DEVELOPMENT OF MANGANESE OXIDE BASED CATALYSTS FOR THE
OXYGEN REDUCTION AND OXYGEN EVOLUTION REACTIONS

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I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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Abstract

Development of active catalytic materials for the oxygen reduction reaction (ORR, $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) and the oxygen evolution reaction (OER, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is one of the major challenges in energy conversion and storage technologies such as fuel cells, metal-air batteries, electrolysis cells, and solar fuel synthesis. The majority of industrially relevant active materials are precious metals and metal oxides, whose high cost and scarcity limits the widespread adoption of these important technologies. Manganese oxides ($MnO_x$) catalysts are an interesting alternative to the precious metal based electrodes under alkaline conditions due to their abundance, low cost, and a demonstrated ability to catalyze both the ORR and the OER at high pH values.

To accelerate the development of $MnO_x$ catalysts with improved activities for the ORR and the OER, it is important to increase understanding of the surface properties at the ORR and the OER relevant potentials. Spectroscopy techniques, including x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS), are among the possible methods to monitor surface chemistry of catalytic materials. Both XPS and XAS can offer information on the electronic structure of the surface, while XAS can also probe the short-range order of the catalysts.

This dissertation focuses on development of $MnO_x$ catalysts for the ORR and the OER and uses ex-situ XPS, ex-situ Mn L-edge XAS, and in-situ Mn K-edge XAS to correlate measured catalytic activity to the surface oxidation state of Mn. It first discusses the development of an active $MnO_x$ catalyst on glassy carbon support exhibiting bifunctional activity for the ORR and the OER and identifies its initial state as a Mn (III)
oxide with alpha-Mn$_2$O$_3$ crystallinity. Next, application of *ex-situ* XPS to characterization of the Mn surface oxidation state after exposure to the ORR and the OER relevant potentials reveals that the Mn (III) state is maintained under both sets of reaction conditions, although previous reports have demonstrated significant variations in Mn oxidation state in a similar potential window of characterization.

To investigate the possible effects of the preparation route on the surface properties of MnO$_x$ under reaction conditions, the catalyst was subjected to five different heat treatment conditions to produce surfaces with different starting Mn oxidation states. *Ex-situ* Mn L-edge XAS characterization of the resulting catalytic samples demonstrates that the increase in heat treatment temperature leads both to an increase in catalytic activity for the two reactions and to a decrease in the ability of Mn to change oxidation state. These results highlight the importance of preparation route to electrochemical properties of MnO$_x$. Adaptation of the original synthesis procedure of MnO$_x$ on glassy carbon electrode to a silicon nitride window modified with gold (Au-Si$_3$N$_4$) for *in-situ* Mn K-edge XAS characterization further confirms the importance of synthesis conditions to the resulting surface properties of MnO$_x$. Replacement of glassy carbon support with Au-Si$_3$N$_4$ results in formation of a different phase, a mixture of Mn$_3$O$_4$ and MnO$_2$, and significant changes in Mn oxidation state with reaction conditions.

Finally, to simplify the complexity of the catalytic samples, size-selected nanoparticulate samples were prepared on glassy carbon and the activity of the nanoparticles for the OER and the ORR was investigated. These studies, which rely on *ex-situ* Mn L-edge XAS characterization of catalytic samples, discuss possible
contribution of gold to the OER activity on composite electrodes consisting of both 
MnO\textsubscript{x} and gold and identify Mn\textsubscript{3}O\textsubscript{4} as a phase with high ORR activity.

The discussed spectroscopic characterization of MnO\textsubscript{x} catalysts with high activity 
for the ORR and the OER demonstrates the influence of preparation conditions and the 
underlying support on the properties of MnO\textsubscript{x} surface under reaction conditions. 
Although the current studies are limited to MnO\textsubscript{x} for oxygen electrocatalysis, these 
considerations are also expected to extend to other transition metal oxide catalysts and 
electrochemical reactions.
Acknowledgements

During the six years at Stanford, I have felt a great deal of support in pursuit of my Ph.D. and would like to thank all the fantastic people who have had a positive impact on me as a person and as a scientist. My adviser, Professor Tom Jaramillo, has been a wonderful mentor, always ready to give advice on topics ranging from potentiostats and catalytic pathways to Friday weddings and the best restaurants in Santa Barbara. His never-ending positive attitude has created a friendly working environment in our lab, and it has been a true pleasure to come into work throughout the years. Tom’s enthusiasm for research has also been incessant and has helped shape my projects into terrific contributions to oxygen electrocatalysis. Zhebo Chen was my first colleague in Tom’s lab, and I would not have been able to progress as far or as quickly into my research project without his help and support. The two of us shared many hours in the laboratory, first ordering equipment and then jump-starting the experiments. Even after all the set-up was complete, Zhebo had continued to be a big part of my days, whether he was helping me run x-ray diffraction experiments, teaching me how to use a new software, or initiating happy hour gatherings. Kendra Kuhl joined the lab right when Zhebo and I were getting started on our projects, and her chemistry skills, of which we had very few, were invaluable to the expansion of the lab and the build-up of in-house synthesis techniques utilized in my work. Her openness, sense of humor, and a friendly love of competition contributed to the development of a fun and enjoyable work environment in our laboratory. Kendra was always happy to talk me through any challenge, whether it was a failed experiment or a search for the best physical therapist in Palo Alto.
As Jaramillo group expanded, the new members have all turned out to be fantastic co-workers. Although it is impossible to detail everyone’s impact on my graduate school experience, I would like to mention some of the most important contributions. Blaise Pinaud and Dr. Jakob Kibsgaard participated in the compilation of the crystal structures and (photo)electrochemical activities of different manganese oxide (MnO₅) phases and made the somewhat tedious process both interesting and fun. Blaise Pinaud was also a wonderful conference buddy and a great resource for all things related to creme brulee. Dr. Shin-Jung Choi and visiting Prof. Sung-Hyeon Baeck shared their extensive MnO₅ knowledge with me and worked toward synthesis of various manganese oxide phases, which eventually served as model compounds in spectroscopy characterization presented in Chapters 4-6. Jesse Benck contributed to preparation and imaging of catalysts described in Chapters 5 and 6 and was always happy to read the latest draft of my manuscript or listen to an update on my research progress. Jesse also became a close friend with whom I could discuss any personal issue or debate the nuances of anchoring, decision making, and the meaning of personality. Helpful discussion of x-ray photoelectron spectroscopy (XPS) with Ben Reinecke helped me complete the XPS analysis detailed in Chapter 3. All other Jaramillo members – Etosha Cave, David Abram, Ariel Jackson, Linsey Seitz, Desmond Ng, Toru Hatsukade, Pong Chakthranont, Peter Vesborg, and Arnold Forman have not only been great scientific resources, but have also enriched my life through their love for movies, Danish Christmas lunches, frisbee, sour beer tastings, and fish smoking.

My development as a scientist was strengthened by the opportunity to mentor several undergraduate and graduate students. Tom Brennan and Bobby Liu, my first two
graduate rotation students, contributed to the set-up of the laboratory and initiated research of oxygen electrocatalysis by precious metal nanoparticles. My undergraduate researchers, AJ Medford, Jeffrey Lou, Meghali Chopra, and Vikram Bali expanded upon the precious metal catalytic systems started by Tom B. and Bobby and studied oxygen reduction and evolution reactions on platinum, platinum-iridium, and platinum-yttrium nanoparticles and thin films. I would like to thank AJ, Jeff, Meghali, and Vik for their enthusiasm for research and the opportunity to guide them in their projects. Next, I would like to acknowledge Felix Mbuga, Elyse Coletta, and the now current Jaramillo group members, Desmond Ng and Pong Chakthranont, who, as rotation students, participated in the development and characterization of manganese oxide catalysts and contributed to increased understanding of the results discussed in my dissertation.

My understanding of oxygen electrocatalysis on MnO$_x$ electrodes also benefitted from my involvement in Center on Nanostructuring for Efficient Energy Conversion (CNEEC). After joining CNEEC in 2009, I participated in a collaborative project on nanoparticulate MnO$_x$ catalysts with Chia-Jung Chung and Prof. Bruce Clemens, the details of which are presented in Chapters 6 and 7. I feel lucky to have collaborated with Chia-Jung, who was always ready to prepare another batch of nanoparticulate samples, discuss the latest results, or brainstorm new project ideas. As part of CNEEC, I also had the pleasure of working with Katie Pickrahn and Prof. Stacey Bent on atomic layer deposition of active manganese oxide catalysts. Throughout our fruitful collaboration, Katie has also become a good friend and a reliable supplier of my favorite food items during late night work sessions. The work presented in Appendix C was the result of collaboration with CNEEC Professor Jens Norskov and Technical University of Denmark.
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详细的锰氧化状态表征在锰氧化物催化剂中是通过使用同步辐射进行 X 射线吸收光谱（XAS）来实现的，该研究在斯坦福同步辐射光源（SSRL）和高级光源（ALS）上进行。我想感谢 Marcus Lundberg，Hodgson 团队的前博士后研究员；SSRL 科学家 Dennis Nordlund；以及 Lawrence Berkeley 国家实验室（LBNL）科学家 Benedikt Lasalle-Kaiser，Sheraz Gul，Junko Yano，Vittal Yachandra，以及 Matthew Marcus 在 XAS 表征和数据解释中的角色。Marcus L. 为我介绍了 Mn L 边 XAS，并展示了该技术在识别平均 Mn 氧化状态中的能力。Dennis 在 ex-situ Mn L 边 XAS 实验中起到了关键作用，这些实验描述在第 4、6 和 7 章节中，他不仅提供了实践帮助，而且提供了必要的科学背景来执行实验并解释数据。Junko 的 Mn K 边 XANES 和 EXAFS 数据对我的理解至关重要，如果没有她的参与，第 5 章中的工作将无法完成。Benedikt，在 Matthew M. 和 Sheraz 的协助下，带领了 Mn K 边 x 射线吸收光谱的原位表征，这些光谱在第 5 章中被呈现，他是一位伟大的导师和同事，他在我在 ALS 的漫长工作日中给予耐心、亲切和清晰的交流，结合
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Chapter 1

Introduction

1.1 Motivation: Oxygen Electrode Electrochemistry

Oxygen reduction reaction (ORR, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) and oxygen evolution reaction (OER, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) are important in emerging energy generation and storage technologies. Oxygen reduction reaction is the limiting reaction in polymer electrolyte membrane fuel cells and metal-air batteries, while oxygen evolution reaction is the limiting reaction in electrolysis cells and photoelectrochemical hydrogen production. These technologies, which offer ways to generate, store, and utilize carbon neutral energy, are especially relevant today, in the age of increasing energy demand and carbon dioxide emissions. As shown in Table 1.1, both global energy consumption and carbon dioxide production is projected to increase by more than 50% in the next two decades, which necessitates rapid development of catalytic materials for the ORR and the OER.

Table 1.1: Projected increases in world energy consumption and carbon dioxide production.

<table>
<thead>
<tr>
<th></th>
<th>Energy Consumption (TW)</th>
<th>CO₂ Production (billion Metric Tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>18</td>
<td>32</td>
</tr>
<tr>
<td>2035</td>
<td>26</td>
<td>43</td>
</tr>
</tbody>
</table>

The important properties of industrially relevant catalytic materials include activity, stability, price, and availability. Due to large overpotentials associated with
both the ORR and the OER when even the best catalytic materials are considered, the majority of current research has focused either on improvement the activity of scarce and expensive precious metal catalysts or development of active non-precious metal catalysts, which are less costly and more abundant, while stability concerns have received less attention. To guide the rational design of potential catalysts for the two reactions, theoretical investigations have attempted to address the origin of high overpotentials associated with the ORR and the OER and predict catalysts with improved catalytic activities. These studies identified the strength of oxygen adsorption on the catalytic surface as a descriptor of both ORR and OER activity. The selection of an accurate descriptor characteristic of the binding strength of intermediates of the reaction of interest allowed for a construction of theoretical volcano relationships, which visually represented the well-known Sabatier principle. The theoretically constructed volcano plots matched the experimental observations of the best performing catalysts, identifying platinum and ruthenium oxide as materials at the top of the ORR and OER volcanoes plots, respectively.

Platinum has long been known as the most active ORR catalyst and is the current industry standard in low temperature fuel cells. More recently, alloys of platinum have been shown to achieve activities higher than that of pure platinum and non-precious metal catalysts have begun to approach the activity of platinum, with nitrogen-coordinated iron prepared in a carbon matrix and perovskite catalysts showing remarkable ORR activity in acidic and alkaline electrolytes, respectively. Ruthenium oxides, together with iridium oxides, have been used in industrial electrolyzers as part of dimensionally stable anodes (DSAs) since 1960s and their OER activity and stability
has remained unmatched in acidic environment.\textsuperscript{20,21} In alkaline environment, the industrial standard for OER is nickel oxide.\textsuperscript{22,23} More recently, other catalytic materials including perovskites\textsuperscript{24} and cobalt oxides\textsuperscript{25-27} have also shown high OER in basic electrolyte. More research is necessary, however, to develop catalysts with high activity and appropriate stability, cost, and availability to facilitate widespread commercialization of fuel cells, metal-air batteries, and photoelectrochemical reactors.

1.2 Background: Manganese Oxides

Manganese oxides and oxyhydroxides (MnO$_x$) catalysts are an interesting alternative to the precious metal based electrodes in basic conditions due to their abundance,\textsuperscript{28} low cost,\textsuperscript{29} and a demonstrated ability to catalyze both the ORR\textsuperscript{30} and the OER\textsuperscript{31} at high pH values. Comparison of abundance and cost of manganese to platinum and iridium, shown in Table 1.2, demonstrates that manganese is approximately six orders of magnitude more abundant in the earth’s crust\textsuperscript{28} and three to four orders of magnitude cheaper than the precious metals, such as platinum and iridium.\textsuperscript{29} These large differences indicate that even if manganese does not approach the activity of the best catalysts for the ORR and the OER, it may present a feasible cost-effective alternative to precious metal catalysts.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Abundance (mg/kg)$^{28}$</th>
<th>Price ($/kg)$^{29}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>$5.0 \cdot 10^{-3}$</td>
<td>45600</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>$1.0 \cdot 10^{-3}$</td>
<td>3500</td>
</tr>
<tr>
<td>Manganese</td>
<td>$9.5 \cdot 10^{2}$</td>
<td>3</td>
</tr>
</tbody>
</table>

In addition to being earth-abundant and cheap, manganese can take on several oxidation states, including 2, 3, 4, 6, and 7,\textsuperscript{28} and exists in a variety of structures.\textsuperscript{32}
allowing for a large number of possible catalysts. Table 1.3 summarizes the most common MnOₓ oxidation states and phases and lists examples of naturally occurring minerals. Out of possible oxidation states, MnO₂ is by far the most diverse state, with at least seven different known phases. Examples of MnO₂ structures are provided in Figure 1.1.

