ELECTRODEPOSITION OF HIGHLY ACTIVE LITHIUM COBALT OXIDE THIN FILM ANODES IN PLATINUM METAL GROUP-FREE PHOTOELECTROCHEMICAL CELLS

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ABSTRACT OF THE THESIS

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In the development of high-performance, commercially-scalable photoelectrochemical cells (PECs) for solar-driven hydrogen production, effective and low-cost anodes must be engineered for long-term operation in alkaline solution. Lithium cobalt oxide (LiCoO$_2$) has been studied as a highly active and stable catalyst for the anodic oxygen evolution reaction (OER) in its delithiated cubic spinel polymorph, LiCo$_2$O$_4$.

Drawing inspiration from the dimensionally stabilized anode (DSA) configuration used for continuous electrochemical chlorine generation, a thin film of Li$_x$CoO$_2$ has been electrodeposited onto a passivated TiO$_x$/Ti support for functional integration as the dark anode in the PEC device. Kinetic performance as evaluated by cyclic and linear sweep voltammetry resulted in geometric current densities of 10 mA/cm$^2$ (corresponding to 10% photoelectrochemical conversion) achieved at 430 mV overpotential. Long-term stability measurements evaluated at 10 mA/cm$^2$ demonstrate continuous operation for up to 13 days with minimal loss in activity. Characterization via x-ray diffraction, x-ray photoelectron spectroscopy, and scanning electron microscopy coupled with electron dispersive spectroscopy give insight into the structure-property relationships responsible for the measured high electrochemical performance.
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I would also like to thank Shinjae Hwang, current senior graduate student in the Dismukes Solar Fuels Group, and Dr. Anders Laursen, current research associate, who have both not only provided extensive project guidance through this past year, but who have also provided the x-ray photoelectron spectroscopy and scanning electron microscopy-electron dispersive spectroscopy measurements, respectively, presented in this study. I additionally thank Prof. George Tsilomelekis for providing the preliminary Raman spectroscopy measurements utilized in this study.

I would finally like to acknowledge the prior work of former Dismukes Group member, Dr. Graeme Gardener: Structural Basis for Differing Electrocatalytic Water Oxidation by the Cubic, Layered and Spinel Forms of Lithium Cobalt Oxides. Energy Environ. Sci. 2016, 9(1), 184–19, and prior unpublished work by Shinjae Hwang on the electrodeposition of lithium cobalt oxide on fluorinated tin oxide substrates that together provided the primary groundwork for this study.
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DEDICATION

This work is dedicated to my parents, Sandhya and Ramesh Kashi, and sisters, Suma and Shwetha Kashi, for their constant love and encouragement toward my academic pursuits. I cannot thank them enough for all of the support they have given me to have reached these professional milestones and toward my future career endeavors.
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1. INTRODUCTION

1.1. Motivation and Broader Impact

Renewable energy sources, particularly solar- and wind-derived energy have seen a steady 2.5-3% growth rate in global primary energy supply and market share.\(^1\) Both the desire to capitalize on this growth rate as well as the urgent environmental need to displace fossil fuels as the backbone of the global economy requires a portfolio of flexible energy storage solutions to efficiently and scalably utilize intermittent solar and wind energy as chemical fuels. Figure 1-1 below from the DOE-EERE illustrates the 24-hour cycle of average grid load overlaid with the hourly profile of renewable energy supply.\(^2\) Simply put, storage solutions must be flexible enough to balance between peak energy supply and peak energy demand.

![Figure 1-1: Hourly Profile of Average Load and Average Wind and Solar Generation\(^2\)]

Lifecycle analysis studies by Barnhart et al. indicate that photovoltaic-based electrochemical energy storage devices, capable of harvesting solar energy and converting to a chemical fuel, exhibit the greatest “Energy-Return-on-Energy-Investment” (EROI).\(^3\) Of the chemicals that can be electrochemically generated to store solar energy, hydrogen (H\(_2\)) stands
as a viable candidate. H\textsubscript{2} not only combusts cleanly, without the emission of dominant greenhouse gases, but also has a mass-specific energy density that is nearly three times that of methane (CH\textsubscript{4}) / liquefied natural gas or other higher alkanes.

The viability of a hydrogen-driven economy requires production of hydrogen many orders above that conventionally produced via methane steam reformation. Electrolysis of water has been proposed to have the capability of supplying this need, but currently requires expensive, Platinum metal-group (PGM) electrocatalysts in order to efficiently lower the energy input and bring it closer to the thermodynamic minimum.\textsuperscript{[4]} The use of more earth-abundant, non-PGM catalysts that achieve the electrolysis of water at energy inputs on par with that of PGM catalysts can help to dramatically lower the cost and thus increase the scalability of electrolytic devices for renewable H\textsubscript{2} production. The focus of this study is the development of a scalable and active electrocatalyst configuration that is conducive to integration into a photoelectrochemical cell, a device capable of directly harvesting and converting solar energy into H\textsubscript{2}.

1.2. The Photoelectrochemical Cell

A photoelectrochemical cell (PEC) is a multi-junction tandem photoabsorber that is outfitted with water-splitting catalysts to perform the electrolysis of water from solar-derived electricity. Achieving both scalability and long-term stability of non-PGM electrocatalysts requires that the PEC operates under alkaline pH conditions.\textsuperscript{[5]} Scalable engineered tandem photoabsorber materials must be able to achieve best-in-class quantum efficiencies with low bandgap modulations required for efficient hole and electron transport to the electrodes’ catalytic surfaces while also remaining highly stable in the environment with minimal leaching of toxic substances.\textsuperscript{[6]} Figure 1-2 below illustrates a schematic of a PEC.
The primary objective of this study is the development of a high-performance anode configuration for effectively catalyzing the oxygen evolution reaction (OER).

