molecular hydrogen makes H₂ ideal as a carrier of stored energy which can later be used to drive a fuel cell to recover the stored energy as electricity.⁵⁻⁹ Electricity has been used to split water into molecular hydrogen and oxygen since the invention of the voltaic cell ¹⁰ and this water splitting technique offers a promising means to store solar energy into hydrogen fuels. A solar photovoltaic (PV) cell can operate in tandem with a non-photoactive, or "dark", electrochemical (EC) water-splitting cell to power the cathodic hydrogen evolution reaction (HER, eq 1.1) and anodic oxygen evolution reaction (OER, eq 1.2) with solar-derived electricity.^{7,11–13} Alternatively, sunlight can be converted directly into hydrogen fuels via photoelectrochemical (PEC) water splitting, where energetic electrons and/or holes generated upon the absorption of light drive HER or OER directly at a semiconductor-liquid interface.^{6,14–17} There has been a global effort to optimize the performance of an EC or PEC cell, however, the selection of reactants and the actual economic value added by the EC or PEC reaction are rarely considered under most circumstances. In this thesis, I demonstrate the importance of choosing proper reactants for EC and PEC reactions and generating value-added products compared to reactants.

$$HER: 2 H^{+} + 2 e^{-} \rightarrow H_{2} \qquad (eq \ 1.1)$$
$$OER: 2 H_{2}O \rightarrow 4 H^{+} + O_{2} + 4 e^{-} (eq \ 1.2)$$

Water electrolysis is a well-established commercial technology; however, the economical production of hydrogen is curbed by the large overpotential required to overcome sluggish kinetics of the anodic OER,^{5,7,11} and moreover the anodic production of oxygen gas which are not very valuable.^{3,18,19} One solution may be to produce a more valuable product at the anode to satisfy the industrial demand for chemicals of global importance. Both of these challenges can be addressed by choosing a suitable electrochemical reaction that occurs at a lower redox potential. In Chapter 3, I report a facile way to

reduce the overpotential required to drive PEC water oxidation on bismuth vanadate (BiVO₄) photoanode. In Chapters 4 and 5, I show a new strategy to drive PEC organic oxidations on BiVO₄ photoanode as an alternative to OER and generate products that are more useful than oxygen.

On the cathode side of an electrolyzer, even at the strikingly cheap clean electricity prices that are known today,^{5,7} hydrogen still costs approximately twice as much to produce through the electrolysis of water as it does when extracted from fossil fuels.^{20,21} This scenario has constrained electrolytically produced hydrogen to merely ~5% of total global hydrogen production.²⁰⁻²² Cathodic reduction of carbon dioxide (CO₂) is therefore an appealing alternative to HER for long-term energy storage because the carbon-containing products can penetrate a wider range of global fuels and chemicals markets that have the requisite infrastructure in place.^{8,9,23-26} In Chapter 6, I demonstrate that the overall value of electrode products for a CO₂ electrolyzer can be improved by pairing CO₂ reduction with organic oxidation in a sing electrochemical cell to produce valuable carbon products on both electrodes. In Chapter 7, I propose the viability of a new type of carbon reduction chemistry on cathode, bicarbonate and carbonate reductions (instead of CO₂ reduction), which provides a new strategy for carbon capture and utilization schemes by directly converting bicarbonate or carbonate into valuable commodities without the need to first extract CO₂ gas from a bicarbonate or carbonate solution by an energy-intensive step.

1.2. Structure of the thesis

This Chapter gives a brief overview of EC and PEC reactions and a summary of motivation for this work. A tutorial of the fundamental principles for EC and PEC reactions is provided in Chapter 2, as well as a literature review of recent advances on the anodic oxidations of water and organic molecules and the cathodic reductions of CO_2 . The research Chapters 3-7 are each adapted from published or submitted work in which I played a primary role. These chapters are based on four different combinations of cathodic and anodic reactions, where the cathodic reaction is HER or CO_2 /bicarbonate reduction and anodic reaction is OER or organic oxidation. Chapter 8 summarizes this work and outlines future directions.



Figure 1.1 Structure of Chapters 3-7. Four different configurations for PEC or EC cell are discussed, including HER + OER (Chapter 3), HER + organic oxidation (Chapters 4 & 5), CO₂ reduction + organic oxidation (Chapter 6) and bicarbonate reduction + OER (Chapter 7). Organic oxidation refers to the oxidation of organic reactant (organic R) to organic product (organic P). Chapters 3-5 are based on PEC cell with a photoanode and sunlight irradiation while Chapters 6-7 are based on EC cell without utilizing sunlight. The half electrode reaction of interest in each chapter is highlighted in orange.

The structure of the research Chapters is shown in Figure 1.1. Chapters 3-5 focus on the anode side of a PEC cell and utilize the reactive power of a photoanode to drive either OER (Chapter 3) or organic oxidations (Chapters 4 & 5). Chapter 3 is a study on improving the performance of traditional PEC water splitting cell (HER at cathode and OER at photoanode) by decreasing the overpotential for OER. Chapter 4 shows a new PEC cell design where the photoanode drives alternative anodic reaction, organic oxidation, to produce something more useful than oxygen. Two types of organic oxidations, alcohol oxidation and C-H oxidation, are presented as a proof-of-concept study for PEC organic oxidation. In Chapter 5, I further apply this PEC organic oxidation system to the decomposition of lignin biomass,

which is a more complicated organic transformation and bears higher economic values. Chapters 6-7 mainly discuss the cathode side an EC cell (without sunlight irradiation) and use cathode electrocatalyst to drive the reduction of CO_2 or bicarbonate towards carbon fuel, e.g. carbon monoxide (CO) in this thesis. In Chapter 6, cathodic CO_2 reduction is shown to occur in tandem with anodic organic oxidation to form higher-valued carbon products at both electrodes. Chapter 7 shows bicarbonate (and carbonate), the alternative carbon species to CO_2 , can also be reduced to CO at cathode and give comparable CO production rate compared to conventional CO_2 reduction. My research work in this thesis highlight the importance of selecting a proper target PEC or EC reaction for the generation of value-added products.
Chapter 2: Literature Review

This chapter will first give a short tutorial on the physics of EC and PEC water splitting and then discuss several challenges of OER at the anode side of water splitting cell (2.1). Based on those challenges, I introduce alternative anodic reactions, organic oxidations, in 2.2. A brief description on the basic principle of EC and PEC organic oxidation will be provided, followed by several examples of recent reports on two common EC and PEC organic oxidations: alcohol oxidation and C-H oxidation. Cathodic CO₂ reduction, an alternative to HER, will be discussed in 2.3. The selectivity of CO₂ reduction chemistry and relevant reaction mechanism will be highlighted in that part and the recent advance on cathodic CO₂ reduction will be reviewed. I will finally put the cathodic carbon reduction chemistry into a bigger picture of carbon capture and utilization process and provide some discussions on choosing a proper carbon species as the reactant for cathodic carbon reduction.

2.1. Electrochemical and photoelectrochemical water splitting

2.1.1. Fundamental physics of electrochemical and photoelectrochemical water splitting

In a typical electrochemical water-splitting cell, protons from the electrolyte are reduced at the cathode to produce dihydrogen while water oxidation at the anode generates protons to complete the circuit and balance proton consumption at the cathode (Figure 2.1a). Water splitting requires an applied voltage (V_{app}) of at least 1.23 V (the difference between the standard electrochemical potentials of OER ($E_{H2O/O2}$) and HER ($E_{H2/H2O}$)), but a voltage closer to 2 V is required in practice to overcome any voltage inefficiencies inherent to the cell. Although this *overpotential* can be associated with both anode and cathode reactions, it is the sluggish kinetics of the four-electron transfer process of OER and the large energy barrier of dioxygen formation that limits the overall reaction rate of water electrolysis.^{5,8,11,12} Significant research efforts have aimed to develop more efficient OER catalysts to reduce the high overpotential required for water splitting.²⁷⁻³³

The direct conversion of sunlight into chemical fuels in a PEC water splitting cell is enabled by semiconducting photoelectrodes at the semiconductor-liquid junction (Figure 2.1b). Non-equilibrium charge populations are created in the conduction band (CB) and valence band (VB) of the semiconductor as a result of the separation of electrons and holes that occurs when photons of appropriate energy strike the photoanode.^{6,14,15} The overall photovoltage (V_{ph}) that can be extracted from the photoanode is determined by the potential difference between the quasi Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$).^{2,6,34,35} Water is oxidized at the photoanode by holes and reduced on cathode by the photo-generated electrons that travel from the photoanode to the cathode under the applied external bias. An external voltage (V_{app}) is still required in a PEC cell; however, this potential is much smaller than that required in an electrochemical cell due to the photovoltage supplied by captured solar energy.



Figure 2.1 Schematics of (a) electrochemical (EC) and (b) photoelectrochemical (PEC) water oxidation processes at the (photo)anode and corresponding proton reduction processes at the cathode. A voltage must be applied to tune the Fermi level (E_F) of anode aligned with the electrochemical potential of water oxidation. Solar energy capture supplies part of this voltage to the photoanode in a photoelectrochemical cell. Electrons and holes are created in the conduction band (CB) and valence band (VB) of the semiconductor, respectively. The quasi Fermi levels of electrons ($E_{F,n}$) and holes ($E_{F,p}$) define the photovoltage (V_{ph}) that can be extracted from the photoanode.

2.1.2. Challenges of anodic water oxidation and opportunities for anodic organic chemistry

A key challenge in designing an OER catalyst is the long-term stability of the anode in aqueous media. The stability of the electrode material during water electrolysis is a more serious issue for photoelectrocatalytic materials. Very few non-precious metal OER electrocatalysts have been reported which can retain high catalytic activity over 1000 hours 31,36 Even fewer photoanode materials are able to retain high OER performance (photocurrent density > 10 mA cm⁻²) over 100 h of operation.^{37,38} The mechanism of photoanode degradation is not yet fully understood; however, it has been widely observed that the surface of the photoanode begins to dissolve in aqueous solution within hours of PEC electrolysis and generally leads to a loss of PEC activity.^{37,39–41}

The large overpotential required for OER remains a key challenge, thus providing the impetus to prepare (photo)electrocatalysts that can facilitate OER at lower overpotentials. Different strategies have been applied to mediate OER more effectively; *e.g.*, the use of amorphous mixed-metal electrocatalysts to reduce the overpotential of OER.^{28,42} Catalyst stability and activity in neutral pH conditions has been promoted via formation of the active electrocatalyst *in-situ*.²⁷ Recent reports have described $IrO_x/SrIrO_3$,³¹ and $Fe(PO_3)_2/Ni_2P$ foam³⁶ electrocatalysts for OER that exhibit a current density of 10 mA cm⁻² with an applied voltage of less than 1.5 V.

Improvements in PEC OER activity have focused on the design of composite photoanodeelectrocatalyst assemblies^{38,43,44} as well as the application of high-surface-area, nanostructured photoanode materials which may suppress charge recombination.^{45,46} Photoanodes comprising layers of BiVO₄/FeOOH/NiOOH or NiO_x/CoO_x/n-Si have recently achieved photocurrent densities of 3 mA cm⁻² (0.6 V applied voltage)⁴⁵ and 30 mA cm⁻² (1.3 V voltage under illumination),³⁸ respectively. My research also found a simple strategy to improve PEC OER activity by treating the photoanode with ultraviolet (UV) light, which is going to be discussed in Chapter 3. Additionally, Grätzel and colleagues reported a perovskite PV-electrolyzer tandem apparatus in 2014 that achieved a solar-to-hydrogen efficiency of 12.3% using nickel-iron oxide electrodes.¹³ However, the persistence of the higher overpotential of water oxidation compared to the hydrogen evolution potential raises the question of whether there is a highervalue alternative to driving anode reaction.

In most water splitting architectures, the anodic product, oxygen gas, is vented rather than captured.^{3,18,19} The fundamental purpose of OER as the anodic water-electrolysis reaction is simply to complete the electrical circuit and to provide protons to offset the proton consumption at cathode. Many chemical oxidation reactions can be achieved electrochemically and are typically accompanied by a deprotonation process.^{47,48} Replacement of anodic OER with an alternative organic oxidation reaction has the potential to generate products with higher economic value than oxygen gas (*e.g.*, fine chemicals, pharmaceutical precursors). My studies in Chapters 4-6 show how anodic OER can be replaced by useful PEC/EC organic transformations. Furthermore, using the anode to drive organic transformations can also provide an opportunity to alleviate the degradation of photoelectrodes that occurs during water oxidation (see Chapter 4). In the following section, the anodic oxidation of organic substrates will be discussed as a promising strategy to address the limitations of the traditional anodic oxidation of water.

2.2. Anodic chemistry: organic oxidation

2.2.1. Principles of (photo)electrochemical organic oxidation

The high-value commodity chemicals afforded by electrochemical organic oxidation makes this class of reaction ideal for pairing with cathode reaction. Electrochemical oxidation reactions afford the use of catalytic rather than stoichiometric amounts of oxidizing reagents via electrochemical regeneration, offering an environmentally friendly alternative to traditional chemical oxidation methods.⁴⁹ Furthermore, an electricity-driven redox process affords the ability to tune the oxidative strength of the reaction to the redox potential of a substrate so that catalytic redox reagents are not necessarily required.⁵⁰ *Electricity* drives the electron transfer processes instead of chemical oxidants, shuttling electrons between the surface of anode and the organic substrates. Selectivity between different functional groups is controlled by the electric potential applied to the working electrode and/or a redox mediator (see discussions below) rather than the oxidative strength of a selected chemical oxidant.⁵⁰ The relatively mild reaction conditions

required for electrochemistry—along with the ability to target desired functional groups for oxidation are features of anodic oxidation which can impart high selectivity alongside operational simplicity.

Electron transfer between electrode and substrate is an interfacial heterogeneous process that may be expected to be kinetically slower than a homogeneous chemical reaction. The surface area of the electrode can be increased, or a redox shuttle or "mediator" can be employed, to more efficiently transfer electrons between anode and substrate (Figure 2.2a), (analogous to the role of redox photosensitizers in photocatalytic oxidation reactions, Figure 2.2c). The redox mediators can promote the *indirect* EC oxidation of organic substrates at lower applied potentials than the *direct* electrolysis (i.e. without redox mediator) would require. The advantage is twofold: (i) a relatively lower applied voltage avoids the oxidation of functional groups with lower standard potentials; and (ii) transient interactions or chemical bonding occurring between the substrate and mediator can show selectivity for particular functional groups.⁴⁷ Some examples of redox mediators used for organic oxidation will be provided in 2.2.2. My research in Chapters 4 and 6 also use redox mediator to drive the PEC or EC organic oxidation. The *direct* electrolysis, on the other hand, has the advantage of avoiding the separation of homogeneous mediator from reaction mixture and thus enabling a more straightforward product separation. My study in Chapter 5 shows an example of *direct* PEC organic transformation (lignin decomposition) without a redox mediator.

Photoelectrochemical oxidation of an organic substrate (Figure 2.2b) follows a similar electron transfer mechanism to the EC system. A lower potential is required to drive electron transfer between the photoanode and substrate, owing to the photovoltage generated by the semiconductor. Both photocatalytic and electrocatalytic oxidations are promising for environmentally friendly, sustainable and cost-effective syntheses of organic commodity chemicals; however, my thesis will focus solely on using EC and PEC systems to drive organic transformations.



Figure 2.2 General principles of (a) electrocatalytic, (b) photoelectrocatalytic, and (c) photocatalytic oxidations of an organic substrate. In (a) and (b) the potential supplied to the anode results in the oxidation of a redox mediator (Mediator_{red} \rightarrow Mediator_{ox}) that subsequently oxidizes the substrate at a comparable chemical potential (this oxidation of substrate can also occur directly at the surface of anode/photoanode without redox mediator). In photocatalytic cells the process is mediated by a photo redox senisitizer molecule (Sens) through an analogous mechanism.

2.2.2. Two common types of (photo)electrochemical organic oxidation

It is important to consider a few key criteria in selecting an oxidation reaction to replace OER. Namely, the organic substrate must be soluble and have a lower (less positive) anodic oxidation potential than solvent to prevent the oxidation of solvent. Furthermore, the feedstock chemical should be chosen to maximize the value of the oxidation product. The reaction should be selective to avoid costly separation steps where multiple oxidation products are possible. A repertoire of organic reactions exist which fulfill some or all of these criteria and can readily be applied to an electrochemical reforming process. Baran and colleagues have exhaustively reviewed a large scope of electrochemical organic transformations that have been developed since 2000.⁴⁸ This section will focus on two model reactions that have been developed for electrochemical reforming purposes and fulfill most or all of the criteria for effectively replacing OER: alcohol oxidation and C-H functionalization. Some recent EC/PEC organic oxidation reports that are related to my research will be discussed.

2.2.2.1. Electrochemical alcohol oxidation

Alcohol oxidation reactions are important chemical transformations for synthetic chemistry. Primary alcohols are typically oxidized at an anodic potential between 0.5-1.3 V affording aldehyde and carboxylic acid products that can be used as building blocks for a multitude of commodity chemicals. Some recent reports on EC and PEC oxidation of alcohols will be reviewed in this section.

A redox mediator might be required for oxidation of alcohols in cases where direct anodic oxidation fails due to the high overpotential required (the solvent will be oxidized first), or where selectivity is needed in the presence of other functional groups. For example, the aerobic oxidation of alcohols by nitroxyl radical cations is well known,⁵¹ leading to the ubiquitous employment of 2,2,6,6-tetramethylpiperidine nitrosonium (TEMPO) compounds as chemical oxidants and, later, electrochemical mediators. TEMPO is known to selectively oxidize primary alcohols over secondary alcohols in basic conditions, whereas secondary alcohols are favoured over primary alcohols in acidic conditions. Stahl's group has explained this selectivity by the interactions between the substrate and mediator.⁵² The selectivity in basic conditions is attributed to the large steric effect of the secondary alcohol when a chemical bond is formed between the nitrogen atom of TEMPO and the oxygen atom of the alcohol (Figure 2.3a). The mechanism of TEMPO-mediated alcohol oxidation under acidic conditions, however, is believed to involve hydride transfer between TEMPO and the alcohol, favouring electron-rich secondary alcohols (Figure 2.3b).⁵²



Figure 2.3 The mechanism of TEMPO-mediated alcohol oxidation proceeds through an alkoxide adduct under basic conditions, or through a bimolecular hydride transfer under acidic conditions, to impart substrate chemoselectivity. Copyright 2015, American Chemical Society.⁵²

Based on previous EC oxidations of alcohol mediated by TEMPO and derivatives,^{52–55} Choi and coworkers applied this TEMPO chemistry to a PEC cell and reported the first example of PEC alcohol oxidation.¹⁸ While PEC oxidative degradation of organic wastes is widely known,^{56–59} Choi's work was the first report of PEC conversion of organic substrates into commodity chemicals. In this study, the PEC oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA, a key monomer to produce polymer materials) was achieved using a BiVO₄ photoanode and TEMPO redox mediator (Figure 2.4a). The onset potential for TEMPO-mediated oxidation of HMF was negatively shifted by ~0.7 V compared to water oxidation (Figure 2.4b), indicating that the organic oxidation chemistry was more favourable than the oxidation of water. HMF oxidation was achieved with nearly 100% faradaic efficiency whereas the competing water oxidation reaction was completely suppressed.



Figure 2.4 (a) Schematic depiction for the PEC oxidation of 5-hydroxymethylfurfural (HMF) into 2,5furandicarboxylic acid (FDCA) on a BiVO₄ photoanode mediated by TEMPO. (b) Linear sweep voltammograms obtained in aqueous buffer solution (black), buffer solution containing TEMPO (blue), and buffer solution containing TEMPO and HMF (red). Copyright 2015, Nature Publishing Group.¹⁸

The PEC oxidation of HMF reported by Cha and Choi demonstrated a proof-of-concept design for producing value-added products at the photoanode; however, the use of aqueous media continues to limit the scope of possible organic chemical reactions and can lead to extensive photoanode degradation. My study demonstrated the PEC oxidation of organic substrates in organic media,³ where MeCN was used as solvent to broaden substrate scope (*e.g.*, alcohol, hydrocarbons, lignin model, see Chapters 4 and 5) and suppress corrosion of the BiVO₄ photoanode. The PEC oxidations of alcohols were also recently achieved without using redox mediator, e.g. oxidation of methanol to formaldehyde on hematite photoanode.⁶⁰, oxidation of 1-phenylethanol to acetophenone on BiVO₄|WO₃ composite photoanode.⁶¹. HER at the cathode may also be replaced with an alternative electrochemical reduction reaction that yields more valuable chemicals than hydrogen. My study has demonstrated the electrochemical reduction of CO₂ to CO paired with anodic oxidation of different types of alcohols mediated by TEMPO (see Chapter 6).³

2.2.2.2. Electrochemical C-H oxidation

C-H oxidation can be achieved electrochemically with the proper selection of electrode materials and redox mediators to overcome the high C-H oxidation potential.^{48,63} In a typical EC C-H oxidation, a radical cation intermediate is generated by anode and redox mediator, followed by reaction with an oxidant (*e.g.*, O_2 , ¹BuOOH) to yield a oxygenated product. The high-value commodity chemicals afforded by electrochemical C-H functionalization makes this class of reaction ideal for pairing with cathodic HER. Common C-H activation reactions can be divided into three types based on the reactivity of the C-H bond: aryl (activated) C(sp²)-H; benzylic and allylic (activated) C(sp³)-H; and unactivated C(sp³)-H. This section will mainly discuss reviews recent reports of electrochemical oxidation of benzylic and allylic activated C–H bonds.