**Table 1.3: Oxidation states and phases of MnOₓ.**

<table>
<thead>
<tr>
<th>MnOₓ</th>
<th>Mineral Example</th>
<th>Valence</th>
<th>Type of Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₁₋ₓO</td>
<td>Manganosite</td>
<td>+2</td>
<td>non-stoichiometric</td>
</tr>
<tr>
<td>Mn(OH)₂</td>
<td>Pyrochroite</td>
<td>+2</td>
<td>n/a</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>Hausmannite</td>
<td>+2, 3, 3</td>
<td>α, β</td>
</tr>
<tr>
<td>MnOOH</td>
<td>Manganite</td>
<td>+3</td>
<td>α, β, γ</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>Bixbyite</td>
<td>+3</td>
<td>α, γ</td>
</tr>
<tr>
<td>MnO₂</td>
<td>Pyrolusite</td>
<td>+4</td>
<td>α, β, γ, δ, ε, ρ, λ</td>
</tr>
</tbody>
</table>

Although not all phases listed in Table 1.3 have been extensively characterized for the ORR and the OER, ex-situ spectroscopy and x-ray diffraction studies have linked gamma-MnOOH, alpha-MnO₂, beta-MnO₂, and delta-MnO₂ to have high activity for the ORR and alpha-Mn₂O₃, gamma-MnOOH, and amorphous manganese oxides to have high activity for the OER. MnOₓ is also found in a biological enzyme, which catalyzes the OER in photosystem II. The enzyme, known as the oxygen evolving center (OEC), contains four manganese, one calcium, and four oxygen ions and forms a cubane like CaMn₃O₄ structure with the fourth manganese ion connected to the cubane via a mono-µ-oxo bridge. Due to the large possibilities of different MnOₓ catalysts and the precedent for ORR and OER activity in MnOₓ based catalysts, it is important to continue investigating oxygen reduction and evolution activities of MnOₓ and identify design principles for the development of highly active catalysts.
1.3 Spectroscopy Techniques: Characterization of Mn Oxidation State

To accelerate the development of manganese oxide and oxyhydroxide (MnO_x) catalysts with improved activities for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), it is important to develop understanding of the chemical state and structure of MnO_x active surfaces at or after exposure to ORR and OER relevant potentials. Characterization of MnO_x surface under reaction conditions, however, has been so far limited only to a handful of studies. In this section two possible methods of surface characterization are discussed: x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS).

Both XPS and XAS can offer information on the electronic structure of the surface, while XAS can also probe the short-range order of the catalysts. Spectroscopy characterization of the catalysts can be performed ex-situ, after exposing the catalysts to specific electrochemical conditions, or in-situ, by controlling the electrochemical reaction...
conditions as the spectroscopic measurements are performed. Although *in-situ* studies provide direct evidence that the measured surface properties of the catalysts exist under specific electrochemical reaction conditions, they require advanced experimental set-ups. Electrolyte presents a particular challenge for ultra-high vacuum conditions typically employed in both XPS and soft x-ray absorption spectroscopy which offer surface sensitivity.\(^4\) *In-situ* electrochemical cells have already been developed for hard x-ray absorption spectroscopy measurements,\(^4\) which lose surface sensitivity but allow for characterization of the electronic structure and the short-range order of the bulk of the electrode as a function of applied potential.

### 1.3.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique, which can provide information on the chemical state of the catalytic surface. In the technique, the incident x-ray energy is absorbed by the atoms, resulting in ejection of core electrons. Electrons close to the surface of the sample are able to escape into the vacuum and their kinetic energy is measured using an energy analyzer. From the measured kinetic energy the binding energy of the electron, a value specific to the electronic structure of an element, can be calculated using equation 1.1:

\[
E_B = h\nu - E_K - \varphi_{sp} \quad (1.1)
\]

where \(E_B\) refers to the binding energy of the core electron, \(h\nu\) to the photon energy of the x-ray source, \(E_K\) to the measured kinetic energy of the ejected electrons, and \(\varphi_{sp}\) to the work function of the spectrometer.\(^5\) The intensity of the electrons is usually plotted as a function of binding energy, providing quantitative and qualitative information about the composition of the surface and the chemical state of the components. The probe depth of
XPS is proportional to the electron attenuation length and can be estimated using mean free path of the electrons and the universal mean free path curve. \(^51\) For most samples and instrument configurations XPS measures the top 10 nm or less.

![Figure 1.2: High resolution x-ray photoelectron spectroscopy of (a) Mn 2p region and (b) Mn 3s region, demonstrating an increasing \(\Delta E_{2p_{1/2}}\) and decreasing \(\Delta E_{3s}\) with increasing Mn oxidation state.](image)

A typical spectrum of \(\text{MnO}_x\) surface will contain Mn 2s, 2p\(_{3/2}\), 2p\(_{1/2}\), 3s, and 3p peaks, O 1s peak, both due to oxygen in the sample and adventitious oxygen, and C 1s peak due to surface contamination with adventitious carbon. The strongest Mn XPS peak is Mn 2p\(_{3/2}\), but resolving the Mn oxidation state using its energy position is challenging due to the large full width half maximum (FWHM) of the peak and the small separation of 2 eV between the peak maxima of Mn (II), Mn (III), and Mn (IV) oxides. \(^{52-54}\) Instead, previous studies have identified the relative magnitude of Mn 3s multiplet splitting (\(\Delta E_{3s}\)), \(^{55-57}\) the relative position of Mn 2p\(_{1/2}\) satellite (\(\Delta E_{2p_{1/2}}\)), \(^{56,58}\) and de-convolution of O 1s peak into contributions from Mn-O-Mn, Mn-OH, and H-O-H for cases where the expected components are MnOOH and MnO\(_2\) \(^{59-61}\) as promising methods to monitor Mn oxidation state. High resolution x-ray photoelectron spectra of three \(\text{MnO}_x\) powders: MnO, \(\text{Mn}_2\text{O}_3\), and MnO\(_2\) illustrate the expected \(\Delta E_{2p_{1/2}}\) and \(\Delta E_{3s}\) in Figure 1.2.
1.3.2 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is another technique which can offer surface sensitive information about the chemical state of the catalyst. In the technique, the surface is irradiated by a tunable x-ray source. When the energy of the incident x-ray is equal or greater to the energy of a core electron, absorption of the energy results in an excitation of the core electron into an empty electronic state. The event produces an edge, which is characteristic to the electronic structure of the element and incident x-ray energy.49

XAS experiments can be classified into two types: surface sensitive soft x-rays experiments typically done with x-ray energies below 1000 eV and bulk sensitive hard x-rays experiments typically done with x-ray energies above 3000 eV.62 These two types of experiments require different instrumentation and often use different detection modes. Soft x-ray XAS experiments are performed in ultra-high vacuum (UHV) environment and usually measure absorption indirectly in total, auger, or partial electron yield modes.48 In contrast, hard x-ray XAS experiments are performed in atmosphere and usually measure absorption in transmission or fluorescence mode.49

The energies of Mn K-edge and L-edge are 6500 eV and 600 eV, falling into hard x-ray and soft x-ray regimes, respectively. The L-edge corresponds to an allowed 2p-3d transition, producing sharp peaks, while the K-edge corresponds to 1s-3d dipole-forbidden transition, producing features that are less sharp, but that are often more sensitive to local geometric structure.63-65 Examples of Mn L-edge and K-edge spectra are shown in Figure 1.3. In Figure 1.3 (a) Mn L-edge spectrum of Mn (III) oxide, alpha-Mn$_2$O$_3$, has a distinct shape from the spectra of the Mn (IV) oxides, beta-MnO$_2$ and
lambda-MnO$_2$, allowing for straightforward differentiation between Mn (III) and (IV) oxidation states. The differences between the Mn (IV) phases in the Mn L-edge are slight and difficult to resolve. Mn K-edge spectra, on the other hand, allows for differentiation between both different oxidation states and phases, as shown in Figure 1.3 (b).

![Figure 1.3](image_url)

**Figure 1.3:** X-ray absorption spectroscopy of (a) Mn L-edge and (b) Mn K-edge, illustrating the spectra of different MnO$_x$ powders: alpha-Mn$_2$O$_3$, beta-MnO$_2$, and lambda-MnO$_2$.

Measurements of the Mn L-edge are performed in UHV environment and can offer information about the oxidation state of the top few nanometers of the catalytic surface. The hard x-rays necessary for the Mn K-edge measurements, however, penetrate the bulk of the sample and lose surface sensitivity. Although the loss in surface sensitivity introduces a large number of spectator species located in the bulk of the
sample, it also creates an opportunity to easily configure XAS measurements for in-situ electrochemical characterization and provide information on the oxidation state and phase of the catalyst under applied potentials relevant to the ORR and the OER.\textsuperscript{49,66,67} In the forthcoming chapters, Mn L-edge XAS measurements will be used ex-situ to extract surface oxidation state of Mn after exposure of the MnO$_x$ catalytic surface to the ORR and OER relevant potentials, while Mn K-edge measurements will be used in-situ to monitor the changes in the structure and phase of MnO$_x$ catalyst as the electrochemical conditions switch from the ORR to the OER potentials.

1.4 Dissertation Overview

This dissertation focuses on development of manganese oxide (MnO$_x$) catalysts for the two oxygen electrode reactions: oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The two major themes of the work are: identification of active materials for the ORR, the OER, or both and characterization of the Mn oxidation state in an attempt to correlate measured catalytic activity to material properties.

Specifically, the second chapter describes development of a Mn (III) oxide with alpha-Mn$_2$O$_3$ crystallinity with bifunctional activity for the ORR and the OER. The third, fourth, and fifth chapters focus on understanding of surface conditions of electrodeposited MnO$_x$ at the ORR and the OER relevant potentials using a variety of spectroscopic techniques. The third chapter describes application of ex-situ X-ray photoelectron spectroscopy (XPS) to characterization of the Mn surface oxidation state after exposure of the catalyst to the ORR and the OER relevant potentials. The fourth chapter explores the effect of preparation route on the extent of change in Mn surface oxidation state of MnO$_x$ using ex-situ Mn L-edge X-ray absorption spectroscopy (XAS).
The fifth chapter details the adaptation of the original synthesis procedure on glassy carbon electrode to a silicon nitride window modified with gold to track the changes of Mn oxidation state as a function of reaction conditions in-situ using Mn K-edge XAS. Together, the third, fourth, and fifth chapters utilize three different techniques: ex-situ XPS, ex-situ L-edge XAS, and in-situ K-edge XAS to characterize the oxidation state of Mn either after exposure to or under the ORR and the OER reaction conditions.

The sixth and seventh chapters shift focus from electrodeposited MnO₅ resulting in a complex morphology on glassy carbon support to a more defined system consisting of nanoparticulate MnO₅. In the sixth chapter, the OER activity of MnO₅ nanoparticles is characterized in the presence and absence of gold, and the possible direct and indirect effects of MnO₅ and Au on the observed OER activity are considered. In the seventh chapter, Mn₃O₄ phase is identified as a phase capable of 4-electron reduction of oxygen on glassy carbon support. The eighth chapter summarizes the findings from both electrodeposited MnO₅ and nanoparticulate MnO₅ catalysts and presents the directions for future research. At the end of the dissertation, a study detailing a collaborative effort based on density function theory (DFT) calculations and electrochemistry is included in Appendix C.

### 1.5 Collaborations

Several parts of this dissertation were conducted in collaboration with other researchers and research groups. Preliminary ex-situ Mn L-edge X-ray absorption spectroscopy (XAS) measurements on electrodeposited Mn (III) oxide were performed in collaboration with Marcus Lundberg and Samuel Wilson, postdocs in Keith Hodgson’s group in Chemistry. Mn L-edge XAS data described in chapters four, sixth, and seven
were measured, normalized and interpreted with the help from Dennis Nordlund, a staff scientist at SLAC national accelerator laboratory. *In-situ* XAS measurements described in chapter five were performed in collaboration with Joint Center for Artificial Photosynthesis (JCAP) scientists Benedikt Lassalle-Kaiser, Sheraz Gul, Junko Yano, and Vittal Yachandra. Preparation of MnO\textsubscript{x} nanoparticles studied in chapters six and seven was performed by Chia-Jung Chung, a graduate student in Bruce Clemens’ group in Material Science. Jesse Benck, a graduate student in Jaramillo group, participated in the preparation and characterization of catalytic samples described in chapters five and sixth. The DFT study presented in the Appendix C was a result of collaboration with Jens Norskov and Technical University of Denmark scientists Hai-Yan Su, Isabela C. Man, Federico Calle-Vallejo, and Jan Rossmeisl. When applicable, detailed description of author contributions is available at the end of the chapter or appendix.

### 1.6 Conclusions

Development of active catalytic materials for the oxygen reduction and evolution reactions is extremely important to widespread commercialization of emerging energy storage and conversion technologies. Manganese oxides are interesting catalysts for the two reactions due to their abundance and availability, ability to exist in a variety of oxidation states and structures, and previously demonstrated high oxygen electrode activity both in biological enzymes and in solid state surfaces. This dissertation will focus both on development of new MnO\textsubscript{x} electrocatalysts active for the ORR and the OER and on characterization of ORR and OER relevant surfaces using x-ray photoelectron spectroscopy and x-ray absorption spectroscopy.
Chapter 2

Development of a Bifunctional Nonprecious Metal Catalyst for the Oxygen Reduction and Water Oxidation

2.1 Abstract

There is a growing interest in oxygen electrochemistry as conversions between O₂ and H₂O play an important role in a variety of renewable energy technologies. Drawing inspiration from a cubane-like CaMn₄Oₓ, the biological catalyst found in the oxygen evolving center (OEC) in photosystem II, nanostructured manganese oxide surfaces were investigated for these reactions. Thin films of nanostructured manganese oxide were found to be active for both oxygen reduction and water oxidation, with similar overall oxygen electrode activity to the best known precious metal nanoparticle catalysts: platinum, ruthenium, and iridium. Physical and chemical characterization of the nanostructured manganese oxide bifunctional catalyst reveals an oxidation state of Mn (III), akin to one of the most commonly observed Mn oxidation states found in the OEC.

2.2 Introduction

This chapter focuses on the development and characterization of a bifunctional manganese oxide (MnOₓ) catalyst exhibiting activities for the oxygen reduction reaction
(ORR) and the oxygen evolution reaction (OER). A bifunctional catalyst, with significant catalytic activity for these reactions, could be employed in a unitized regenerative fuel cell (URFC), an energy storage device that can be coupled to intermittent renewable energy such as wind or solar to peak-shift electricity to the grid. As discussed in Chapter 1, catalyst development is critical in these fields. The best catalysts for the ORR consist of platinum (Pt), but Pt has only moderate activity for the OER. Ruthenium (Ru) and iridium (Ir) oxides are the best OER catalysts, but they are not as active for the ORR as Pt. Alloys of Pt, Ir, and Ru have consequently been evaluated for bifunctional oxygen electrode activity, and they were shown to perform better than the pure metals or metal oxides. Nevertheless, bifunctional catalyst development remains a major challenge as the best catalysts require significant overpotentials for both reactions and consist of precious metals that are both scarce and expensive.

In search of catalysts with lower overpotentials for the ORR or the OER, researchers have turned to understanding the properties of the oxygen evolving complex (OEC), an enzyme consisting of a cubane-like CaMn₄Oₓ active site known to catalyze the OER during photosynthesis. Density functional theory (DFT) calculations have helped explain the high activity of the enzyme: each step in the reaction is close to thermoneutral, a requirement for a reversible catalyst. This funding motivates investigation of manganese oxide (MnOₓ) surfaces and molecular mimics as potential materials for bifunctional oxygen catalysis. A number of Mn-based molecular mimics and MnOₓ surfaces discussed in Chapter 1 have already demonstrated activity for the OER, particularly the alpha-Mn₂O₃ phase. Though alpha-Mn₂O₃ has not previously shown activity for the ORR, other MnOₓ phases are ORR active, particularly
MnOOH,\textsuperscript{76} beta-MnO\textsubscript{2},\textsuperscript{38} and alpha-MnO\textsubscript{2}.\textsuperscript{36} The upcoming sections describe the development and characterization of an active MnO\textsubscript{x} bifunctional catalyst, a nanostructured thin film with such high activity in alkaline media that it nearly reaches that of the most active precious metals.