1.3. Lithium Cobalt Oxide: Structural Dependence on Electrocatalytic OER

The primary kinetic limitation of electrolytic watersplitting occurs at the anode in which the endothermic OER requires an additional activation energy. The thermodynamic half-reaction potential of OER is 1.23 V vs. the reversible hydrogen electrode (RHE). PGM electrocatalysts, primarily Iridium- and Ruthenium-based, IrO$_2$ and RuO$_2$, drive OER at pH 14 at overpotentials around 330 mV.$^7$ In seeking active PGM-free alternative OER catalysts, molecular metal oxide catalysts have been developed to model the [CaMn$_4$O$_5$]$^{n+}$ cubane core found in photosynthetic organisms’ Photosystem II.$^8$ Furthering the extensive prior work on evaluating the electrochemical performance of lithium cobalt oxide, LiCoO$_2$ as a cathode material in Li-ion batteries, Graeme Gardner from the Dismukes Group has elucidated a structural dependence on its anodic OER activity based on the initial bio-inspired hypothesis.$^{8,9}$

Figure 1-2: Schematic of a Photoelectrochemical Cell for Solar-to-Hydrogen Watersplitting
LiCoO$_2$ exhibits two polymorphs, a cubic structure with a $F\overline{3}dm$ space group and a layered rhombohedral phase with a $R\overline{3}m$ trigonal space group. The primary application of layered LiCoO$_2$ as a Li-ion battery material relies on the reversible intercalation chemistry of labile Li$^+$ between the alternating lattice sheets of Co-O and Li-O octahedrons. On the other hand, the high activity for OER demonstrated by cubic LiCoO$_2$ is attributed to the presence of a Co$_4$O$_4$ core (analogous to the aforementioned CaMn$_4$O$_5$ cluster found in Photosystem II). Upon onset of OER, cubic LiCoO$_2$ undergoes a structural transformation accompanied by irreversible delithiation to form a highly OER-active cubic spinel phase, LiCo$_2$O$_4$. The Co$_4$O$_4$ units found in the cubic structure not only allow oxidation to the Co$^{4+}$ state at accessible overpotentials in ambient conditions, but also provide low intercubane mobility of holes to allow the concerted four-electron reaction on a single center necessary for water oxidation.$^{[8,9]}$

*Figure 1-3: (a) Cubic LiCoO$_2$ ($Fd\overline{3}m$) (b) Layered LiCoO$_2$ ($R\overline{3}m$)$^{[8]}$*

Due to high ligand field stabilization, the active Co$^{3+}$ centers in the cubic phase are present in the octahedrally-coordinated sites. Based on post-catalysis HRTEM studies, upon further delithiation of the active spinel during long-term OER operation (beyond 60% delithiation),
auto-reduction to Co$^{2+}$ is accompanied by migration to tetrahedrally-coordinated sites, until full delithiation when the catalyst degrades via formation of Co$_3$O$_4$. While exhibiting moderate OER activity, Co$_3$O$_4$ is not a stable phase during long-term OER operation and will further decompose to form inactive CoO$_2$.[9]

The half-reaction OER activity of cubic LiCoO$_2$ was evaluated and benchmarked against best-in-class IrO$_x$ and Co$_3$O$_4$ in the format of a spincoated ink on glassy carbon consisting of the ground calcined pure catalyst powder, a Nafion$^\text{®}$ ionmeric binder, and activated acetylene black suspended in water and ethanol. Activity was evaluated at a geometric current density of 10 mA/cm$^2$, which roughly corresponds to 10% solar-to-hydrogen (STH) efficiency.

![Figure 1-4: OER LSV Activity Comparison of Cubic LiCoO$_2$, 20% Ir@C, and Co$_3$O$_4$](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ @ 10 mA cm$^{-2}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic LiCoO$_2$</td>
<td>430</td>
</tr>
<tr>
<td>20% Ir@C</td>
<td>330</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>470</td>
</tr>
</tbody>
</table>

Table 1-1: Comparison of Cubic LiCoO$_2$, 20% Ir@C, and Co$_3$O$_4$ Overpotentials at 10 mA/cm$^2$
As shown in Figure 1-4 and Table 1-1 above, LiCoO$_2$ outperforms Co$_3$O$_4$ but still falls short of the activity of the Ir catalyst by 100 mV overpotential.

However, when operating in a full-cell, membrane electrode assembly (MEA) configuration at higher current densities typical of commercial-scale electrolyzers, the trend is reversed with LiCoO$_2$ outperforming IrO$_x$ by achieving overall lower full cell potentials at each respective geometric current density. LiCoO$_2$ maintains its stability of operating at 500 mA/cm$^2$ for up to 1000 hours.$^{[9]}$

![Figure 1-5: MEA Configuration Comparison of LiCoO$_2$ Anode/Pt cathode to PGM (Ir) Anode/Pt Cathode$^{[9]}$](image)

1.4. Dark Anode Integration of Cubic LiCoO$_2$ into PEC

The objective of this study is integration of the cubic LiCoO$_2$ OER catalyst into the PEC as a dark, anode in order to first benchmark its electrolytic kinetics and interfacial stability on a non-photo-illuminated support. Based on scalability and kinetic metrics outlined by DOE-EERE-FCTO for tandem photoabsorber electrolyzers and fuel cells, the PGM-free anode must meet at least the following three performance requirements: (1) 10 mA/cm$^2$ achieved at overpotentials ($\eta$) < 500 mV, (2) stable OER operation at 10 mA/cm$^2$ for a minimum of 1000
hours of bulk electrolysis, and (3) tunability to eventually surpass the activity of best-in-class IrO$_x$.$^{[10]}$

The design requirements of the anode that would meet these performance requirements include: (1) a high surface area (from either the catalyst or support) at the optimal mass loading to maximize the performance:cost ratio, (2) high interfacial conductivity, (3) and high interfacial stability, i.e. optimal adhesion to the substrate. As will be introduced in the following section, the initial approach taken by this study was to develop a dimensionally controlled architecture, a catalytic geometry that maximizes the total number of catalytically-active facets across a single dimension or domain. The dimensionally controlled architecture proposed is the dimensionally stabilized anode (DSA) configuration.