Oxygenation of benzylic and allylic C–H bonds plays an important role in the synthesis of fine chemicals or pharmaceuticals, especially for the production of pharmaceutical precursors containing heterocycles.^{64,65} In chemical systems, C-H oxidation can be achieved by employing metal-ion catalysts (*e.g.*, Co²⁺, Mn²⁺, Cu²⁺); however, this process typically requires extreme reaction conditions (high temperature and/or pressure) and yields multiple oxygenation products for substrates having more than one activated C-H group.^{65,66} Chelation of the metal-ion catalyst or co-catalyst may also occur for substrates bearing a Lewis basic group adjacent to the functionalized C-H group; this chelation is detrimental to catalyst turnover.⁶⁷

In 2017, Stahl and colleagues identified a cobalt(II)/N-hydroxyphthalimide (NHPI) catalyst system for the aerobic oxidation of benzylic C-H bonds.⁶⁷ The chemical oxidations were typically run for 12 h in organic solvent at 90-100 °C under 1 atm O₂. This method was tolerant of heterocycles and highly selective for benzylic methylene groups; however, the reaction was low yielding for some benzyl pyridines and imidazoles due to chelation of the cobalt co-catalyst (Figure 2.5). The authors developed an electrochemical oxidation system for the oxygenation of these substrates which did not require the cobalt co-catalyst nor the high operating temperature (reduced to 50 °C) of the chemical system.⁶⁷

Electrochemical oxidation was instead achieved using a NHPI redox mediator and carbon anode (Pt cathode) in an undivided 3-electrode cell at 0.65-0.75 V (vs. Ag/AgCl) under 1 atm O₂. EC oxidation of the benzylic C-H bonds in absence of Co²⁺ gave substantially higher product yields than the aerobic oxidation system that was prone to catalyst chelation.⁶⁷



Figure 2.5 Chemical oxidation (with $Co^{2+}/NHPI$; NHPI = *N*-hydroxyphthalimide) and electrochemical oxidation (with NHPI only) of benzylic C-H to yield benzyl ketones. NHPI is anodically oxidized to the phthalimido-*N*-oxyl (PINO) radical which mediates the selective abstraction of benzylic C-H bonds to generate an organic radical, affording the oxygenated products on quenching with dioxygen. Copyright 2017, Royal Society of Chemistry.⁶⁷

EC oxidation of allylic C-H bonds is more difficult to achieve than benzylic C-H bonds due to the higher redox potential of allylic C-H.⁶⁸ Direct EC allylic C-H oxidation (without redox mediator) was first reported in 1968 on α -pinene,⁶⁹ followed by the first report of indirect allylic oxidation mediated by NHPI in 1985.⁷⁰ Unfortunately, EC strategies toward allylic C-H activation have been limited by relatively low product yields. This challenge could potentially be overcome by developing a more reactive mediator (i.e. higher redox potential) to activate allylic C-H bonds. In 2016, Baran and coworkers reported a study

which evaluated a series of redox mediators for the allylic C-H oxidation of the sesquiterpene valencene into the corresponding α,β -unsaturated ketone nootkatone (Figure 2.6).⁷¹ In addition to the selection of a new mediator, the authors identified another modification to improve EC allylic oxidation: use of *tert*butyl hydroperoxide ('BuOOH) as oxygen source instead of air or O₂. Among the different mediators tested, tetrachloro-*N*-hydroxyphthalimide (Cl₄NHPI) showed the best performance with a 20% increase in yield for compared to simple NHPI. The presence of the electron-withdrawing Cl groups on Cl₄NHPI afforded a +0.1 V gain in redox potential compared to NHPI, resulting in a more reactive Cl₄NHPI radical. A scope of 40 allylic C-H substrates were electrochemically oxidized to enones on 0.5 mmol scale with moderate to high yields (40–90%). Three of these substrates were converted at 100-gram scale in a beaker open to the air, demonstrating a scalable and operationally-simple EC oxidation of allylic C-H bonds without using toxic or expensive chemical reagents.

Inspired by Baran's EC C-H oxidation system, my study in Chapter 4 applied this technology to a PEC cell and demonstrated the first example of a PEC C-H oxidation. In addition, Baran and coworkers reported a similar EC protocol to drive the C-H oxidation of unactivated C-H by using a modified redox mediator, quinuclidine, and achieved up to 50% yield of oxygenated product.⁶⁸ The oxidation of unactivated C-H bonds was recently achieved in a PEC cell,⁷² where the direct oxidation of cyclohexane occur on the surface of WO₃ photoanode without a redox mediator and produce cyclohexanol and cyclohexanone.



Figure 2.6 (a) Scope of redox mediators explored for electrochemical allylic C-H oxidation of valencene into nootkatone. Conditions: Cl_4NHPI redox mediator (0.2 equiv.), ^{*t*}BuOOH co-oxidant (1.5 equiv.), pyridine base (2 equiv.), LiClO₄ electrolyte (0.6 equiv.), acetone solvent (0.16 M in substrate), carbon electrodes. (b) Large-scale allylic C-H oxidation of selected substrates in a beaker open to air (pictured in inset). Copyright 2016, Nature Publishing Group.⁷¹

2.3. Cathodic Chemistry: CO₂ reduction

Section 2.1.2. has discussed the challenges of anodic OER in a water splitting cell and proposed alternative anode reaction (organic oxidation) to solve those problems. Ihere introduce an alternative cathode reaction: CO_2 reduction reaction (CO_2RR).

The rising level of CO₂ in atmosphere has provided the impetus to develop technologies for efficient carbon capture and the downstream carbon storage/utilization, where electrochemical CO₂RR stands out an attractive strategy to create useful chemical feedstocks from CO₂ and clean electricity and close the carbon cycle.^{8,9,23–26} Another motivation to study CO₂RR as a replacement of cathodic HER in electrochemical cell is the price of hydrogen. Electrolytic hydrogen produced from water splitting costs twice as much as the commercial hydrogen extracted from fossil fuels.^{20,21} CO₂RR is therefore an appealing alternative to HER for the storage of renewable electricity into carbon chemicals with higher market price than hydrogen.^{73,74} The following sections will review the basic principles of CO₂RR and some recent efforts to enhance the performance of CO₂RR.

2.3.1. Principles for electrochemical CO₂ reduction

Unlike HER that only produces H₂ on cathode, CO₂RR usually generate multiple carbon products. The product selectivity of CO₂RR is mainly determined by the catalyst property and the electrical voltage applied. Table 2.1 shows the standard potentials (E°) of some common products of CO₂RR, including formic acid (HOOH), carbon monoxide (CO), methanol (CH₃OH), methane (CH₄), ethylene (C₂H₄) and ethanol (C₂H₅OH). Notably, HER (E° = 0 V versus RHE) usually also occurs during CO₂RR and produce H₂ as a byproduct. Due to the narrow potential window where the standard potentials of multiple CO₂RR products fall in, it is very important to develop electrocatalyst to facilitate the formation of single product.

Product	Reaction	E° (V versus RHE)
Formic acid (HOOH)	$\rm CO_2 + 2 \ e^- + 2 \ H^+ \rightarrow \rm HCOOH$	-0.20
Carbon monoxide (CO)	$CO_2 + 2 e^- + 2 H^+ \rightarrow CO + H_2O$	-0.10
Methanol (CH ₃ OH)	$CO_2 + 6 e^- + 6 H^+ \rightarrow CH_3OH + H_2O$	0.02
Methane (CH ₄)	$\mathrm{CO}_2 + 8 \ \mathrm{e}^{-} + 8 \ \mathrm{H}^+ \rightarrow \mathrm{CH}_4 + 2 \ \mathrm{H}_2\mathrm{O}$	0.17
Ethylene (C ₂ H ₄)	$2 \text{ CO}_2 + 12 \text{ e}^- + 12 \text{ H}^+ \rightarrow \text{C}_2\text{H}_4 + 4 \text{ H}_2\text{O}$	0.08
Ethanol (C ₂ H ₅ OH)	$2 \text{ CO}_2 + 12 \text{ e}^- + 12 \text{ H}^+ \rightarrow \text{C}_2\text{H}_5\text{OH} + 3 \text{ H}_2\text{O}$	0.09

Table 2.1 Common products of electrochemical CO_2 reduction and their standard redox potentials (E°) versus reversible hydrogen electrode (RHE). Potential data from reference.⁷⁵

While the CO₂ reduction catalysts can be divided into two types: homogeneous and heterogeneous catalysts, I will focus on heterogeneous catalyst because homogeneous CO₂ reduction catalysts are usually limited by low turnover number and poor recyclability.²³ Heterogeneous CO₂ reduction catalysts are mainly metals, which can be divided into four groups based on the ability to form a metal-carbon bond (M-C) with surface-adsorbed carbon species (CO₂ or CO), ^{75,76} as shown in Figure 2.7. Group I includes metals that do not form a M-C bond with CO₂ (In, Bi, Sn, Pb, Pd, Hg) and favour the formation of formic acid because the poor interaction between CO₂ and metal is not able to mediate the dissociation of C-O bond in CO₂. Metals that form weak M-C bonds with CO₂ (Group II, including Au, Ag, Zn) produces CO as major product, where CO₂ is adsorbed on the surface of metal, followed by the reduction towards surface-bound CO. The CO molecule is then released as the final product due to the relatively weak bonding strength of M-C between metal and CO. Group III consists of Cu only, which forms medium M-C bond that enables the formation of products that require more than two electrons. The

 CO_2 is first adsorbed and reduced to CO intermediate, which can reside on the surface of Cu and be further reduced to hydrocarbons (e.g. CH_4 , C_2H_4) or alcohols (e.g. C_2H_5OH). Group IV includes metals that bind too strongly to CO (Pt, Fe, Co, Ni) and end up with CO poisoning the metal catalyst. The CO bound metal sites are inaccessible for further CO_2 reduction and HER becomes dominant, making Group IV metals good HER catalyst instead of CO_2RR catalyst. The CO adsorption enthalpy (ΔH_{CO}) ⁷⁷ can quantitatively represent the bonding strength of M-C and predict the major product of CO_2RR on the surface of a certain metal (see 2.3.2).



Figure 2.7 CO₂RR pathways for different metal catalysts, including Group I that does not form M-C bond and produces formic acid, Group II that forms weak M-C bond and produces CO, Group III that forms medium M-C bond and produces hydrocarbons or alcohols, and Group IV that forms strong M-C bond and produces H₂. Reaction pathways adapted from reference.^{75,76}

The product selectivity is therefore one of the figures of merits in CO₂RR. Faradaic efficiency (F.E.) is widely used to represent the selectivity towards a certain product (X), which is the ratio of electrons utilized to create X over the total number of electrons (eq 2.1). Total current density (J_{total}) stands for the overall reaction rate while the partial current density for X (J_X), defined by eq 2.2, is used to represent the reaction rate of producing X. Another key value is the overpotential, defined as the potential in excess of the standard potential of the reaction (eq. 2.3). An ideal CO₂RR is able to achieve a high total current density with a high Faradaic efficiency towards a single product at a low overpotential. I will review some recent efforts to enhance the performance of CO₂RR in the following section.

$$F.E._{X} = \frac{number of electrons used to produce X}{total number of electrons} \quad (eq \ 2.1)$$

$$J_X = J_{total} * F. E_{\cdot X} \qquad (eq \ 2.2)$$

overpotential = $E - E^\circ$ (eq 2.3)

2.3.2. Efforts to enhance performance of CO₂ reduction

There has been a global effort to improve the performance of CO₂RR and many parameters have been studied and optimized. In this section, I will mainly discuss some recent work on the optimizations of *catalyst* and *cell configuration*. Cu has been widely studied as a CO₂RR catalyst in the last 20 years because it is able to mediate the formation of almost every possible CO₂ reduction product,^{75,76} but the performance of Cu-catalyzed CO₂RR was limited by low current density and Faradaic efficiency. In 2012, Kanan and coworkers reported an oxide-derived Cu catalyst that achieves a total current densities > 1 mA cm-2 and Faradaic efficiencies > 50% at overpotentials < 0.4 V for the first time.⁷⁸ Polycrystalline Cu foil was annealed at 500 °C to give Cu₂O, followed by electrochemical reduction to the oxide-derived Cu, which created nanostructured Cu particles and greatly increased surface roughness of Cu electrode (Figure 2.8). The resulting oxide-derived Cu exhibited significantly higher total current densities and Faradaic efficiencies for CO and HCOOH compared to polycrystalline Cu. This work gave the first example of a metal catalyst that can mediate CO_2RR at meaningful current density and Faradaic efficiency and opened a new research area for electrochemical CO_2 reduction chemistry.



Figure 2.8 Oxide-derived Cu catalyst for CO₂RR. a) Total current densities and b) Faradaic efficiencies of CO and HCOOH for oxide-derived Cu and polycrystalline Cu. c) Preparation of oxide-derived Cu and scanning electron microscopy (SEM) images of the annealed Cu₂O and oxide-derived Cu. Copyrights 2012, American Chemical Society.⁷⁸

Following Kanan's work, our group prepared oxide-derived alloy catalysts with different compositions of metals and studied the influence of metal composition on the selectivity of CO₂RR.⁷⁷ A series of alloy catalysts were made by mixing stoichiometric amounts of metal precursor solutions, followed by near-infrared driven decomposition ³² of metal precursors to form mixed metal oxides and

electrochemical reduction to give mixed metal catalysts. As mentioned in 2.3.1, the selectivity of CO₂ reduction catalyst depends on the strength of M-C bond between metal surface and carbon species (CO₂ or CO) and can be reflected by CO adsorption enthalpy (ΔH_{CO}). Figure 2.9a shows the relationship of major product for CO₂RR and the ΔH_{CO} values of different catalysts. The best CO production catalysts are often characterized by a ΔH_{CO} value of around 10 kcal mol⁻¹.⁷⁹ It was postulated that combining In, a Group I metal that has low ΔH_{CO} and favours HCOOH, with Group III and IV metals that have higher ΔH_{CO} can give a mixed metal catalyst with proper value of ΔH_{CO} that favours CO formation. ΔH_{CO} of $M_x In_{1-x}$ (M = Fe, Co, Ni, Cu, Zn) was calculated by a linear combination of the ΔH_{CO} of each component (Figure 2.9b). The orange region (ΔH_{CO} between 7 and 12 kcal mol⁻¹) was expected to show optimized selectivity towards CO. Figure 2.9c shows the partial current densities for CO measured on $M_x In_{1-x}$ catalysts, where the experimental results closely match the theoretical prediction. This method indicates that ΔH_{CO} can provide a facile means of predicting the selectivity of CO₂RR catalyst and accelerate the selection of mixed metal catalysts. The metal composition with highest CO partial current density (Cu_{0.75}In_{0.25}) was chosen as cathode to perform CO₂RR in my study in Chapter 6.



Figure 2.9 a) General relationship between the primary product and ΔH_{CO} for metal (black) and mixed metal (orange) catalysts. b) Estimated ΔH_{CO} for $M_x In_{1-x}$ alloys (M = Fe, Co, Ni, Cu, Zn). ΔH_{CO} of $M_x In_{1-x}$ was calculated by a linear combination of the ΔH_{CO} of each component. The orange region (ΔH_{CO} between 7 - 12 kcal mol⁻¹) was expected to show optimized selectivity towards CO. c) The partial current densities for CO at -0.7 V (vs RHE) for $M_x In_{1-x}$ samples. Copyright 2017, Wiley-VCH.⁸⁰

Another important factor that may influence CO_2RR performance is the configuration of the electrochemical cell. Most reports (> 1000 papers) on CO_2RR use a three-electrode "H cell" configuration (Figure 2.10a), consisting of a working electrode (cathode), a counter electrode (anode), a reference electrode (e.g. Ag/AgCl) and a membrane that separates cathode and anode compartments. CO_2 gas is bubbled into the catholyte solution and reduced to carbon products. The H cell configuration is easy to operate but this system is largely limited by mass transport, confining the partial current density for carbon products (e.g. J_{CO}) to 10 mA cm⁻². Therefore, there are recently some reports (< 40 papers) on using a "flow cell" to perform CO_2RR .²⁶ Figure 2.10b shows the architecture of a typical flow cell, where

a membrane electrode assembly (MEA, consisting of a cathode catalyst, a membrane and an anode catalyst) is sandwiched between flow plates. The cathode is continuously fed with CO_2 and the carbon products flow away from the cell, which serves to overcome the mass transport limitation and enables large scale CO_2 electrolysis. OER occurs on the anode side in a similar way and completes the electrical circuit. Our group has reported liquid-phase CO_2 (circulating CO_2 -saturated solution)⁸¹ and gas-phase CO_2 (circulating humidified CO_2 gas)⁸² reductions to CO in flow cells, where the MEA consists of a Ni anode, a bipolar membrane and a Ag cathode (known to be a CO_2 reduction catalyst towards CO). Based on that flow cell configuration, I performed electrochemical reduction of bicarbonate without CO_2 feed in Chapter 7.



Figure 2.10 Two common cell configurations used for CO_2RR . a) An H cell where the working electrode, counter electrode and reference electrodes are immersed in electrolyte solution and the CO_2 -saturated catholyte is separated with anolyte by a membrane. b) A flow cell that consists of a membrane electrode assembly (MEA) and two flow plates of anode and cathode. Electrodes are continuously fed with reactants and products are brought away from electrodes. Copyright 2018, American Chemical Society.²⁶

2.3.3. Insights into a proper reactant for carbon reduction chemistry: CO₂ vs bicarbonate

In section 2.3.2 I have discussed some recent progress on improving the performance of electrochemical CO_2RR , with the presupposition that CO_2 is the best (or even the only) carbon species for cathodic reduction. In this section, however, I will put the electrochemical CO_2RR into a bigger picture of carbon capture and utilization/storage (CCU/CCS) industry and raise up the question that not many CO_2RR studies have noticed before: is CO_2 a proper reactant for carbon reduction chemistry?

In a typical CCU/CCS process, waste CO_2 gas is captured by alkaline solution to form bicarbonate (HCO₃⁻) and/or carbonate (CO₃²⁻) solution, followed by a thermally-driven process to recover CO_2 gas from HCO_3^{-7}/CO_3^{-2-3} solution (Figure 2.11). The recovered CO_2 gas is then either utilized to form carbon chemicals or stored in deep geological formations (e.g. oil fields).⁸³⁻⁸⁵ Electrochemical CO₂RR is one of the downstream strategies to utilize the recovered CO₂ gas. This CCU/CCS technology, however, is expensive, risky and not economic viable, mainly due to the energy-intensive step of recovering CO_2 gas from carbon-rich solution, where an extreme temperature (> 800 $^{\circ}$ C) and a great amount of thermal energy (~ 10 GJ per ton CO₂) is required.⁸⁵ Therefore, a direct utilization of bicarbonate/carbonate solution towards carbon chemicals that bypasses the CO2 recovery step would save the total amount of energy required for converting waste CO₂ into carbon chemicals, provided that the electrical energy required for bicarbonate/carbonate reduction is similar to that of CO₂ reduction. My study in Chapter 7 shows an electrochemical flow cell that can directly reduce bicarbonate and carbonate solutions into carbon monoxide without CO₂ feed, and the reduction of bicarbonate requires even less electrical energy than CO₂ reduction. This work could provide new opportunities for CCU industry and change the conventional view that CO₂ is the only carbon species that can be reduced on cathode (I show that CO₂ is not the only reducible carbon species, and may not even be the best carbon species for reduction because bicarbonate could be better than CO_2).



Figure 2.11 A typical carbon capture and utilization/storage process. Waste CO_2 gas is captured to form bicarbonate (HCO₃⁻) and/or carbonate (CO₃²⁻) solution, followed by an energy-intensive thermal process to recover CO_2 gas for downstream utilization or storage. I here propose a direct utilization of HCO₃⁻/ CO_3^{2-} solution towards carbon chemicals that bypasses the CO₂ recovery step.

In addition, choosing HCO_3^{-1} or $CO_3^{2^-}$, instead of CO_2 , as the reactant for carbon reduction also have the following advantages in terms of electrochemistry. First, the low solubility of CO_2 in water (0.033 M) limits the maximum current density that can be achieved for electrochemical CO_2RR , while the solubilities of HCO_3^{-1} and $CO_3^{2^-}$ in water are significantly greater (~3.3 M for KHCO_3; 8.1 M for K₂CO₃), which overcomes the mass transport limitations in large scale electrolysis. Secondly, the addition of CO_2 into electrolyte solution causes a lowering in pH, thus providing conditions that favour the competing HER instead of the desired CO_2RR .^{86–88} Thirdly, less than 50% of the CO_2 gas injected into electrochemical cell is converted into carbon products in most cases of CO_2RR , which means the rest of CO_2 is released into air again and a separation of gas products from unreacted CO_2 gas is required. The electrochemical reduction system for HCO_3^{-1} and $CO_3^{2^-}$ in Chapter 7 is also able to solve these problems.

Chapter 3: Exposure of Photoanodes to Ultraviolet Light Enhances Photoelectrochemical Water Oxidation

3.1. Introduction

Section 2.1.1 has introduced how the solar-driven PEC oxidation of water stores sunlight as hydrogen and oxygen. The efficient, direct conversion of photons to these fuels requires a semiconducting material that is competent in both absorbing sufficient amounts of sunlight and mediating the catalytic oxidation of water, potentially augmented by an electrocatalyst layer.^{5,6,14} Among the materials that have been tested in this context, BiVO₄ stands out as one of the best photoelectrocatalysts due to an absorption edge of 520 nm, band edges appropriately positioned to accommodate the oxygen evolution reaction (OER).⁸⁹ The OER onset potential for the BiVO₄ photoanode is high, however, thereby requiring nanostructuring of material ^{45,90} or an additional metal oxide layer (e.g., CoO_x, NiO_x, and FeO_x) to help mediate the multi-electron reaction more effectively.^{44,45,91,92} These secondary metal oxide coatings serve to improve photoelectrocatalysis by either suppressing charge recombination within the photoanode^{44,45,89,90,93,94} and/or mediating the OER reaction more effectively.^{91,95} The mechanism of action notwithstanding, these composite systems will inherently suffer from some efficiency losses due to the additional interface and a masking of the photoactive layer to incident sunlight, ^{96,97} thus providing the impetus to discover a photoelectrocatalyst that does not require an additional electrocatalyst coating.

Pursuant to the ultraviolet-driven-decomposition (UVDD) strategy to access metal oxide electrocatalyst for EC water oxidation previously reported by our group,²⁸ I set out to understand how the OER PEC performance of BiVO₄ photoanodes is affected by extended exposure to UV radiation. I show herein the unexpected observation that exposure of BiVO₄ photoanodes to sustained UV radiation yields a change in electrode morphology that yields a markedly cathodic potential shift of ~400 mV at 1 mA/cm². Notably, this photolysis procedure is found to enhance the photocurrent of BiVO₄ to the same extent as a Co-Pi cocatalyst,^{44,91} and provides a fundamentally different yet simple approach for achieving high

performance photoanodes compared to previously tested methods. This demonstration of enhanced performance during extended illumination is aligned with the need to develop solar energy conversion technologies that display temporal stability.

3.2. Results and discussions

3.2.1. Physical characterizations of BiVO₄ photoanode

The BiVO₄ photoanodes under investigation were synthesized in accordance with a protocol developed by Gamelin and coworkers,⁴⁴ where appropriate stoichiometric amounts of bismuth nitrate hexahydrate, vanadyl acetylacetonate and tungsten hexachloride dissolved in a solution of acetic acid and acetylacetone were spin-cast onto a conducting layer of fluorine-doped tin oxide (FTO) prior to an annealing step at 500 °C. The resultant films were then exposed to UV radiation ($\lambda_{max} \sim 185$ and 254 nm, $\sim 10 \text{ mW/cm}^2$) in air for up to 20 hours.