2.3 Experimental Methods

2.3.1 Synthesis of the Manganese Oxide Thin Film

Manganese oxide (MnO\textsubscript{x}) thin film was synthesized by potentiostatic electrodeposition using a Bio-Logic potentiostat (VMP3) in a 3-electrode electrochemical cell in a rotating disk electrode configuration (RDE, Pine Instruments). A modified version of a procedure developed by Tench et al was employed.\textsuperscript{77} A glassy carbon disk (0.196 cm\textsuperscript{2}, SigradurG HTW Hochtemperatur-Werkstoffe GmbH) was first polished with alumina to a 0.05 μm finish and used as a substrate. An Ag|AgCl electrode was used as a reference electrode, and platinum mesh was used as a counter electrode. The deposition solution consisted of 2.15 g of sodium sulfate (Sigma-Aldrich, >99.0%) and 3.70 g of manganous acetate (Aldrich, 99.99%) dissolved in 150 mL of Millipore water at room temperature, yielding a solution pH of 7.4. The deposition solution was then allowed to age for 6 days, until the pH dropped to 7.1. To deposit the manganese oxide thin film, 30 mL of the deposition solution was added to a 50 mL beaker. The polished glassy carbon substrate described above was inserted into an interchangeable RDE tip, and the tip was subsequently immersed into the deposition solution. The platinum mesh was positioned 1 cm underneath and parallel to the substrate. The resistance between working and reference electrodes was measured to be 37.9 Ω. During the electrodeposition, potential was cycled 9 times at a sweep rate of 20 mV·s\textsuperscript{-1} between 0 V and 0.6 V versus an
Ag|AgCl reference electrode (with iR compensation) at 900 revolutions per minute (rpm) rotation speed. After the 9th cycle, the RDE tip was removed from the deposition solution and the carbon electrode was thoroughly rinsed with Millipore water. The substrate was then placed into a ceramic boat (Fisher Scientific) and heated at 480°C in air for 10 hours in a quartz tube furnace (Thermolyne 21100).

2.3.2 Electrochemical Characterization of Catalytic Materials

Electrochemical activity of all catalytic materials was studied using cyclic voltammetry (CV) in a 3-electrode electrochemical cell in a RDE configuration. All CVs were iR-compensated and measured in 0.1 M KOH electrolyte at 23°C and 1600 rpm, with a sweep rate of 5 mV·s⁻¹, using a platinum wire counter electrode and Hg|HgO reference electrode. The electrolyte (0.1 M KOH) was prepared from high purity KOH pellets (Sigma-Aldrich, 99.99%) by adding 5.60 g of pellets to 1 L of Millipore water. The potential scale was calibrated to a reversible hydrogen electrode (RHE). RHE calibration was performed at the end of each characterization in a hydrogen saturated electrolyte with platinum nanoparticles at the working electrode (20-wt.% Pt on Vulcan XC-72, Etek). The potential at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. To benchmark the activity of the MnOₓ thin film, electrochemical characterization was also performed on commercial carbon-supported (Vulcan XC-72) precious metal nanoparticles: 20 wt % Pt (Etek), 20 wt % Ru (Premetek), and 20 wt % Ir (Premetek). Catalyst dispersions of Pt, Ir, and Ru nanoparticles were prepared using standard procedures for fuel cell catalyst testing to achieve a metal concentration of 28 μg·cm⁻² on a GC substrate. Measurements of the electrochemically active surface area (ECSA) showed that ECSAₘₙₒₓ ≤
ECSA_{precious metals}. A bare GC substrate, heat treated to 480 °C as with the MnO\textsubscript{x} sample, was examined as a control.

Oxygen electrode activities were measured in oxygen saturated electrolyte. Initially, the potential was scanned from 0.05 V to 1.1 V vs RHE and the oxygen reduction activity was measured. After the oxygen reduction activity was obtained, the potential window was extended to 1.9 V for the MnO\textsubscript{x} thin film, 1.7 V for iridium and ruthenium nanoparticles, 2.2 V for platinum nanoparticles, and 2.6 V for glassy carbon substrate to measure both oxygen reduction reaction and oxygen evolution reaction activities. Multiple cycles of cyclic voltamograms were recorded for each catalytic material, but only the initial anodic sweep is reported.

2.3.3 Physical and Chemical Characterization of the Manganese Oxide Thin Film

The morphology of the manganese oxide thin film was studied using scanning electron microscopy (SEM, FEI XL30 Sirion). A beam current of 5 kV, spot size of 3 nm, and a secondary electron detector were used. The manganese oxidation state was studied by X-ray photo-electron spectroscopy using Al K\textalpha\ 1486.6 eV x-rays (XPS, PHI 5000 VersaProbe). High resolution spectra of C-1s, Mn-2p and Mn-3s regions were collected on the manganese oxide thin film and the four manganese oxide powders: MnO, Mn\textsubscript{3}O\textsubscript{4}, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2} (Sigma-Aldrich). Prior to characterization, the MnO powder standard was sputtered with argon ions for 1 minute to remove surface oxidation. All spectra were calibrated using 285.0 eV as the line position of adventitious carbon. During data acquisition runs, a pass energy of 23.5 eV, an energy step of 0.1 eV, and a time of 20 ms per step were used. The energy regions and the number of scans for each spectrum are
shown in Table 2.1. As discussed in Chapter 1 and previous literature, the absolute positions of the Mn-2p and Mn-3s peaks are not a robust metric for determining the oxidation state of Mn in MnO$_x$.\textsuperscript{55,56} Consequently, the relative position of 2p$_{1/2}$ satellite structure and the magnitude of 3s multiplet splitting were used to determine the oxidation state of manganese in the manganese oxide thin film.

<table>
<thead>
<tr>
<th>XPS Region</th>
<th>Lower (eV)</th>
<th>Range (eV)</th>
<th>Repeats</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1s</td>
<td>278</td>
<td>32</td>
<td>80</td>
</tr>
<tr>
<td>Mn-2p</td>
<td>632</td>
<td>40</td>
<td>80</td>
</tr>
<tr>
<td>Mn-3s</td>
<td>75</td>
<td>35</td>
<td>400</td>
</tr>
</tbody>
</table>

The crystal structure of the MnO$_x$ thin film was investigated using x-ray diffraction with Cu K$_{\alpha1}$ radiation and $\lambda=1.54$ Å, operated at 45 kV and 40 mA (XRD, Phillips X'Pert 2). 2θ scans from 20 to 70 degrees were performed at 0.01 degrees per step and 2 seconds per step.

2.4 Results and Discussion

The oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) activities of the manganese oxide (MnO$_x$) thin film, precious metal nanoparticles, and glassy carbon (GC) support are shown in Figure 2.1. From the figure, which exhibits the initial linear sweep in an anodic direction for each catalytic material, it is evident that MnO$_x$ was found to be highly active for both the ORR and the OER. The MnO$_x$ thin film was more active for the ORR than both Ru and Ir nanoparticles and only $\sim$130 mV less active than Pt at the half-wave potential. Regarding OER activity, the MnO$_x$ thin film was clearly more active than Pt with activity that approached those of Ir and Ru. As expected, the GC support itself showed little catalytic activity.
Figure 2.1: Oxygen electrode activities of the MnO\textsubscript{x} thin film, nanoparticles of Pt, Ir, and Ru supported on Vulcan carbon, and the glassy carbon (GC) substrate. The MnO\textsubscript{x} thin film shows excellent activity for both the ORR and the OER.

Table 2.2 quantitatively compares the bifunctional oxygen electrode activity of the MnO\textsubscript{x} thin film to those of the precious metal nanoparticles. The figure of merit used to quantify ORR is the potential at which an ORR current density of 3 mA·cm\textsuperscript{-2} is reached, which approximates the half-wave potential. Activities for the OER are judged by the potential required to oxidize water at a current density of 10 mA·cm\textsuperscript{-2}, a convention commonly used in the OER literature,\textsuperscript{78} and a metric relevant to solar fuel synthesis, discussed in Appendix A. Two values are recorded for Pt nanoparticles as degradation of the carbon support complicates measurement of the potential needed for 10 mA·cm\textsuperscript{-2} on Pt (see the note below Table 2.2). To assess the overall oxygen electrode activity, the difference between the ORR and the OER metrics is tabulated. The smaller the difference, the closer the catalyst is to an ideal reversible oxygen electrode. By this metric, the nanostructured MnO\textsubscript{x} thin film has an oxygen electrode activity of 1.04 V, which compares favorably to the precious metal catalysts.
Table 2.2. Oxygen electrode activities.

<table>
<thead>
<tr>
<th>Catalyst Material</th>
<th>ORR: E(V) at I=-3 mA·cm⁻²</th>
<th>OER: E(V) at I=10 mA·cm⁻²</th>
<th>Δ(OER-ORR): E (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20wt.% Ir/C</td>
<td>0.69</td>
<td>1.61</td>
<td>0.92</td>
</tr>
<tr>
<td>20wt.% Ru/C</td>
<td>0.61</td>
<td>1.62</td>
<td>1.01</td>
</tr>
<tr>
<td>20wt.% Pt/C</td>
<td>0.86</td>
<td>2.02 (1.88)ᵃ</td>
<td>1.16 (1.02)ᵃ</td>
</tr>
<tr>
<td>MnOₓ</td>
<td>0.73</td>
<td>1.77</td>
<td>1.04</td>
</tr>
</tbody>
</table>

ᵃExtrapolated value using the same Tafel slope as that at 1.74 V, where negligible corrosion occurs and the Pt is active for the OER.

To investigate the nature of this material’s bifunctional activity, X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were employed. XRD revealed some crystallinity, a weak peak at 32.9° consistent with alpha-Mn₂O₃ (222), as shown in Figure 2.2. The fact that this material does not behave as previously reported alpha-Mn₂O₃ may be explained by the SEM images shown in Figure 2.3 (a) and 2.3 (b), which exhibit a highly nanostructured surface with features that likely distinguish this surface from that of standard preparations.

![Figure 2.2: XRD of the glassy carbon (GC) support and the MnOₓ thin film deposited on GC. A weak reflection at 32.9° is attributed to alpha-Mn₂O₃ (222). The other features observed pertain to GC.](image)

XPS was used to probe the Mn oxidation state at the surface, Figure 2.3 (c) and 2.3 (d), by means of the relative position of the 2p₁/₂ satellite structure (ΔE₂p₁/₂) and the
magnitude of the 3s multiplet splitting (ΔE3s). Powder standards of MnO, Mn₃O₄, Mn₂O₃, and MnO₂ were measured for comparison and are shown in Figure 2.4. Table 2.3 lists the measured values for the four standards along with previous measurements from literature. For the active MnOₓ catalyst, ΔE₂p₁/₂ and ΔE₃s were 10.0 and 5.2, respectively, which correspond to Mn (III) in Mn₂O₃, the most common oxidation state in the OEC.

![Figure 2.3: SEM images of the MnOₓ thin film in two locations: (a) and (b), revealing a nanostructured morphology. High resolution XPS spectra of Mn-2p and Mn-3s regions are shown in (c) and (d), respectively. The relative positions of the 2p₁/₂ satellite and the magnitude of 3s multiplet splitting were 10.0 and 5.2. These values indicate a Mn (III) oxide surface.](image)

This nanostructured Mn (III) oxide demonstrates bifunctional activity unlike other MnOₓ catalysts, whose activities are detailed in Appendix B. Its OER activity is on par with the best reported MnOₓ OER catalyst, while its ORR activity matches or surpasses the activities of the best reported MnOₓ ORR catalysts. More importantly, its bifunctional activity is comparable to that of precious metals. Its OER activity also
outperforms that of recently reported Co-based OER electrodes.\textsuperscript{27} The observed excellent catalytic activity likely stems from the nanostructured nature of the catalyst, which can facilitate the presence of the appropriate MnO\textsubscript{x} active surfaces or sites at the relevant potentials to drive either the ORR or the OER. To understand the appropriate active surfaces under reaction conditions spectroscopic surface characterization techniques and Density Functional Theory (DFT) calculations were employed. The details of those studies are presented in Chapters 3-5 and Appendix C.

![Figure 2.4](image)

**Figure 2.4:** (a) Mn-2p\textsubscript{1/2} satellite structure and (b) Mn-3s splitting of the four MnO\textsubscript{x} powders (Sigma-Aldrich) plotted on the binding scale relative to Mn-2p\textsubscript{1/2} peak and the low binding energy multiplet, respectively.

**Table 2.3:** XPS values for Mn \(\Delta E\text{2p}_{1/2}\) and Mn \(\Delta E\text{3s}\) splitting for four MnO\textsubscript{x} standards, obtained in this work and in Dicastro et al.\textsuperscript{56}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>(\Delta E\text{2p}_{1/2})</th>
<th>(\Delta E\text{3s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO\textsubscript{2}</td>
<td>this work</td>
<td>11.8</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Dicastro</td>
<td>11.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Mn\textsubscript{2}O\textsubscript{3}</td>
<td>this work</td>
<td>10.0</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>Dicastro</td>
<td>10.5</td>
<td>5.4</td>
</tr>
<tr>
<td>MnO</td>
<td>this work</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>Dicastro</td>
<td>5.4</td>
<td>6.1</td>
</tr>
<tr>
<td>Mn\textsubscript{3}O\textsubscript{4}</td>
<td>this work</td>
<td>10.5\textsuperscript{a}</td>
<td>6.0\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td>Dicastro</td>
<td>11.3</td>
<td>5.3</td>
</tr>
<tr>
<td>MnO\textsubscript{x} thin film in Fig. 2.1, 2.2, &amp; 2.3</td>
<td>10.0</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}A very broad peak is observed.
2.5 Conclusions

Inspired by nature’s catalyst for water oxidation, a thin-film analogue consisting of a nanostructured Mn (III) oxide was developed and characterized. This inexpensive and earth-abundant catalyst exhibited excellent bifunctional oxygen electrode activity similar to that of the best known precious metal catalysts: Pt, Ru, and Ir. Such a catalyst could potentially be employed as the oxygen electrode in an alkaline exchange membrane (AEM) URFC or AEM-PEM (proton exchange membrane) hybrid URFC. This result opens up new avenues for energy conversion technologies based on earth abundant, scalable, nonprecious metal catalysts. Efforts to understand the properties of MnO\(_x\) surfaces under reaction conditions are detailed in Chapters 3-5 and Appendix C.

2.6 Copyright

Chapter 3

Investigation of Surface Oxidation Processes on a Bifunctional Manganese Oxide Electro catalyst Using Electrochemical Methods and $\textit{Ex-situ}$ X-ray Photoelectron Spectroscopy

3.1 Abstract

This chapter first identifies key electrochemical features of the bifunctional manganese oxide catalyst using cyclic voltammetry and then probes the changes in the surface oxidation state of manganese in the potential region between the oxygen reduction reaction (ORR) and the oxygen evolution (OER) using $\textit{ex-situ}$ x-ray photoelectron spectroscopy (XPS). Despite the surface sensitivity of XPS, these measurements do not reveal any differences in surface oxidation state between samples tested at ORR potentials and those examined at potentials relevant to the OER. Re-insertion of the samples into an electrochemical cell after the completion of $\textit{ex-situ}$ XPS measurements, however, demonstrates that electrochemical methods can discern a
difference in oxidation states of the two samples. These results suggest that the surface oxidative processes associated with the change from the ORR to the OER conditions are extremely shallow, likely on the order of one monolayer.

3.2 Introduction

Chapter 2 detailed the development of a bifunctional manganese oxide (MnO\textsubscript{x}) catalyst, exhibiting significant activity for the oxygen reduction and evolution reactions and identified the starting catalyst as Mn (III) oxide with alpha-Mn\textsubscript{2}O\textsubscript{3} crystallinity.\textsuperscript{82} In the upcoming sections, the changes in the MnO\textsubscript{x} surface upon exposure to potentials relevant to the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) catalysis are studied using ex-situ x-ray photoelectron spectroscopy (XPS).