1.5. Dimensionally Stabilized Anodes

For the past 40 years, the dimensionally stabilized anode (DSA) has been a common dimensionally controlled electrocatalytic architecture used for industrial chlorine generation via electrolysis.$^{[11]}$ As shown in Figure 1-6 below, the DSA consists of an inert metal, a high-surface area anodically-grown oxide of that metal, and a calcined catalytic metal oxide dopant. This metal oxide-metal oxide interface gives high interfacial stability in basic media, allowing for long-term operation. The chloro-alkali industry standard IrO$_2$-RuO$_2$ doped-TiO$_2$/Ti DSA has demonstrated service lifetimes of up to 14 years at 2 kA/m$^2$.$^{[11,12]}$

*Figure 1-6: Preparation of an IrO$_2$-RuO$_2$ doped-TiO$_2$/Ti Dimensionally Stabilized Anode*
Accelerated lifetime tests (ALTs) conducted by Hoseinieh et al on the IrO$_2$-RuO$_2$@TiO$_2$/Ti DSA show stable operation for over 250 hours, operating at 400 times the geometric current density of normal operation, as shown in Figure 1-7 below.$^{[12]}$

Shin et al has reported higher geometric OER activity for high-surface area microporous and nanotubular TiO$_2$/Ti DSA architectures when compared to the same electrocatalyst cast onto the passivated native oxide TiO$_x$ or bare Ti substrates.$^{[13]}$
In order to cast cubic LiCoO$_2$ onto the DSA architecture, three main strategies were considered. The first of which is in direct relation to the primary way in which the intrinsic activity of LiCoO$_2$ was studied – via a spincoated Nafion/activated C ink. While this method has shown to involve facile preparation, it has also demonstrated poor adhesion to substrates with less relative surface roughness over the course of a single day’s continuous operation. The second option considered is via pulsed laser deposition (PLD), which follows prior work by Shinjae Hwang et al from the Dismukes Group, in which he has successfully shown the capability of this physical vapor deposition technique to produce uniform crystalline thin films of the layered phase – which can then be converted to the OER-active cubic spinel phase via alkaline electrolysis.\textsuperscript{[14]} While this method would address the issue of adhesion, conformal deposition on top of the DSA morphology would be difficult as PLD is a line-of-sight deposition technique. Finally, the third and ultimately implemented option was electrodeposition of spinel Li$_x$CoO$_2$ on the DSA electrode. Unpublished work by Shinjae Hwang has demonstrated successful electrodeposition of Li$_x$CoO$_2$ on fluorinated tin oxide (FTO) substrates which are relatively rough. However this prior work also showed that the deposited material has very low Li-content ($x<0.5$), and may require a post-intercalation step of Li in order to the stability of the catalyst.

Section 2-1 will detail the DSA preparation attempted in this study.
2. EXPERIMENTAL METHODS

2.1. DSA Preparation

The DSA preparation was developed via an adapted procedure by Deviliers et al, utilizing milder conditions than the +200V and HF treatment required for anodic growth of microporous TiO$_2$. Rather, a +20V applied bias was applied for 2 minutes in the presence of 2 M H$_2$SO$_4$ to anodically grow 60-80 nm TiO$_2$ nanotubes.$^{[15]}$ Prior to anodization, Ti foils were hole-punched out of a 0.127 mm-thick annealed foil (Alfa Aesar Product No. 00927), pressed under 12 metric tons, and mechanically-polished on an 800-grit dry polishing pad for 15 minutes each. This removes much of the surface passivated native oxide, leaving behind only a 6-8 nm layer.

![Figure 2-1: 20 μm and 200 nm SEM micrographs of anodized TiO$_2$ morphology$^{[15]}$](image)

X-ray photoelectron spectroscopy (XPS) measurements of the Ti(2p) core shell orbital then gave confirmation that the native oxide surface was conformally coated by TiO$_2$, as shown in Section 3-1. Going forward for the rest of this work, this configuration will be known as TiO$_2$@TiO$_x$/Ti.
2.2. Electrodeposition of Li$_x$CoO$_2$

The electrodeposition of Li$_x$CoO$_2$ on top of the DSA TiO$_2$@TiO$_x$/Ti electrode follows the process illustration shown below in Figure 2-2.

![Figure 2-2: Electrodeposition of Li$_x$CoO$_2$ Process](image)

Here, the anodized Ti substrate is first mounted into an electrode configuration which consists of a copper tape back contact and Teflon tape mask, exposing only the surface area of the foil. Then, in a piranha solution-cleaned 5-compartment electrochemical cell, 100 mL total electrolyte consisting of 3.5 M LiOH, 2.5 mM Co(NO$_3$)$_2$, and 3 mM L-tartaric acid is purged under N$_2$ bubbling. The cell is heated in an oil bath to 95°C, measured by a thermometer with a reflux condenser connected to a water chiller to minimize electrolyte evaporation during the course of the electrodeposition. The counter-electrode is a Ti mesh and the reference electrode is a double-junction Ag/AgCl electrode, to give highly reference potentials over the course of deposition. Based on the Pourbaix diagram of Co, Co(NO$_3$)$_2$ upon addition to the LiOH will immediately precipitate out of solution as Co(OH)$_2$ solid at pH 14 and application of the relevant anodic potentials. Therefore, tartaric acid (tartrate in solution) is used to complex the Co$^{2+}$ ions in order to keep it soluble and electrochemically active for deposition under anodic bias. To further minimize the irreversible precipitation, a stock solution prepared in advance of the Co(NO$_3$)$_2$ and L-tartaric acid was prepared such that only 1.25 mL added drop-wise to the heated LiOH bath would need to be added in order to achieve the desired concentrations.
The proposed mechanism of deposition goes via the precipitation/nucleation of Co$^{3+}$ on the surface, forming a Co$_3$O$_4$ lattice, followed by in-situ intercalation of Li from the reduction of Li(OH)$_2$, forming a spinel-type Li$_x$CoO$_2$ deposited film.

2.2.1. Cyclic Voltammetric (CV) Deposition

The first mode of electrodeposition evaluated was a cyclic voltammetric (CV) deposition carried out on a potentiostat interface (CH Instruments, PARStat, and BioLogic) in a sweep range of 0.9 V to 1.55 V vs. RHE at 50 mV/s for 10 cycles.

![Cyclic Voltammetric (CV) Deposition](image)

*Figure 2-3: Cyclic Voltammetric (CV) Deposition of Li$_x$Co$_2$ for 10 cycles at 50 mV/s between 0.9 V – 1.55 V vs. RHE*

As shown above in Figure 2-3, as the CV proceeds in time, OER activation is observed with increasing currents across cycles and OER activation seen at the higher anodic potentials which corresponds to film growth. In addition, the redox peaks corresponding to Co$^{2+}$/Co$^{3+}$ and Co$^{3+}$/Co$^{4+}$ are observed, along with the in-situ delithiation step upon OER onset.

2.2.2. Chronoamperometric (CA) Pulsed Deposition
The next mode of deposition considered was a pulsed fixed deposition mode carried out via pulsed chronoamperometry (CA). Rather than cycling across a range of anodic potentials, the deposition was carried out via a 2-step pulse sequence, consisting of a 1 second deposition pulse at the observed Co\textsuperscript{2+}/Co\textsuperscript{3+} oxidation potential (from the CV scan) of 1.2 V vs. RHE, followed by a 15-second rest period at a cathodic potential determined to give minimal (< +/− 50 uA) faradaic current. This sequence was considered in order to give a rest time for lateral diffusion of oxidized Co\textsuperscript{3+} ions across the substrate surface following each pulse, to yield a more uniform and conformal film.