Figure 3.1 SEM images of $BiVO_4$ films coated on FTO glass before (a) and after (b) exposure to 20 h of UV curing.

Scanning electron microscopy (SEM) images of the $BiVO_4$ films not subjected to UV curing (Figure 3.1a) reveal morphological features consistent with previous descriptions of $BiVO_4$.⁴⁴ Images of the films after photolysis reveal a change in features that suggests fusion of the crystalline domains

towards a less textured surface (Figure 3.1b). Atomic force microscopy (AFM) images of BiVO₄ also indicate a lower roughness factor after irradiation (Figure 3.2). These macroscopic modifications during UV photolysis did not render any changes in atomic structure that were detectable by X-ray diffraction (XRD) techniques, as the photoactive monoclinic phase of BiVO₄ was measured before and after curing (Figure 3.3a). Moreover, absorption spectra recorded on the photoanodes before and after photolysis were superimposable (Figure 3.3b), thus ruling out differences in film absorptivities being responsible for any changes in PEC performance after photolysis of BiVO₄.



Figure 3.2 AFM images of BiVO₄ with exposure to UV radiation of 0 h (left) and 20 h (right). (c) and (d) show the 3D view (from the side) of the BiVO₄ surface with 0 h and 20 h UV radiation, respectively, and the roughness factors of each sample, including the average area roughness (S_a) and root mean square area roughness (S_q).



Figure 3.3 (a) Powder XRD diffractograms and (b) UV-vis absorption spectra recorded on $BiVO_4$ films coated on FTO glass before and after exposure to 20 h of UV curing. Diffraction signals attributed to FTO are indicated by black diamonds in (a).

3.2.2. Ultraviolet radiation on BiVO₄ photoanode enhances photoelectrochemical activity

The PEC current densities of the BiVO₄ photoanodes cured by UV radiation for 0 (control), 5 and 20 h in air were then measured, in the dark and under AM1.5 front-side illumination, in a three electrode cell containing a 0.1 M potassium phosphate solution buffered to pH 7 (KPi) (Figure 3.4a). The films that were not exposed to UV radiation displayed an onset potential of 0.65 V vs RHE and a current density of 1.0 mA/cm² at 1.52 V vs RHE. While this electrocatalytic response is commensurate with previously reported BiVO₄ films,⁴⁴ progressively larger cathodic shifts in onset potentials were measured as the films were exposed to increasing durations of UV curing: The potential required to reach a photocurrent of 1 mA/cm² was reduced to 1.12 V vs RHE after 20 h of UV curing. This ~400-mV reduction in overpotential is striking in that it is comparable to the effects of metal oxide co-catalysts deposited on BiVO₄ (e.g., 440 mV for Co-Pi on BiVO₄).⁴⁴ The photocurrent densities progressively increase with UV radiation exposure times up to 20 h, with nominal differences over the next 10 h of photolysis (Figure A3.1). Notably, this enhancement of photocurrent is stable after the cured BiVO₄ samples are kept in air and open circuit condition in KPi solution (Figure 3.5a).



Figure 3.4 (a) Dark current (dashed) and photocurrent (solid; AM1.5 front-side illumination) densities of BiVO₄ photoanodes after being subjected to 0 (black), 5 (blue), and 20 (orange) hours of UV curing. Data was recorded in a three-electrode cell in KPi buffered solutions (pH 7). (b) Open-circuit potentials (V_{OC}), measured in the dark (black) and under AM1.5 illumination (red), of BiVO₄ photoanodes before and after 20 h of UV curing. The values indicated correspond to the photovoltages generated by BiVO₄, calculated by the difference of V_{OC} between dark and illumination conditions.



Figure 3.5 (a) Photocurrent (AM1.5 front-side illumination) densities of $BiVO_4$ photoanodes after being subjected to 0 (black), 20 (red) h of UV curing, and then being kept in air for 5 days (green), in open circuit (OC) condition in KPi solution for 20 h (blue). (b) Anode stability under 1.5 AM illumination of $BiVO_4$ with 0 h (a) and 20 h (b) exposure to UV radiation, measured at 1.23 V vs. RHE in KPi buffered solution (pH 7) for 6000 s.

The dark currents of the water oxidation reaction are suppressed after UV curing (Figure 3.3a inset and Figure 3.6d), an observation consistent with a lower number of electrochemically active sites on the surface; this conclusion is corroborated by the less textured surface in SEM images. The charging currents are also suppressed after photolysis (Figure 3.6), consistent with the lower specific surface area indicated by SEM and AFM. On this basis, I rule out the enhancement of photocurrent densities of the cured films being a result of a higher concentration of active sites or a larger specific surface area. The measured photovoltages increase from 0.17 V to 0.41 V after 20 h of UV curing (Figure 3.4b), and the photovoltages measured in the presence of H_2O_2 , which is capable of proceeding through more facile oxidative chemistry than water, also displayed a ~230-mV cathodic shift in onset potential (Figure 3.7a). These collective data indicate that the cathodic shift is due to a larger photovoltage emanating from a shift in flat-band potential upon UV curing, and not electrocatalytic efficacy.⁹⁸



Figure 3.6 Cyclic voltammetry (recorded in the dark) for $BiVO_4$ (a) before and (b) after 20 h of UV radiation at different scan rates (5, 10, 20, 50, 100, 200 mV/s) show no enhancement of charging current during photolysis. (c) Charging current densities of $BiVO_4$ at different scan rates; the slope reflects the capacitance, which is proportional to the specific surface area. (d) Cyclic voltammetry with a scan rate of 10 mV/s.



Figure 3.7 (a) Photocurrent densities of $BiVO_4$ photoanodes, before and after exposure to 20 h of UV curing, in KPi buffered solutions (solid) and after the addition of 0.1 M H₂O₂ (dashed). (b) Photocurrent transients measured at 1.23 V vs. RHE of $BiVO_4$ before (black, solid) and after (orange, solid) UV curing in KPi. Data for the sample not exposed to UV curing measured in a KPi solution containing H₂O₂ is also shown (black, dashed).

Recombination at the BiVO₄ surface was interrogated by measuring the photocurrent transients of BiVO₄ photoanodes at 1.23 V vs. RHE (Figure 3.7b). Temporal measurements in KPi solutions show a sharp spike in photocurrent, consistent with an accumulation of photo-generated holes at the photoanode/electrolyte interface, followed by a slow decay induced from charge recombination.⁴⁴ The spikes in current are suppressed in the presence of H_2O_2 due to the lower activation barrier associated with mediating the reaction. This behaviour is different after UV curing, where photocurrent density in KPi of ~1.2 mA/cm² is twice that measured for the films not exposed to UV curing (Figure 3.7b). These photocurrents are stable in 2 h (Figure 3.5b). Moreover, the photocurrent transient profile reveals a significant diminution in current spikes that point to a reduction in surface recombination processes being responsible for the enhanced PEC activity.

3.2.3. Surface states of BiVO₄ photoanode are removed by ultraviolet radiation

Electrochemical impedance spectroscopy (EIS) was measured on the BiVO₄ before and after 20 h of UV curing to better characterize the surface chemistry. Nyquist plots recorded at potentials of 0.5, 0.7 and 0.9 V vs RHE (Figure 3.8a; plots recorded under the full potential range are shown in Figure A3.2) reveal two semicircles at lower potentials, where the second is diminished at higher potentials. These features have been modeled to an equivalent circuit model (Figure 3.8a inset),⁹⁹ where the first semicircle is ascribed to bulk processes and the second to surface processes. The capacitance of the bulk solid, C_{bulk} , follows the regulation of depletion layer capacitance¹⁰⁰ while the second capacitance value, C_{ss} , progressively increases over the 0.5-1.1 V range (Figure 3.8b, the substantial increase in photocurrent does not commence until the surface state resistance is lowered to some extent, pointing to the increase in photocurrent being regulated by the energy barrier associated with the surface states.



Figure 3.8 (a) Nyquist plots of BiVO₄ with 0 h (dashed) and 20 h (solid) UV curing under 0.5 V (black), 0.7 V (orange) and 0.9 V (blue) vs RHE. The first and second semicircles correspond to the bulk (R_{bulk} and C_{bulk}) and surface states (R_{ss} and C_{ss}) shown in the inset image of equivalent circuit model, respectively. (b) Resistance-potential plots of the bulk BiVO₄ (R_{bulk} , triangles) and surface states (R_{ss} , circles) with 0 h (black) and 20 h (orange) UV curing, and the current densities-potential curve of PEC water oxidation.

Mott-Schottky plots prepared from C_{bulk} values of EIS spectra, which exhibit slopes that are inversely proportional to the charge carrier densities,^{100,102} show a strikingly lower slope for the photolyzed photoanodes relative to those not exposed to light (Figure 3.9a). The photolysis treatments leading to a higher charge carrier density (1.4×10^{20} cm⁻³ to 1.9×10^{21} cm⁻³) is corroborated by the diminution in resistance (Figures 3-8). The flat band potential (E_{fb}) of BiVO₄ extracted from the *x*-axis intercept of the Mott-Schottky plots is negatively-shifted by 0.25 V after 20 h of UV exposure. This value corresponds reasonably closely to the cathodic shift of onset potential measured in KPi/H₂O₂ (0.23 V, Figure 3.7a). (Note that Mott–Schottky plots derived from C_{bulk} values of EIS spectra are known to be positively shifted relative to idealized V_{fb} values.^{100,103}) A more negative flat band potential provides a higher quasi-Fermi level of electrons ($E_{F,n}$) that drives a greater separation with the quasi-Fermi level of holes ($E_{F,p}$), that leads to a difference of photovoltage generation (0.24 V, Figure 3.4b). A qualitative energy level diagram summarizing the potential shifts and photovoltage generation is provided in Figure 3.10.



Figure 3.9 (a) Mott-Schottky plots of BiVO₄ with 0 h (black) and 20 h (orange) UV curing. The intercepts on X-axis represent the flat band potentials and the slopes are inversely proportional to the charge carrier densities. (b) O 1s and V 2p peaks of BiVO₄ with 0 h (black) and 20 h (orange) UV curing in XPS spectra normalized to V $2p_{3/2}$ signal. The inset images represent the possible structures of crystalline oxygen (530.3 eV) and oxygen-based defect sites (532.3 eV) on the surface. The red spheres represent O atoms and gray spheres represent V atoms.



Figure 3.10 Band gap structures of BiVO₄ with 0 h (black) and 20 h (red) exposure to UV radiation. Gray and black lines show the band edges in dark and under AM 1.5 illumination, respectively. The shift of the conduction band edges (0.23V) represents the negative shift of flat band potential in Figure 3.7a. The quasi Fermi levels of holes ($E_{F,p}$) and electrons ($E_{F,n}$) are measured by the open-circuit potentials under AM 1.5 illumination and in the dark, respectively, and the difference between the two quasi Fermi levels is the photovoltage (V_{ph}).⁶

The foregoing data suggest that passivation of surface states by UV curing is responsible for the lower onset potentials. I therefore set out to gain structural information of the surface by examining the films by X-ray photoelectron spectroscopy (XPS; Figure 3.9b). The spectra obtained on the samples before and after curing contained the signature oxygen 1*s*, vanadium 2*p* (Figure 3.9b), and bismuth 4*f* (Figure A3.4) signals. While the vanadium and bismuth signals displayed no changes before and after photolysis, the oxygen 1*s* spectroscopic signals were affected. The oxygen 1*s* peaks at 530.3 eV and 532.3 eV have been ascribed to lattice oxygen and non-uniform surface sites (such as dangling oxygen), respectively (Figure 3.9b).^{104,105} It has been purported that the peaks at ~532 eV correspond to defect sites (e.g., dangling oxo or hydroxyl groups) at the surface.^{105–107} These are believed to introduce half-filled energy states in the band gap that result in a trapping of charges on the interface of electrode/electrolyte and a Fermi level pinning effect. This situation leads to a lower charge carrier density (Figure 3.9a). It also consumes of external bias by the surface states (in addition to the depletion layer ^{98,100,103}), which is

corroborated by the high onset potential in H_2O_2 (Figure 3.7a). The non-uniform surface sites were confirmed by high-resolution transmission electron microscopy (HRTEM),¹⁰⁸ with a higher level of crystallinity being observed on the film after 20 h of photolysis (Figure 3.11).



Figure 3.11 High-resolution transmission electron microscopy (HRTEM) images of $BiVO_4$ (a) before and (b) after being subjected to 20 h of UV irradiation to highlight the higher crystallinity after photolysis. The fringe spacing of 0.26 nm is ascribed to (200) lattice plane of $BiVO_4$.

Table 3.1 Relative contents of Bi and O atoms at the surface before and after 20 h UV radiation. The data

 was based on the integration of XPS peaks.

UV radiation time	Atom % of Bi 4 <i>f</i>	Atom % of O 1s	Ratio of O:Bi
0 h	8.00	48.84	6.105
20 h	9.29	39.71	4.274

This 532.3-eV XPS signal was significantly diminished for the photolyzed film (Figure 3.9b), and the ratio of O and Bi atoms at the surface also decreased significantly after UV radiation (from 6:1 to 4:1; Table 3.1), offering direct evidence that UV light has induced a process that has reduced the number of
oxygen atoms. This atomic rearrangement not only releases the charges trapped in the surface states, and thusly a higher charge carrier density in Mott–Schottky plots (Figure 3.9a), but also minimizes potential loss at the surface to require a relatively lower bias to drive water oxidation.

3.3. Conclusion

This chapter shows that UV curing of the BiVO₄ photoanode leads to a marked improvement in OER PEC properties. The exposure to UV radiation is found to diminish the number of defect sites at the surface (possibly dangling oxygen centers) that are purported to be deleterious to PEC performance. This structural arrangement is corroborated by SEM images that show distinctive morphologies before and after photolysis that reflect surface chemistry. An important outcome of this study is that UV photolysis of bare BiVO₄ yields a cathodic shift in onset potential and corresponding photocurrent enhancement that is comparable to the effect of coating photoanodes with cocatalysts. This finding may prove useful in resolving the mechanism of action for composite electrodes in photoelectrocatalysis schemes.

3.4. Experimental details

3.4.1. Materials

Bismuth nitrate hexahydrate (98%, Strem Chemicals), vanadyl acetylacetonate (98%, Strem Chemicals) tungsten hexachloride (99.9%, Strem Chemicals), acetic acid (99.7%, Fisher Scientific) acetylacetone (99.5%, Sigma Aldrich) were used as received.

3.4.2. Electrode preparation

Photoanodes of BiVO₄ were prepared according to a previously documented metal-organic decomposition method.⁴⁴ Bismuth nitrate hexahydrate (0.346 g, 0.713 mmol), vanadyl acetylacetonate (0.176 g 0.663 mmol) and tungsten hexachloride (0.02 g, 0.05 mmol) were added to a 10-mL mixture of acetic acid and acetylacetone (1:8.25 v/v). The dark green solution was sonicated for 15 min and then

spin-coated onto an FTO substrate (TEC 15, Hartford Glass Co.) at 1000 rpm for 30 s. Each of the successive 16 coats was annealed at 500 °C for 10 min, with an 8-h annealing step at 500 °C for the last step. The photolysis protocol involved exposing the BiVO₄ samples, in transparent Petri dishes sealed by parafilm, to a UV lamp (Model#: GPH436T5VH, Atlantic Ultraviolet Co.; $\lambda_{max} \sim 254$ nm and 185 nm; flux = 0.12 mW/cm² at 1 m from lamp, ~10 mW/cm² at 5.5 cm in my experiment) for variable periods of time.

3.4.3. Physical methods

All PEC and photovoltage measurements were performed with a CHI 660D potentiostat in a three-electrode photoelectrochemical cell with the photoanode as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire mesh as the counter electrode (cell configuration is shown in Figure A3.5). Photoelectrochemical measurements were conducted under 1 Sun simulated sunlight with an Oriel 94011A-ES solar simulator integrating a 100-W Xenon arc lamp and AM1.5 filter. Experiments were performed in 0.1 M potassium phosphate (KPi) buffered to pH 7, unless otherwise stated. Potentials are reported as measured vs Ag/AgCl, and adjusted to vs RHE using the Nernstian relation $E_{RHE} = E_{Ag/AgCl}$ + 0.0591 pH + 0.166 V. For the dark and photocurrent measurements, linear sweep voltammetry (LSV) was used and the scan rate was maintained at 10 mV/s. For photovoltage measurements, dioxygen was bubbled into the electrolyte and each open circuit potential was read after a stabilization time of 30 min with magnetic stirring. Electrochemical impedance measurements were performed for a frequency range from 1000000 Hz to 0.1 Hz with 5 mV oscillation amplitude. Film morphologies were investigated using a Helios NanoLab 650 Focused Ion Beam Scanning Electron Microscope (SEM), with the accelerating voltage kept at 1 kV and the current at 50 pA for imaging. X-ray diffraction (XRD) characterization was conducted using a Bruker F8 Focus X-ray diffractometer. Data were collected between 2θ angles of 5° and 90° with a step size of 0.04° and the step time was 0.6 s. Atomic Force Microscopy (AFM) was performed in non-contact dynamic mode on Nanosurf EasyScan 2 Atomic Force Microscope. The UV-vis absorptivity data was collected with a PerkinElmer Lambda 35 UV/Vis spectrometer with a solid sample holder accessory. Baseline scans were recorded on clean FTO. X-ray photoelectron spectroscopy (XPS) data were collected on a Leybold MAX200 spectrometer using Mg K α radiation. The pass energy used for the survey and narrow scans were 192 eV and 48 eV, respectively. High Resolution Transmission Electron Microscopy (HRTEM) was performed on an FEI Tecnai G2 200kV Transmission Electron Microscope with a LaB6 emitter. The camera used for the HRTEM images was an FEI Eagle 4K CCD camera. To prepare samples for HRTEM, BiVO₄ samples were put into ethanol and ultrasonicated for 1 h to remove BiVO₄ from the FTO.

Chapter 4: Photoelectrochemical Oxidation of Organic Substrates in Organic Media

4.1. Introduction

As mentioned in Chapters 2 and 3, interfacial photoelectrochemistry at a semiconductor-liquid junction enables the direct conversion of light into chemical energy. The highly energetic electrons and holes that are created through the absorption of visible light by semiconducting electrodes are capable of driving the energetically demanding conversion of water into oxygen and hydrogen fuels.^{5,6,14} While there has been a large global effort to reduce the relatively large energy losses associated with producing oxygen at the anode, including the UV-curing strategy in Chapter 3, strikingly few photoanodes are known to be capable of both absorbing incident sunlight and mediating efficient and sustained water oxidation catalysis.^{38,45,46,98,109}

The technical challenges of using a photoanode to form dioxygen that has little economic value provides the imperative to explore alternative reactions that generate higher value products with lower energy input. Choi and coworkers recently demonstrated that the photoelectrochemical oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid could be realized with a BiVO₄ photoanode in the presence of a redox mediator.¹⁸ A key challenge of this distinctive approach, however, is that the aqueous medium limits the scope of chemistry available and induces high rates of BiVO₄ photocorrosion.^{39,41} While photocorrosion in H₂O can be suppressed by a protective (electrocatalytic) layer (e.g., CoO_x, NiO_x, FeO_x),^{37,39,40,110} these layers tend to suppress the oxidation of organic compounds in favor of competitive oxygen evolution.^{18,111}

I therefore set out to explore conditions where the photoelectrochemically-driven oxidation of organic compounds in non-aqueous media could be achieved. Two classes of well known organic transformations were chosen to test this concept: alcohol oxidation and the much more challenging C–H functionalization/oxidation (Figure 4.1). The oxidation of alcohols can be readily achieved using chemical

oxidizing agents that include transition metals, hypervalent iodine reagents, and activated sulfur transformations.^{112,113} Some of these alcohol oxidation reactions have also been conducted using an electrode,^{54,55,114} photo-oxidized dyes immobilized on TiO₂,¹¹⁵ and, as mentioned above, a photoanode.¹⁸ The activation and subsequent functionalization of C–H bonds is a greater challenge.¹¹⁶ The respective transformation of olefin and alkylbenzene compounds into α , β -unsaturated and aryl ketones, for example, usually requires toxic reagents (e.g., CrO₃, SeO₂) and/or expensive metal catalysts (e.g., Rh, Pd),^{116,117} but allylic C–H oxidation can also be driven electrochemically at a carbon electrode.^{71,118} Note that the electrochemical study by Baran and coworkers was performed in non-aqueous media, thereby enabling them to oxidize a large set of substrates with reasonable yields (40-90%).⁷¹



Figure 4.1 Summary of reaction conditions for alcohol oxidation and C-H functionalization. Three types of reaction conditions (chemical oxidation, electrochemical oxidation at an electrode,^{54,55,71,114} and photoelectrochemical oxidation ¹⁸) that have been used for alcohol oxidation and C–H functionalization are shown. I report here C–H functionalization and oxidation by PEC.

I report here the use of a PEC cell to mediate organic oxidation reactions using a photoanode immersed in organic media. The photoelectrochemical oxidation of benzyl alcohol, cyclohexene, and tetralin into their corresponding carbonyl compounds were demonstrated in a PEC cell containing a BiVO₄ photoanode immersed in MeCN containing appropriate reaction mediators (e.g., electrolyte, base, electron transfer reagent). Product formation can be achieved using a 60% reduction in the applied voltage compared to a purely electrochemical oxidation. Furthermore, no significant degradation of the photoanode was observed.

4.2. Results and discussions

4.2.1. Photoelectrochemical stability of BiVO4 in non-aqueous media

The BiVO₄ photoanodes used in this chapter were synthesized in accordance with Chapter 4. Appropriate stoichiometric amounts of bismuth nitrate hexahydrate and vanadyl acetylacetonate precursors dissolved in a solution of acetic acid and acetylacetone were spin-coated onto fluorine-doped tin oxide (FTO), annealed at 500 °C, and then subjected to UV irradiation ($\lambda_{max} \sim 185$ and 254 nm, flux $\sim 10 \text{ mW cm}^{-2}$) in air for 20 h. This UV radiation step renders higher activity for aqueous PEC.^{2,119} The UV-vis absorption spectra and surface morphology of the films are consistent with previous descriptions of BiVO₄ prepared by this protocol (Figures 4.2 and 4.3).^{2,44}



Figure 4.2 Demonstration of lower BiVO₄ photocorrosion in MeCN than in H₂O. (a) UV-vis absorption spectra of BiVO₄ photoanodes before (black) and after 96 h of PEC in H₂O (blue) or MeCN (orange). (b) Photocurrents of BiVO₄ photoanodes before (solid line) and after (dashed line) 96 h of PEC electrolysis in H₂O (blue) or MeCN (orange).