Ex-situ XPS has been successfully used to monitor Mn oxidation state changes in a number of manganese oxides electrodes.\textsuperscript{59-61,83-85} To determine the oxidation state of Mn as a function of potential, researchers have relied on several spectral features. As the discussed in Chapter 1, the magnitude of Mn 3s multiplet splitting (\(\Delta E_{3s}\)),\textsuperscript{55,56,60,61,95-97} the relative position of Mn 2p\textsubscript{1/2} satellite (\(\Delta E_{2p_{1/2}}\)),\textsuperscript{56,58} and de-convolution of O 1s peak into contributions from Mn-O-Mn, Mn-OH, and H-O-H\textsuperscript{59-61,83,85} can all be used to estimate the average Mn oxidation state.\textsuperscript{55,56,60,61,83-85} In this chapter, the relative position of 2p\textsubscript{1/2} satellite structure and the O 1s line are used to monitor the changes in Mn oxidation state in the nanostructured Mn (III) oxide as the reaction conditions change from the ORR to the OER relevant potentials. The results of the ex-situ XPS study are interfaced with electrochemical characterization of the catalyst, and conclusions are drawn about the properties of the MnO\textsubscript{x} surface under the ORR and the OER reaction conditions.
3.3 Experimental Methods

3.3.1 Synthesis of the Manganese Oxide Thin Film

The manganese oxide thin film was electrodeposited onto a polished glassy carbon electrode (0.196 cm$^2$, SigradurG HTW Hochtemperatur-Werkstoffe GmbH) as described previously, using a modified procedure developed by Tench and co-workers. Briefly, the potential was cycled between 0.0 V and 0.6 V (Bio-Logic, VSP) vs. a Ag|AgCl reference electrode at 20 mV·s$^{-1}$ and 900 revolutions per minute (rpm) rotation speed in a three electrode electrochemical cell in a rotating disk electrode configuration (RDE, Pine Instruments). The deposition solution contained manganous acetate and sodium sulfate in concentrations of 0.1 M each; platinum mesh was used as a counter electrode. After the 9th cycle, the RDE tip was removed from the deposition solution, and the carbon electrode was thoroughly rinsed with Millipore water. The substrate was then placed into a ceramic boat (Fisher Scientific) and heated at 480°C in air for 10 hours in a quartz tube furnace (Mellen Company SC13).

3.3.2 Electrochemical Characterization of the Manganese Oxide Thin Film

The manganese oxide thin film was characterized using cyclic voltammetry in a three electrode electrochemical cell in a RDE configuration in both nitrogen and oxygen saturated environments. All experiments were performed in 0.1 M KOH electrolyte at room temperature, using a sweep rate of 20 mV·s$^{-1}$ and a rotation rate of either 0 rpm or 1600 rpm. A carbon rod was used as a counter electrode, and Ag|AgCl was used as a reference electrode. The potential scale was calibrated to a reversible hydrogen electrode
(RHE), and all the potentials were iR-compensated to 85% and reported vs. RHE. Cyclic voltammetry in nitrogen was performed between 0.05 and 1.35 V at 0 rpm and was used to identify electrochemical features of the catalyst; multiple cycles were performed to obtain stabilized electrochemical features. Cyclic voltammetry in oxygen was performed on an identically prepared sample between 0.05 and 1.75 V at 1600 rpm and was used to identify potential regions relevant to the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER).

### 3.3.3 Investigation of Surface Oxidation States of Mn

To probe the oxidation state of the manganese oxide thin film catalyst under conditions relevant to the ORR and the OER, the film was cycled from 0.05 V to a vertex potential of either 0.70 V or 1.35 V, held at the vertex potential for 10 minutes, extracted from the electrochemical cell under potential control, and characterized using ex-situ XPS (PHI 5000 VersaProbe). During XPS characterization, monochromated Al Kα 1486.6 eV x-rays were used to collect high resolution spectra of the Mn 2p region (632 eV to 675 eV), the O 1s region (520 to 535 eV), and the C 1s region (275 to 295 eV) of the MnOₓ thin film as well as for two control samples: Mn₂O₃ and MnO₂ powders (Sigma-Aldrich). During the measurements, the electron detector was positioned at 45° with respect to surface normal, and a pass energy of 23.5 eV, an energy step of 0.1 eV, and a time of 20 ms per step were used. All spectra were calibrated to the position of adventitious carbon at 285.0 eV. To identify a change in the oxidation state between oxidized and reduced surfaces, the distance between manganese 2p₁/₂ peak and its satellite (Δ2p₁/₂) was monitored, and the O 1s peak of the two samples was compared. After the completion of XPS measurements, the samples were re-inserted into a nitrogen saturated electrolyte at a
controlled potential of 1 V. The samples were then cycled three times from 1 V to 1.35 V at 20 mV·s⁻¹ and 0 rpm.

3.4 Results and Discussion

Electrochemical characterization of the nanostructured Mn (III) oxide with alpha-Mn₂O₃ crystallinity in nitrogen and oxygen saturated environments revealed features suggesting a change in the Mn oxidation state in the region between the onset potentials for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), as shown in Figure 3.1. During the initial cycle in the N₂ saturated environment, the catalyst exhibited an oxidation feature around 0.8-1 V. Upon further cycling, the feature decreased in size and shifted toward higher anodic potentials. This behavior has been previously observed with gamma-MnO₂ and beta-MnO₂ phases after application of similar reducing potentials of less than 0.45 V.⁸⁷ At potentials below 0.45 V, Mn(OH)₂ becomes the thermodynamically stable phase.⁸⁷,⁸⁸ After formation, it has been shown to oxidize first to Mn (III) species and then to delta-MnO₂, independently of the original MnO₂ phase.⁸⁷ Since the oxidation of Mn (III) oxide to MnO₂ is expected and has been shown to occur at around 1 V,⁸⁷,⁸⁸ it was hypothesized that, during the ORR, the oxidation state of the nanostructured Mn (III) oxide surface was Mn (III), while, during the OER, the oxidation state of the MnOₓ surface was Mn (IV). Previous x-ray absorption spectroscopy studies have demonstrated this reduction in Mn oxidation state in-situ for MnOₓ dispersed on Vulcan carbon.³⁸,⁴⁶ To explicitly probe the oxidation state of the nanostructured Mn (III) oxide catalyst with alpha-Mn₂O₃ crystallinity as a function of potential, catalyst samples were held at potentials on either side of the oxidation feature. One sample was held before the oxidation feature, at an ORR relevant potential of 0.70
V, while the other sample was held after the oxidation feature at 1.35 V, close to the onset potential of OER, as shown in Figure 3.2 (a). After each electrochemical experiment, the sample was extracted under potential control, and XPS was used to estimate the Mn oxidation state of the electrodes held at each condition.

![Cyclic voltammetry graph](image)

**Figure 3.1:** Cyclic voltammetry in oxygen (O₂) revealed the potential regions relevant to the ORR and the OER, while cyclic voltammetry in nitrogen (N₂) revealed initial and stabilized oxidation/reduction features. Cyclic voltammetry was performed in 0.1 M KOH electrolyte at 20 mV·s⁻¹ and 1600 rpm rotation rate.

Although bulk sensitive *in-situ* XAS measurements previously performed on MnOₓ catalysts dispersed on Vulcan carbon could detect changes in Mn oxidation state in a similar potential window,³⁸ the surface sensitive *ex-situ* XPS experiments, detailed in this chapter, showed no discernible differences between the samples exposed to 0.70 V and 1.35 V. As shown in Figure 3.2 (b), the Δ2p₁/₂ value was the same for both samples and corresponded to the Mn (III) oxide value of 10 eV.⁵⁶,⁸² The O 1s spectra for the two samples also overlapped with one another, a further indication of similar Mn oxidation states in each sample. These observations suggest that the surface of the nanostructured Mn (III) oxide with alpha-Mn₂O₃ crystallinity maintains the same Mn (III) state under both the ORR and the OER conditions and thus, behaves differently from the previously studied MnOₓ dispersed in Vulcan carbon.³⁸
Figure 3.2: Preparation of the nanostructured Mn (III) oxide catalyst for XPS characterization: (a) a stabilized cyclic voltammogram in nitrogen and linear sweep voltamograms from 0.05 V to vertex potentials of 1.35 V and 0.70 V performed at 20 mV·s⁻¹, followed by holding at the vertex potential for 10 minutes; (b) and (c) Mn 2p₁/₂ and O 1s XPS analysis of the oxidation state of 1.35 V and 0.70 V, where in (b) vertical lines indicate the expected Δ2p₁/₂ of 10.0 eV for the Mn₂O₃ control.
To interpret the *ex-situ* XPS results in the context of the observed redox features in the N$_2$ CVs, which indicated a change in the Mn oxidation state in the region between 0.7 V and 1.35 V, it was considered whether or not the two MnO$_x$ surfaces equilibrate with their surroundings (e.g. air, vacuum, and/or the underlying bulk MnO$_x$ phase) upon removal of the sample from the electrochemical cell and transfer to the XPS chamber. In fact, this is how Toupin and co-workers explained similar results in their studies of electrochemical oxidation of MnO$_x$ electrodes as a function of thickness.$^{61}$ For thin MnO$_x$ films of less than 2 μm thick, *ex-situ* XPS successfully confirmed that exposing their MnO$_x$ electrodes to oxidizing and reducing potentials corresponded to a significant change in the Mn oxidation state from 4.0 to 2.9, respectively. For thicker films on the order of 100 μm, however, a constant oxidation state of 3.5 was observed in the same potential window. To increase spectroscopic surface sensitivity, Toupin et al. performed additional angle-resolved XPS experiments, which also failed to detect any differences in the oxidation state of electrochemically reduced and oxidized samples. The authors suspected that the electrochemically reduced and oxidized surface layers of thick MnO$_x$ films had equilibrated with the bulk of the electrode after removal of the films from the electrochemical cell. Open circuit measurements, which yielded the same value of +0.45 V for both reduced and oxidized samples, provided support for the above hypothesis.

In this study, the thickness of the MnO$_x$ electrodes is ~ 400 nm, which is within the thin film regime where the differences in oxidation state are expected to be observed by *ex-situ* XPS based on the results of Toupin et al. The results of Toupin et al., however, may not translate to the bifunctional MnO$_x$ thin film catalyst, due to the heat treatment of the catalyst at 480°C and the resulting dehydration of the electrode. Although in a fully
hydrated electrode, a large fraction of atoms can participate in pseudocapacitative processes, thermal treatment of catalysts is known to limit such processes to the sample surface. To determine if the depth of electrochemical oxidation in the bifunctional MnO$_x$ catalyst is too thin to be determined by XPS or if the surface of the sample oxidized at 1.35 V had equilibrated with the bulk Mn (III) oxide phase upon exposure to air or the ultra-high vacuum (UHV) environment of the XPS chamber, further electrochemical characterization was performed after ex-situ XPS measurements.

**Figure 3.3:** After XPS, the MnO$_x$ samples were re-inserted into electrochemical cell at a controlled potential of 1 V. MnO$_x$ previously oxidized at 1.35 V, shown in (a), lacks an oxidation feature in the region from 1 V to 1.35 V, while the MnO$_x$ previously held at a more reducing potential of 0.70 V, shown in (b), undergoes oxidation in the same region. This indicates a difference in their surface oxidation states. Characterization was performed in 0.1 M KOH N$_2$ saturated electrolyte at 20 mV·s$^{-1}$ and without rotation.
In the experiments, immediately after XPS characterization was completed each sample was re-inserted into an electrochemical cell at a controlled potential of 1 V, a potential at which neither oxidation nor reduction is favored based on the N₂-stabilized CV of Figure 3.1. Then, three cyclic voltammograms were collected in the region between 1 V and 1.35 V for both samples. As shown in Figure 3.3, the sample held at 0.70 V showed a strong oxidation feature in this potential window, while the sample held at 1.35 V did not. This indicated that the surface of the sample originally held at 1.35 V must have remained oxidized before, during, and after XPS characterization despite exposure to air and the UHV environment. This experiment confirmed that the surface of the MnOₓ catalyst held at oxidizing potentials was in fact distinct from the surface of the MnOₓ catalyst held at the reducing potentials, despite their similar XPS spectra. Considering the well-known surface-sensitive nature of XPS measurements, the observed electrochemical oxidation was concluded to be an extremely shallow process involving the top-most layer(s) of the surface, too thin for the differences to be discerned by XPS.

This result prompted a calculation of the minimum thickness of a surface oxidation process on the MnOₓ catalyst that could be distinguished by conventional XPS measurements with Al Kα emission. The calculation assumed a model Mn₂O₃ thin film with a surface MnO₂ layer of thickness d, illustrated in Figure 3.4 (a). The photoelectron intensities of Mn in MnO₂ oxidation layer and Mn₂O₃ bulk layer are given by equations 3.1 and 3.2:

\[
I_{Mn}^{\text{MnO}_2} = N_{Mn}^{\text{MnO}_2} \sigma_{Mn,E} E_K \int_0^d e^{-\frac{z}{\lambda_{\text{MnO}_2}}} \cos \theta \, dz = N_{Mn}^{\text{MnO}_2} \sigma_{Mn,E} E_K \lambda_{\text{MnO}_2} \cos \theta \left[1 - e^{-\frac{d}{\lambda_{\text{MnO}_2}}} \cos \theta \right]
\]

\[
I_{Mn}^{\text{Mn}_2\text{O}_3} = N_{Mn}^{\text{Mn}_2\text{O}_3} \sigma_{Mn,E} E_K \int_d^{\infty} e^{-\frac{z}{\lambda_{\text{Mn}_2\text{O}_3}}} \cos \theta \, dz = N_{Mn}^{\text{Mn}_2\text{O}_3} \sigma_{Mn,E} E_K \lambda_{\text{Mn}_2\text{O}_3} \cos \theta \left[e^{-\frac{d}{\lambda_{\text{Mn}_2\text{O}_3}}} \cos \theta \right]
\]
where $N$ is the atomic density of Mn element in either MnO$_2$ surface layer or Mn$_2$O$_3$ bulk layer, $\sigma$ is the photoionization cross-section of Mn for monochromated Al K\(\alpha\) 1486.6 eV x-rays, $K$ is the constant which encompasses instrumentation effects, including the transmission function of the spectrometer, the efficiency of the electron detector, and the effects of stray magnetic fields, $\lambda$ is the electron attenuation length of Mn emitted from either the Mn$_2$O$_3$ bulk layer or the MnO$_2$ surface layer, $\theta$ is the angle of electron emission with respect to the surface normal, and $z$ is the escape depth of emitted electrons.$^{90,91}$ Although the above model assumes a flat surface, it was previously shown to be valid for rough samples if $\theta$ is between 40° and 45°.$^{92}$ Assuming $\lambda_{\text{MnO}_2} = \lambda_{\text{Mn}_2\text{O}_3} = \lambda$, which is approximately true for oxides of the same element involving the same photoelectron line,$^{91}$ the ratio of MnO$_2$ and Mn$_2$O$_3$ intensities can be written as

$$\frac{I_{\text{MnO}_2}}{I_{\text{Mn}_2\text{O}_3}} = \frac{N_{\text{MnO}_2}}{N_{\text{Mn}_2\text{O}_3}} \left[ e^{-\lambda \cos \theta} - 1 \right]$$

(3.3)

The relationship between XPS intensities of the MnO$_2$ overlayer on Mn$_2$O$_3$ described in Equation 3.3 is visually represented in Figure 3.4 (b) for the $\theta = 45^\circ$ photoemission angle used in the XPS studies. The atomic density of Mn in MnO$_2$ was estimated to be 0.036 atoms/Å$^3$ assuming a beta-MnO$_2$ lattice, while the atomic density of Mn in Mn$_2$O$_3$ was estimated to be 0.038 atoms/Å$^3$, assuming alpha-Mn$_2$O$_3$ lattice. The electron attenuation length, $\lambda$, was approximated by the inelastic mean free path of electrons for monochromated Al K\(\alpha\) 1486.6 eV x-rays and found to be 4 nm from the mean free path universal curve.$^{51}$ Figure 3.4 (b) shows that for the case where the thickness of the surface MnO$_2$ layer is 0.3 nm (about one monolayer), the vast majority of the measured photoelectron intensity comes from the Mn$_2$O$_3$ bulk material underneath. If the thickness of the surface MnO$_2$ layer is increased to 2 nm (about seven monolayers),
however, approximately equal intensity is measured from the surface MnO$_2$ and the bulk Mn$_2$O$_3$ material underneath. These calculations suggest that after electrochemical oxidation at 1.35 V the surface MnO$_2$ layer must be < 2 nm thick.