![Figure 2-4: CA Pulsed Deposition Sequence of Li\textsubscript{x}CoO\textsubscript{2}](image)

**2.2.3. Continuous Chronoamperometric (CA) Deposition**

The last mode of deposition considered was simply fixing and holding the anodic potential at the Co\textsuperscript{2+}/Co\textsuperscript{3+} oxidation for a designated total period of time. While this does not allow for a rest period as material continually deposits on preferentially-oriented nucleation sites, it allows for a diagnostic of the film activity and composition in the absence of other faradaic and capacitive processes that would otherwise occur during a CV sweep.
2.3. Electrochemical Measurements of OER Kinetics

2.3.1. Cyclic and Linear Sweep Voltammetry

The primary method by which the kinetics of OER for the electrodeposited Li$_x$CoO$_2$ films are evaluated is via cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Following standard measurement of the reference potential with respect to RHE in 0.5 M H$_2$SO$_4$, a cell is prepared with 1 M (pH 14) NaOH, Pt counter-electrode in an embedded glass/Teflon tape-lined compartment outfitted with an anion exchange membrane, and a Ag/AgCl reference electrode. A CV scanning at 50 mV/s in a scan window of 0.9 V – 2.05 V vs. RHE first gives the redox features occurring on the surface at the lower (pre-OER) potentials, followed by OER currents corresponding up to 100 mA/cm$^2$ geometric current densities after the OER onset overpotential is achieved. The iR compensation at open circuit potential is then measured and used to correct the measured OER potentials. An LSV is then run at 50 mV/s and used to deduce the overpotential at which 10 mA/cm$^2$ is achieved, following normalization of the measured currents to the geometric surface area. The geometric surface
area is measured via ImageJ software, which correlates a photo of the electrode and a ruler scale bar to the number of measured pixels in order to give a 2-D projected area in cm$^2$.

**2.3.2. Electrochemical Surface Area Determination**

In order to measure the electrochemically active surface area (ECSA), CVs are run in a scan window of 0 V to +100 mV vs. RHE corresponding to the double-layer capacitive region where no faradaic processes are occurring. The scan rate is then varied over 5 mV/s, 10 mV/s, 20 mV/s, 30 mV/s, 40 mV/s, and 50 mV/s in order to then measure the proportional increase in average current width of the CV. Normalizing these currents to the geometric surface area, plotting the output current densities against scan rate, and taking the slope of this line gives the specific capacitance of the electrode. This specific capacitance is then normalized to that of pristine glassy carbon (as a flat, electrochemically inert substrate), 40 uF/cm$^2$, in order to yield a roughness factor. The geometric current densities measured from the original CV and LSV can then be re-normalized to this roughness factor in order to yield an activity measurement that only takes into the electrochemically active surface for catalysis. This method provides an in-situ alternative to BET normalization.

**2.3.3. Chronoamperometric Bulk Electrolysis**

Finally, in order to evaluate long-term OER stability, a CA scan is run at the overpotential corresponding to 10 mA/cm$^2$ for a set period of time (24 hours to several days). The profile of the CA scan, followed by a post-CA CV, LSV, and ECSA measurement is then taken again and compared against the initially measured data in order to evaluate the stability of OER operation / mode of degradation. Because of glass etching and release of contaminants in alkaline conditions, for longer term OER studies, a Teflon cell is used in lieu of a glass cell.
**2.4. X-Ray Photoelectron Spectroscopy (XPS)**

XPS was the primary surface characterization tool used in this work. The operating principle behind XPS is incident x-ray excitation of each designated element present in the sample’s core-shell electrons in ultrahigh vacuum. Spectral data collected on the kinetic energy and number of electrons escaping across the top 5 nm of the surface allows probing of the relative shielding effects of the core electrons as a function of binding energy. The higher the shielding, the lower the binding energies measured, and vice-versa. These binding energies roughly correlated with the relative concentrations of oxidation states present of the particular element as well as information about their respective binding and coordination environments. As a diagnostic, this technique allows probing of the deposition conditions that give rise to the specific and relative concentrations of Li, Co, O, and C surface states present.

**2.5. Scanning Electron Microscopy and Electron Dispersive Spectroscopy**

Micrographs taken on a Phenom Tabletop SEM-EDS setup and a high-resolution ZEISS SEM-EDS setup allowed topographical visualization of the electrodeposited films from a 200 μm resolution to 200 nm resolution, which allows an understanding of how the deposition conditions affect the top-surface morphology of the catalytic material. Coupled with SEM imaging is EDS, which provides elemental mapping of the surface. An electron beam probes into the surface and the difference in the outer shell and inner shell energies in the form of an emitted x-ray gives rise to a unique elemental emission spectrum. Integrating multiple elemental spectra allows calculation and tabulation of the relative atomic and mass-specific concentrations of each element present within the sample. Combining this information with the estimated element-specific probe depth as calculated by Castaing’s formula, it is possible to infer mass loading concentrations on a geometric surface area basis.
2.6. Grazing Angle X-Ray Diffraction (XRD)

Grazing x-ray diffraction measurements were conducted in the Wright-Riemann Crystallography Laboratory with the assistance of Dr. Tom Emge in order to detect the crystalline phases present in the electrodeposited films. The thin film configuration requires the need for higher resolution detection of grains in order to yield sufficiently high signal-to-noise ratio diffraction patterns, and thus necessitates the grazing angle setup, as shown in the photo below.

2θ ranges of 20°, +/- 10° from a preset 0° position delivers this higher resolution. Integrating each 2θ region yields the full spectrum in the range of diffractions expected for the relevant reference patterns of LiCoO₂ and TiOₓ/Ti.

2.7. Raman Spectroscopy

Preliminary Raman spectroscopy studies were conducted on the electrodeposited LiₓCoO₂ films by Prof. George Tsilomelekis in the Chemical and Biochemical Engineering Department using a 532 nm green laser in backscattering mode. Relying on the principle of inelastic Raman scattering, a structural fingerprint can be elucidated from the active, low-frequency Raman active molecular vibrational modes present in the spectrum. The spectra collected in
this study were used to provide evidence for the local coordination chemistry in the Li\textsubscript{x}CoO\textsubscript{2} responsible for its OER activity.