The photoelectrochemical stability of BiVO₄ in aqueous and non-aqueous media was tested by measuring the absorptivity changes before and after 96 h of illumination under an applied potential. The photoanodes were immersed in 25 mL H₂O containing 0.1 M NaHCO₃ or 25 mL MeCN with 0.1 M LiClO₄ and exposed to simulated AM1.5G sunlight for 24 h and an applied potential of 0.1 or 1.6 V, respectively (all potentials reported herein are referenced against Ag/AgCl). The anodes were then left in solution in the dark for 24 h at open-circuit prior to a subsequent 24 h of PEC electrolysis at these same potentials. UV-vis absorption spectra of the photoanodes recorded after four successive cycles in H₂O (i.e. \sim 96 h of cumulative exposure to PEC conditions) showed a much more significant reduction in intensity over the 400-600 nm range than those in MeCN (Figure 4.2a). This reduced absorptivity is consistent with a decrease in $BiVO_4$ film thickness, while the nominal changes in absorptivity of the photoanode in MeCN after PEC indicate insignificant photocorrosion. The solvent-dictated differences in photoanode stability were corroborated by photocurrent measurements of BiVO₄ before and after PEC in both solvents (Figure 4.2b): The anode tested in H₂O exhibited a striking drop in photocurrent after 96 h of PEC electrolysis whereas the photocurrents recorded in MeCN did not change. The photoanodes tested in MeCN with increasing amounts of water also showed an increasing propensity for photocorrosion (Table 4.1).

Table 4.1 Relative decay of photocurrents (measured at 1.2 V vs Ag/AgCl) of BiVO₄ after 96 h of PEC electrolysis in a mixture of H₂O and MeCN.

H ₂ O:MeCN	Relative decay of photocurrent		
0:10	7%		
1:9	18%		
2:8	21%		
3:7	26%		
10:0	56%		

The accelerated photocorrosion of BiVO₄ in H₂O was confirmed by scanning electron microscope (SEM) images of photoanodes before and after 96 h of PEC. Full coverage of FTO by spherical grains of BiVO₄ (Figure 4.3) are retained for the photoanodes subjected to 96 h of PEC electrolysis in MeCN, with visible FTO providing evidence for less uniform coverage in films exposed to aqueous PEC. This morphology change during PEC electrolysis in H₂O is widely known.^{39,40} While organic solvents increase the resistance of the PEC cell (~ 10-20 Ω with MeCN *c.f.* <10 Ω using water), merely ~ 30 mV in additional voltage is required at the low currents (~ 3 mA) relevant to this study. This is a modest energy penalty for the much higher photoanode stability.



Figure 4.3 SEM images before and after 96 h PEC electrolysis of H_2O , MeCN or tetralin show full surface coverage of BiVO₄ on FTO before PEC and after PEC electrolysis of MeCN, and more surface corrosion of BiVO₄ after PEC electrolysis of H_2O relative to tetralin.

4.2.2. Photoelectrochemical alcohol oxidation

Having validated the photostability of BiVO₄ in MeCN, I tested the oxidation of organic substrates using a PEC cell. All experiments were carried out in MeCN containing LiClO₄ electrolyte. Other organic solvents (e.g. acetone and CH₃NO₂) and electrolytes (e.g. Bu₄NClO₄ and Bu₄NPF₆) were tested but did not yield any discernible benefit in photocurrent or product yield. MeCN was utilized as the solvent because because the boiling point (82 °C) is sufficiently high to minimize evaporation during electrolysis and sufficiently low to circumvent interfering with the GC-MS analysis. LiClO₄ was selected on the basis of it being a cheap electrolyte that is soluble in organic media.

Linear sweep voltammetry (LSV) was measured under AM1.5G light prior to performing PEC electrolysis (Figure 4.4). Photocurrent profiles recorded on the BiVO₄ working electrode in 25 mL of

MeCN containing 0.1 M LiClO₄, a glassy carbon counter electrode, and an Ag/AgCl reference electrode generated nominal current below *ca.* 1 V. For each of the organic reactions in this study, pyridine served as the requisite base to accommodate deprotonation of *N*-hydroxysuccinimide (NHS), a soluble, transparent, and electrochemically active species that proved effective at mediating hole transfer from the electrode to the organic substrate. Baseline photocurrent profiles were measured prior to addition of 0.5 mmol of substrate: 4 equiv. pyridine (162 μ L; 2 mmol) caused a small but detectable change in LSV photocurrent below 1 V (Figure 4.4), while the subsequent addition of 40 mol% NHS (23 mg; 0.2 mmol) caused a more dramatic rise in current. The shoulder at 0.8 V (indicated by the vertical dashed lines in Figure 4.4) is assigned to the oxidation of NHS⁻ to electrochemically-active NHS[•].¹²⁰ All organic oxidation reactions in this report were therefore carried out under an applied voltage of 0.8 V (denoted V_{app}), which is sufficiently low to avoid solvent and pyridine oxidation yet sufficiently positive to generate the NHS[•] species required for oxidation of the organic substrates.



Figure 4.4 LSV curves of PEC organic oxidation profiles. Photocurrents correspond to PEC oxidations of (a) benzyl alcohol to benzaldehyde, (b) cyclohexene to cyclohexanone, and (c) tetralin to 1-tetralone using a BiVO₄ photoanode immersed in 25 mL MeCN containing 0.1 M LiClO₄ and subjected to AM1.5G light (scan rate = 10 mV/s). Photocurrent profiles correspond to the solvent and electrolyte solution (black) after the successive addition of 2 mmol pyridine (green), 0.2 mmol NHS (orange), 1.5 mmol of 'BuOOH (red) and 0.5 mmol of the respective substrate (blue). The reaction yields determined by GC-MS are indicated. The dashed line indicates the NHS⁻ \rightarrow NHS[•] oxidation; this potential was used as the applied voltage, V_{app} , for PEC electrolysis experiments.

The facile oxidation of benzyl alcohol to benzaldehyde was selected as a proof-of-concept experiment because alcohol oxidation was previously shown to proceed at a BiVO₄ photoanode in H_2O .¹⁸ The photocurrent increased after the addition of 0.5 mmol benzyl alcohol to the PEC cell described above (Figure 4.4a). This increase is assumed to be due to the consumption of NHS[•] (which oxidizes benzyl alcohol) driving a faster NHS⁻ oxidation. The oxidation of benzyl alcohol into benzaldehyde was confirmed by gas chromatography-mass spectrometry (GC-MS), with a reaction yield of 41% after 8 h of PEC electrolysis (Figure A4.1). While further optimization is still needed to make the yield of benzaldehyde competitive with the best available synthetic methods, the result demonstrates the viability of performing PEC in a non-aqueous medium. These experiments also demonstrate that NHS can act as a useful redox mediator in tandem with a BiVO₄ photoanode.

4.2.3. Photoelectrochemical C-H oxidation

With evidence of a successful photoelectrochemical oxidation in non-aqueous media, I next explored the more synthetically challenging oxidation of cyclohexene to cyclohexenone (Figure 4.4b) and tetralin to 1-tetralone (Figure 4.4c). In addition to using NHS as a redox mediator, an external oxygen source, *tert*-butyl hydroperoxide ('BuOOH), is used to form the requisite 'Bu peroxide-substrate adduct.⁷¹ (Figure 4.5) Prior to addition of 0.5 mmol of substrate, 3 equiv. of 'BuOOH were shown to produce larger photocurrents than what was measured for pyridine, presumably due to the oxidation of 'BuOOH. The PEC electrolysis experiments afforded cyclohexanone from cyclohexene (38% yield after 8 h, Figure A4.2) and 1-tetralone from tetralin (75% yield after 24 h; Figure 4.5). The conversions were quantified by GC-MS to confirm 93% conversion of tetralin to 1-tetralone, which is corroborated with the coulombic charge passed through the PEC cell (Figures 4.5). The BiVO₄ photoanodes after 96 h of PEC with substrate exhibit minor differences in absorptivity and LSV photocurrents consistent with negligible photocorrosion (Figures 4.3 and Figure 4.6), but not to a degree that compromises these experiments.



Figure 4.5 (a) GC-MS traces of PEC oxidation of tetralin into 1-tetralone. Carvone was used as the internal standard. (b) Relative concentrations of tetralin (blue) and 1-tetralone (orange), and charges passed through the PEC cell (black) during the PEC oxidation of tetralin. Concentrations were quantified by internal standard calibration on GC-MS.



Figure 4.6 (a) UV-vis absorption spectra for $BiVO_4$ photoanodes before (black) and after 96 h of PEC electrolysis of tetralin (orange) or H_2O (blue). (b) Photocurrents of $BiVO_4$ photoanodes before (solid line) and after 96 h (dashed line) of PEC electrolysis of tetralin (orange) or H_2O (blue).

The PEC oxidations of each of the compounds appear to be mediated by NHS. In each of these schemes, a quasi-static equilibrium of photo-generated electron and hole populations leads to the separation of the BiVO₄ Fermi level (E_F) into quasi-Fermi levels for electrons ($E_{F,p}$) and holes ($E_{F,p}$).⁶ The

difference between these two quasi-Fermi levels represents the photovoltage (V_{ph}), which serves to reduce the applied voltage (V_{app}) required to drive the reaction. The interfacial chemistry is then driven by the oxidation of deprotonated NHS to form NHS[•], which reacts with the substrate. (Control experiments ruled out a meaningful rate of oxidation without NHS; the replacement of NHS with *N*methoxysuccinimide, which is not able to generate a radical, also did not show reactivity.) In the case of tetralin (a conjectured mechanism for tetralin photooxidation is provided in Figure 4.7), NHS[•] abstracts a hydrogen atom from tetralin to ostensibly form a stable benzylic radical species that ultimately leads to a peroxide intermediate that eliminates 'BuOH to yield 1-tetralone. The reductive chemistry at the cathode is assumed to involve pyridinium. This proposal is in line with known chemistry,⁷¹ but experiments are underway to validate the proposed reaction steps and energetic profiles for each of these reactions.



Figure 4.7 Proposed mechanism of PEC oxidation of tetralin in MeCN. $E_{F,n}$ and $E_{F,p}$ = quasi-Fermi levels of photo-generated electrons and holes, respectively; V_{ph} = photovoltage; V_{app} = external voltage applied. It is likely that the reaction proceeds through a cationic intermediate (pathway 2), however, I cannot rule out the possibility of a pure radical mechanism (pathway 1) for the oxidation process.

4.2.4. Voltage reduction provided by photoelectrochemical cell

I also quantified the electrical energy savings provided by AM1.5G light for the oxidation of tetralin in the PEC cell versus an electrochemical (EC) cell with a glassy carbon electrode (Figure 4.8). The oxidation of NHS⁻ to NHS[•] was measured at 0.8 V and 1.8 V for the PEC and EC cell, respectively. These potentials each produced currents of ~ 3.8 mA and thus similar 75% yields of 1-tetralone after 24 h of (photo)electrolysis (Figure A4.3a). This comparison indicates that illumination of the PEC cell enables V_{app} to be reduced by 1 V compared to that of the EC cell corresponding to a 60% reduction in energy savings.



Figure 4.8 Contrasting the photoelectrochemical and electrochemical oxidation processes. The NHSmediated oxidation of tetralin in a PEC cell (orange) is cathodically shifted by 1 V compared to an electrochemical cell (EC; blue). The (photo)currents measured after adding pyridine and NHS to MeCN are denoted NHS, while the (photo)currents measured after adding 'BuOOH and tetralin are denoted tetralin. The shoulder at 0.8 V and peak at 1.8 V (dashed lines) are attributed to the oxidation of NHS⁻ to NHS[•] under PEC and EC conditions, respectively.

The solar-to-electricity efficiency (η_{STE}) of traditional PEC water oxidation can be calculated by the following relationship: $\eta_{\text{STE}} = J^*(1.23 \text{ V} - V_{\text{app}}) / P_{\text{in}}$, where J = photocurrent density, 1.23 V = E^o (O₂/H₂O), $V_{\text{app}} =$ applied potential in the PEC cell, and $P_{\text{in}} =$ power density of illumination (100 mW cm⁻²) in this study). State-of-the-art BiVO₄ photoanodes ⁴⁵ that mediate PEC water oxidation at a V_{app} of 0.6 V generate J = 2.73 mA cm⁻² and therefore yield $\eta_{STE} = 1.7\%$. In my experiments in MeCN, the PEC cell was driven at 0.8 V to produce J = 3.8 mA / 3 cm² = 1.3 mA cm⁻². Given that my EC cell required 1.8 V to yield the same J value of 1.3 mA cm⁻², I assumed 1.8 V to effectively be the pseudo standard potential of NHS. Given that my illuminated photoanode area was 3 cm² and my light intensity was 100 mW cm⁻², the η_{STE} of my cell is therefore 1.3%. This analysis shows that my PEC organic oxidation system offers high-valued organic products at approximately the same energy efficiency as traditional PEC water oxidation.

4.3. Conclusions

In summary, I have demonstrated that illumination of BiVO₄ immersed in organic media drives both alcohol oxidation and C-H activation/oxidation. The use of light can reduce the applied voltage of an electrochemical oxidation process by 1 V. The use of organic media in place of water affords markedly higher semiconductor photostability, thereby enabling sustained photochemical conversion over at least one day. This alternative PEC cell design highlights the potential to generate higher-value small molecules compared to traditional PEC cells.

4.4. Experimental details

4.4.1. Materials

Bismuth nitrate hexahydrate (98%), vanadyl acetylacetonate (98%), and tungsten hexachloride (99%) were purchased from Strem Chemicals and used as received. All other chemicals were purchased from commercial vendors (Acros Organics, Alfa Aesar, Fisher Scientific, or Sigma-Aldrich) and used as received. Fluorine-doped tin oxide (FTO) substrates (TEC 15) were purchased from Hartford Glass Co. Glassy carbon electrodes were purchased from Alfa Aesar.

4.4.2. Electrode preparation

BiVO₄ photoanodes were prepared in accordance with previous reported procedures.^{2,44} Bismuth nitrate hexahydrate (0.346 g, 0.713 mmol), vanadyl acetylacetonate (0.176 g 0.663 mmol) and tungsten hexachloride (0.02 g, 0.05 mmol) were added to a 10 mL mixture of acetic acid and acetylacetone (1:8 v/v). The solution was sonicated for 15 min and then spin-coated onto a FTO substrate at 1000 rpm for 30 s. Each of the successive 16 coats was annealed at 500 °C for 10 min prior to a final 8 h annealing step at 500 °C. The BiVO₄ samples were irradiated with UV light (Model #: GPH436T5VH, Atlantic Ultraviolet Co.; $\lambda_{max} \sim 254$ nm and 185 nm; flux ~ 10 mW cm⁻² at 5.5 cm in my experiment) for 20 h. The geometric surface areas of all working electrodes (BiVO₄ photoanodes and glassy carbon electrodes) in this study were 3 cm².

4.4.3. Photoelectrochemical and electrochemical oxidation

PEC and EC electrolysis were performed with a CHI 660D potentiostat in a three-electrode photoelectrochemical cell with a BiVO₄ photoanode (for PEC experiments) or glassy carbon (electrochemistry experiments) as the working electrode, Ag/AgCl as the reference electrode, and glassy carbon as the counter electrode. PEC measurements and electrolysis were conducted under AM1.5G simulated sunlight with an Oriel 94011A-ES solar simulator integrated with a 100-W xenon arc lamp and AM1.5G filter. An infrared water filter was applied to prevent the solution from heating up during PEC electrolysis. Experiments were performed in 0.1-M LiClO₄ in 25 mL MeCN or 0.1-M NaHCO₃ in H₂O (buffered to pH 7). Potentials were measured vs Ag/AgCl, which was calibrated to 0.196 V vs NHE in aqueous media. For the dark and photocurrent measurements, linear sweep voltammetry (LSV) was measured prior to performing electrolysis, and the scan rate was maintained at 10 mV/s. For PEC and EC oxidations of organic substrates: pyridine (2 mmol, 4 equiv.), *N*-hydroxysuccinimide (NHS, 0.2 mmol, 40 mol%), 'BuOOH (70% in H₂O, 1.5 mmol, 3 equiv. for cyclohexene and tetralin oxidations) and substrate (0.5 mmol, 1 equiv.) were added successively to a 0.1-M LiClO₄ solution in 25 mL MeCN. Control experiments were performed under the same condition, except that each of the said reagents was added in

exclusivity. PEC/EC electrolysis was performed at room temperature, using a constant potential method (0.8 V and 1.8 V vs Ag/AgCl for PEC and EC electrolysis, respectively) with magnetic stirring.

4.4.4. Product analysis

Samples were taken during and after electrolysis and carvone was added as an internal standard. GC-MS measurements were run on an Agilent GC-MS instrument with a HP-5ms GC column and electron ionization (EI) ion source. A 1-µL aliquot was injected with an auto-sampler using split mode with a split ratio of 20:1, and carried by He gas at a flow rate of 1 mL/min. The oven temperature started at 60 °C for 1 min, then ramped from 100 to 150 °C at 20 °C/min and from 150 to 250 °C at 40 °C/min. Detection was not performed for the first 1.75 min of the run, or the solvent delay time. GC-MS peaks were identified using the NIST Mass Spectrometry Data Center database (all peak identifications exhibited a probability match of >90%) and compared with peaks in standard solutions. For quantitative analysis, a series of standard solutions with known concentrations of reactants and products were prepared and carvone was added as an internal standard. Standard solutions were normalized to the internal standard peak. Linear calibration curves were plotted to quantify the concentrations of reactants and products.

4.4.5. Physical methods

Absorptivity measurements of BiVO₄ samples were collected with a PerkinElmer Lambda 35 UV/Vis spectrometer with a solid sample holder accessory. Baseline scans were recorded on clean FTO. Film morphologies were investigated using a Helios NanoLab 650 Focused Ion Beam SEM, with the accelerating voltage kept at 1 kV and the current at 50 pA for imaging.

Chapter 5: Lignin Decomposition at a Photoanode

5.1. Introduction

Chapter 4 discussed using a photoanode to drive some relatively simple organic transformations (alcohol oxidation and C-H oxidation). In this chapter, I aim to apply this PEC organic chemistry to lignin decomposition, a more complicated organic transformation and generate products with higher commercial value. Lignin biomass, a complex bio-polymer which comprises ~25% of the mass of lignocellulose, is one of the most abundantly available raw materials on the planet.¹²¹⁻¹²⁴ However, 98% of the 50 million tons of lignin isolated from the pulp and paper industry each year is simply burned.^{122,124,125} The more effective utilization of lignin would represent a major step towards satisfying the urgent need to identify renewable sources of carbon.^{121,123,124} The catalytic decomposition of lignin into its small-molecule components has therefore emerged as a highly-promising avenue to generate valuable chemical feedstocks from biomass in a scalable and profitable manner.^{121,123,124,126}

Lignin biomass consists of complex three-dimensional networks that link different aromatic building blocks. A " β -O-4" bond, which represents >50% of the linkages between the building blocks in native lignin biomass,^{121–124} contains a secondary hydroxyl group on the α carbon, and a β carbon linked to the oxygen of the adjacent phenolic unit at the 4 position (Figure 5.1a). The majority of lignin decomposition studies therefore use the " β -O-4" unit as a model compound for examining how to cleave the C β -O and/or C α -C β bonds.^{121–126} A number of catalysts for the oxidative decomposition of such lignin model compounds under chemical and electrochemical conditions have been reported.^{121–124} A typical chemical lignin decomposition route (Figure 5.1b) involves the oxidation of the secondary alcohol to the ketone, followed by the cleavage of the high-energy C-O and/or C-C bonds mediated by a catalyst (e.g., iridium complexes,^{127,128} or formic acid¹²⁹). Single-step lignin decomposition strategies, which avoid the formation of the ketone intermediate, have been developed with the use of homogeneous vanadium^{130–132} or ruthenium^{133,134} catalysts. Single-step lignin decomposition has also been demonstrated electrolytically (Figure 5.1b) using electrocatalytic materials that include metal/metal oxide electrodes,^{135–138} iodide ions,¹³⁹ or *N*-hydroxyphthalimide¹⁴⁰. All current catalysis protocols for lignin degradation, however, are challenged by: (i) expensive and/or toxic metal complex catalysts; (ii) difficulties in catalyst separation from reaction mixtures; (iii) relatively low catalyst turnover numbers; or (iv) poor recyclability.^{126,141} The use of a photoelectrochemical (PEC) cell has the potential to mitigate these challenges by harnessing the reactive power of electricity and light towards chemical degradation on a heterogeneous surface. The PEC decomposition of lignin has, to my knowledge, not been previously documented.



Figure 5.1 (a) Representative fragment of lignin, highlighting the β -O-4 unit that constitutes more than 50% of the linkages in native lignin. (b) Previously reported strategies for lignin decomposition by chemical or electrochemical catalysts, including 2-step chemical decomposition,^{127–129} 1-step chemical decomposition^{130–134} and 1-step electrochemical decomposition.^{135–140} (R and R' can be one of number of different functional groups corresponding to various lignin model compounds.) I show in this work a 1-step photoelectrochemical decomposition strategy of alcohol lignin model compounds into aryl aldehyde and phenol derivatives using a photoanode in organic solvent.

As shown in Chapters 2-4, PEC systems provide a direct pathway to convert photons absorbed by a semiconductor into highly-energetic electrons and holes that can drive kinetically-demanding chemical transformations under ambient conditions.^{5,6,14} Water splitting, for example, is a well-studied target for PEC cells because there exists the potential to convert abundant solar electricity to hydrogen fuel.^{7–}

^{9,38,45,46,98} Despite the voltage savings that are offered by the light-absorbing semiconductor photoelectrode, this process remains challenged by the sluggish anodic kinetics intrinsic to the evolution of a dioxygen byproduct that ultimately holds little economic value.^{1,5,7,114,142} Efforts to overcome this challenge have provided the impetus to explore alternative PEC reactions at the anode that form products more valuable than dioxygen.^{1,6,12,143} Choi, for example, demonstrated anodic PEC oxidation of alcohols using a redox mediator and a BiVO₄ photoanode in aqueous media.¹⁸ my own studies in Chapter 4 demonstrated these reactions could also be performed in organic media, serving to expand the scope of possible PEC reactions (e.g., the oxidation of allylic and benzylic C-H bonds) and improve the lifetime of the photoanode.³ Known PEC organic oxidation chemistry has thus far been limited to simple chemical transformations (e.g., alcohol or C-H oxidations) used to generate products for which there is minimal large-scale demand.^{1,142}

The above observations prompted us to investigate the conversion of various lignin model compounds into low-molecular-weight aromatic chemicals in organic solvents using a PEC cell. The results presented herein demonstrate the viability of this strategy by using a BiVO₄ photoanode immersed in acetonitrile (MeCN). This system is able to catalyze the single-step decomposition of five different alcohol lignin models into aryl aldehyde and phenol derivatives with up to 50% degradation under AM 1.5 simulated sunlight irradiation and a constant applied potential of 2.0 V. No additional redox mediator is required to drive the decomposition of the lignin model compounds. This study constitutes the first report of a photoelectrocatalyst applied towards lignin decomposition.