Figure 3.4. (a) Model Mn$_2$O$_3$ thin film with a surface MnO$_2$ oxidation of thickness d, (b) relationship between the ratio of photoelectron intensities of MnO$_2$ and Mn$_2$O$_3$ and the thickness of MnO$_2$ in the surface oxidation layer, (c) calculated XPS spectra for 2 nm and 0.3 nm thick MnO$_2$ overlayers on Mn$_2$O$_3$, generated from linear combinations of MnO$_2$ and Mn$_2$O$_3$ control spectra. Vertical lines indicate the expected Δ$2p_{1/2}$ for MnO$_2$ (11.8 eV) and Mn$_2$O$_3$ (10.0 eV) controls.
The ratios of photoelectron intensities of surface MnO$_2$ relative to bulk Mn$_2$O$_3$ were used to generate calculated XPS spectra of MnO$_2$ overlayers on top of bulk Mn$_2$O$_3$ based on linear combinations of experimentally measured phase-pure powder control samples of MnO$_2$ and Mn$_2$O$_3$, shown in Figure 3.4 (c). Here, the two constructed spectra corresponding to surface MnO$_2$ overlayer thicknesses of 0.3 nm and 2 nm are directly compared to the spectra of the phase-pure MnO$_2$ and Mn$_2$O$_3$ controls. As seen in the figure, the calculated spectrum corresponding to a 0.3 nm surface oxidation layer shows a \( \Delta 2p_{1/2} \) of approximately 10 eV and is indistinguishable from the spectrum of pure Mn$_2$O$_3$. Changes are more evident in the calculated spectrum corresponding to a 2 nm surface oxidation layer, with a \( \Delta 2p_{1/2} \) of approximately 11 eV, clearly distinguishable from the spectrum of either pure Mn$_2$O$_3$ or pure MnO$_2$, as photoelectron intensity from both contribute about equally. As the electrochemically oxidized sample did not exhibit noticeable changes in the XPS spectra – and recognizing that the surface remained oxidized before, during, and after the XPS measurements based on the electrochemical re-insertion experiments – these modeling results help to quantify the thickness of the oxidized surface layer to be on the order of one monolayer.

3.5 Conclusions

The study detailed in this chapter aimed to understand the surface chemistry of an active manganese oxide bifunctional catalyst under reaction conditions relevant to the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). To achieve the goal, electrochemical characterization was combined with \textit{ex-situ} XPS measurements to monitor how the oxidation state of the catalyst, identified in its initial state as a Mn (III) oxide thin film with alpha-Mn$_2$O$_3$ crystallinity, changed as a function of applied
potential. Using cyclic voltammetry in nitrogen and oxygen saturated environments, an electrochemical oxidation of the catalyst was detected in the region between the ORR and the OER, but *ex-situ* XPS measurements employing incident Al Kα 1486.6 eV x-rays could only discern the Mn (III) oxide phase both before and after electrochemical oxidation. Additional electrochemistry performed after XPS measurements confirmed that the catalysts exposed to the ORR and the OER conditions had distinct surfaces, despite their similarity in the XPS spectra. It was therefore postulated that the thermal treatment of the manganese oxide thin film at 480°C dehydrated the catalyst, leaving only the top-most surface layer(s) accessible to electrochemical processes. These top-most surface layers are too thin for XPS to distinguish from the bulk Mn$_2$O$_3$ phase, despite the well-known surface sensitivity of XPS.

Calculations performed to determine how thick the MnO$_2$ surface needed to be for conventional XPS to differentiate it from bulk Mn$_2$O$_3$ showed that a 2 nm thick surface layer of MnO$_2$ could be distinguished from the bulk Mn$_2$O$_3$, but that distinguishing the two phases became increasingly difficult with thinner MnO$_2$ surface layers. In particular, the calculated spectrum of a 0.3 nm thick MnO$_2$ layer on bulk Mn$_2$O$_3$ was virtually identical to that of the pure Mn$_2$O$_3$ spectrum. It was concluded that the electrochemical oxidation of the nanostructured Mn (III) oxide catalyst with alpha-Mn$_2$O$_3$ crystallinity must penetrate less than two nanometers into the surface, to a depth likely on the order of one monolayer. For future studies, it would be interesting to investigate the effect of heat treatment on the thickness of the electrochemically oxidized overlayer, and to use synchrotron radiation. The tunable incident x-ray energy and increased signal of synchrotron methods could allow for improved surface sensitivity and higher-resolution
measurements, helping identify the extent of electrochemical oxidation of the catalytic surface.

3.6 Copyright

Chapter 4

Effect of Heat Treatment on the Surface Oxidation State and Oxygen Electrode Activity of Electrodeposited Manganese Oxide Thin Films on Glassy Carbon

4.1 Abstract

Manganese oxides (MnO$_x$) are promising catalysts for the oxygen reduction reaction (ORR) in air-cathodes of alkaline fuel cells and metal-air batteries and oxygen evolution reaction (OER) in anodes of electrolysis cells and photoelectrochemical hydrogen production. Different types of phases have been linked to high activity for each type of reaction and little is known about active sites and surface properties under reaction conditions. In this chapter, we investigate the effect of preparation route on the oxidation state of the surface after its exposure to the electrochemical potentials relevant to the ORR and the OER. We prepare five different catalysts by electrodepositing MnO$_x$ on glassy carbon electrodes and then heat treating them at five different conditions: no heat treatment (“no ht”), 250°C, 350°C, 450°C, and 500°C. We first confirm that we prepare different types of surfaces using scanning electron microscopy (SEM), x-ray
photoelectron spectroscopy (XPS), and x-ray absorption spectroscopy (XAS) and then cycle each sample to a vertex potential of either 0.7 V or 1.65 V to obtain an ORR and OER relevant surfaces, respectively. Using *ex-situ* XAS characterization, we find that “no ht” catalyst is capable of the largest changes in Mn oxidation state as the potential switches from 0.7 V to 1.65 V, but has the least activity for both reactions. As the heat treatment temperature increases, the changes in Mn oxidation state as a function of potential decrease, while the activity for both reactions increases. Specifically, heat treatment at 450°C and 500°C is associated with a change in the ORR mechanism from 2 electron reduction observed with no ht, 250°C, and 350°C to 4 electron reduction, while increasing the temperature to 350°C leads to significant increase in the OER activity. These effects could not be attributed solely to the changes in the electrochemical activity of glassy carbon support or to the surface area effects and therefore, demonstrate that the changes in surface properties achieved through different heat treatment conditions influence the activity of MnOx catalyst for the ORR and the OER.

4.2 Introduction

As discussed in Chapter 1, manganese oxides and oxyhydroxides (MnOx) can exist in over 15 types of phases with Mn taking on 2+, 3+, 4+, and mixed valent oxidation states and various structural configurations.32 Recently, an increasing number of phases has been linked to high activity for the oxygen reduction reaction (ORR)35-38,82 and the oxygen evolution reaction (OER),39,40,42,44,47,93 raising the importance of MnOx catalysts to energy storage and conversion devices. To develop improved MnOx based catalysts for these important technologies, it is necessary to determine the properties of active surfaces under reaction conditions.
Thermodynamic calculations, presented in Appendix C, have identified the relevant ORR and OER bulk phases in alkaline conditions as Mn$_2$O$_3$/MnOOH and MnO$_2$ and the relevant ORR and OER surfaces as Mn$_2$O$_3$ covered with ½ monolayer of adsorbed OH and MnO$_2$ covered with adsorbed O based on density functional theory calculations of surface Pourbaix diagrams and reaction energetics. Experimental characterization of MnO$_x$ ORR and OER relevant surfaces, however, has been limited to a handful of studies. In an in-situ x-ray absorption spectroscopy (XAS) experiments, Lima and co-workers have detected formation of Mn (III) species under ORR relevant potentials in MnO$_x$ catalyst dispersed on Vulcan carbon, while Hocking and co-workers have demonstrated formation of disordered Mn (III)/Mn (IV) phase similar to birnessite-MnO$_2$ from a homogeneous MnO$_x$ catalyst under OER relevant potentials. Using ex-situ x-ray photoelectron spectroscopy (XPS), on the other hand, we have shown in Chapter 3 that Mn(III) oxide is maintained as the major phase under both ORR and OER conditions in a bifunctional MnO$_x$ catalyst electrodeposited on glassy carbon. These seemingly conflicting reports indicate that the observed phases under reaction conditions may differ from the expected thermodynamically stable phase calculated in a Pourbaix or a surface Pourbaix diagram of MnO$_x$, presented in Appendix C, and suggest that MnO$_x$ surface at the ORR and the OER potentials depends on the starting phase or preparation route.

Previous studies, which consider electrochemical changes in MnO$_x$ phase as a function of potential, provide further evidence that the Mn oxidation state at a particular potential may vary among different MnO$_x$ electrodes. For example, an ex-situ x-ray diffraction (XRD) experiment performed in combination with electrochemical
characterization of MnOₓ electrodes has successfully demonstrated that the starting phase of MnO₂ will have an influence on the reduction products. Additionally, ex-situ XPS and in-situ XAS studies of MnOₓ supercapacitors have indicated that the change in Mn oxidation state in ~1 V potential window may differ from no observed or little change to a change of up to 1 unit of valency depending on the considered electrode. The observed variability in the surface properties of MnOₓ electrodes exposed to the same electrochemical potentials warrants examination of Mn surface oxidation state in a variety of MnOₓ based catalysts under ORR and OER reaction conditions.

In this chapter, we investigate the effect of preparation route on the changes in surface oxidation state in the potential region between the ORR and OER and correlate the properties of the surface to catalytic activity. We synthesize different types of MnOₓ surfaces by electrodepositing MnOₓ on glassy carbon (GC) and exposing the electrodes to five different heat treatment conditions: no heat treatment (no ht), heat treatment at 250°C, 350°C, 450°C, and 500°C. We then hold each of the five samples at an ORR relevant potential of 0.7 V or an OER relevant potential of 1.65 V and track the resulting surface oxidation states of MnOₓ samples using ex-situ x-ray absorption spectroscopy (XAS). By interfacing the XAS spectra with electrochemical characterization we determine how the surface properties influence the activities for the ORR and the OER.

4.3 Experimental Methods

4.3.1 Preparation of Electrode Substrates

Rotating disk electrodes for the study of manganese oxide (MnOₓ) thin films were prepared using 200 mm long glassy carbon rods (dia 5 mm, Sigradur G) purchased from
HTW Hochtemperatur-Werkstoffe GmbH. Before deposition of MnO\textsubscript{x}, the rods were processed by Stanford crystal shop to produce 4 mm pieces with one side lapped and chamfered and the other side polished to a surface roughness of less than 50 nm.

**4.3.2 Synthesis of Manganese Oxide Catalysts**

MnO\textsubscript{x} thin film catalysts were electrodeposited onto polished glassy carbon electrodes using a modified procedure originally developed by Tench et al.\textsuperscript{77,82} In the synthesis, the potential was cycled between 0.0 V and 0.6 V (Bio-Logic, VSP) vs. a Ag|AgCl reference electrode at 20 mV·s\textsuperscript{-1} and 900 revolutions per minute (rpm) rotation speed in a three electrode electrochemical cell in a rotating disk electrode configuration (RDE, Pine Instruments). The deposition solution contained manganous acetate and sodium sulfate in concentrations of 0.1 M each; graphite foil was used as a counter electrode. After the 9th cycle, the RDE tip was removed from the deposition solution, and the carbon electrode was thoroughly rinsed with Millipore water. Representative cyclic voltammetry curves demonstrating 9 cycles of deposition are shown in Appendix D. After electrodeposition the electrodes were stored or heat treated in air for 10 hours in a quartz tube furnace (Mellen Company SC13) at temperatures ranging from 250°C to 500°C. This synthesis produced five sets of MnO\textsubscript{x} thin films corresponding to five heat treatment conditions: no heat treatment (no ht), 250°C, 350°C, 450°C, and 500°C.

**4.3.3 Electrochemical Characterization of Manganese Oxide Catalysts**

The activity for the oxygen reduction and evolution reactions of the five differently prepared MnO\textsubscript{x} thin film catalysts were characterized using cyclic
voltammetry with a scan rate of 20 mV·s⁻¹ in a three electrode electrochemical cell in a RDE configuration. All experiments were performed at room temperature in 0.1 M KOH electrolyte, using a carbon rod counter electrode and Ag|AgCl reference electrode. The potential scale was calibrated to a reversible hydrogen electrode (RHE), and all the potentials were iR-compensated to 85% and reported vs. RHE. Oxygen reduction reaction activity was studied in an oxygen saturated electrolyte in the potential window between 0.05 V and 1.1 V, while oxygen evolution reaction activity was studied in the potential window between 0.05 V to 1.8 V in a nitrogen saturated environment.

4.3.4 Preparation of Oxygen Reduction and Evolution Relevant Surfaces

To prepare surfaces for ex-situ XAS characterization, three types of samples were prepared for each of the five temperature conditions: oxygen reduction reaction (ORR) sample, oxygen evolution reaction (OER) sample, and ORR sample after exposure to OER potentials (ORR after OER). To prepare ORR and OER samples, the potential was scanned from 0.05 V to vertex potentials of 0.7 V and 1.65 V, respectively and held at the vertex potential for 30 min. To prepare ORR after OER sample, MnOₓ thin film was first exposed to an OER potential of 1.8 V and then subjected to the same ORR condition described above.

4.3.5 Physical and Chemical Characterization of Manganese Oxide Catalysts

Morphology of the MnOₓ thin film catalysts and GC support were determined using scanning electron microscopy (SEM, FEI Magellan 400XHR). The images were
obtained using a secondary electron detector, a beam current of 25 pA, and beam voltage of 5 kV. The oxidation state of Mn in the MnOx thin film catalysts subjected to five different heat treatment conditions was characterized using ex-situ x-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) and ex-situ x-ray absorption spectroscopy (XAS, Stanford Synchrotron Radiation Lightsource), while the surface oxidation state of ORR and OER samples was characterized exclusively by ex-situ XAS. In XPS experiments, monochromatized Al Kα 1486.6 eV x-rays were used to collect Mn 3s, Mn 2p, and C 1s x-ray photoelectron spectra and all spectra were calibrated to 285.0 eV, the line position of adventitious carbon. To acquire the spectra, a pass energy of 23.5 eV, an energy step of 0.1 eV, and a time of 20 ms per step were used; the corresponding resolution of the XPS measurement was 0.6 eV. Oxidation state of Mn in the thin films was monitored using the relative the magnitude of the 3s multiplet splitting (ΔE3s) and the distance between manganese 2p1/2 peak and its satellite (ΔE2p1/2) which have been previously shown to provide information on the oxidation state of Mn.