3. RESULTS AND DISCUSSION

3.1. Electron Conduction Barrier in Anodized TiO\textsubscript{2}

Following preparation of the anodized TiO\textsubscript{2}/Ti DSA, Ti(2p) XPS was used to confirm conformal coverage of TiO\textsubscript{2} across the foil, as shown below in Figure 3-1.

\textit{Figure 3-1: Ti(2p) XPS Taken (a) Before and (b) After Anodization of Polished TiO\textsubscript{2}/Ti Foil}

The successful anodization is confirmed via the disappearance of the satellite peak near 454 eV, which corresponds to Ti\textsuperscript{0} or Ti metal, with only peaks corresponding to the Ti\textsuperscript{4+} surface states present.

The CV electrodeposition procedure of Li\textsubscript{x}CoO\textsubscript{2} outlined above was then attempted on the anodized surface. Little to no deposited material was present. We then noted that under an oxidative bias in the absence of UV-illumination, the band-bending of TiO\textsubscript{2} produced an electron conduction barrier too large to surmount or tunnel through. In essence, the 60-80 nm
layer of TiO$_2$ is too thick for electron conduction. This phenomenon is illustrated by a band diagram of the (attempted) electrochemistry occurring at the interface, as shown below.

Electron injection into the TiO$_2$ layer is inhibited by this high barrier, which decreases the number of available holes in the electrolyte, rendering the interface unable to access the minimum Co$^{2+}$/Co$^{3+}$ oxidation potential. In the traditional RuO$_2$ and IrO$_2$-doped DSA format, the conductivity of these catalytic oxides is high enough to circumvent this band-bending.

This band-bending was experimentally observed in the CV itself, by the absence of the redox features that are present on the bare TiO$_x$/Ti substrate, as shown to the right.

**Figure 3-2: Band Diagram Illustrating Band-bending of Anodized TiO$_2$ Causing Electron Transfer Barrier**

**Figure 3-3: CV-Deposition on Anodized TiO$_2$ (black) and Bare TiO$_x$/Ti (purple)**
TiO$_x$ has a sufficiently large number of degenerate gap states for facile electron extraction. Studies by Sahasrabudhe et al have shown that it is possible to dope bulk particulate TiO$_2$ with 3 mol% metallic Nb to improve its conductivity by a million fold.\cite{16} Investigation to see if this may applied to the anodically grown (primarily anatase)\cite{17} TiO$_2$ via solid-state reaction with a suitable Nb precursor is currently ongoing. However, for the purposes of this study, the anodized TiO$_2$ DSA configuration was abandoned in lieu of simply electrodepositing Li$_x$CoO$_2$ directly on TiO$_x$/Ti.

3.2. CV Deposition of Li$_x$CoO$_2$ on TiO$_x$/Ti

3.2.1. OER Activity and Stability

Investigation into the electrodeposition of Li$_x$CoO$_2$ and its OER activity/interfacial stability was moved forward by directly working on the mechanically-polished TiO$_x$/Ti substrates. Shown below are overlaid LSVs and tabulated activity data of the CV-deposited Li$_x$CoO$_2$@TiO$_x$/Ti and that of the Nafion/C ink-casted cubic LiCoO$_2$@GC.

![Figure 3-4: OER LSVs of the CV-Deposited Li$_x$CoO$_2$@TiO$_x$/Ti and Ink-Casted Cubic LiCoO$_2$@GC](image)

*Figure 3-4: OER LSVs of the CV-Deposited Li$_x$CoO$_2$@TiO$_x$/Ti and Ink-Casted Cubic LiCoO$_2$@GC; Scan rate = 10 mVs*
Comparing the initial OER activity of the two Li$_x$CoO$_2$ formats, it is clear that the CV-deposited Li$_x$CoO$_2$ performs on par with that of the cubic spinel LiCoO$_2$ ink, achieving 10 mA/cm$^2$ at ~430 mV overpotential. However, the double layer specific capacitance and roughness factor of the CV-deposited film are double that of the ink, indicating twice the useable electrochemical surface area for OER catalysis. These roughness factors are utilized with data from EDS mapping to then correlate the effective utilization of Co for catalysis, as will be reported in Section 3.2.2.

Table 3-1: Activity Comparison of CV-Deposited Li$_x$CoO$_2$@TiO$_x$/Ti and LiCoO$_2$ Ink@GC

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ @ 10 mA/cm$^2$ (mV)</th>
<th>Double Layer Capacitance (µF/cm$^2$)</th>
<th>Roughness Factor (norm. to pristine GC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic LiCoO$_2$ Ink @ GC</td>
<td>430 +/- 14</td>
<td>18360</td>
<td>459</td>
</tr>
<tr>
<td>CV-Dep Li$_x$CoO$_2$ @ TiO$_x$/Ti</td>
<td>430 +/- 10</td>
<td>36190</td>
<td>905</td>
</tr>
</tbody>
</table>
Below is the chronoamperometric bulk electrolysis measurement used to evaluate the long-term stability of the CV-deposited Li$_x$CoO$_2$. The stability measurement was run for about 13 days in a Teflon cell exposed to ambient airflow.

![Figure 3-5: 13-Day Bulk Electrolysis at 1.67 V vs. RHE (430 mV overpotential)](image)

As seen, the signal shows high amounts of fluctuation in the current densities measured over time. As will be elucidated with the LSVs reported below for before and after the stability measurement, these fluctuations can be ascribed to high convection from the stir bar and bubble formation on the surface. Below are the OER LSVs measured before and after 13-day bulk electrolysis, normalized to geometric surface area and the electrochemical surface area.
As can be seen, the geometric area-normalized LSVs before and after the stability test shows a slight deactivation, with a shift to 440 mV overpotential at 10 mA/cm$^2$. On the other hand, the ECSA-normalized before and after traces overlap almost entirely over one another, especially at higher current densities. This indicates that the mode of deactivation seen on the geometric basis is due to delamination of the top layers of the film that are not in intimate contact with the interfacial TiO$_x$ layer, and not from intrinsic catalyst poisoning.

### 3.2.2. SEM-EDS Mapping

Below is a 100 μm SEM image of the mechanically-polished TiO$_x$/Ti substrate as a point of reference.