5.2. Results and discussions

5.2.1. Photoelectrochemical decompositions of lignin models at BiVO₄ photoanode

BiVO₄ photoanodes were synthesized in accordance with Chapter 4. The lignin model compounds were synthesized by coupling 2-bromoacetophenone with the corresponding phenol derivative in the presence of potassium carbonate, followed by α -formylation and ketone reduction

(Scheme A5-1). The final lignin model compounds were characterized by ¹H and ¹³C NMR (see Appendix). Detailed experimental and synthetic procedures can be found in 5.4. and Appendix. The PEC decomposition of lignin model compounds were performed in a three-electrode cell with a BiVO₄ photoanode working electrode subjected to simulated AM 1.5 sunlight, a glassy carbon counter electrode and a Ag/AgCl reference electrode. All potentials reported in this paper are referenced against Ag/AgCl.

PEC decompositions of five alcohol lignin model compounds with different substitutional groups, 2-phenoxy-1-phenylethan-1-ol (1), 1-(4-methoxyphenyl)-2-phenoxyethanol (2), 2-phenoxy-1-1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol phenylpropane-1,3-diol (3), (4) and 2-(4methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (5) were successfully achieved at a $BiVO_4$ photoanode with degradation yields ranging between 12 and 47% (Figure 5.2). Yields of the aryl aldehyde products were used to reflect the extent of decomposition of lignin models (yields of phenol products and formic acid can be found in Table A5.1). In each experiment, one of the five lignin model compounds 1 to 5 (0.25 mmol) was added to 0.1 M LiClO₄ in 25 mL MeCN and subjected to a constant potential of 2.0 V with a BiVO₄ photoanode under simulated AM 1.5 sunlight. The reaction mixture after PEC electrolysis for 20 h was analyzed by GC-MS with carvone as an internal standard to quantify yields of products.

	P_{R_2} –	BiVO ₄ PEC 20 h R ₁	о н + но	() <mark>R</mark> 2 + НСООН
Lignin model compounds Degradation products				
Lignin model	R ₁	R ₂	R ₃	Degradation
1	Н	Н	Н	12 ± 1%
2	OCH_3	н	н	14 ± 1%
3	н	н	CH₂OH	38 ± 2%
4	OCH ₃	н	CH ₂ OH	41 ± 2%
5	OCH_3	OCH ₃	CH ₂ OH	47 ± 2%

Figure 5.2 Scope of BiVO₄-catalyzed photoelectrochemical (PEC) decomposition of five alcohol lignin models (**1-5**) carried out with a BiVO₄ working electrode under simulated AM 1.5 sunlight and a constant applied potential of 2.0 V, a glassy carbon counter electrode and Ag/AgCl as a reference electrode. Yields of the aryl aldehyde products (quantified by GC-MS) were used to measure the extent at which the lignin model compounds were degraded.

Lignin model compounds with no functionalization at the C β position (1 and 2) underwent conversion to the respective aryl aldehyde and phenol products with yields up to 14 ± 1% after 20 h PEC decomposition. The introduction of an electron-donating methoxy group at the R₁ position of 1 to give 2 had a nominal effect on the reactivity of the model.¹⁴⁴ Compounds containing a hydroxymethyl group at the C β position (i.e., **3-5**) were also tested for activity towards PEC decomposition. This functionalization is known to provide a better resemblance of a full lignin structure.^{121–124} These compounds demonstrated significantly enhanced decomposition yields between 38-47%. The introduction of methoxy groups at either the R₁ position (**4**) or the R₁ and R₂ positions (**5**) again served to enhance the reactivity of the lignin substrate towards PEC decomposition up to a maximum yield of 47 ± 2%. These collective results show the successful lignin decomposition achieved by applying PEC methodology on a BiVO₄ photoanode surface. Baseline cyclic voltammetry (CV) scans were recorded in 25 mL of MeCN containing 0.1 M LiClO₄ electrolyte and showed an onset potential at approximately 1.0 V and a photocurrent density of 0.6 mA cm⁻² at 2.0 V. This behaviour is consistent with my study of a BiVO₄ photoanode in MeCN (Chapter 4) and confirms the PEC activity of the BiVO₄ photoanode. The addition of ~0.25 mmol of a lignin model compound (1 to 5) caused a significant increase in photocurrent density. The addition of 4, for example, resulted in a photocurrent density of 2.8 mA cm⁻² at 2.0 V (Figure 5.3a). The redox peak observed at 1.8 V is likely due to the oxidation of hydroxyl groups in the lignin model substrate.¹²⁸ This increase in photocurrent density measured with the lignin model compound *versus* the background indicates viable electron transfer between the illuminated BiVO₄ photoanode and lignin model compound without the need for a redox mediator in solution. Figure 5.3b shows the decomposition of 4 over the 20 h experiment (yields of aryl aldehyde product was used to represent the decomposition extent), confirming the successful and complete PEC decomposition of the lignin model compound.



Figure 5.3 (a) Cyclic voltammetry profiles for the decomposition of compound **4** recorded on a BiVO₄ photoanode immersed in 25 mL MeCN containing 0.1 M LiClO₄ electrolyte and subjected to simulated AM 1.5 sunlight. Photocurrent densities correspond to the blank MeCN solution (black trace), and the solution after the addition of 0.25 mmol of lignin model (orange trace). (b) The degradation of **4** during 20 h reaction under AM 1.5 sunlight and a constant applied potential of 2.0 V. Yields of the aryl aldehyde product were used to measure the extent to which **4** was degraded. GC-MS measurements at each time point were carried out in triplicate; error bars denote the standard deviation of each set of measurements.

5.2.2. Influence of surface vanadium on lignin decomposition

A series of control experiments tracking the conversion of lignin model compound **4** into degradation products *p*-anisaldehyde (**6**) and phenol (**7**) were used to probe the role of vanadium sites during PEC decomposition. Four electrodes consisting of either bare FTO, bismuth-free V_2O_5 , BiVO₄, or BiVO₄ with an overlayer of V_2O_5 (denoted BiVO₄| V_2O_5) were synthesized (see 5.4.2.) and tested as electrodes for the degradation of **4** under either PEC conditions (i.e., AM 1.5 sunlight and applied potential of 2.0 V) or strictly electrochemical (EC) conditions (i.e., applied potential of 2.0 V; Figure 5.4). Yields of *p*-anisaldehyde (**6**) were used to reflect the extent of decomposition of **4** in each experiment. The yields of phenol (**7**) and formic acid are provided in Table A5.2.



Figure 5.4 The influence of vanadium studied by the decompositions of alcohol lignin model (4) with different anode materials under photoelectrochemical (PEC) or electrochemical (EC) condition. Decompositions of **4** were performed under a constant potential of 2.0 V for 20 h with different anodes, including a BiVO₄ photoanode, a BiVO₄ photoanode coated with an additional layer of V_2O_5 , a V_2O_5 anode and a bare fluorine-doped tin oxide (FTO) glass anode. Yields of product **6** (quantified by GC-MS) were used to reflect the decomposition degrees of lignin models while the yields of **7** and formic acid were provided in Table A5.2. Error bars indicate standard deviations of triplicate GC-MS measurements.

Bare FTO electrodes decompose 4 under both PEC and EC conditions with degradation yields of $12 \pm 2\%$ in both cases. Similar yields ($11 \pm 2\%$) are observed for a BiVO₄ photoanode under EC conditions. This same material under PEC conditions exhibits a 4-fold increase in degradation yield to 41 $\pm 2\%$, demonstrating that sunlight is essential to achieving high reactivity with a BiVO₄ photoanode. A layer of bismuth-free V₂O₅ improves the degradation yield of 4 relative to bare FTO to approximately 27

 \pm 3% under EC conditions. This value does not increase upon exposure to light under PEC conditions (26 \pm 3%), indicating that this non-photoactive material acts exclusively as an electrocatalyst for lignin decomposition. I were able to leverage the electrochemical activity of V₂O₅ by coating a layer of V₂O₅ onto a BiVO₄ photoanode, which results in increased PEC activity towards lignin degradation relative to a BiVO₄ photoanode (52 \pm 2% *versus* 41 \pm 2%). UV-Vis absorption spectra and X-ray fluorescence signals (Figure 5.5) confirm that similar amounts of V₂O₅ were deposited onto FTO and BiVO₄.



Figure 5.5 (a) UV-Vis absorption spectra and (b) relative X-ray fluorescence (XRF) signals for vanadium in FTO, V_2O_5 , BiVO₄ and BiVO₄| V_2O_5 . Vanadium signals in BiVO₄ were normalized to 100%. Error bars indicate standard deviations in triplicate film preparations.

Electrochemical impedance spectra of the four different types of electrodes were collected on a solution of 4 (10 mM) in 0.1 M LiClO₄ in MeCN and modeled to an equivalent circuit model (Figure 5.6). Coating V_2O_5 on either FTO or BiVO₄ decreased the conductivity of the electrode (i.e., larger resistance of bulk electrode) relative to the uncoated electrode, indicating that the higher degradation yields in the presence of vanadium were not a result of increased conductivity. By contrast, the additional V_2O_5 layer led to a clear enhancement for charge transfer at the electrode-solution interface that is consistent with more effective catalysis. The coating of V_2O_5 on FTO or BiVO₄ also led to larger capacitance compared



to the uncoated electrode, suggesting that the surface roughness was also enhanced by the V2O5 layer.

Figure 5.6 Electrochemical impedance spectra of (a) FTO and V_2O_5 (in dark); (b) BiVO₄ and BiVO₄| V_2O_5 (under AM 1.5 sunlight) measured at 1.2 V vs. Ag/AgCl. Electrodes were immersed in 0.1 M LiClO₄ in 25 mL MeCN with 0.25 mmol of lignin model compound **4**. Impedance spectra were modeled to an equivalent circuit model where the first semicircle is ascribed to bulk electrode (R_{bulk} and C_{bulk}) and the second to charge transfer across the electrode-solution interface (R_{ct} and C_{ct}). Experimental data were shown as points while fitting results were shown as curves.

Electrochemical active surface areas (ECSAs) of the four electrodes were investigated by measuring the charging current densities in 0.1-M LiClO₄ in MeCN with different scan rates (Figure 5.7). The results indicated increased surface roughnesses after coating V_2O_5 onto FTO or BiVO₄, which may also contribute to the higher yield of lignin decomposition shown in Figure 5.4. Scanning electron microscopy (SEM) images also showed a more porous surface morphology after coating V_2O_5 onto FTO or BiVO₄ (Figure 5.8). These observations suggest that V_2O_5 enhances the yield of lignin decomposition

by both (i) acting as an electrocatalyst layer and (ii) increasing surface roughness of the composite electrode.



Figure 5.7 (a) Charging current densities $BiVO_4$ at different scan rates (10, 50, 100, 150, 200 mV s⁻¹). (b) Charging current densities of FTO, $BiVO_4$, V_2O_5 and $BiVO_4|V_2O_5$ measured at 0.6 V vs. Ag/AgCl. R² for all linear fittings are 0.999. Electrodes (in dark) were immersed in 0.1 M LiClO₄ in 25 mL MeCN.



Figure 5.8 SEM images of $BiVO_4$, $BiVO_4|V_2O_5$ and V_2O_5 . Islands on $BiVO_4$ or FTO were assigned as V_2O_5 particles.

The reactivity of a ketone model compound 3-hydroxy-1-(4-methoxyphenyl)-2- phenoxypropan-1-one (8) was also tested for susceptibility towards degradation using a BiVO₄ photoanode under PEC conditions. This experiment did not yield any decomposition products (Figure 5.9), nor did I detect degradation of 8 when the system was illuminated by sunlight without an externally applied voltage. This result rules out the possibility of a 2-step photoassisted pathway *via* oxidation of the benzylic hydroxyl group to first form a ketone (see Figure 5.1b^{123,128}). Degradation of the alcohol lignin model compounds under PEC conditions is more likely to proceed *via* oxidation of the benzylic hydroxyl group to form an aryl aldehyde.^{132,145} Likewise, the degradation of **4** does not occur at a BiVO₄ photoanode without an externally-applied voltage. From these results, I can conclude that lignin degradation is driven by reaction with light-generated holes of the semiconductor rather than direct photochemical degradation.



Figure 5.9 Control experiments where alcohol (**4**) and ketone (**8**) lignin models showed no decomposition reaction. PEC control experiment of the ketone lignin model 3-hydroxy-1-(4-methoxyphenyl)-2-phenoxypropan-1-one (**8**) was performed on a BiVO₄ photoanode and denoted as "BiVO₄, PEC". Photochemical control experiments were carried out for **4** and **8** where BiVO₄ photoanode was immersed into solution and irradiated by simulated AM 1.5 sunlight for 20 h but no electric voltage was applied (denoted as "BiVO₄, photo").

5.3. Conclusion

The proven viability of photoelectrochemically driving the decomposition of lignin into the component aryl aldehydes and phenols at the surface of $BiVO_4$ (and $BiVO_4|V_2O_5$) photoanodes provides a means of producing alternative sources of aromatic chemical feedstocks from lignin biomass. While the degradation of lignin is established for catalytic and electrochemical methods,^{127,129,132} the use of photoelectrochemical (PEC) cells to drive this reaction has not been previously demonstrated. I have also

shown that the vanadium atoms at the surface of $BiVO_4$ photoanode likely acts as a heterogeneous catalyst for lignin decomposition in PEC system. This report serves as the first example of a photoelectrocatalyst for lignin decomposition and the "dual role" of vanadium in $BiVO_4$ acting as both a photoanode materials and a heterogeneous catalyst for organic transformation. This strategy highlights a new utility of PEC cells to produce valuable chemical feedstocks from solar energy and biomass.

5.4. Experimental details

5.4.1. Materials

Bismuth nitrate hexahydrate (98%), vanadyl acetylacetonate (98%), and tungsten hexachloride (99%) were purchased from Strem Chemicals and used as received. Chemicals for lignin synthesis including 2-bromoacetophenone (98%), 1-bromo-4'-methoxyacetophenone (97%), phenol (99%), 4-methoxyphenol (99%) and formaldehyde solution 37 wt% were purchased from Sigma-Aldrich and used as received. FTO substrates (TEC 15) were purchased from Hartford Glass Co. Glassy carbon electrodes were purchased from Alfa Aesar.

5.4.2. Electrode preparation

BiVO₄ photoanodes were prepared in accordance with previously reported procedures.² Bismuth nitrate hexahydrate (0.346 g, 0.713 mmol), vanadyl acetylacetonate (0.176 g 0.663 mmol), and tungsten hexachloride (0.02 g, 0.05 mmol) were added to a 10 mL mixture of acetic acid and acetylacetone (1:8 v/v). The solution was sonicated for 15 min and then spin-coated onto a FTO substrate at 1000 rpm for 30 s. Each of the successive 16 coats was annealed at 500 °C for 10 min prior to a final 8 h annealing step at 500 °C. The BiVO₄ samples were irradiated with UV light (Model #: GPH436T5VH, Atlantic Ultraviolet Co.; $\lambda_{max} \sim 254$ nm and 185 nm; flux ~10 mW cm⁻² at 5.5 cm in my experiment) for 20 h. V₂O₅ anodes were prepared in a similar protocol but with only vanadium precursor in the solution for spin-coating and only one layer of coating, where vanadyl acetylacetonate (0.176 g 0.663 mmol) in 10 mL mixture of acetic acid and acetylacetone (1:8 v/v) was spin-coated onto a FTO substrate and annealed at 500 °C for 8 h. Similar

treatment was applied to prepare $BiVO_4|V_2O_5$ assembly, where vanadium precursor solution was spin-coated onto a $BiVO_4$ photoanode. The geometric surface areas of all working electrodes ($BiVO_4$ photoanodes, V_2O_5 and FTO electrodes) in this study were 2 cm².

5.4.3. Photoelectrochemical and electrochemical degradations of lignin models

PEC and EC degradations of lignin models were performed with a CHI 660D potentiostat in a threeelectrode photoelectrochemical cell with a BiVO₄ photoanode or BiVO₄|V₂O₅ assembly (for PEC experiments), V₂O₅ or FTO electrode (for electrochemistry experiments) as the working electrode, Ag/AgCl as the reference electrode, and glassy carbon as the counter electrode. AM 1.5 simulated sunlight for PEC experiments were provided by an Oriel 94011A-ES solar simulator integrated with a 100-W xenon arc lamp and AM 1.5 filter. An infrared water filter was applied to prevent the solution from heating up during PEC experiment. All degradation experiments were performed in 0.1 M LiClO₄ in 25 mL MeCN added with 0.25 mmol of lignin substrate. Potentials were measured vs. Ag/AgCl, which was calibrated to 0.196 V vs. NHE in aqueous media. Degradation was performed at room temperature, applying a constant potential of 2.0 V vs. Ag/AgCl with magnetic stirring. Photochemical control experiments were performed under the same condition as PEC experiments except that no voltage was applied.

5.4.4. Physical methods

The UV-vis absorptivity data was collected with a PerkinElmer Lambda 35 UV/Vis spectrometer with a solid sample holder accessory. X-ray fluorescence measurements were performed with a Thermo Fisher Scientific Niton XL3t analyzer utilizing a shielded test stand. The X-ray source was run with an accelerating voltage of 50 kV and a current of 40 μ A. Scan time was 30 s for each sample. Electrochemical impedance experiments were performed with a CHI 660D potentiostat in a three-electrode cell with a bare FTO or V₂O₅ electrode (in dark), BiVO₄ or BiVO₄|V₂O₅ photoanode (under AM 1.5 sunlight) as the working electrode, Ag/AgCl as the reference electrode, and glassy carbon as the counter electrode. Electrodes were immersed in 0.1 M LiClO₄ in 25 mL MeCN with 0.25 mmol of lignin model compound **4**. Measurements were performed for a frequency range from 1000000 Hz to 0.1 Hz with 5 mV oscillation amplitude. Impedances were measured at a constant potential of 1.2 V vs. Ag/AgCl. Charging current densities were measured in 0.1 M LiClO₄ in 25 mL MeCN at 0.6 V vs. Ag/AgCl. Scanning electron microscopy was carried out on all samples using an FEI Helios NanoLab 650 dual beam scanning electron microscope. For creating the cross-sections, a pit was first bored out with an ion beam current of 0.8 nA. The edge of the resulting pit was cleaned using an ion beam current of 80 pA. Cross-sectional images were taken at an angle of 52 degrees. All images were taken using secondary electrons with an accelerating voltage from 1 kV and a current of 50 pA. The working distance was 4 mm. All images were corrected for tilt.

5.4.5. Product analysis

Reaction samples were taken during and after electrolysis and carvone was added as an internal standard, and then analyzed by gas chromatography-mass spectrometry (GC-MS). GC-MS measurements were run on an Agilent GC-MS instrument with a HP-5ms GC column and electron ionization ion source. A 1- μ L aliquot was injected with an auto-sampler using split mode with a split ratio of 20:1, and carried by He gas at a flow rate of 1 mL min⁻¹. The oven temperature started at 60 °C for 1 min, then ramped from 100 to 150 °C at 20 °C min⁻¹ and from 150 to 250 °C at 40 °C min⁻¹. Detection was not performed for the first 1.75 min of the run, or the solvent delay time. GC-MS peaks were identified using the NIST Mass Spectrometry Data Center database (all peak identifications exhibited a probability match of > 90%) and compared with peaks in standard solutions. For quantitative analysis, a series of standard solutions with known concentrations of reactants and products were prepared and carvone was added as an internal standard. Standard solutions were run by GC-MS using the same method, and the relative peak areas of reactants and products.

Chapter 6: Electrolytic CO₂ Reduction in Tandem with Oxidative Organic Chemistry

6.1. Introduction

Chapters 3-5 have studied the anode chemistry in a PEC cell. In this chapter, I start to discuss the cathode chemistry in an EC cell. Significant resources have been committed to realizing scalable and cost effective cathodic hydrogen production as a means of storing electrical energy,^{5,7} but there remain economic challenges in using electrolyzer technologies to store renewable energy.^{7,22} Even at the strikingly cheap clean electricity prices that are known today,⁷ hydrogen still costs approximately twice as much to produce through HER as it does when extracted from fossil fuels.^{20,21} This scenario has constrained electrolytically produced hydrogen to merely ~5% of total global hydrogen production.²⁰⁻²² Cathodic CO₂ electrolysis is therefore an appealing alternative to water electrolysis for long-term energy storage because the carbon-containing products can penetrate a wider range of global fuels and chemicals markets that have the requisite infrastructure in place.^{73,74} Electrolyzer technologies for CO₂ conversion are, however, at an early stage of development and innovative technology solutions are needed.^{8,9,23-26,146}

In a conventional water electrolyzer where HER takes place at the cathode, it is still the OER at the anode that requires the larger overpotential due to the kinetic and thermodynamic barriers associated with dioxygen formation.^{5,6} As mentioned in Chapter 2, the negligible economic value of dioxygen has prompted several groups to consider whether alternative reactions can be driven at the anode to lower the operating voltage while generating a higher-value product. Choi ¹⁸ and Sun ¹¹⁴ have independently demonstrated a successful embodiment of this concept by driving alcohol oxidation at the anode in tandem with HER at the cathode to produce carbonyl compounds and hydrogen fuels (Figure 6.1). Baran recently reported the more synthetically challenging allylic oxidation at the anode while performing HER at the cathode.⁷¹ Choi ¹⁸ and our group (Chapters 4 and 5) have also independently demonstrated the photoelectrochemical oxidation of organic compounds coupled with HER.



Figure 6.1 Summary of cathodic reactions [hydrogen evolution reaction (HER); CO₂ to CO, formic acid, or methane] that have been performed in tandem with the oxygen evolution reaction (OER) and the oxidation of organic substrates (e.g., alcohols;^{18,54,114} allylic oxidation ⁷¹) in a single electrochemical cell. I report here the integration of CO₂ reduction and organic oxidation in a single cell.