Ex-situ XAS measurements were performed on the 31-pole wiggler beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 350 mA and a 1000 l·mm−1 spherical grating monochromator with 40 μm entrance and exit slits, providing ~10¹¹ ph·s⁻¹ at 0.3 eV resolution in a 1 mm² beam spot. During the measurements, all samples were attached to an aluminum sample holder using conductive carbon, and data were acquired in a single load at room temperature and under ultra-high vacuum (10⁻⁹ torr). Detection was performed in either total electron yield (TEY) mode, where the sample drain current was normalized by the current from of a reference sample in a form of freshly evaporated gold on a thin grid positioned upstream of the sample
chamber, or Auger electron yield (AEY) mode with the electron analyzer window set at 575 eV and the collected current normalized by the current of the reference sample. The measurements were performed on the MnOₓ thin films subjected to 5 different heat treatment conditions and on the thin films held at ORR and OER relevant potentials.

4.3.6 Preparation of Manganese Oxide Standards

To determine the average oxidation state of Mn in the differently prepared thin films, XPS and XAS measurements were also performed on five different standards: MnO, Mn₃O₄, gamma-MnOOH, Mn₂O₃, and MnO₂. Gamma-MnOOH powder was synthesized by preparing 8 mM solution of MnSO₄ adjusted to pH 10 using 1 M KOH and heating it in a sealed autoclave for 10 hours; the resulting powder was then washed and dried under vacuum. MnO, Mn₃O₄, Mn₂O₃, and MnO₂ powders were purchased from Sigma Aldrich and used as received with exception of MnO standard. Prior to collecting XPS spectra on MnO standard, the powder was sputtered to remove the oxidized surface known to form on MnO in air. MnO powder also oxidized during sample preparation for XAS measurements and therefore was not used as an XAS standard. Instead, MnO nanoparticles synthesized using inert gas condensation technique and confirmed to have MnO phase served as MnO reference. XAS measurements were also performed on four MnO₂ polymorphs: alpha-MnO₂, beta-MnO₂, delta-MnO₂, and lambda-MnO₂. Alpha-MnO₂ phase was prepared by dissolving 0.5 g of KMnO₄ in 30 mL of Millipore water, followed by drop-wise addition of ethanol under stirring, drying the resulting powder at 60 °C overnight, and calcining the powder at 400°C for 3 hours. Beta-MnO₂ phase was prepared by dissolving Mn(NO₃)₂·H₂O in water, drying the solution at 60 °C for 24 hours, and calcining the powder for 3 hours at 200 °C. Gamma-MnO₂ and lambda-MnO₂
phases were prepared using digestion of LiMn$_2$O$_4$ at 75°C or room temperature following the procedure of Xue et al.$^9$ X-ray diffraction data of synthesized powders is shown in Appendix E.

4.3.7 Normalization of XAS Spectra

The energy was carefully calibrated in two steps. First, all spectra were corrected for the drift in the beam energy by aligning the Mn L-edge spectra of a beamline reference sample, positioned upstream of the sample chamber to intercept a small part of the beam. We estimate that the resulting relative energy scale for all spectra is accurate within 50 meV. Second, the energy of the first peak of the Mn$_3$O$_4$ powder control was fixed to the literature value 639.6 eV,$^6$ and all spectra were shifted accordingly. Data were taken over the extended range of 610-690 eV to facilitate normalization. Normalization was performed by fitting a linear background to the spectra of all samples using the following two constraints: the area from 636 eV to 660 eV was specified to be the same in every spectrum and the edge jump in the 660 eV to 665 eV region of each spectrum was fixed to match the edge jump of MnO$_2$ powder standard.

4.4 Results and Discussion

In our work we aimed to investigate the effect of starting surface conditions on the surface oxidation state of manganese oxide (MnO$_x$) electrodes under oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) conditions. To obtain different starting surfaces, we varied preparation route of the electrodes by means of five heat treatment conditions of an electrodeposited MnO$_x$ thin films on glassy carbon support: no heat treatment (“no ht”), heat treatment at 250°C, 350°C, 450°C, and 500°C. Scanning electron microscopy (SEM) characterization of the bare glassy carbon support,
shown in Figure 4.1 (a), and the five MnO$_x$ films, shown in Figure 4.1 (b)-(f), demonstrates how each heat treatment condition influences the surface of MnO$_x$. MnO$_x$ electrodeposits on polished GC (Figure 4.1 (a)) in needle-like morphology illustrated in Figure 4.1 (b). Initial heat treatment at 250°C and 350°C increases the compactness of the needles, as illustrated in Figures 4.1 (c) and 4.1 (d), while a further increase in temperature to 450°C results in agglomeration of MnO$_x$ needles and formation of spherical particles, shown in Figure 4.1 (e). Heat treatment at 500°C leads to roughening of the support, due to evolution of CO and CO$_2$ gases, and formation of a complex nanostructured morphology, demonstrated in Figure 4.1 (f).

**Figure 4.1:** Scanning electron microscopy images of bare glassy carbon substrate (a) and manganese oxide thin films showing morphology prior to heat treatment (b) and after heat treatment at 250°C (c), 350°C (d), 450°C (e), and 500°C (f). Initial needle-like morphology presented in (b) undergoes little change until the temperature is increased to 450°C. After heat treatment at 450°C and 500°C, the needles agglomerate into larger particles and the underlying glassy carbon support begins to corrode, creating complex nanostructured morphology.

To determine if changes in the film morphology triggered by the specific heat treatment conditions corresponded to changes in the starting surface oxidation state of MnO$_x$...
Mn, we first used x-ray photoelectron spectroscopy (XPS). High resolution x-ray photoelectron Mn 2p spectra for the five different synthesis conditions are shown in Figure 4.2 (a), and the observed ΔE2p\textsubscript{1/2} values are presented in Table 4.1. From the spectra, it is clear that the morphological changes after heat treatments at 250°C and 450°C are accompanied by a change in the surface oxidation state of Mn in the MnO\textsubscript{x} thin film. Similarly, heat treatments at 350°C and 500°C, which result in little change in MnO\textsubscript{x} morphology when compared to 250°C and 450°C samples, respectively, maintain the same surface oxidation state formed after 250°C and 450°C treatments.

It has been shown previously that ΔE2p\textsubscript{1/2} values increase with oxidation state, with MnO, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2} values varying from 5.7-6.0 eV to 10.0-10.5 eV to 11.8-11.9 eV.\textsuperscript{56,58} The spectra of Mn\textsubscript{3}O\textsubscript{4} and MnOOH phases has also been studied previously,\textsuperscript{56,58,101} but offered less consistent results. Mn\textsubscript{3}O\textsubscript{4} spectrum is characterized by relatively broader peaks, and its 2p\textsubscript{1/2} satellite position falls between Mn\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2}, despite its lower oxidation state than that of either Mn\textsubscript{2}O\textsubscript{3} or MnO\textsubscript{2}.\textsuperscript{56,58} MnOOH 2p spectrum has been shown to be similar both to MnO\textsubscript{2},\textsuperscript{58} likely due to decomposition of MnOOH in vacuum, and to Mn\textsubscript{2}O\textsubscript{3}.\textsuperscript{101}

Our measurements of the five MnO\textsubscript{x} standards: MnO, Mn\textsubscript{3}O\textsubscript{4}, MnOOH, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2} support previous results, showing a clear trend of an increase in ΔE2p\textsubscript{1/2} with increasing oxidation state for MnO, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2} in Figure 4.2 (b) and a large FWHM for Mn\textsubscript{3}O\textsubscript{4}. Our MnOOH spectrum has ΔE2p\textsubscript{1/2} similar to MnO\textsubscript{2} and agrees with results from Oku et al., which suggests that our MnOOH powder decomposes in vacuum. Although ΔE2p\textsubscript{1/2} values of Mn\textsubscript{3}O\textsubscript{4} and MnOOH powders do not conform to the overall trend observed with MnO, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2} powders, making assignment of average
Mn oxidation state in electrodeposited thin films difficult, we can conclude that heat treatment at 250°C and 350°C results in an increase in Mn oxidation state, forming a phase closer to MnO₂, while further increase in temperature to 450°C and 500°C, results in reduction in Mn oxidation state forming a phase consistent with Mn₂O₃ and Mn₃O₄.

Analysis of Mn 3s spectra of MnOₓ thin films and powder standards, shown in Figures 4.2 (c) and 4.2 (d), provides further support to the above conclusion. The
multiplet splitting values of the samples, listed in Table 4.1, demonstrate that $\Delta E_{3s}$ decreases with heat treatment at 250°C and 350°C and then increases after heat treatment at 450°C and 500°C. Inspection of the $\Delta E_{3s}$ trend of the standards shows that the splitting distance decreases with increasing oxidation state and thus allows to link the changes in the Mn 3s spectra of MnO$_x$ thin films to initial increase in Mn oxidation state after heat treatment at 250°C followed by a decrease in Mn oxidation state after heat treatment at 450°C. To determine the average Mn oxidation state for each of the five samples further characterization was necessary.

**Table 4.1:** Mn $\Delta E_{2p_{1/2}}$ and Mn $\Delta E_{3s}$ values for manganese oxide thin films and powder standards.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>Mn $\Delta E_{2p_{1/2}}$</th>
<th>Mn $\Delta E_{3s}$</th>
<th>Standard</th>
<th>Mn $\Delta E_{2p_{1/2}}$</th>
<th>Mn $\Delta E_{3s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>no ht</td>
<td>10.5</td>
<td>5.2</td>
<td>MnO</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>250°C</td>
<td>11.5</td>
<td>5.0</td>
<td>Mn$_3$O$_4$</td>
<td>10.3</td>
<td>5.8</td>
</tr>
<tr>
<td>350°C</td>
<td>11.5</td>
<td>5.1</td>
<td>MnOOH</td>
<td>11.1</td>
<td>4.6</td>
</tr>
<tr>
<td>450°C</td>
<td>10.0</td>
<td>5.4</td>
<td>Mn$_2$O$_3$</td>
<td>10.0</td>
<td>5.1</td>
</tr>
<tr>
<td>500°C</td>
<td>10.0</td>
<td>5.3</td>
<td>MnO$_2$</td>
<td>11.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Mn L-edge x-ray absorption spectroscopy has been previously identified as a sensitive probe for resolving Mn oxidation states.$^{64}$ Figure 4.3 (a) shows the spectra of five different standards: MnO, Mn$_3$O$_4$, gamma-MnOOH, Mn$_2$O$_3$, and MnO$_2$ in total electron yield (TEY) mode. Unlike XPS spectra of MnO$_x$ standards, where all samples have similar features with small differences in the splitting values, L-edge XAS spectra contains distinctive absorption features associated with each standard, resulting in a straightforward differentiation between the phases. Our results indicate that the spectra of two Mn (III) oxides, MnOOH and Mn$_2$O$_3$, are distinct. Since our XPS measurements suggested that MnOOH powder may decompose in vacuum, we attempted to fit the spectrum of MnOOH using linear combinations of other standards. We could not obtain
a successful fit and therefore are treating MnOOH spectrum as a unique spectrum characteristic to the phase.

Figure 4.3: Total electron yield (TEY) x-ray absorption spectroscopy (XAS) measurements of (a) five standards: MnO, Mn₃O₄, MnOOH, Mn₂O₃, and MnO₂ and (b) manganese oxide thin films exposed to five different heat treatment conditions: no heat treatment (no ht), heat treatment at 250°C, 350°C, 450°C, and 500°C. X-ray absorption spectra confirm initial increase in oxidation state with heat treatment at 250°C/350°C and subsequent decrease in oxidation state with heat treatment at 450°C/500°C determined by XPS.

The spectra of the samples are shown in Figure 4.3 (b). To determine the average oxidation state for each heat treatment condition, the data was fitted using linear combination of standards. The resulting fits could be improved using the spectrum of
alpha-MnO$_2$ instead of commercial MnO$_2$ powder purchased through Sigma-Aldrich (comparison of TEY Mn L-edge spectra of MnO$_2$ polymorphs as well as commercially available MnO$_2$ is presented in Appendix F) and consequently, alpha-MnO$_2$ spectrum was used in all the fits. The average oxidation state of the five samples is summarized in Table 4.2. Electrodeposited sample without subsequent heat treatment is successfully fitted by the spectrum of MnOOH with small contributions from MnO and alpha-MnO$_2$ for an average oxidation state of 3.1. Heat treatment at 250°C and 350°C results in an increase of Mn oxidation state to 3.4-3.5, while increasing the temperature to 450°C and 500°C converts the film to pure Mn$_2$O$_3$ phase.

**Table 4.2:** Mn valency calculated from linear combination fitting of XAS spectra of five powder standards: MnO, Mn$_3$O$_4$, Mn$_2$O$_3$, gamma-MnOOH, and alpha-MnO$_2$.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>As prepared</th>
<th>ORR</th>
<th>OER</th>
<th>ORR-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>no ht</td>
<td>3.1 (MnOOH)</td>
<td>3.3</td>
<td>3.6</td>
<td>3.1</td>
</tr>
<tr>
<td>250°C</td>
<td>3.5 (Mn$_2$O$_3$)</td>
<td>n/a</td>
<td>3.6</td>
<td>n/a</td>
</tr>
<tr>
<td>350°C</td>
<td>3.4 (Mn$_2$O$_3$)</td>
<td>3.5</td>
<td>3.6</td>
<td>3.5</td>
</tr>
<tr>
<td>450°C</td>
<td>3.0 (Mn$_2$O$_3$)</td>
<td>3.0</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>500°C</td>
<td>3.0 (Mn$_2$O$_3$)</td>
<td>3.0</td>
<td>3.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

MnO$_x$ phase listed in the parenthesis indicates the Mn(III) phase used in the fitting. Fittings for ORR, OER, and ORR-2 conditions were performed by considering the spectra of as prepared samples and the five powder controls.

Due to more clear distinctions between different MnO$_x$ phases using Mn L-edge XAS than $\Delta E_{2p_{1/2}}$ and $\Delta E_{3s}$ of XPS, we focused on XAS characterization in an attempt to understand how the starting surface conditions influence the surface oxidation state under the ORR and the OER potentials. In the experiments, the samples were cycled from 0.05 V to a vertex potential of either 0.7 V or 1.65 V and held at the vertex potential for 30 minutes. An additional sample, which has previously been exposed to OER potentials of up to 1.8 V was cycled from 0.05 V to a vertex potential of 0.7 V to test electrochemical reversibility of the electrode. The resulting chronoamperometry curves
are shown in Figure 4.4 and the XAS spectra of the samples are presented in Figure 4.5. Only OER spectrum is shown for 250°C sample due to instability of the sample under ORR conditions resulting in loss of catalytic material and poor XAS signal. The average oxidation state of all ORR and OER samples was obtained by linear combination of the spectra from as prepared samples and the spectra from five MnOₓ standards (MnO, Mn₃O₄, Mn₂O₃, gamma-MnOOH, alpha-MnO₂) and is summarized in Table 4.2.

Inspection of the spectra reveals the influence of the starting material on the Mn surface oxidation state under reaction conditions. Under ORR potentials, “no ht” sample maintains its similarity to MnOOH phase, but shows a decrease in contributions from MnO and an increase in contribution from alpha-MnO₂. The sample heat treated at 350°C shows a slight increase in Mn oxidation state due to a larger contribution from alpha-MnO₂ phase. The samples heat treated at 450°C and 500°C do not change the phase and remain as pure Mn₂O₃. Exposure to OER potentials further increases contribution from alpha-MnO₂ in “no ht,” 250°C and 350°C samples and results in a similar average oxidation state of 3.6 in the three samples. The spectra of OER samples heat treated at 450°C and 500°C is similar to the spectra of the corresponding as prepared catalysts, but the fit of the spectra can be improved by addition of ~10% alpha-MnO₂ to Mn₂O₃, suggesting slight oxidation of the surface. Interestingly, although “no ht,” 250°C, and 350°C have similar surface oxidation state under OER conditions, repetition of the ORR hold after previous exposure to anodic potentials (ORR-2) results in spectra that are similar to the original ORR spectra. This indicates that the samples have a memory of their previous state and the starting properties of the film matter even after exposure to high oxidizing potentials. Repetition of the ORR hold experiment with 450°C and 500°C
samples also results in spectra that are similar to the corresponding as prepared catalysts, with the fit of 500°C sample showing improvement after addition of a small alpha-MnO₂ component.