![SEM of Bare Mechanically-Polished TiO$_x$/Ti Foil (100 μm)](image)

Below are SEM images taken at 100 μm, 1 μm, and 200 nm resolutions of the CV-deposited Li$_x$CoO$_2$ film on top of the TiO$_x$/Ti.
On the 100 μm scale, film coverage already appears quite uniform and conformal across the foil substrate. Moving to the 1 μm scale, large aggregates of particles are visible that cluster and stack up on smaller particles, forming almost flower-like patterns. Moving to the 200 nm scale, it can be seen that ~180 nm-size clusters are being formed from ~50 nm-size particles. This indicates that while the film is quite dense and that there is a large size regime, the individual particles are still depositing on the nanoscale. The delamination seems quite readily possible given the stacking of particles, which may easily lose contact with the metal oxide interface. ICP may help to deduce the percentage of initial Li and Co content lost to solution.

<table>
<thead>
<tr>
<th>Element Symbol</th>
<th>Atomic Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>76.31</td>
</tr>
<tr>
<td>Co</td>
<td>4.24</td>
</tr>
<tr>
<td>Ti</td>
<td>18.69</td>
</tr>
<tr>
<td>Si</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*Table 3-2: EDS Data on the Relative Atomic Concentrations of O, Co, Ti, and Si*
Taking the elemental ratio of Co to Ti to be 4.24/18.69, or about 0.227, along with the Co probe depth calculated using Castaing’s formula to be 1.58 μm into the surface, the Co loading was calculated to be about 17.1 μg/cm².

<table>
<thead>
<tr>
<th>Sample</th>
<th>η @ 10 mA/cm² (mV)</th>
<th>Roughness Factor (ECSA norm. to pristine GC)</th>
<th>Mass Loading (μg/cm²)</th>
<th>Co-Utilization (Roughness / μg Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂ Ink @ GC</td>
<td>430</td>
<td>459</td>
<td>184</td>
<td>2.49</td>
</tr>
<tr>
<td>CV-Dep Li₅CoO₂ @ TiOₓ/Ti</td>
<td>430</td>
<td>905</td>
<td>17.1</td>
<td>52.9</td>
</tr>
</tbody>
</table>

*Table 3-3: Mass-normalized OER Activity Comparison of LiCoO₂ Ink@GC and CV-Deposited Li₅CoO₂@TiOₓ/Ti*

Table 3-3 above again shows the overpotentials at which 10 mA/cm² is reached for the two electrode configurations, along with their respective roughness factors, and the Co mass loadings calculated for each preparation. By dividing the electrochemical roughness factors by the respective Co loadings, it is possible to calculate the effective utilization of Co within the Li₅CoO₂ thin film framework being used for OER catalysis. And here, it is shown that the CV-deposited Li₅CoO₂ utilizes Co 21x more effectively for OER than the LiCoO₂ ink preparation. The implication of this is the ability to achieve a highly-stable OER operation at 21x less mass loading of Co required.
3.2.3. Grazing Angle XRD Phase Characterization

Below is the integrated 2θ range of individual grazing angle diffraction measurements on the as-made CV-deposited Li₇CoO₂ film, overlaid with the program pattern match stoichiometry and a reference pattern for cubic-phase LiCoO₂.

![XRD Pattern of Sample, Overlaid with Pattern Match and Reference LiCoO₂](image)

The high diffraction peaks resolved from the sample exactly match up to the Ti₆O suboxide pattern match from the database. These peaks do not match up at all to the reference pattern for cubic LiCoO₂. This indicates that the only long-range crystalline periodicity present is from the native TiOₓ layer underneath the electrodeposited catalyst, and that the electrodeposited layer shows no long-range periodicity, indicating an amorphous metal oxide structure. Reports have shown the facile electrodeposition of highly crystalline Co₃O₄ under similar conditions as the electrodeposition carried out here, and so the main reason for the amorphous nature of this film may come from the forced reduction and insertion of Li during the deposition process,
breaking down the initial lattice and lowering the overall crystallinity of the resulting film. XPS and Raman spectroscopy must now be the main characterization tools to elucidate the structure-property relationships responsible for the high OER activity.

3.2.4. XPS Characterization

Below are the Li(1s), O(1s), and Co(2p) XPS spectra of the as-made and OER-cycled CV-deposited Li$_x$CoO$_2$@TiO$_x$/Ti films.

![Figure 3-10: Li(1s), O(1s), and Co(2p) XPS Spectra of As-Made and OER-Cycled CV-Deposited Li$_x$CoO$_2$@TiO$_x$/Ti](image)

With only one electron in the Li core shell, it is relatively easy to make out that Li$^+$ is very much present in the as-made sample, but falls below the detection limit of XPS after OER cycling. The O(1s) spectrum also includes the deconvolution to the three similarly-shielded states of oxygen. Shifted most to the right (highest-shielded) is the lattice O$^2_-$, present in the as-made sample, but shifted into the defect O peak in the OER-cycled sample. Ascribing the charge balance of Li$_x$CoO$_2$ to O, this indicates a change in the Co-O binding environment as a result of delithiation. However, when comparing the Co(2p) spectra of the as-made and OER-
cycled samples, there is an identical match of only Co$^{3+}$ corresponding peaks, with no satellites, which would otherwise also indicate the presence of Co$^{2+}$ on the surface. This presents some initial insight into the local coordination environment at work during OER.

### 3.2.5. Raman Spectroscopy

To further elucidate the local coordination environment in the CV-deposited Li$_x$CoO$_2$, Raman spectroscopy was conducted in the 400-800 cm$^{-1}$ range where Raman-active modes for spinel-type coordination can be found. However, before presenting the Raman spectrum obtained, it is important to first outline a thermodynamic argument for the use of battery-literature-obtained Raman shifts for layered LiCoO$_2$ to correlate to the coordination chemistry of the cubic spinel polymorph.

Both thermodynamic and experimental evidence exists for the transformation of layered phase LiCoO$_2$ ($R\overline{3}m$) to spinel-type ($F\overline{3}dm$) coordination after 50% delithiation, as shown in Figure 3-11 below.[18]
Figure 3-11: (a) Calculated Phase Diagram at $T = 270 \, \text{K}$ Illustrating Layered LiCoO$_2$ Decomposition via the Spinel Phase; (b) Calculated Reaction Enthalpy as a Function of Li$^{[18]}$

Figure 3-11(a) shows that the layered phase of LiCoO$_2$ undergoes an irreversible transformation and decomposition after delithiation via a meta-stable spinel phase. Figure 3-11(b) correlates this spinel phase to lie on a reaction enthalpy pathway after 50% delithiation. After 75% delithiation, thermodynamic calculations predict a larger driving force toward the formation of Co$_3$O$_4$ spinel. Based on these modes, it is possible to reference Raman spectra data for delithiated layered phase LiCoO$_2$ to that of the electrodeposited film in order to find evidence for local spinel-type coordination.