Given that each of the preceding oxidative studies rely on the HER at the cathode, I set out to explore the possibility of instead driving the electrochemical reduction of CO₂. This notion was inspired by the significant recent advances in converting CO₂ to CO at a metal (alloy) electrode at moderate temperatures and pressure conditions. For example, Kanan and coworkers have shown that CO₂ can be electrochemically reduced into various types of chemical fuels (e.g., formic acid, CO, methane, etc.) with high current densities and selectivities on oxide-derived metal cathodes.^{78,86,147} Jaramillo and co-workers electrocatalytically converted CO₂ into hydrocarbons (e.g. methane, ethylene) and/or alcohols (e.g. methanol, ethanol) at transition metal surfaces.^{148,149} Yang and Chang have developed an efficient nanoparticle/nanowire system for the (photo)electrochemical reduction of CO₂,^{150–152} while Sargent and coworkers demonstrated an enhanced electrocatalytic CO₂ reduction via a high local CO₂ concentration created by nanostructured electrode.¹⁵³ Of relevance to this study is the recent report our group that efficient electrochemical reduction of CO₂ reduction studies relied on OER at the counter-electrode, studies of molecular CO₂ reduction catalysts have utilized sacrificial oxidizing
reagents such as ferrocene to bypass the use of OER as the oxidative half reaction.^{154,155}

These preceding observations prompted us to contemplate whether sacrificial oxidative chemistry could be bypassed during CO₂ reduction for sustained electrolytic formation of useable products at both the anode and cathode. Following this line of inquiry, I report herein tandem CO₂ reduction and organic oxidation in a single electrochemical cell using an NaHCO₃ electrolyte where the anode and cathode are separated by a Nafion® membrane. This proof-of-concept study focuses on the conversion of CO₂ into CO at a copper-indium cathode, and oxidative chemistry at a platinum anode with the redox mediator 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)^{18,54} to mediate the oxidation of alcohols. Four different types of alcohols were investigated; namely, the primary and secondary benzylic and aliphatic alcohols listed in Figure 6.2 I were able to electrochemically convert each of these alcohols to their corresponding carbonyl compounds with >78% yield in less than 3 h while maintaining Faradaic efficiencies for both the cathode and anode at >70% prior to reagent depletion. These experiments represent the first demonstration of CO₂ reduction in tandem with oxidation of organic compounds, and provide an alternative strategy for generating economically valuable products at both electrodes.



Figure 6.2 Reactions tested herein to demonstrate the oxidations of primary and secondary benzylic alcohols, and primary and secondary aliphatic alcohols.

6.2. Results and discussions

6.2.1. Individual electrochemistry on cathode and anode

A two-compartment electrochemical cell was used for all electrochemistry experiments where each compartment contains 25 mL of 0.5 M NaHCO₃ in water and are separated by a Nafion® proton exchange membrane (Figure 6.3). A platinum mesh served as the anode and a copper-indium alloy film on titanium was used as the cathode for all experiments. The cathode catalyst layer was synthesized by irradiating copper (II) chloride dihydrate (0.075 mmol) and indium acetylacetone (0.025 mmol) dissolved in 6 mL of methanol that were spin-coated on planar titanium substrates with near infrared light prior to electrochemical reduction.⁷⁷ Powder X-ray diffractrograms displayed dominant crystalline phases of Cu₂In and Cu, confirming the composition and structure of the Cu-In films as previously reported (Figure 6.4).⁷⁷ The solution in the cathodic compartment was purged with CO₂ at a rate of 5.0 sccm for 30 min prior to and during electrochemical measurements. All potentials were measured against an Ag/AgCl reference electrode and reported versus reversible hydrogen electrode (RHE).



Figure 6.3 Illustration of the overall electrolysis scheme. CO_2 is reduced to CO at the Cu-In cathode (in competition with protons reducing protons to hydrogen). Each alcohol is oxidized by TEMPO, which is oxidized at the Pt anode (in competition with OER). The catholyte and anolyte are separated by a Nafion membrane.



Figure 6.4 Powder XRD diffractrogram of Cu-In film on Ti substrate. Peaks attributed to the Ti substrate (*) and each phase of Cu (red), Cu₂In (green), CuIn (blue), and In (orange) are indicated. The dominant phases for my Cu-In film are Cu₂In and Cu.

The cathode and anode reactions were each investigated independently by cyclic voltammetry. The cyclic voltammogram for CO₂ reduction at a copper-indium cathode shows an onset potential at approximately -0.36 V and a current density of 3.7 mA cm⁻² at -0.70 V (Figure 6.5a). The Faradaic efficiency at -0.70 V was confirmed to be 80% based on the relative amounts of CO and hydrogen detected by gas-chromatography (GC).⁷⁷ While superior CO₂ reduction electrocatalyst activity has been observed for complex nanostructures or with ionic liquids,^{153,156} the current density of 3.7 mA/cm² for the copper-indium samples is among the highest activity reported to date for CO₂ reduction by a planar thin film, providing a reliable foundation for studying tandem CO₂ reduction and organic oxidation.

I then investigated the oxidative electrochemistry of each of the four alcohols indicated in Figure 6.2. The data for 1-phenylethanol (1-PEA) are provided in Figure 6.5b; the other three alcohols exhibit similar behavior and the data are included in Figure A6.1. The oxidative scans of the alcohols in 0.5-M NaHCO₃ aqueous solutions (without TEMPO present) did not show any redox activity over the 0.7-2.1 V range using a platinum anode (Figure A6.2). Data recorded on 0.20 mmol of TEMPO in the same

electrolyte (no alcohol present) produced a reversible redox couple at 1.3 V in accordance with literature values.^{18,54} Following these control experiments, 0.25 mmol of 1-phenylethanol was added to the electrolyte solution containing TEMPO and a small increase in current was observed, suggestive of charge transfer between TEMPO and the alcohol (Figure 6.5b). This response was observed for each of the acids. The much larger current response measured with TEMPO and the alcohol over that of the background indicates that TEMPO-mediated alcohol oxidation is more favorable than water oxidation over the 1.2-1.8 V potential window.¹⁸



Figure 6.5 a) Reductive scan of a copper-indium cathode immersed in 25 mL H_2O containing 0.50-M NaHCO₃ where CO₂ is bubbled through at a rate of 5.0 sccm. b) Cyclic voltammetry profiles of a blank 0.50 M NaHCO₃ aqueous solution (black) prior to the successive addition of 0.20 mmol TEMPO (orange) and 0.25 mmol 1-phenylethanol (1-PEA, blue). All data recorded at a scan rate of 10 mV/s in 25 mL aqueous solution.

6.2.2. Tandem electrolysis

The two half reactions were then tested in tandem by performing chronoamperometry of a twoelectrode cell where CO_2 was bubbled into the catholyte, and 0.20 mmol of TEMPO and 0.25 mmol of an alcohol was added to the anolyte. Electrolysis carried out at a constant potential of -0.70 V maintained a stable current density of ~3.7 mA cm⁻² for 3 h (Figure 6.6a). During electrolysis, gases in the cathodic compartment were automatically vented into the gas-sampling loop of a gas chromatograph (GC) and analyzed every 30 min. Aliquots of the liquid in the anodic compartment were manually collected by syringe and analyzed by proton nuclear magnetic resonance (¹H NMR) every 30 min (Figures A6.3, A6.4, A6.5, and A6.6). The competing HER and OER reactions at the cathode and anode, respectively, were accounted for by measuring the relative amounts of hydrogen and oxygen formation by GC. The Faradaic efficiencies for CO₂ to CO conversion were maintained at >70% over the course of the 3-h experiment (Figure 6.6a). The Faradaic efficiency of the anodic oxidation of 1-phenylethanol (1-PEA) to acetophenone (ACP) was ~95% for the first 30 min of the reaction, but then started to diminish towards ~70% at 1.5 h into the experiment (Figure 6.6b). The OER was dominant for the last half of the 3-h experiment and thus the Faradaic efficiency for ACP formation was merely ~36% over the course of the anotic or starting with higher concentrations. These collective data indicate that the formation of CO and ACP are favored over the competing HER and OER reactions until substrate depletion and are therefore poised for sustained tandem electrolysis.



Figure 6.6 a) Rate of product formation (blue trace) and Faradaic efficiencies (columns) over 3 h of tandem electrolysis at an external bias of -0.70 V that converts CO_2 into CO and 1-phenylethanol (1-PEA) into acetophenone (ACP). The Faradaic efficiencies for the cathodic products CO (green) and H₂ (black) and anodic products acetophenone (orange) and O₂ (grey) are indicated. b) Relative concentrations of 1-phenylethanol (blue) and acetophenone (orange) over the course of the 3-h experiment that were quantified by ¹H NMR spectroscopy.

The four alcohols chosen to demonstrate the viability of oxidizing different classes of alcohols were all oxidized with meaningful yields (78%-93%) after 3 h reaction (Figure 6.7). Product selectivity is one of the key figures of merit for alcohol oxidation, particularly for primary alcohols that can be oxidized to aldehydes or oxidized further to carboxylic acids (aldehydes can be hydrated to geminal diols in aqueous solution and subsequently oxidized to carboxylic acids).¹⁵⁷ The oxidation of secondary alcohols (1-phenylethanol and isopropanol) in my study yielded the respective ketones in exclusivity, whereas the oxidation of primary alcohols (4-methoxybenzyl alcohol and ethanol) produced mixtures of the aldehydes and carboxylic acids during the initial stages of the reaction but yielded higher product selectivity over 3 h of electrolysis. For the ethanol oxidation reaction, acetaldehyde was accumulated over the first 1 h of reaction (yield ~ 16%, Figure 6.8a) prior to further oxidation to acetic acid. Acetic acid was the dominant product after 3 h of electrolysis, suggesting a relatively fast oxidation of acetaldehyde into acetic acid.¹⁵⁷ The oxidation of 4-methoxybenzyl alcohol, however, terminated at the corresponding

aldehyde to yield 4-methoxybenzaldehyde as the major products (Figure 6.8b). This observation indicates that the oxidation rate of 4-methoxybenzaldehyde is much slower than that of 4-methoxybenzyl alcohol. The divergent oxidation product selectivity of ethanol and 4-methoxybenzyl alcohol is consistent with previous studies on TEMPO-mediated oxidation of primary alcohols.^{52,54} The differences were attributed to the strongly electron-donating effect and steric encumbrance of the methoxybenzyl group that render hydration of 4-methoxybenzaldehyde much more unfavourable than that of acetaldehyde (hydration constant of acetaldehyde $\sim 10^{0.1}$, whereas the hydration constant of 4-methoxybenzaldehyde is $< 10^{-2}$, Figure 6.9).¹⁵⁷



Figure 6.7 Yields of alcohol oxidation following 3 fours of sustained electrolysis.



Figure 6.8 (a) Relative concentrations of 4-methoxybenzyl alcohol (blue), 4-methoxybenzaldehyde (orange) and 4-methoxybenzoic acid (green). (b) Relative concentrations of ethanol (blue), acetaldehyde (orange) and acetic acid (green). Concentrations were determined by ¹H NMR spectroscopy over the course of a 3 h electrolysis experiment.



Figure 6.9 Mechanism of oxidations of 4-methoxybenzyl alcohol and ethanol in water. The methoxyphenyl group (with strong electron-donating and steric effects) makes a much smaller hydration constant ($K_{hydration}$) of 4-methoxybenzaldehyde compared to acetaldehyde.

6.3. Conclusion

These results collectively demonstrate that my integration of CO_2 reduction and oxidative electrochemistry can be used to form CO and convert alcohols with high product selectivity and high Faradaic efficiencies. This cell architecture successfully converted four primary and secondary aliphatic and benzylic alcohols into their corresponding carbonyl compounds with yields >70% within the first hour of the experiment. At the current densities investigated here, the losses in cell efficiency are due to the depletion of the organic reagents. Future studies will test the efficacy of these reactions in a flow cell configuration that enables constant delivery of the substrate to the electrode. This electrochemical study showcases the opportunity to create an electrolyzer that generates products at both electroles that are of higher commercial value than the hydrogen and oxygen fuels produced in a conventional electrolyzer.

6.4. Experimental details

6.4.1. Materials

Indium acetylacetone (98%), copper (II) chloride dihydrate (98%), methanol (98%), NaHCO₃ (99%), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 98%), 4-methoxybenzyl alcohol (98%), 4-methoxybenzaldehyde (98%), 4-methoxybenzoic acid (98%), 1-phenylethanol (racemic, 98%), acetophenone (99%), ethanol (dried, 99%), acetaldehyde (99%), acetic acid (99%), isopropanol (99%), acetone (99%), benzene-1,3,5-tricarboxylic acid (98%), deuterium oxide (D₂O, 99.9 atom% D) were purchased from commercial vendors (Alfa Aesar, Fisher Scientific, or Sigma-Aldrich). No unexpected or unusually high safety hazards were encountered.

6.4.2. Electrode preparation

Copper-indium cathodes were prepared in accordance with the procedures previously reported by our group.³⁶ Solutions of metal precursor complexes were prepared by dissolving 0.075 mmol of copper (II) chloride dihydrate and 0.025 mmol of indium acetylacetone in 6 mL methanol, and 0.75 mL precursor

solution was drop onto titanium substrate (T2 standard) each time, followed by irradiation under infrared (IR) lamp (Phillips, 175 W) for 1 h before the drop of next layer. The final sample is left under IR lamp for overnight. The resulting metal oxide film is electrochemically reduced to the metal phase at a steady bias of - 0.7 V vs RHE) for 30 min in 0.5 M NaHCO₃ aqueous solution. Cu-In electrode was confirmed by powder XRD techniques (Bruker F8 Focus X-ray diffractometer, data collected between 2θ angles of 5° and 90° with a step size of 0.04° and a step time of 0.6 s).

6.4.3. Electrochemistry experiments

A CHI 660D potentiostat and a gastight two-compartment electrochemical cell with a piece of Nafion® proton exchange membrane as a separator were used for all electrochemistry experiments. Each compartment contained 25 mL 0.5 M NaHCO₃ aqueous solution. The solution in the cathodic compartment was purged with CO₂ for 30 min prior to electrochemical measurements. All potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl) and converted to the RHE reference scale using E (vs RHE) = E (vs Ag/AgCl) + 0.22 V + 0.059 V*pH. For cyclic voltammetry of CO₂ reduction, copper-indium working electrode and platinum counter electrode were used. For cyclic voltammetry of alcohol oxidation, platinum working electrode and copper-indium counter electrode were used, and 0.20 mmol TEMPO and 0.25 mmol alcohol were added successively into anolyte. For overall electrolysis, copper-indium working electrode (immersed surface area of 2.7 cm²) and platinum counter electrode were used, and 0.20 mmol TEMPO and 0.25 mmol alcohol were added into anolyte; a constant bias of - 0.7 V vs RHE was applied over 3 h. During electrolysis, CO₂ gas was delivered into the cathodic compartment at a rate of 5.0 sccm and gas sample in cathodic compartment was taken into analysis by gas chromatography (GC) every 30 min; whereas liquid sample in anodic compartment were taken into analysis by proton nuclear magnetic resonance (¹H NMR) every 30 min.

6.4.4. Product analysis

GC (SRI Instruments) was equipped with a packed MolSieve 5A column with an interior

diameter of 2 mm and a length of 0.274 mm. Argon (Praxair, 99.999%) was used as the carrier gas and set at a flow rate of 20 sccm. A flame ionization detector (FID) with methanizer was used to quantify CO and a thermal conductivity detector (TCD) was used to quantify H₂. Calibration curves for CO and H₂ were created by plotting peak area versus concentration in standard calibration gas purchased from Norlab. ¹H NMR spectroscopic data were collected on a Bruker AV III HD 400 MHz spectrometer equipped with Bruker BBFO smart probe with ATMA at 25 °C. Benzene-1,3,5-tricarboxylic acid was added to reaction sample taken from anolyte as internal standard and deuterium oxide (D₂O) was added to make a H₂O:D₂O (1:9 ν/ν) solution for ¹H NMR measurements. Water signal was suppressed by using watergate W5 pulse sequence with double gradient echos.¹⁵⁸ A series of standard solutions with known concentrations of pure reactants and products were prepared and analyzed by ¹H NMR, and the relative peak areas of reactants and products were normalized to the peak of benzene-1,3,5-tricarboxylic acid (singlet, $\delta = 8.29$ ppm). Calibration curves were created by plotting relative peak areas versus concentration of standard solutions.

Chapter 7: Electrolytic Conversion of Bicarbonate and Carbonate into CO in a Flow Cell

7.1. Introduction

As mentioned in Chapter 6, electrochemical CO₂ reduction at ambient temperatures and pressures offers a method to store abundant clean electricity by converting CO₂ into a variety of commodity chemicals.^{4,23,25,148,153,159,160} A number of different cell configurations have been proposed in an effort to reach the high current densities and product selectivities that would be required by a commercial CO₂ electrolyzer, yet there is no low-temperature CO₂ electrolyzer available on the market. The majority of cell configurations supply CO₂ to the cathode of the electrochemical cell as a saturated solution in a supporting aqueous electrolyte.^{23,25,148} (There are also examples where gas phase CO₂ is delivered directly to the electrode.^{81,82,161–163}) Electrolyte CO₂ saturation is typically achieved by bubbling gaseous CO₂ into the electrolyte to a maximum [CO₂] of ~0.033 M at ambient temperature and pressure prior to and during electrolysis. This saturation point fundamentally limits the maximum current density that can be achieved for CO₂ reduction in the bulk liquid phase. Furthermore, the addition of CO₂ to the electrolyte causes a lowering in pH, thus providing conditions that favour the competing HER instead of the desired CO₂RR (i.e., selectivity for a desired carbon product is lowered).^{86–88} These characteristics of CO₂-saturated electrolyte systems provide the impetus to explore alternative pathways for accessing electrolytically-reduced carbon products at high current densities.

A system capable of directly reducing either bicarbonate (HCO_3^{-}) or carbonate (CO_3^{2-}) is compelling because the maximum concentrations of these carbon species in a saturated aqueous solution are greater in each case than for saturated CO_2 (~3.3 M for KHCO₃; 8.1 M for K₂CO₃). The electrochemical reduction of a HCO_3^{-} or CO_3^{2-} solution would also provide an opportunity to avoid electrolyte acidification caused by the addition of gaseous CO_2 . However, very few examples of systems capable of these electrochemical transformations currently exist. A study by Hori in 1983 showed that formate could be produced from the electrochemical reduction of a 1.0-M sodium bicarbonate solution without CO₂ supply in an H-cell architecture containing a mercury catalyst, albeit with a partial current density for formate (J_{formate}) of less than 1 mA cm⁻².¹⁶⁴ Kanan and coworkers reported in 2015 that a palladium catalyst in an H-cell was able to reduce 2.8-M potassium bicarbonate into formate without a CO₂ feed at $J_{\text{formate}} = 3.2 \text{ mA cm}^{-2}$ (*c.f.* 6.1 mA cm⁻² in a CO₂-fed bicarbonate solution). To my knowledge, these results set the benchmark for bicarbonate reduction to a reduced carbon product in a system without supply of CO₂.⁸⁶

The mechanism for the reduction of bicarbonate into formate (or any carbon product) without CO_2 feed is widely debated: There is disagreement over either an *indirect* (i.e., bicarbonate first dissociating to form CO_2 that is then reduced; eqs 7.1a and 7.1b) ^{86,164} or *direct* (i.e., no CO_2 molecule is formed prior to reduction; eq 7.2) ^{88,165,166} reduction mechanism. The exact role of bicarbonate in a CO_2 -fed system is also unclear: Bicarbonate may enhance the rate of CO_2 reduction by increasing the concentration of dissolved CO_2 via rapid equilibrium exchange;^{167,168} and/or by increasing the pH of the electrolyte solution to suppress HER.⁸⁶ Alternatively, bicarbonate may simply act as a proton donor and have no direct influence on the rate of CO_2 reduction.¹⁶⁹ These points notwithstanding, all reports of bicarbonate reduction chemistry show: (i) lower current densities and Faradaic efficiencies (F.E.s) compared to a CO_2 -fed system; and (ii) that formate is the only product that has been reported from the reduction of bicarbonate without a CO_2 feed. The electrochemical reduction of bicarbonate into CO without CO_2 supply, for example, is not currently known. Moreover, there is no previous report of a flow cell to promote the direct reduction of either carbonate or bicarbonate to a reduced carbon product.

Indirect reduction:
$$HCO_3^- + H^+ \rightleftharpoons CO_2 + H_2O$$
 (eq 7.1a)
 $CO_2 + H^+ + 2 e^- \rightarrow HCOO^-$ (eq 7.1b)
Direct reduction: $HCO_3^- + 2 H^+ + 2 e^- \rightarrow HCOO^- + H_2O$ (eq 7.2)

I report herein data within an electrochemical flow reactor^{81,82} that shows the formation of CO from either a KHCO₃ or a K₂CO₃ solution without the need to supply the electrolyte with gaseous CO₂. A 3.0-M potassium bicarbonate electrolyte demonstrates a F.E. for CO of 67% at 20 mA cm⁻² that is greater

than a system wherein the electrolyte is saturated with CO_2 gas (62%). A 3.0-M potassium carbonate electrolyte also shows reasonable performance for electrochemical reduction with a F.E. for CO of 18% at 20 mA cm⁻². I also demonstrate an electrolysis performance dependency that is related to the concentration of HCO_3^- in the electrolyte, and not that of dissolved CO_2 . My results cannot definitively distinguish between the two reaction pathways; however, they do invoke the possibility of a mechanism for the direct reduction of bicarbonate, which goes against the current dogma in the field. To my knowledge, I report here for the first time: (i) the electrochemical reduction of bicarbonate into a carbon product other than formate; (ii) the electrochemical reduction of carbonate electrolytes with and without saturation from a gaseous CO_2 feed; and (iv) the electrochemical reduction of bicarbonate or carbonate to form carbon products in a continuous flow reactor. These results provide a potential breakthrough for carbon capture and utilization schemes.