Figure 4.4: Chronoamperometry curves for manganese oxide thin films at vertex potentials of 0.7 V (a), 1.65 V (b), and 0.7 V after exposure to high anodic potentials of up to 1.8 V (c).
Figure 4.5: Total electron yield (TEY) x-ray absorption spectroscopy (XAS) measurements of manganese oxide thin films exposed to five different heat treatment conditions: no heat treatment (no ht), heat treatment at 250°C, 350°C, 450°C, and 500°C and electrochemical potentials relevant to the oxygen reduction reaction (ORR) (a), oxygen evolution reaction (OER) (b), or ORR after previous exposure to OER (ORR-2) (c). ORR and ORR-2 spectra of the film heat treated at 250°C are not shown due to instability of the film at ORR relevant potentials.
The differences in the sampling depths of TEY and AEY collection modes can allow for a better understanding of the depth of surface oxidation. Distinct TEY and AEY spectra for a particular sample correspond to a shallow surface oxidation that is less than 2 nanometers deep. Overlapping TEY and AEY spectra, on the other hand, correspond either to an oxidation that is at least several nanometers deep or, if no difference is detected from the as prepared material, to no oxidation at all. As shown in Figure 4.6, for “no ht,” 250°C, and 350°C, TEY and AEY spectra overlap, demonstrating that the measured oxidation in these three samples is several nanometers deep. For 450°C and 500°C samples, the TEY and AEY spectra show small differences that might correspond to a shallow surface oxidation. Comparison of TEY and AEY spectra of Mn₂O₃ standard, presented in Figure 4.6 (f), also shows differences between TEY and AEY, which are likely due to signal saturation during AEY measurements. Since the differences between TEY and AEY spectra were observed both with a powder control and catalytic samples, these results do not provide conclusive evidence for the oxidation of Mn₂O₃ surface in 450°C and 500°C samples after exposure to high anodic potentials.

Our XAS spectra of ORR and OER relevant surfaces on MnOₓ samples exposed to five different heat treatment conditions has demonstrated a decreased ability of the surface to change oxidation state with increasing heat treatment temperature. This is likely caused by a decrease in the hydration of the samples, which can limit the pseudocapacititative processes to the very top surface. We confirmed the decrease in hydration of MnOₓ thin films with increasing heat treatment temperature by monitoring O 1s spectra of the five samples. From Figure 4.7, it is seen that the electrodeposited MnOₓ thin film with no subsequent heat treatment has a large proportion of Mn-OH species
Figure 4.6: Comparison of total electron yield (TEY, solid colors) and auger electron yield (AEY, dotted black lines) for manganese oxide thin films (a)-(e) and powder controls (f). For manganese oxide thin films, XPS spectra is shown for initial surfaces and after exposure to electrochemical potentials relevant to the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), or ORR with prior introduction to OER potentials up to 1.8 V. Only initial surface and OER condition are shown for the thin film heat treated at 250°C, due to instability of the film at ORR relevant potentials.

relative to Mn-O-Mn species, while heat treatment at all temperatures results in a significant decrease in Mn-OH species. To determine the effect of heat treatment and decreased ability to change oxidation state as the conditions switch from ORR and OER
potentials on the activity of the surface for the two reactions, we electrochemically characterized the five samples using cyclic voltammetry in RDE configuration.

![O 1s spectra of MnOₓ samples exposed to five different heat treatment conditions: no heat treatment (no ht), 250°C, 350°C, 450°C, and 500°C. The spectrum of the sample no heat treatment is de-convoluted into Mn-O-Mn, Mn-OH, and H-O-H contributions to the O 1s signal.](image)

Figure 4.7: O 1s spectra of MnOₓ samples exposed to five different heat treatment conditions: no heat treatment (no ht), 250°C, 350°C, 450°C, and 500°C. The spectrum of the sample no heat treatment is de-convoluted into Mn-O-Mn, Mn-OH, and H-O-H contributions to the O 1s signal.

Cyclic voltammetry characterization of the catalysts for ORR and OER is shown in Figures 4.8. MnOₓ samples heat treated at the highest temperatures of 450°C and 500°C, which correspond to the samples of Mn₂O₃ phase with least ability to change Mn oxidation state, have the best activity for both reactions. From the ORR CVs shown in Figure 4.8 (a), it is clear that after heat treatment at 450°C, there is a distinct change in the diffusion limited current. This change corresponds to an increase in the number of electrons transferred from about 2 to closer to 4, linking the formation of Mn₂O₃ phase to a favorable change in the ORR mechanism toward 4-electron reduction. The OER CVs in Figure 4.8 (b) also demonstrate the trend of increasing catalytic activity with increasing heat treatment temperature. In this case, the initial enhancement in OER activity is observed with 350°C sample, and the activity continues to increase with 450°C and 500°C samples. The improvement in both the ORR and the OER activities with rising
heat treatment temperature indicates that a lower ability to cycle between oxidation states is associated with high catalytic performance.

Although the surface oxidation state is likely important to the activity of the catalyst for both the ORR and the OER, other factors including the effects of the electrochemical surface area and the background activity of the support will also influence observed geometric activity. Inspection of N\textsubscript{2} CVs, shown in Figure 4.8 (c) reveals that MnO\textsubscript{x} sample heat treated at 500°C has the largest capacitance/pseudo-capacitance, which is proportional to the electrochemical surface area, and the highest electrochemical activities for the reactions of interest. To extract the contribution of increasing electrochemical surface area in the observed increasing geometric activities of the catalysts, we focused on 450°C and 500°C samples. These samples were confirmed to be the same phase by XAS, and therefore the differences in their capacitive current are likely to be solely explained by the differences in the electrochemical surface area. To compare the normalized catalytic activities 450°C and 500°C samples, we first determined the kinetic current by compensating for the remaining 15% of ohmic resistance of the electrolyte for both the ORR and the OER. For the ORR, we performed additional adjustments by subtracting capacitive contributions using N\textsubscript{2} scans, shown in Figure 4.8 (c), and correcting for mass transport losses using equation 4.1,

\[ \frac{1}{i_m} = \frac{1}{i_k} + \frac{1}{i_d} \]  

(4.1)

where \( i_m \) corresponds to the measured current in the ORR CV in anodic direction corrected for ohmic resistance and capacitance current, \( i_k \) corresponds to the kinetic current, and \( i_d \) corresponds to the diffusion limited current measured experimentally. We then normalized the kinetic current by the magnitude of capacitance/pseudocapacitance
Figure 4.8: Cyclic voltammetry characterization of manganese oxide thin films showing the oxygen reduction reaction (ORR) activity in O\textsubscript{2} (a), the oxygen evolution reaction (OER) activity in N\textsubscript{2} (b), and oxidation/reduction features as well as pseudocapacitance in N\textsubscript{2} (c). The film heat treated at 500°C shows the highest activity for both the ORR and the OER on geometric basis, while also having the largest pseudocapacitance.
Figure 4.9: Tafel plots of 450°C and 500°C samples before (solid lines) and after (dotted line) normalization of 450°C current to the ratio of capacitive/pseudocapacitive current of the two samples. Due to the variation in the magnitude in capacitive/pseudocapacitive with potential, ORR kinetic current was normalized by the ratio of magnitudes at 0.5 V, while OER kinetic current was normalized by the ratio of magnitude at 1.4 V. Normalization results in similar activities, illustrating that the differences observed in cyclic voltammograms of these two Mn$_2$O$_3$ samples are largely explained by the differences in the surface area.

at 0.5 V for the ORR and 1.4 V for the OER and constructed Tafel plots, which in Figure 4.9 illustrate the relationship between the kinetic current and the applied potential. The Tafel plots demonstrate that the two samples have similar intrinsic catalytic activities and indicate that the higher geometric activity of 500°C sample relative to 450°C sample for the ORR and the OER could be explained by a larger surface area of the catalyst. To explore possible contributions of the GC support to the observed catalytic activities for
Figure 4.10: Oxygen reduction reaction (ORR) activity (a) and oxygen evolution reaction (OER) activity (b) of glassy carbon (GC) after heat treatment at 250°C, 350°C, 450°C, 500°C, demonstrating that the catalytic current for both the ORR and the OER increases with heat treatment.

The ORR and the OER, we exposed bare GC to the same five heat treatment conditions as MnO$_x$ thin films and characterized the resulting electrodes electrochemically for both reactions, as shown Figure 4.10. We found that although both the ORR and the OER activity of GC increases with heat treatment temperature, it remains significantly lower than the activity of the best performing MnO$_x$ catalysts. Heat treatment of GC in the absence of MnO$_x$, however, does not result in formation of the porous structure observed in Figure 4.1 (f). We therefore prepared an additional sample by electrodepositing MnO$_x$, heat treating the electrode at 500°C, and then dissolving MnO$_x$ using concentrated
hydrochloric acid to form a porous GC (pGC) support shown in Figure 4.11. As shown in
Figure 4.10, pGC has the most favorable ORR onset potential among GC electrodes and
the highest OER current at 1.8 V. When its activities are compared to the activities of
MnOₓ thin film heat treated at 500°C, shown in Figure 4.12, however, it is evident that
the presence of Mn₂O₃ phase is more important to 4-electron oxygen reduction and high
OER activity than the pGC surface.

![Figure 4.11: Scanning electron microscopy (SEM) image of porous glassy carbon (pGC) electrode
prepared by depositing MnOₓ, heat treating the sample at 500°C, and subsequently removing MnOₓ using
concentrated hydrochloric acid.](image)

To better understand the contribution of GC to the electrochemical activity of
MnOₓ catalysts, we studied the electrochemical activity of the catalysts for the ORR after
previous exposure to high anodic potentials necessary for the OER. As discussed
previously, exposure to the OER relevant potentials followed by the ORR hold (ORR-2)
resulted in a similar surface oxidation state of MnOₓ as after the initial ORR hold
experiment for all five MnOₓ surfaces. These results indicated that there was little change
in MnOₓ surface properties with exposure to OER potentials, suggesting that the
electrochemical activity for the ORR should not be dependent on previous exposure to
high anodic potentials. Measurement of the ORR activity after the exposure to the OER
potentials, however, revealed a significant decrease in electrochemical activity as shown in Figure 4.13 (a). Characterization of the ORR activity of GC and pGC samples after exposure to OER potentials, shown in Figure 4.13 (b), also revealed the same drop in activity. Therefore, the drop in ORR activity in MnO$_x$ samples is most likely explained by a change in GC surface and suggests that although the phase of MnO$_x$ is important to ORR activity, the contribution of GC is not negligible. The contributions of carbon and MnO$_x$ to ORR activity are further explored in Chapter 7.

**Figure 4.12:** Oxygen reduction reaction (ORR) activity (a) and oxygen evolution reaction (OER) activity (b) of glassy carbon after heat treatment at 500°C (GC 500°C), porous glassy carbon (pGC), and manganese oxide thin film on glassy carbon after heat treatment at 500°C (MnO$_x$ 500°C), demonstrating that pGC has higher activity for both the ORR and the OER than GC 500°C, but negligible activity for both reactions when compared to the best performing manganese oxide catalyst.
4.5 Conclusions

In our study we characterized the effect of preparation route of manganese oxide (MnO_x) thin films on the surface properties of the films in the potential region between the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). To obtain different types of MnO_x surfaces we electrodeposited MnO_x on glassy carbon and subjected the resulting electrodes to five heat treatment conditions: no heat treatment (“no ht”), heat treatment at 250°C, 350°C, 450°C, and 500°C. We found that increasing heat
treatment temperature resulted first in an increase and then a decrease in the starting Mn oxidation state and a continuous decrease in the extent of changes in Mn oxidation state with changes in the electrochemical potential. At the two highest heat treatment temperatures of 450°C and 500°C, the surface of MnOx displayed an oxidation state close to its starting Mn$_2$O$_3$ phase both at the ORR and the OER potentials and demonstrated the highest ORR and OER activities. Although the electrochemical surface area and the properties of GC were also found to change with increasing heat treatment temperature, the phase of MnOx was determined to be most important to the ORR and OER activities.

4.6 Collaborations

Dennis Nordlund assisted in x-ray absorption spectroscopy (XAS) data acquisition and was instrumental in XAS data normalization and interpretation.
Chapter 5

*In-situ* X-Ray Absorption Spectroscopy

Investigation of a Bifunctional Manganese Oxide Catalyst with High Activity for the Oxygen Reduction and Evolution Reactions

5.1 Abstract

*In-situ* x-ray absorption spectroscopy (XAS), in combination with electrochemistry, is a powerful technique that can elucidate the chemical nature of electrocatalysts under reaction conditions, providing design principles for the development of improved catalysts. In this study, we perform *in-situ* XAS measurements on a bifunctional manganese oxide (MnOₓ) catalyst with high electrochemical activity for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Using x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS), we find that exposure to an ORR relevant potential of 0.7 V produces a disordered Mn₃O₄ phase with negligible contributions from other phases. After the
potential is increased to a highly anodic value of 1.8 V relevant to the OER, we observe an oxidation of the disordered Mn$_3$O$_4$ phase to a mixture of phases consisting of a major phase similar to birnessite MnO$_x$ and a minor phase, likely corresponding to Mn$_3$O$_4$. Investigation of a catalyst with a thinner layer of MnO$_x$ showed a similar composition of MnO$_x$ phases at the OER condition, but smaller OER activity, demonstrating that the OER catalysis occurs throughout the catalytic layer and not at the top most geometric layer of the film.

5.2 Introduction

Chapter 1 highlighted the development of catalytic materials for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) as a major challenge in energy conversion and storage technologies and introduced *in-situ* x-ray absorption spectroscopy (XAS) as a characterization tool that can help develop improved electrocatalysts for these important reactions. *In-situ* XAS experiments are performed using hard x-rays, which probe both the electronic structure of the catalyst in the x-ray absorption near edge structure (XANES) region and the short-range order of catalyst in the extended x-ray absorption fine structure (EXAFS) region. In the past, *in-situ* XAS measurements have been applied to a variety of ORR and OER systems. For example, the method has been used to track oxidation state of platinum as a function of potential in the ORR region\textsuperscript{102} and correlate d-band vacancies on platinum alloy catalysts to oxygen reduction activity.\textsuperscript{103} *In-situ* XAS has also been used to understand the valency and structure of a cobalt phosphate and nickel borate OER catalysts,\textsuperscript{66,67} study ORR mechanism on manganese oxide catalysts,\textsuperscript{38,46} and probe the photochemical oxygen evolution on a manganese-based catalytic material.\textsuperscript{47}
No previous *in situ* XAS study, however, has focused on changes in the active catalyst phase between the ORR and OER regimes using the same material. The significant overpotentials associated with the two reactions make it unlikely for the same surface to form under both reductive and oxidative potentials, and no known metal or metal oxide has yet been shown to approach the activity of an ideal reversible oxygen electrode. Due to the large number of MnO\textsubscript{x} phases associated with high ORR\textsuperscript{35-38,82} and OER activities\textsuperscript{39,41,42}, it could be possible for MnO\textsubscript{x} based catalysts to change surface structure as a function of potential and yet exhibit high activity for both reactions. In our work, we perform *in-situ* XAS measurements on a bifunctional manganese oxide (MnO\textsubscript{x}) catalyst with high electrochemical activity for both the ORR and the OER. To prepare a bifunctional MnO\textsubscript{x} catalyst, we adopt a synthesis procedure previously developed for the deposition of MnO\textsubscript{x} on glassy carbon (GC),\textsuperscript{82} discussed in Chapter 2, to deposition on a gold-coated silicon nitride (Au-Si\textsubscript{3}N\textsubscript{4}) window. Using information from *in-situ* XANES and EXAFS we find that the switch from ORR to OER potentials results in a structural change in MnO\textsubscript{x}/Au-Si\textsubscript{3}N\textsubscript{4} catalyst and identify MnO\textsubscript{x} phases relevant to each set of conditions. We also collect data on a thinner catalyst to investigate the thickness of the MnO\textsubscript{x} layer that is able to participate in electrochemical processes. Our results link specific MnO\textsubscript{x} phases to ORR and OER conditions, thus increasing understanding of oxygen electrocatalysis on MnO\textsubscript{x} electrodes.