Figure 3-12: Obtained Raman Spectrum for As-Made CV-deposited Li$_x$CoO$_2$
From Figure 3-12, it is evident that the CV-deposited Li$_x$CoO$_2$ shows the presence of A$_{1g}$, E$_g$, and F$_{2g}$ active modes, which are characteristic of spinel-type coordination. Also seen are peaks located at 470 cm$^{-1}$ and 590 cm$^{-1}$ that correspond to the anodically-grown anatase and rutile polymorphs of TiO$_2$ during the oxidative deposition.\cite{20} By examining the Raman shifts of the delithiated layered LiCoO$_2$ as shown in Figure 3-13 as a function of delithiation from 18% to 60%, it can be seen that the A$_{1g}$ and E$_g$ modes are shifted to the left toward lower wavenumbers with further delithiation. By correlating this shift to the wavenumbers at which these respective peaks appear in the sample spectrum, it is possible to infer that the lithium content in CV-deposited Li$_x$CoO$_2$ is less than 0.5. A more rigorous Raman study of the as-made material compared against the OER-cycled material, along with reference spectra for the fully-lithiated structure and that of spinel Co$_3$O$_4$ can help to spectroscopically expound on the loss of Li during continuous OER operation, and whether this degradation mode will continue to proceed toward complete delithiation and thus total loss of catalytic activity. Nevertheless, Raman spectroscopy provides a first glance at the spinel-type local coordination chemistry in the electrodeposited Li$_x$CoO$_2$, making it possible to establish a similar structure-property relationship as that of the crystalline cubic LiCoO$_2$.

3.3. CA-Pulsed Deposition of Li$_x$CoO$_2$ on TiO$_x$/Ti

3.3.1. OER Activity Dependence on Total Deposition Time

As discussed in Sections 2.2.2, a fixed potential pulsed deposition method conducted via chronoamperometry was also used to deposit Li$_x$CoO$_2$. The number of pulse cycles (1s “on”, 15s “off”) was manipulated to give the intended total deposition time. OER activity was measured as a function of total deposition time in order to begin initial optimization of this
process. However, as seen below, at any given time interval, the deposition and rest period currents displayed unsteady-state behavior.

![Figure 3-14: Unsteady Deposition and Rest Currents during Pulsed Sequence](image)

Over time, an increase in average cathodic current could be seen at the rest potential (-0.05 V vs. RHE), while the deposition currents fluctuated in magnitude. However, as a starting way to evaluate if these unsteady-state behaviors affect the OER activity of the deposited films, several different total deposition times were held and the overpotentials measured at 10 mA/cm² were plotted as a scatter.
While the lowest average overpotential of 447 mV is achieved at a total deposition time of 30 seconds, this method does not produce films that are as active for OER as the CV-deposition.
3.3.2. SEM Mapping

Figure 3-16: SEM Images of Pulsed-Deposited Li\textsubscript{x}CoO\textsubscript{2}@TiO\textsubscript{x}/Ti (200 μm, 10 μm, 2 μm)

By naked-eye visual inspection, the pulsed-deposited films are translucent and not opaque as that of the CV-deposited films. SEM images of the pulse-deposited Li\textsubscript{x}CoO\textsubscript{2} further reveal the much thinner layer of deposited material compared to the CV-deposited films. All of the defects and abrasions on the TiO\textsubscript{x}/Ti surface can be clearly visualized, with several larger, sparsely-distributed particles agglomerated on the surface. Cross-sectional SEM may be able to further probe the morphology of the thin (<50 nm) layer, but from the top-down views shown above, it is clear that these films are thinner than what can be resolved fully by conventional SEM.
3.3.3. XPS Characterization

![Li(1s) and Co(2p) XPS Spectra](image)

Figure 3-17: Li(1s) and Co(2p) XPS Spectra of As-Made Pulsed-Deposited Li₅CoO₂@TiO₂/Ti

Li(1s) and Co(2p) XPS spectra were taken of the best-performing 30 second total deposition time pulsed sample. As seen above, the Li(1s) reveals no detectable presence of Li⁺ on the pulsed-deposited Li₅CoO₂ surface. The Co(2p) scan, in contrast to that of the CV-deposited Li₅CoO₂, now shows the presence of satellite peaks for both the 2p₃/₂ and 2p₁/₂ signals, no longer allowing the main peaks to solely correspond to Co³⁺. Instead, the presence of the satellite peaks interprets to a mixture of similarly-shielded Co³⁺ and Co²⁺ surface states. And without the detectable presence of Li⁺, this spectrum may correspond to the formation of Co₃O₄ on the surface during the pulsed-deposition, either due to the reducing effects of the increasing cathodic currents between each pulse, or the inability to access high enough energy at the fixed deposition potential to fully oxidize Co²⁺ to Co³⁺ on the surface. These potentially synergistic effects are decoupled in Section 3.4 where the CA deposition is evaluated in a continuous mode at the fixed anodic potential.

3.4. Continuous CA Deposition of Li₅CoO₂ on TiO₂/Ti
3.4.1. SEM Mapping

As seen with the SEM images of the pulsed-deposited samples, the SEM images of the continuous CA-deposited Li$_x$CoO$_2$ similarly show a highly thin film through which the morphology of the underlying TiO$_x$/Ti substrate can be clearly visualized. However, a higher density of sparsely distributed agglomerated particles can be seen candy-coating the surface, as seen under 10 μm resolution. The surface shows pronouncedly larger agglomerates on the 1 μm scale, demonstrating that the preferential, non-uniform nucleation akin to holding a steady deposition potential.
3.4.2. XPS Characterization

As stated previously, the deposition potential was fixed at 1.2 V vs. RHE where the Co$^{2+}$/Co$^{3+}$ oxidation peak was observed during the CV deposition.