7.2. Results and discussions

7.2.1. Flow cell setup for bicarbonate and carbonate reduction

A two-electrode liquid flow-cell electrolyzer previously reported by our group was used for all electrochemistry experiments (Figure 7.1).⁸² The flow cell was built in-house and consists of housing, gaskets, anode and cathode flow-field plates and a membrane electrode assembly (MEA). The anode and cathode housings are made from stainless steel and serve to deliver liquid electrolyte to anode and cathode. The titanium cathode flow plate and stainless steel anode flow plate sandwich the 4-cm² MEA. The anode (316 stainless steel) and cathode (grade 2 titanium) flow-field plates (active area = 4 cm²) contain serpentine channels 1.5 mm wide and 1.5 mm deep with 1-mm ribs. The MEA consists of a nickel foam anode (2.5×2.5 cm), a bipolar membrane (3×3 cm), and a silver nanoparticle-coated porous carbon support as the cathode (2.5×2.5 cm). The entire assembly is sandwiched between the two stainless housings fastened with 8 bolts. The silver-coated carbon cathode was prepared by spray coating

carbon paper with a mixture of commercially-available silver nanopowder and NafionTM solution. The anode feed was 1.0-M KOH delivered at 50 mL min⁻¹ and the cathode feed was an aqueous solution of either 3.0-M K₂CO₃ or 3.0-M KHCO₃ delivered at 50 mL min⁻¹ continuously bubbled with either N₂ or CO₂ gas at a rate of 50 sccm. Cyclic voltammetry measurements of the two-electrode flow cell were collected over the -1.5 to -3.5 V range (reported as the cell potential). Faradaic efficiencies for CO production were measured at constant current densities of 20, 40, 60, 80, and 100 mA cm⁻². Gas chromatography (GC) analysis of the gaseous headspace at the electrolyzer outlet showed CO and H₂ as the only detectable products. The cathode solution was analyzed by ¹H NMR after electrolysis and no liquid products were detected. F.E. for CO is reported with the remainder of products confirmed as H₂. Further description of the setup and full cell dimensions are shown in Figure A7.1. Control experiments were also applied using an analogous flow cell architecture with an anion exchange membrane (AEM) in place of the bipolar membrane. A second control experiment using a two-compartment H-cell was also performed wherein the anode (platinum mesh) and cathode (Ag-coated carbon paper) compartments both contained 30 mL of 3.0-M KHCO₃ (catholyte saturated by N₂ gas) separated by a proton exchange membrane (NafionTM).



Figure 7.1 Experimental setup of the electrochemical flow cell represented by (a) a schematic diagram, (b) a solid model, and (c) a detailed dimensional diagram of the cathode & anode flowplates. Nickel foam (anode) and silver deposited on a porous carbon support (cathode) were separated by a bipolar membrane. 1.0-M KOH electrolyte was circulated through the stainless flow plate and oxidized into O_2 gas at the anode. Either KHCO₃ or K₂CO₃ electrolyte solutions bubbled with N₂ or CO₂ were circulated through the titanium flow plate and reduced into CO at the cathode. The cathodic products were analyzed by gas chromatography (GC). Electrolyte flows were driven by peristaltic pumps at 50 mL min⁻¹. Gas flows (N₂ or CO₂) were set to 50 sccm. All dimension in (d) are in cm.

7.2.2. Cell performance for bicarbonate and carbonate reductions

The flow cell setup described above was used to test the electrochemical activity towards CO production from three solutions (3.0-M KHCO₃ bubbled with CO₂ gas; 3.0-M KHCO₃ bubbled with N₂ gas; 3.0-M K₂CO₃ bubbled with N₂ gas; Figure 7.2). Cyclic voltammograms (CVs) were collected between potentials of -1.0 and -3.5 V (Figure 7.2a) in a two-electrode flow cell, and the F.E. for CO (F.E._{CO}) was measured between current densities of 20 and 100 mA cm⁻² in 20-mA cm⁻² increments (Figure 7.2b). The viability of the flow cell towards CO₂ reduction was confirmed by results from the CO₂-saturated 3.0-M KHCO₃ solution (Figure 7.2, black): The CV exhibits a sharp rise in current density at -2.5 V and a current density of 90 mA cm⁻² at -3.5 V was measured. The moderate F.E._{CO} of 62% exhibited at low current densities (20 mA cm⁻²) is further reduced at higher current densities (e.g. 21% at 100 mA cm⁻²). The F.E._{CO} for CO₂ reduction was stable at 20 mA cm⁻² over 3 hours (Figure 7.3). These results are consistent with previous reports of CO₂-to-CO reduction in liquid-fed flow cells.^{81,170,171}



Figure 7.2 Electrochemical reduction behaviours of CO₂-saturated 3.0-M KHCO₃; N₂-saturated 3.0-M KHCO₃; and N₂-saturated 3.0-M K₂CO₃ solutions using a electrolyzer flow cell. (a) Cyclic voltammogram profiles recorded in each electrolyte solution between -1.5 and -3.5 V (scan rate = 100 mV s⁻¹); (b) Faradaic efficiencies of CO (F.E._{CO}) measured at constant current densities between 20 and 100 mA cm⁻². Cathode: silver deposited on porous carbon support ; anode: nickel foam; catholyte: 3.0 M-KHCO₃ or K₂CO₃; anolyte: 1.0-M KOH.

Having validated the CO_2 reduction activity of my flow cell, I then investigated the electrochemical reduction of bicarbonate and carbonate solutions in the absence of a CO₂ supply. CVs were collected in the -1.0 to -3.5 V cell potential range which show similar reductive sweep profiles to the CO₂-saturated solution (Figure 7.2a). Peak current densities of 100 and 60 mA cm⁻² were measured for the KHCO₃ and K₂CO₃ solutions, respectively. Electrochemical reduction of N₂-saturated 3.0-M KHCO₃ solution showed a F.E._{CO} of 67% at a current density of 20 mA cm⁻², and 26% at 100 mA cm⁻² (Figure 7.2b, orange). Note that the F.E._{CO} is greater for the N₂-saturated 3.0-M KHCO₃ solution compared with the analagous CO₂-saturated solution at every current density between 20 and 100 mA cm⁻². This result is the first observation of KHCO3 reduction to CO in the absence of a gaseous CO2 feed, and the first example of KHCO₃ reduction to a reduced carbon product other than formate. It is also noteworthy that the electrochemical performance of a CO_2 -free KHCO₃ solution marginally exceeds that of the analogous CO₂-saturated solution. Electrochemical reduction of the N₂-saturated 3.0-M K₂CO₃ solution showed a F.E._{CO} of 18% at 20 mA cm⁻², 5% at 100 mA cm⁻² (Figure 7.2b, blue). This is the first example of the production of a reduced carbon product (CO) from a carbonate electrolyte in the absence of gaseous CO₂ supply. The F.E._{CO} for N₂-saturated K₂CO₃ and KHCO₃ solutions were stable at 20 mA cm⁻² during 3 h sustained electrolysis (Figure 7.3).



Figure 7.3. Faradaic efficiencies of CO production at a constant current of 20 mA cm⁻² over 3 h for N₂-saturated 3 M KHCO₃, CO₂-saturated 3 M KHCO₃ and N₂-saturated 3 M K₂CO₃.

The concentrations of dissolved CO₂ in each of the three electrolytes were calculated in an effort to determine the most likely species in solution undergoing electrochemical reduction. [CO₂] values in bulk solution were resolved using the bicarbonate and carbonate equilibria equations (eqs 7.4 and 7.5, respectively) in conjunction with the pH as measured by pH meter (Table 7.1). The pH for CO₂-saturated 3.0-M KHCO₃ solution was measured to be 8.2 giving a [CO₂] = 33 mM. This concentration is consistent with the reported value of saturated CO₂ aqueous solution.^{86,172} The pH values of N₂-saturated 3.0-M KHCO₃ and 3.0-M K₂CO₃ electrolytes were measured to be 9.0 and 13.7, respectively, giving [CO₂] = 6.6 mM and 4.8×10^{-8} mM, respectively, both significantly lower than [CO₂] in the bicarbonate solution bubbled with CO₂.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$
 $pK_{a1} = 6.4$ (eq 7.4)
 $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H^+$ $pK_{a2} = 10.3$ (eq 7.5)

Despite the ~5-fold difference in $[CO_2]$ between the CO₂-saturated and N₂-saturated bicarbonate solutions, these two solutions exhibit similar performance for the electrochemical production of CO in the flow cell. Furthermore, N₂-saturated K₂CO₃ exhibits moderate electrochemical reduction performance despite containing CO₂ concentrations of merely 10⁻⁸ mM. These results collectively suggest that KHCO₃ may be undergoing electrochemical conversion to CO via a direct reduction pathway (eq 7.6) at the surface of the electrode in my flow cell. This observation is in stark contrast with more recent mechanistic reports that suggest that only CO₂ is the electrochemically active species.^{86,169}

$$HCO_3^- + 3 H^+ + 2 e^- \rightarrow CO + 2 H_2O$$
 (7.6)

Table 7.1. pH values and corresponding CO_2 concentrations in the different electrolytes in Figure 2: CO_2 -saturated 3.0-M KHCO₃, N₂-saturated 3.0-M KHCO₃ and N₂-saturated 3.0-M K₂CO₃. pH values were measured with a pH meter. [CO₂] was calculated according to eqs. 4 and 5 (Table A7-1).

Electrolytes	3.0 M KHCO ₃ + CO ₂	3.0 M KHCO ₃ + N ₂	$3.0 \text{ M K}_2 \text{CO}_3 + \text{N}_2$
Measured pH	8.2	9.0	13.7
Calculated [CO ₂] (mM)	33	6.6	4.8×10 ⁻⁸

The above measurements on the electrolyte pH can be used to estimate CO_2 concentration in bulk solutions; however, the chemical environment at the surface of the electrode (i.e., where the conversion reactions actually take place) is more challenging to define due to a lack of *in operando* physical tools that can readily integrate with my flow cell. I therefore combined my bulk solution measurements with predictions from previously-reported mathematical models for cathode surface CO_2 concentrations in a bicarbonate electrolyte ^{173,174} in an effort to qualitatively assess electrode surface conditions. These models predict that the environment at the surface of the electrode is likely to have a higher pH compared to the bulk solution due to the consumption of protons during the electrochemical formation of either H₂ or CO, resulting in a lower localized concentration of CO_2 . This prediction infers that bicarbonate could be directly reduced to CO, rather than first forming CO_2 at the surface of electrode. It is worth noting, however, that the bipolar membrane transports protons to the surface of cathode, raising the question of whether this material feature of the flow cell creates an increased local CO_2 concentration near the electrode surface, which would instead correspond to an indirect bicarbonate reduction mechanism.

I next performed electrochemical experiments with N₂-saturated 3.0-M KHCO₃ electrolyte in flow cell containing an anion exchange membrane (AEM), wherein no proton transport to the cathode is expected to occur. The results showed a moderate F.E._{CO} of ~35% at 20 mA cm⁻² (Figure 7.4) demonstrating that bicarbonate reduction is viable without proton supply from membrane (i.e., without

 CO_2 formation). The inferior performance of the AEM system relative to the bipolar membrane system could point to an indirect bicarbonate reduction mechanism, but could also be explained by a decreased concentration of bicarbonate due to bicarbonate anion transport across AEM from cathode to anode. A second control experiment performed in an H-cell (i.e., no membrane adjacent to the cathode surface) with N₂-saturated 3.0-M KHCO₃ also gave moderate F.E._{CO} ~38% at 20 mA cm⁻² (Figure 7.4). These results, while not entirely definitive, do suggest a possible mechanism effectuated by my flow cell for bicarbonate reduction to CO that does not pass through a CO₂ intermediate.



Figure 7.4. Faradaic efficiencies of CO (F.E._{CO}) measured at constant current densities between 20 and 100 mA cm⁻² for a flow cell with a bipolar membrane (BPM), a flow cell with anion exchange membrane (AEM) and an H-cell.

In-situ attenuated total reflectance infrared spectroscopy (ATR-IR) was also performed upon the catalyst surface during electrolysis in an effort to qualitatively assess $[CO_2]$ at the surface of the Ag cathode (Figures 7.5 and 7.6). The *in-situ* ATR-IR spectra of CO₂-saturated 3.0 M KHCO₃, N₂-saturated 3.0 M KHCO₃ and N₂-saturated 3.0 M K₂CO₃ solutions were measured with a potential of 2.0 V applied between silver cathode and platinum anode (Figure 7.5). The ATR-IR spectra of deionized water is also provided as a reference. The spectra measured between 1200 and 3800 cm⁻¹ (left in Figure 7.6) show the peaks of H₂O at 3300 cm⁻¹ and 1640 cm⁻¹ (for all solutions), HCO₃⁻ at 1360 cm⁻¹ (for CO₂-saturated and N₂-saturated 3.0 M KHCO₃) and CO₃²⁻ at 1380 cm⁻¹ (for N₂-saturated 3.0 M K₂CO₃). The peak at 2345

 cm^{-1} correlated to the asymmetric stretching of CO₂ (right in Figure 7.6) is only observed in the CO₂saturated 3.0-M KHCO₃ experiments, but is absent from the spectra in the case of the N₂-saturated 3.0-M KHCO₃ and K₂CO₃ solutions. This observation suggests that the surface concentrations of CO₂ in the latter two cases are significantly lower than in the CO₂-saturated solution, which further supports the possibility for direct bicarbonate reduction.



Figure 7.5 Experimental setup of the *in-situ* attenuated total reflectance infrared (ATR-IR) spectroscopy. Silver nanoparticles were deposited onto the diamond prism of the Fourier transform infrared spectrometer and served as cathode for reduction of CO_2 /bicarbonate/carbonate electrolyte. Platinum mesh was used as anode and a potential of 2.0 V was applied between anode and cathode.



Figure 7.6 Attenuated total reflectance infrared (ATR-IR) spectra of CO_2 -saturated 3.0 M KHCO₃ (black), N₂-saturated 3.0 M KHCO₃ (orange), N₂-saturated 3.0 M K₂CO₃ (blue) solutions and deionized water (grey). *In-situ* ATR-IR signals (except H₂O) were measured with a potential of 2.0 V applied between silver cathode and platinum anode. Peaks for H₂O, HCO₃⁻ and CO₃²⁻ near the surface of silver cathode are labeled in the figure on the left and the figure on the right is zoomed into 2200-2600 cm⁻¹ to show the peak for CO₂ at the surface of silver cathode.

7.2.3. Dependence of Faradaic efficiency for CO on concentrations of bicarbonate and CO₂

The relationship between F.E._{CO} and the [HCO₃-] and [CO₂] in solution was investigated by measuring the F.E._{CO} at 20 mA cm⁻² for a series of N₂-saturated and CO₂-saturated KHCO₃ solutions prepared with bicarbonate concentrations ranging from 0.5 M to 3.0 M (Figure 7.7a). The results show that increasing the concentration of KHCO₃ increases the F.E._{CO} from 14% at 0.5 M to 67% at 3.0 M. The same solutions bubbled with CO₂ show a similar (but less pronounced) increase in F.E._{CO} from 37% at 0.5-M KHCO₃ to 62% at 3.0-M KHCO₃. These trends are also reflected in the results at current densities between 40 and 100 mA cm⁻² (Figure A7.2 to Figure A7.6). The pH of each solution and corresponding [CO₂] were measured (Table 7.2) which show that the increase in F.E._{CO} for the CO₂-fed system is not related to the concentration of CO₂ in solution (which is 33 mM for all solutions), but to the suppression of HER caused by the higher pH at higher [HCO₃⁻].⁸⁶ The F.E._{CO} in solutions with concentrations < 2 M KHCO₃ were greater in each case for the CO₂-fed electrolytes which is within the range where most

previous CO_2RR studies have been carried out. The N₂-saturated solution outperforms that of the CO_2 saturated solution at [KHCO₃] > 2.5 M to exhibit a greater F.E._{CO} despite having a significantly lower concentration of dissolved CO_2 , likely due to the suppression of HER in less acidic solution (pH values in N₂-saturated and CO_2 -saturated 3.0-M KHCO₃ solutions are 9.0 and 8.2, respectively).^{86,88}



Figure 7.7 Faradaic efficiencies for CO (F.E._{CO}) as a function of KHCO₃ and CO₂ concentrations. (a) F.E._{CO} measured at 20 mA cm⁻² in a series of KHCO₃ solutions prepared with different bicarbonate concentrations saturated with CO₂ (black) or N₂ (orange), where F.E._{CO} showed dependence on KHCO₃ concentration. (b) F.E._{CO} (green) measured at 20 mA cm⁻² in a series of electrolyte solutions where different amounts of K₂CO₃ were added to the N₂-saturated KHCO₃ to adjust CO₂ concentration (grey) while keeping bicarbonate concentration constant at 3.0 M, where F.E._{CO} showed independence on CO₂ concentration.

The concentrations of bicarbonate and CO_2 in the N₂-saturated solutions both increase with increasing [HCO₃⁻] at constant pH (Table 7.2). The results from these solutions therefore cannot be used to distinguish between which possible reactants (i.e., bicarbonate or CO_2 corresponding to direct or indirect reduction pathways, respectively) lead to greater F.E._{CO} values. I therefore used a bicarbonate-carbonate buffer system wherein the pH values were adjusted by adding different amounts of K₂CO₃ to the N₂-saturated KHCO₃ solutions (Figure 7.7b), causing [CO₂] to change while [HCO₃⁻] was held constant at 3.0 M.⁸⁶ The solution pH increased from 9.0 to 10.4 (Figure 7.8) as the ratio of [CO₃²⁻]/[HCO₃⁻]

was increased from 0 to 0.4, and $[CO_2]$ correspondingly decreased from 6.6 mM to 0.17 mM (Figure 7.7b, grey). F.E._{CO} measured at 20 mA cm⁻², however, remained unchanged (Figure 7.7b, green) despite a drop in $[CO_2]$ by an order of magnitude. This result indicates that F.E._{CO} of N₂-saturated KHCO₃ system is largely independent of $[CO_2]$. The dependence of F.E._{CO} on $[HCO_3^-]$ (Figure 7.7a) and independence on $[CO_2]$ (Figure 7.7b) collectively provide evidence that supports a direct reduction pathway for bicarbonate to form CO. However, it should be noted that these results do not preclude the existence of an indirect bicarbonate reduction mechanism, and further spectroscopic studies would be needed to fully distinguish between the two pathways.

Table 7.2. pH values and corresponding CO_2 concentrations in a series of electrolyte solutions (in Figure 7.7a) as a function of KHCO₃ concentration saturated with CO_2 or N₂. pH values were measured by pH meter. [CO_2] values were calculated according to eqs. 4 and 5 (see Tables A7.2 and A7.3).

[KHCO ₃] (M)	CO ₂ -saturated		N ₂ -saturated	
	Measured pH	Calculated [CO ₂] (mM)	Measured pH	Calculated [CO ₂] (mM)
0.5	7.4	33	9.0	1.1
1.0	7.5	33	9.0	2.2
1.5	7.6	33	9.0	3.3
2.0	7.9	33	9.0	4.4
2.5	8.0	33	9.0	5.5
3.0	8.2	33	9.0	6.6



Figure 7.8 pH values in a series of electrolyte solutions (in Figure 7.7b) where different amounts of K_2CO_3 was added to N₂-saturated 3.0-M KHCO₃. pH values were measured by pH meter.

7.3. Conclusion

I have demonstrated that bicarbonate and carbonate can be reduced into CO in a flow cell without the supply of gaseous CO₂ to the electrolyte. The 3.0-M KHCO₃ system without a CO₂ feed results in a greater Faradaic efficiency for CO than the CO₂-fed solution. The observations that (i) aqueous carbonate, wherein $[CO_2]$ is negligible, can be reduced into CO; and (ii) bicarbonate reduction shows strong dependence on $[HCO_3^-]$ but no dependence on $[CO_2]$, collectively appear to implicate a pathway for the direct reduction of bicarbonate to form CO. My bicarbonate reduction system requires further optimizations to increase the electrolytic performance towards CO production; however, this study provides a new strategy for directly converting aqueous bicarbonate and carbonate species into valuable commodities without the need to first extract CO₂ gas from a bicarbonate or carbonate solution by an energy-intensive thermally-driven decomposition step.

7.4. Experimental details

7.4.1. Materials

KHCO₃ (99%) and K₂CO₃ (99%) were purchased from Alfa Aesar. Ag nanopowder (trace metal basis, 99%) and Nafion 117 solution (5 wt%, in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Carbon paper was purchased from the Fuel Cell Store and cut into desired dimensions with a blade. Nickel foam gas diffusion electrode material was purchased from MTI. Bipolar membranes (Fumasep FBM) were purchased from FuMA-tech and stored in 1M NaCl Solution.

7.4.2. Electrode preparation

The cathode catalyst ink was prepared by mixing 52 mg of silver nanopowder, 500 μ L of DI water, 500 μ L of isopropyl alcohol and 70 μ l Nafion 117 solution. The catalyst ink was then spray-coated on a 4-cm² area of carbon paper and dried under a gentle air stream. Kapton tape (McMaster-Carr) was used as a mask during the deposition process to avoid catalyst being deposited outside the active area of the carbon paper. The catalyst loading was determined to be 100-120 counts per second by X-Ray fluorescence analysis.

7.4.3. Electrochemical measurement and product analysis

A CH instruments 660D with a picoamp booster was used for all experiments. Electrochemical measurements were made with a two-electrode system with Ni foam as the anode and Ag spray-coated on carbon paper as the cathode. The anode electrolyte was 1 M KOH solution delivered by a peristaltic pump at 50 mL/min. The cathode electrolyte was 3 M K₂CO₃ or $0.5 \sim 3$ M KHCO₃ with 0.02 M ethylenediaminetetraacetic acid (EDTA, 99%, Sigma Aldrich) added to remove impurities.¹⁷⁵ Catholyte solution was bubbled with N₂ (Praxair, 99.9%) or CO₂ (Praxair, 99.9%) gas at 50 sccm in a sealed flask with an outlet into the flow cell. The catholyte solution was delivered by another peristaltic pump at 50 mL/min into the flow cell electrolyzer, which was then vented back into the flask. Samples of the gas headspace in the flask were delivered into a gas chromatograph (GC, Perkin Elmer). The GC was equipped with a packed

MolSieve 5A column and a packed HayeSepD column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector (FID) equipped with a methanizer was used to quantify CO concentrations and a thermal conductivity detector (TCD) was used to quantify H_2 concentrations. Control experiments with a two-compartment H-cell were performed wherein the anode (platinum mesh) and cathode (Ag-coated carbon paper) compartments both contained 30 mL of 3.0-M KHCO₃ separated by a proton exchange membrane (NafionTM). The cathode electrolyte was bubbled with N_2 gas at 50 sccm and gas samples in the headspace of the cathode compartment were analyzed by GC.

7.4.4. In-situ attenuated total reflectance infrared measurements

ATR-IR measurements were conducted on a Bruker Alpha II Fourier transform infrared spectrometer (FTIR) in ATR mode. Silver nanoparticles were deposited onto the diamond prism of the FTIR and served as cathode for reduction of CO₂/bicarbonate/carbonate, enabling simultaneous ATR-IR measurement of species near the surface of silver cathode while performing electrochemistry. CO₂-saturated 3.0 M KHCO₃, N₂-saturated 3.0 M KHCO₃ and N₂-saturated 3.0 M K₂CO₃ solutions were used as electrolytes. Platinum mesh was used as anode and a potential of 2.0 V was applied between anode and cathode. ATR-IR spectra were collected with 4 cm⁻¹ resolution and 16 scans were applied for each measurement.