In contrast to the pulse-deposited Li$_x$CoO$_2$ XPS survey, here, Li$^+$ is clearly detected in the Li(1s) XPS. However as seen in the Co(2p) survey, satellite peaks adjacent to the major 2p$_{3/2}$ and 2p$_{1/2}$ peaks are still present, indicating the presence of both Co$^{2+}$ and Co$^{3+}$ surface states. By preliminary inspection, these satellites are present in a smaller intensity ratio to the main peaks than that for the pulse-deposited Li$_x$CoO$_2$, indicating a lower presence of Co$^{2+}$ with respect to Co$^{3+}$ on the surface (and subsurface). This either suggests that the fixed potential of 1.2 V vs. RHE is not sufficient enough of an anodic bias to completely oxidize the Co$^{2+}$ fully to Co$^{3+}$, and/or that Co$^{2+}$ is being coordinated by another species present in the electrodeposition bath which adsorbs to the surface. If the first hypothesis is correct, combined with the presence of Li$^+$, these XPS surveys reveal a delithiated spinel structure with Co$^{2+}$ occupying the tetrahedral sites which over the course of OER operation may lead to catalyst...
degradation. Evidence for the second hypothesis comes from the C(1s) XPS survey, which shows the presence of a large peak at lower binding energy (strongly shielded). Given that the oxidation potential of tartrate is close to that of the Co$^{2+}$/Co$^{3+}$ oxidation potential, the incomplete oxidation may have been accompanied by incomplete decarboxylation of the tartrate, causing the formation of aqueous CO$_3^{2-}$ ions, which would bind to Co$^{2+}$ and adsorb as CoCO$_3$ onto the surface. In either scenario, the fixed mode of deposition may require probing higher anodic biases in order to complete the Co$^{2+}$ to Co$^{3+}$ oxidation in the Li$_x$CoO$_2$ local spinel framework.

### 3.5. Activity Comparison of Cyclic and Fixed Potential Deposition Modes

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ @ 10 mA cm$^{-2}$ (mV)</th>
<th>Roughness Factor (ECSA norm. to pristine GC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV-Dep Li$_x$CoO$_2$</td>
<td>430 +/- 10</td>
<td>905</td>
</tr>
<tr>
<td>Continuous CA-Dep Li$_x$CoO$_2$</td>
<td>450 +/- 20</td>
<td>108</td>
</tr>
<tr>
<td>Pulsed CA-Dep Li$_x$CoO$_2$</td>
<td>470 +/- 30</td>
<td>65</td>
</tr>
</tbody>
</table>

*Table 3-4: Activity and ECSA Comparison of Li$_x$CoO$_2$ from Cyclic and Fixed Potential Deposition Modes*

As shown above, the CV-deposited Li$_x$CoO$_2$ has been shown to yield the highest OER activity with the largest roughness factor, corresponding to the greatest amount of deposited film material. The lower, moderate activity achieved by the continuous CA and pulsed CA deposited films is comparable to that of bulk particulate Co$_3$O$_4$, but with 9 to 14 times less surface roughness. This demonstrates the viability of producing thin films on TiO$_x$/Ti with thicknesses less than 100 nm. Tuning of anodic potential further toward the OER regime in
either deposition method should help to remove the presence of Co\textsuperscript{2+} surface states, which is detrimental to long-term OER catalysis.

4. CONCLUSIONS

The primary output of this study is the electrodeposition of nanoscale films of Li\textsubscript{x}CoO\textsubscript{2}, x<0.5 via cyclic voltammetry onto TiO\textsubscript{x}/Ti for highly active and stable OER catalysis. The combination of electrochemical double-layer capacitance measurements and SEM-EDS mapping demonstrate high catalytic surface area and enhanced Co utilization when compared against the benchmark preparation of cubic LiCoO\textsubscript{2} particulate/Nafion ink cast onto glassy carbon. The combination of XPS and Raman spectroscopy probed the local coordination environment of Li, Co, and O, giving preliminary evidence of local spinel-type structure responsible for the high and long-term OER catalysis.

Changing the deposition mode to a fixed potential deposition method, achieved either via the pulsed or the continuous CA gave rise to the growth of thin films with thicknesses less than 100 nm with moderate OER activity. Increasing the applied anodic potential beyond the observed CV Co\textsuperscript{2+}/Co\textsuperscript{3+} oxidation peak is necessary to prevent the formation of Co\textsuperscript{2+} surface states that are a hindrance to long-term catalytic operation.

This study hopes to have provided a justification for the use of electrodeposition as the mode for functional integration of high-performance Li\textsubscript{x}CoO\textsubscript{2} into the PGM-free PEC device as a dark anode.
5. ONGOING INVESTIGATIONS AND FUTURE IMPLICATIONS

5.1. Next Steps

As mentioned previously, this study provides initial data and will require the following steps in order to drive the work presented toward a publishable result. Determining the anodic potential required to completely convert Co$^{2+}$ to Co$^{3+}$ under fixed potential deposition conditions, either achieved via the pulsed-scan or the continuous scan will hopefully give rise to thin films that reach the same activity and long-term stability as found for the CV-deposited Li$_x$CoO$_2$ films. Additionally, following a more rigorous analysis of the Raman active modes present in the as-made deposited material compared to the OER-cycled material will be the use of TEM to compare lattice spacing and Co-O bond lengths to those present in the polycrystalline cubic spinel structure.

5.2. Future Project Directions

Several project directions are proposed to carry this work forward. Firstly, revisiting Nb doping strategies for the anodically-grown TiO$_2$ framework (microporous or nanotubular) may allow the viability of re-implementing the DSA configuration as the stable and high-surface area support for the Li$_x$CoO$_2$ deposited material. In addition, other dimensionally-controlled architectures that make advantage of metal oxide interfacial stability.

In addition, as this study has found spectroscopically the presence of low Li content within the pristine CV-deposited sample, another study can employ a post-intercalation step in order to raise the total Li content. Higher Li content in the film may change the crystallinity of the film and its OER activity. As a more fundamental corollary, successful doping of the electrodeposited thin films may also lead to the use of these thin films to probe the
mechanistic role of Li for OER catalysis, specifically regarding the role of the initial
delithiation and transformation of the cubic to the spinel phase upon onset of OER potentials.

Device-oriented studies include integration of the electrodeposited Li$_x$CoO$_2$ thin film
anode into the MEA configuration and benchmarking long-term full-cell operation at current
densities greater than 100 mA/cm$^2$. In addition, Li$_x$CoO$_2$ may also be integrated into the PEC
as a photoanode. This will require devising a strategy to deposit Li$_x$CoO$_2$ onto a hole-
conducting photoabsorber, such as ZnSnN$_2$. Subsequent studies will need to probe the photon
transmittance through the film, as well as the inherent p-type characteristic of Li$_x$CoO$_2$ for
hole transport and recombination with electrons at the surface during photoelectrochemical
catalysis.
6. REFERENCES