Chapter 8: Conclusions and Future Directions

8.1. Conclusions

This thesis set out to study some EC and PEC reactions that can generate useful products and I demonstrated that a proper selection of reactant is very important to make a value-added EC or PEC reaction. Chapters 3 to 5 explored some anode reactions in a PEC cell. Chapter 3 aimed at making a more efficient photoanode (i.e. with higher photocurrent density at a certain voltage) and I proved that UV radiation on BiVO₄ photoanode is capable of improving the PEC activity. The reason for this UV curing effect is believed to be that UV radiation removes the non-lattice oxygen sites at surface and therefore suppresses charge recombination that are deleterious to PEC oxidation of water. By immersing this $BiVO_4$ photoanode into organic solvent, I was able to drive some alternative organic oxidations that created organic products with higher economic values than the O₂ produced by OER in a traditional PEC water splitting cell. In Chapter 4, I demonstrated the first PEC organic oxidation (alcohol oxidation and C-H oxidation) in organic solvent. The use of non-aqueous media in place of water led to significantly higher photoanode stability as well as a broader scope of organic transformations that can be driven in a PEC cell. Chapter 5 extended this PEC organic oxidation technology to lignin decomposition chemistry, which is more complicated and bears higher economic value. I also showed that the vanadium sites at the surface of BiVO₄ photoanode is likely to be catalytic active for lignin decomposition, which precluded the need for a redox mediator in solution.

I also studied carbon reduction chemistry on the cathode side of an EC cell. In Chapter 6, I reported that cathodic CO_2 reduction can occur in tandem with anodic organic oxidation and produce higher-valued products (compared to cathodic HER and anodic OER) at both electrodes. In Chapter 7, I proved that bicarbonate and carbonate can be directly reduced to CO via an electrochemical flow cell without the supply of CO_2 gas. Using bicarbonate/carbonate instead of CO_2 as the carbon species for

cathodic reduction enabled a more energy-saving pathway in carbon capture and utilization schemes by avoiding the energy-intensive thermally-driven step to first extract CO₂ gas from bicarbonate/carbonate.

8.2. Future directions

The study in Chapter 3 requires a further understanding of the mechanism of the UV curing effect. I have proved the removal of non-lattice oxygen and some morphological rearrangements after UV radiation, while it still remains unclear how UV light interact with BiVO₄ surface and remove those oxygen atoms. Some other surface characterization methods (e.g. Raman spectroscopy, X-ray absorption spectroscopy) can be applied to study bond cleavage process of Bi-O and/or V-O and may provide some further information on the mechanism of UV curing effect.

The anodic organic transformations in Chapters 4-6 can be further studied in the following aspects. First, the mechanism of PEC organic oxidations still requires further understandings. We have proved that 'BuOOH play an important role in PEC C-H oxidations, but the mechanism proposed in Figure 4.7 and the existence of the radical/cation species of tetralin still require further experimental evidence. Alternative oxygen source (e.g. O₂, air, H₂O) can be utilized in replace of 'BuOOH to explore the two possible reaction pathways in Figure 4.7 and understand the role of 'BuOOH. Secondly, I can investigate more types of anodic organic reactions on photoanode, e.g. functionalization of olefin,¹⁷⁶ hole-initiated Diels-Alder reaction,¹⁷⁷ decomposition of native lignin biomass etc. Thirdly, the yields of products can be enhanced by optimization of reactions conditions, e.g. finding a more reactive redox mediator, making a more active anode, etc. Finally, larger scale of organic transformations can be achieved in a flow cell. Our group has started pairing cathodic CO₂ reduction with anodic alcohol oxidation in a flow cell and a preliminary paired electrolysis has been successfully achieved. More complicated organic oxidations in flow cell still require further exploration.

The lignin study in Chapter 5 can be further explored in the following ways. We have proved the viability of driving PEC decomposition of lignin models by BiVO₄ photoanode and the special role of surface vanadium in the catalysis process. The mechanism of this BiVO₄-mediated catalysis, however, is

still unclear. The chemical decomposition of lignin was believed to involve the formation of some radical intermediates,^{132,145} raising up the question whether my photoelectrochemical decomposition methodology follows similar reaction pathway. I can study the reaction mechanism by analyzing the reaction mixture with radical trappers and electron paramagnetic resonance spectroscopy, which is able to detect radical intermediate. Secondly, I have only studied the PEC decomposition of *lignin models*, whereas the PEC decomposition of *native lignin biomass* still remained unexplored. The native lignin biomass have poor solubility in most common solvents, which may lead to additional light absorption by the lignin clusters. A new configuration of PEC cell may be required to accommodate the lignin clusters, where simulated sunlight is first absorbed by the photoanode before the light reaches the reaction mixture. In addition, we have only proved the bond cleavage of the " β -O-4" connection in my PEC system, so further studies on the PEC decomposition of other types of connections in lignin polymers are required.

The study on bicarbonate reduction in Chapter 7 can be continued in the following ways. First, I have provided some evidence for a *direct* bicarbonate reduction pathway but further mechanism study is required to prove the *direct* reduction pathway. Simulation can be performed to calculate the concentrations of bicarbonate and CO₂ at the surface of electrode. While this type of simulation has been reported for an H cell,¹⁷⁴ the calculation for a flow cell is more challenging and has never been reported. Our group is developing some temperature and pressure sensors that can probe the electrode surface of a CO₂ flow cell, which can also be applied to a bicarbonate flow cell and study the surface process of bicarbonate reduction. Secondly, the performance (e.g. current density, selectivity, long-term stability) of bicarbonate reduction to CO can be further enhanced by optimizations, e.g. making nanostructured silver, changing catalyst loading, changing catalyst support, etc. Thirdly, our group is studying a flow cell capable of reducing bicarbonate/carbonate into carbon products with higher value than CO (e.g. methane, ethylene, ethanol), where the cathode catalyst is copper instead of silver. Finally, this bicarbonate/carbonate reduction technique can be scaled and applied to the carbon capture and utilization industry.

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Appendix

Appendix data for Chapter 3



Figure A3.1 Photocurrent (AM1.5 front-side illumination) densities of BiVO₄ photoanodes with exposure to UV radiation of 0 (black), 5 (red), 10 (green), 20 (blue) and 30 (orange) hours.



Figure A3.2 Nyquist plots of $BiVO_4$ with 0 h (a) and 20 h (b) exposure to UV radiation over the 0.5-1.0 V vs RHE range.



Figure A3.3 Fitting results of capacitance for first (C_{bulk} , a) and second semicircles (C_{ss} , b) in the Nyquist plots for BiVO₄ with 0 h (black) and 20 h (red) exposure UV radiation.



Figure A3.4. X-ray photoelectron spectrum featuring the bismuth 4f peaks of BiVO₄ with 0 h (black) and 20 h (red) exposure to UV radiation.



Figure A3.5. Cell configuration for PEC water oxidation. PEC experiments were performed in a threeelectrode photoelectrochemical cell with the BiVO₄ photoanode as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire mesh as the counter electrode



Figure A4.1 (a) GC-MS traces of PEC oxidation of benzyl alcohol (BnOH) into benzaldehyde. (b) Calibration curve of benzaldehyde made by plotting the relative peak area versus concentration of benzaldehyde. (Carvone was used as the internal standard.)



Figure A4.2 (a) GC-MS traces of PEC oxidation of cyclohexene into cyclohexenone. (b) Calibration curve of cyclohexenone made by plotting the relative peak area versus concentration of cyclohexenone. (Carvone was used as the internal standard.)



Figure A4.3 (a) GC-MS traces of PEC and EC oxidations of tetralin into 1-tetralone. (b) Calibration curve of 1-tetralone made by plotting the relative peak area of 1-tetralone versus concentration of 1-tetralone. (Carvone was used as the internal standard.)

Syntheses of alcohol lignin model compounds:



Scheme A5.1 Formation of alcohol lignin model compounds using 2-bromoacetophenone derivatives and phenol derivatives.

2-phenoxy-1-phenylethan-1-ol (1)



¹**H** NMR (300 MHz, Chloroform-*d*) δ 7.51 – 7.27 (m, 7H), 6.99 (ddt, *J* = 8.5, 7.3, 1.1 Hz, 1H), 6.96 – 6.90 (m, 2H), 5.14 (dt, *J* = 8.8, 2.8 Hz, 1H), 4.12 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.02 (dd, *J* = 9.6, 8.8 Hz, 1H), 2.80 (d, *J* = 2.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 139.5, 129.2, 128.2, 127.78, 126.0, 120.9, 114.3, 72.9, 72.2. Spectral data are confirmed with those previously reported.¹³³

1-(4-methoxyphenyl)-2-phenoxyethanol (2)



¹H NMR (300 MHz, Chloroform-*d*) δ 7.42 – 7.24 (m, 4H), 7.02 – 6.86 (m, 5H), 5.08 (dt, *J* = 8.7, 2.9 Hz, 1H), 4.17 – 3.96 (m, 2H), 3.82 (s, 3H), 2.77 (d, *J* = 2.5, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 159.3, 158.2,

131.59, 129.4, 127.4, 121.1, 114.4, 113.8, 73.1, 72.0, 55.1. Spectral data are confirmed with those previously reported.¹³³

2-phenoxy-1-phenylpropane-1,3-diol (3, example of detailed synthesis)

Step 1: 2-bromoacetophenone (1.59 g, 8.0 mmol), phenol (0.50 g, 5.3 mmol) and K_2CO_3 (0.50 g, 5.3 mmol) were added to 50 mL round bottom flask equipped with a

reflux condenser in 10 mL dry THF. The resulting suspension was stirred at reflux for 8 h. The suspension was diluted in water (20 mL), then extract with EtOAc (20 mL) twice. The combined organic layers was then washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo* to afford light yellow oil. The crude product was carried forward without purification.

Step 2: The crude product 2-bromoacetophenone (1.06 g, 5.0 mmol) was dissolved in 50 mL ethanol followed by K_2CO_3 (1.04 g, 7.5 mmol) at room temperature. The resulting suspension was stirred for 30 min before adding a water solution (37 wt%) of formaldehyde (0.81 mL, 10 mmol). After all starting material was consumed by monitoring reaction by TLC (50% EtOAc in Hexane), NaBH₄ (0.67 g, 17 mmol) was added in one portion and the reaction mixture was stirred for 1 h. The reaction was concentrated *in vacuo*. The crude oil was was diluted in diethyl ether (100 mL) and quenched slowly with saturated NH₄Cl solution (50 mL), then extracted with diethyl ether (100 mL). The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo* to afford yellow oil. The oil was purified by column chromatography (50% EtOAc in Hexane) to give mixture of diastereomers of compound **3** (0.85 g, 3.5 mmol) in 70% yield over 2 steps.

Erythro: ¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.52 – 7.25 (m, 7H), 7.06 – 6.88 (m, 3H), 5.15 – 5.10 (m, 1H), 4.44 (dq, *J* = 6.7, 3.7 Hz, 1H), 4.01 – 3.88 (m, 1H), 3.83 (dt, *J* = 12.0, 4.4 Hz, 1H), 2.80 (d, *J* = 3.3 Hz, 1H), 2.75 (d, *J* = 3.6 Hz, 1H), 2.14 (t, *J* = 6.5 Hz, 1H);

Threo: ¹**H** NMR (300 MHz, Chloroform-*d*) δ 7.52 – 7.25 (m, 7H), 7.06 – 6.88 (m, 3H), 5.07 (dd, J = 6.7, 3.1 Hz, 2H), 4.44 (dq, J = 6.7, 3.7 Hz, 1H), 3.83 (dt, J = 12.0, 4.4 Hz, 1H), 3.59 (ddd, J = 11.7, 7.1, 4.0 Hz, 1H), 2.80 (d, J = 3.3 Hz, 1H), 1.77 (t, J = 6.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃ mixture of diastereomers) δ 157.8, 157.3, 140.2, 139.5, 129.4, 129.3, 128.2, 128.1, 127.8, 127.7, 126.6, 126.1, 121.2, 121.5, 116.4, 116.3, 82.4, 81.5, 73.7, 73.3, 60.9, 60.6. Spectral data are confirmed with those previously reported.^{178,179}

1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol (4)



Erythro: ¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.22 (m, 4H), 7.04 – 6.95 (m, 2H), 6.95 – 6.84 (m, 3H), 5.06 (dd, *J* = 5.3, 3.5 Hz, 1H), 4.40 (dt, *J* = 7.2, 3.8 Hz, 3H), 4.00 – 3.83 (m, 1H), 3.80 (d, *J* = 3.7 Hz, 3H), 2.72 (d, *J* = 3.5 Hz, 1H), 2.21 (t, *J* = 6.5 Hz, 1H);

Threo: ¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.22 (m, 4H), 7.04 – 6.95 (m, 2H), 6.95 – 6.84 (m, 3H), 5.01 (dd, *J* = 7.0, 3.0 Hz, 2H), 4.40 (dt, *J* = 7.2, 3.8 Hz, 1H), 3.80 (d, *J* = 3.7 Hz, 3H), 3.55 (ddd, *J* = 12.1, 7.5, 3.9 Hz, 1H), 2.78 (d, *J* = 3.0 Hz, 1H), 1.84 – 1.73 (m, 1H). ¹³**C NMR** (101 MHz, CDCl₃ mixture of diastereomers) δ 159.6, 159.4, 158.5, 158.0, 133.1, 132.3, 130.0, 129.8, 128.4, 127.9, 122.1, 122.0, 116.9, 116.8, 114.1, 114.1, 83.0, 82.1, 73.9, 73.4, 61.6, 61.2, 60.8, 55.5. Spectral data are confirmed with those previously reported.¹⁸⁰

2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (5)



Erythro: ¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 2H), 6.99 – 6.75 (m, 6H), 4.98 (dd, *J* = 7.1, 2.9 Hz, 2H), 4.28 – 4.20 (m, 1H), 3.97 – 3.83 (m, 1H), 3.77 (s, 6H), 2.67 (d, *J* = 3.4 Hz, 1H), 2.17 (t, *J* = 6.4 Hz, 1H);

Threo: ¹**H NMR** (300 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 2H), 6.99 – 6.75 (m, 6H), 5.05 – 5.00 (m, 1H), 4.28 – 4.20 (m, 1H), 3.97 – 3.83 (m, 1H), 3.81 (s, 6H), 3.53 (ddd, *J* = 11.8, 7.5, 3.9 Hz, 2H), 2.78 (d, *J* = 3.0 Hz, 2H), 2.17 (t, *J* = 1.76 (dd, *J* = 7.4, 5.2 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃ mixture of diastereomers) δ 159.1, 158.9, 154.4, 154.4, 151.9, 151.5, 132.5, 131.7, 127.9, 127.3, 118.1, 117.9, 114.5, 114.4, 113.6, 113.5, 84.2, 83.2, 73.39, 73.1, 61.0, 60.7, 55.4, 55.0. Spectral data are confirmed with those previously reported.¹⁸¹

Lignin model compound	Yields of phenol products ^a	Yields of formic acid ^b
1	5 ± 1%	2 ± 1%
2	6 ± 1%	$2 \pm 1\%$
3	$20 \pm 1\%$	5 ± 1%
4	23 ± 2%	$5 \pm 1\%$
5	27± 2%	6 ± 1%

Table A5.1 Yields of phenol products from the decompositions of lignin model compounds 1-5.

^a Yields of phenol products were quantified by GC-MS. ^b Yields of formic acid were quantified by ¹H NMR.

Anodes and conditions	Yields of 7 ^a	Yields of formic acid ^b
FTO, PEC	5 ± 1%	2 ± 1%
FTO, EC	5 ± 1%	$2 \pm 1\%$
V ₂ O ₅ , PEC	$10 \pm 2\%$	3 ± 1%
V_2O_5 , EC	$10 \pm 1\%$	3 ± 1%
BiVO ₄ , PEC	23 ± 1%	5 ± 1%
BiVO ₄ , EC	$4 \pm 1\%$	$2 \pm 1\%$
BiVO ₄ V ₂ O ₅ , PEC	$30 \pm 2\%$	$7 \pm 1\%$
BiVO ₄ V ₂ O ₅ , EC	12 ± 2%	3 ± 1%

 Table A5.2 Yields of phenol (7) and formic acid from the decompositions of 4 with different anode

 materials under photoelectrochemical (PEC) or electrochemical (EC) condition.

^a Yields of 7 were quantified by GC-MS. ^b Yields of formic acid were quantified by ¹H NMR.



Figure A6.1 Cyclic voltammetry profiles of a blank 0.50 M NaHCO₃ aqueous solution (black) prior to the successive addition of 0.20 mmol TEMPO (orange), followed by the addition of 0.25 mmol of three others alcohols (independent experiments): ethanol (blue), 4-methoxybenzyl alcohol (red), and isopropanol (green). All data recorded at a scan rate of 10 mV/s in 25 mL aqueous solution.



Figure A6.2 Cyclic voltammetry profiles of a blank 0.50 M NaHCO₃ aqueous solution (black) prior to addition of 0.25 mmol 1-phenylethanol (without TEMPO added).



Figure A6.3 ¹H NMR spectra showing temporal conversion of 4-methoxybenzyl alcohol (blue) into 4methoxybenzaldehyde (orange) over the course of a 3-h electrolysis experiment. Benzene-1,3,5tricarboxylic acid (grey) was added as an internal standard. The signals at 4.8 ppm are water residue peaks from solvent suppression.



Figure A6.4 ¹H NMR spectra showing temporal conversion of 1-phenylethanol (blue) and acetophenone (orange) over course of a 1.5-h electrolysis experiment. Benzene-1,3,5-tricarboxylic acid (grey) was added as internal standard. The signals at 4.8 ppm are water residue peaks from solvent suppression.



Figure A6.5 ¹H NMR spectra showing temporal conversion of ethanol (blue), acetaldehyde (orange) and acetic acid (green) over course of a 3-h electrolysis experiment. Benzene-1,3,5-tricarboxylic acid (grey) was added as internal standard. The signals at 4.8 ppm are water residue peaks from solvent suppression. The rest signals are attributed to the acetaldehyde hydrate (1,1-ethanediol).



Figure A6.6 ¹H NMR spectra showing temporal conversion of isopropanol (blue) and acetone (orange) over course of a 3-h electrolysis experiment. Benzene-1,3,5-tricarboxylic acid (grey) was added as internal standard. The signals at 4.8 ppm are water residue peaks from solvent suppression.



Figure A6.7 Relative concentrations of isopropanol (blue) and acetone (orange) determined by ¹H NMR spectroscopy over the course of a 3 h electrolysis experiment.

Calculation of [CO₂] in solution:

According to the bicarbonate and carbonate equilibria equations (eqs A7.1 and A7.2, respectively), the distribution fraction of CO₂, α (CO₂), in solution can be derived as eq A7.3.

$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$	$pK_{a1} = 6.4$	(eq A7.1)
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$HCO_3^- + H_2O$	$\leftrightarrow CO_3^{2-} + H^+$	$pK_{a2} = 10.3$	(eq A7.2)
	0		· · · /

$$\alpha(CO_2) = [H^+]^2 / \{ [H^+]^2 + K_{a1}[H^+] + K_{a1} * K_{a2} \}$$
 (eq A7.3)

And the CO_2 concentration, $[CO_2]$, can be calculated as eq A7.4.

$$[CO_2] = total carbon concentration * \alpha(CO_2) \qquad (eq A7.4)$$

Where total carbon concentration is the concentration of KHCO₃ and/or K₂CO₃ as prepared.

Electrolytes	3.0 M KHCO ₃ + CO ₂	3.0 M KHCO ₃ + N ₂	$3.0 \text{ M K}_2 \text{CO}_3 + \text{N}_2$
pH	8.2	9.0	13.7
$\alpha(\mathrm{CO}_2)$	0.011	0.0022	1.6×10 ⁻⁸
total carbon concentration (M)	3.0	3.0	3.0
[CO ₂] (mM)	33	6.6	4.8×10 ⁻⁸

Table A7.1 [CO2] data in Figure 7.2.

	[KHCO ₃] (M)					
	0.5	1.0	1.5	2.0	2.5	3.0
pH	7.4	7.5	7.6	7.9	8.0	8.2
$\alpha({ m CO}_2)$	0.066	0.033	0.022	0.0165	0.0132	0.011
total carbon concentration (M)	0.5	1.0	1.5	2.0	2.5	3.0
[CO ₂] (mM)	33	33	33	33	33	33

Table A7.2 [CO₂] data in the CO₂-saturated solutions in Figure 7.3a.

Table A7.3 $[CO_2]$ data in the N₂-saturated solutions in Figure 7.3a.

	[KHCO ₃] (M)					
	0.5	1.0	1.5	2.0	2.5	3.0
рН	9.0	9.0	9.0	9.0	9.0	9.0
$\alpha({ m CO}_2)$	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022
total carbon concentration (M)	0.5	1.0	1.5	2.0	2.5	3.0
[CO ₂] (mM)	1.1	2.2	3.3	4.4	5.5	6.6

	[CO ₃ ²⁻]/[HCO ₃ ⁻]				
	0	0.05	0.1	0.2	0.4
рН	9.0	9.4	9.7	10.0	10.4
$\alpha(\mathrm{CO}_2)$	0.0022	7.9×10 ⁻⁴	3.9×10 ⁻⁴	1.5×10 ⁻⁴	4.0×10 ⁻⁵
total carbon concentration (M)	3.0	3.15	3.3	3.6	4.2
[CO ₂] (mM)	6.6	2.5	1.3	0.55	0.17

Table A7.4 [CO₂] data in Figure 7.3b (different amounts of K₂CO₃ added into 3.0-M KHCO₃ solutions).



Figure A7.1 (a) Expanded view of the bipolar membrane-based electrolyzer cell configuration. (b) Membrane electrode assembly. (c) Dimensions (in cm) of the housing, gasket and flowplate components within the electrolyzer cell.



Figure A7.2 Faradaic efficiency of CO production at constant current densities (20, 40, 60, 80, 100 mA cm⁻²) for N₂-saturated and CO₂-saturated 2.5 M KHCO₃.



Figure A7.3 Faradaic efficiencies of CO production at constant current densities (20, 40, 60, 80, 100 mA cm^{-2}) for N₂-saturated and CO₂-saturated 2 M KHCO₃.



Figure A7.4 Faradaic efficiencies of CO production at constant current densities (20, 40, 60, 80, 100 mA cm^{-2}) for N₂-saturated and CO₂-saturated 1.5 M KHCO₃.



Figure A7.5 Faradaic efficiencies of CO production at constant current densities (20, 40, 60, 80, 100 mA cm^{-2}) for N₂-saturated and CO₂-saturated 1 M KHCO₃.



Figure A7.6 Faradaic efficiencies of CO production at constant current densities (20, 40, 60, 80, 100 mA cm^{-2}) for N₂-saturated and CO₂-saturated 0.5 M KHCO₃.