### 5.3 Experimental Methods

#### 5.3.1 Electrodeposition of Manganese Oxide Catalyst

Prior to manganese oxide (MnO\textsubscript{x}) electrodeposition, silicon nitride membrane (Si\textsubscript{3}N\textsubscript{4}) windows (1000 nm membrane, Silson Ltd.) were sputter coated with a 10 nm
binding layer of titanium and a 100 nm layer of gold to produce a suitable electrode substrate (Au-Si₃N₄). Au-Si₃N₄ substrate was contacted by copper tape and manganese oxide was electrodeposited in a three electrode electrochemical cell using Ag|AgCl reference electrode and a graphite foil counter electrode. The deposition was performed by adopting a known literature procedure in a solution consisting of 0.71 g of sodium sulfate (Sigma-Aldrich, >99.0%) and 1.23 g of manganese acetate (Aldrich, 99.99%) dissolved in 50 mL of Millipore water at room temperature, yielding a solution with pH of 7.4. The solution was then aged for 6 days, until the pH dropped to approximately 7. Before performing electrodeposition, the resistance between the working and reference electrodes was measured to ensure proper electrical contact between copper tape and the gold layer of Au-Si₃N₄. After establishing a proper contact and achieving a resistance of 30-60 Ω, the potential was iR compensated to 85% and cycled nine times between 0.0 and 0.6 V vs Ag|AgCl at a sweep rate of 20 mV·s⁻¹. The Au-Si₃N₄ membrane coated with the resulting thin film was placed in a ceramic boat (Fisher Scientific) and heat treated at 480°C for 10 hours in a tube furnace (Mellen Company SC13).

5.3.2 Electrochemical Characterization

Electrochemical activity of the electrodeposited MnOₓ thin film was first evaluated using cyclic voltammetry (CV) in a three-electrode electrochemical cell. All CVs were iR-compensated to 85% and measured in 0.1 M KOH electrolyte at 23°C with a sweep rate of 20 mV·s⁻¹, using a carbon rod counter electrode and Ag|AgCl reference electrode. The electrolyte (0.1 M KOH) was prepared from high purity KOH pellets (Sigma-Aldrich, 99.99%) by adding 5.60 g of pellets to 1 L of Millipore water. The potential scale was calibrated to a reversible hydrogen electrode (RHE). RHE calibration
was performed at the end of the characterization in a hydrogen saturated electrolyte with platinum nanoparticles at the working electrode (20-wt.% Pt on Vulcan XC-72, Etek). The potential of 0.960 ± 0.002 V, at which the current crossed zero, was taken to be the thermodynamic potential for the hydrogen electrode reactions. All potentials during electrochemical characterization are reported vs. RHE. To characterize activity of the catalyst for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), CVs were performed from 0.05 V to 1.8 V in an oxygen saturated environment.

5.3.3 Physical Characterization

The morphology of MnOₓ/Au-Si₃N₄ catalyst was studied using scanning electron microscopy (SEM, FEI Magellan 400 XHR). A 25 pA beam current of 5 kV and a secondary electron detector were used. The crystal structure of MnOₓ catalyst was investigated using x-ray diffraction with Cu Kα1 radiation and λ=1.54 Å, operated at 45 kV and 40 mA (XRD, Phillips X'Pert 2). 2θ scans from 10° to 90° were performed on the catalyst and the bare Au-Si₃N₄ substrate, at a scan speed of 0.02 degrees per second.

5.3.4 Ex-situ XPS Characterization

The oxidation state of MnOₓ catalyst was initially studied by x-ray photo-electron spectroscopy using monochromated Al Kα 1486.6 eV x-rays (XPS, PHI 5000 VersaProbe). Three samples were investigated: as-prepared sample, an ORR relevant sample, and an OER relevant sample. To prepare ORR and OER relevant samples, MnOₓ on Au-Si₃N₄ was cycled from 0.05 V vs. RHE to a vertex potential of either 0.70 or 1.8 V vs. RHE, held at the vertex potential for 10 minutes, extracted from the electrochemical cell under potential control, and characterized using XPS. During XPS characterization high resolution spectra of Mn 2p, Mn 3s, O 1s, and C 1s were obtained on MnOₓ catalysts.
and two powder standards: Mn₂O₃ and MnO₂ (Sigma-Aldrich), using a pass energy of 23.5 eV, an energy step of 0.1 eV, and a time of 20 ms per step. The energy windows and the number of scans used to acquire each high resolution spectrum are provided in Table 5.1. All spectra were calibrated to the position of adventitious carbon at 285.0 eV. To monitor changes in the Mn oxidation state of MnOₓ catalyst, we compared the distance between Mn 2p₁/₂ peak and its satellite (Δ2p₁/₂), the magnitude of Mn 3s multiplet splitting (ΔE₃s), and the composition of O 1s peak.

**Table 5.1: XPS Acquisition Parameters.**

<table>
<thead>
<tr>
<th>XPS Region</th>
<th>Energy (eV)</th>
<th># of Scans</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>275-310</td>
<td>130</td>
</tr>
<tr>
<td>O 1s</td>
<td>524-539</td>
<td>50</td>
</tr>
<tr>
<td>Mn 2p</td>
<td>632-675</td>
<td>260</td>
</tr>
<tr>
<td>Mn 3s</td>
<td>75-105</td>
<td>260</td>
</tr>
</tbody>
</table>

To extract information from Mn 3s and O 1s high resolution scans, the spectra were analyzed using CasaXPS software. Curves were fit using a Shirley background and 70% Gaussian 30% Lorentzian line shapes. To determine the magnitude of 3s multiplet splitting, we needed to de-convolute Au 4f spectrum from Mn 3s spectrum. In the analysis, the splitting distance between Au 4f₇/₂ and Au 4f₅/₂ was fixed to 3.7 eV and the ratio of Au 4f₇/₂ peak area to Au 4f₅/₂ peak area was fixed to 1.33. To extract information from O 1s spectrum, the relative contributions of Mn-O-Mn, M-OH, and H-O-H bonds to O 1s peak were determined. The analysis assumed the presence of 2 to 3 independent O 1s peaks with full width at half maximum (FWHM) of 2 eV or less. While Mn 2p, Mn 3s, and O 1S spectra can provide an independent estimate of Mn valency, precise information on oxidation state of Mn is difficult to extract using **ex-situ** XPS characterization.
5.3.5 In-situ XAS Characterization

X-ray absorption spectra (XAS) were collected at the Advanced Light Source (ALS) on beamline 10.3.2\textsuperscript{05} at an electron energy of 1.9 GeV with an average current of 500 mA. In the experiments, the radiation was monochromatized by a Si (111) double-crystal monochromator. Intensity of the incident x-ray was monitored by an N\textsubscript{2}-filled ion chamber (I\textsubscript{0}) in front of the sample. Fluorescence spectra were recorded using a seven-element Ge solid-state detector. For electrochemical experiments, no transmission data could be collected. The energy was therefore calibrated using a glitch in the I\textsubscript{0} intensity. All data were collected at room temperature.

Data reduction of the x-ray absorption spectra was performed using custom-made software. Pre-edge and post-edge contributions were subtracted from the XAS spectra, and the results were normalized with respect to edge jump. Background removal in k-space was achieved through a five-domain cubic spline. Curve fitting was performed with Artemis and IFEFFIT software using \textit{ab initio} calculated phases and amplitudes from the program FEFF 8.2.\textsuperscript{106,107} These \textit{ab initio} phases and amplitudes were used in the EXAFS equation:

\[
\chi(k) = S_0^2 \sum_j N_j f_{\text{eff}}(\pi,k,R_j) e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda_j(k)} \sin(2kR_j + \phi_{ij}(k))
\] (5.1)

In the equation, the neighboring atoms to the central atom(s) are divided into \( j \) shells, with all atoms with the same atomic number and distance from the central atom grouped into a single shell. Within each shell, the coordination number \( N_j \) denotes the number of neighboring atoms in shell \( j \) at a distance of \( R_j \) from the central atom. \( f_{\text{eff}}(\pi,k,R_j) \) is the \textit{ab initio} amplitude function for shell \( j \), and the Debye-Waller term \( e^{-2\sigma_j^2 k^2} \) accounts for
damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{-2R_j/\lambda_j(k)}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$ is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term, $\sin(2kR_j + \varphi_{ij}(k))$ where $\varphi_{ij}(k)$ is the \textit{ab initio} phase function for shell $j$. $S_0^2$ is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS equation was used to fit the experimental data using $N$, $R$, and the EXAFS Debye-Waller factor ($\sigma^2$) as variable parameters. For the energy (eV) to wave vector ($k$, Å$^{-1}$) axis conversion, $E_0$ was defined as 6545.0 eV and the $S_0^2$ value was fixed to 0.85.

A schematic of \textit{in-situ} set up is shown in Figure 5.1. In the set-up, the back side of Si$_3$N$_4$ window was exposed to x-rays, while the front side of Si$_3$N$_4$ window with electrodeposited MnO$_x$ on Au/Ti layer faced into the interior of a two-compartment electrochemical cell. Electrochemistry was performed in air using Ag$|$AgCl reference electrode, platinum wire counter electrode, and 0.1 M KOH electrolyte. Although RHE calibration was not performed during \textit{in-situ} XAS characterization, we assumed the same shift of 0.960 V for Ag$|$AgCl reference electrode and report all potentials vs. RHE. After preparing the electrochemical cell for \textit{in-situ} XAS measurements, the resistance between the working and reference electrodes was measured to ensure proper electrical contact between the potentiostat and MnO$_x$ on Au-Si$_3$N$_4$. After achieving a resistance of 150 Ω, a CV was performed from 0.05 to 1.1 V in air, to record electrochemical features of the working electrode. During \textit{in-situ} XAS at ORR relevant conditions, the potential was held at 0.7 V for 3.4 hours. After the completion of the measurement, the resistance between the working and reference electrodes was measured to be 73 Ω and iR-
compensated cyclic voltammetry was performed from 0.05 V to 1.8 V to record bi-functional OER/ORR activity of the working electrode. During in-situ XAS at OER relevant conditions, the iR-compensated potential was held at 1.8 V for 5 hours.

Figure 5.1: In-situ XAS set-up, with the back-side of Si$_3$N$_4$ window facing the x-rays and the front side of the window, with electrodeposited MnO$_x$ on a layer of Au/Ti facing the electrolyte. CE, RE and WE stand for counter, reference and working electrode, respectively.

XAS spectra of MnO$_x$ on Au-Si$_3$N$_4$ was compared to ex-situ XAS spectra of model MnO$_x$ compounds, including Mn$_3$O$_4$ (Sigma-Aldrich), alpha-Mn$_2$O$_3$, beta-MnO$_2$, gamma-MnO$_2$, lambda-MnO$_2$, H$^+$ birnessite, and Mg$^+$ birnessite. Mn$_3$O$_4$ powder was used as purchased. Beta-MnO$_2$ and alpha-Mn$_2$O$_3$ phases were prepared by dissolving Mn(NO$_3$)$_2$·H$_2$O in water, drying the solution at 60 °C for 24 hours, and calcining the powder for 3 hours at 200 °C or 500 °C, respectively. Gamma-MnO$_2$ and lambda-MnO$_2$ phases were prepared using digestion of LiMn$_2$O$_4$ at 75°C or room temperature following the procedure of Xue et al.$^{98}$ XANES spectra of H$^+$ birnessite is available in literature,$^{108}$ while XANES and EXAFS spectra of Mg$^+$ birnessite was provided by Samuel Webb, a
beam scientist at Stanford Synchrotron Radiation Lightsource. Powder XRD was used to confirm the phase of each synthesized compound (Appendix E).

5.4 Results and Discussion

To investigate the material properties of an active manganese oxide (MnOₓ) catalyst under reaction conditions we electrodeposited MnOₓ onto a gold-coated silicon nitride membrane window (Au-Si₃N₄) and heat-treated it at 480°C following a procedure previously developed for a catalyst on glassy carbon (GC) support. The resulting electrode, MnOₓ/Au-Si₃N₄, was electrochemically characterized in an alkaline electrolyte and found to exhibit the expected bifunctional activity for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). To confirm that MnOₓ is the active species responsible for the OER and the ORR, we compared the electrochemical activity of MnOₓ/Au-Si₃N₄ to that of the bare support, Au-Si₃N₄. The catalyst clearly outperforms the bare gold support for the OER, but demonstrates similar ORR activity to Au-Si₃N₄.

To deconvolute contributions from MnOₓ and Au in the observed ORR activity of MnOₓ/Au-Si₃N₄ catalyst, we examined the cyclic voltammograms of MnOₓ/Au-Si₃N₄ and bare Au-Si₃N₄ in the potential region from 1 V to 1.4 V, where gold oxidation and reduction features are prominent. The electrochemical behavior of the electrodes, plotted in the inset of Figure 5.2 (a), demonstrates that the surface in MnOₓ/Au-Si₃N₄ catalyst does not display any of the redox features characteristic to gold, likely indicating that the Au surface is electrochemically inaccessible. This finding links the observed ORR activity of MnOₓ/Au-Si₃N₄ to the MnOₓ surface.

Figure 5.3 (a) compares the bifunctional oxygen electrode activity of MnOₓ/Au-Si₃N₄ to MnOₓ on GC (MnOₓ/GC) catalyst described in Chapter 2, demonstrating that the
Figure 5.2: (a) Cyclic voltammetry of the MnO$_x$ catalyst in O$_2$ showing bifunctional ORR/OER activity and the background activity of the Au-Si$_3$N$_4$ support. Inset shows the disappearance of Au redox features after addition of MnO$_x$. (b) Scanning electron microscopy (SEM) image illustrating needle-like morphology of MnO$_x$. (c) Comparison of Mn 2p spectra of MnO$_x$ on Au-Si$_3$N$_4$ and glassy carbon (GC) supports to the spectra of MnO$_2$, Mn$_2$O$_3$, and MnO powder standards. (d) Comparison of Mn 2p spectra of MnO$_x$ on Au-Si$_3$N$_4$ support to the spectra of the same sample after exposure to ORR or OER relevant potentials.

two catalysts have similar catalytic activity on geometric basis. Physical and chemical characterization of MnO$_x$/Au-Si$_3$N$_4$ catalyst, however, illustrates that this material is distinct from MnO$_x$/GC. As described in Chapter 2, MnO$_x$/GC formed a nanostructured morphology with some alpha-Mn$_2$O$_3$ crystallinity. MnO$_x$/Au-Si$_3$N$_4$, on the other hand, consists of densely packed needles, shown in Figure 5.2 (b), and has no long range order as demonstrated by the absence of the x-ray diffraction peaks in Figure 5.3 (b).

To gain information about the chemical state of the surface of catalyst as synthesized and after exposure to ORR (0.7 V) and OER (1.8 V) conditions, the
Figure 5.3: (a) Comparison of oxygen reduction and evolution activities of manganese oxide on gold coated silicon nitride window (MnOₓ/Au-Si₃N₄) and manganese oxide on glassy carbon (GC) rotating disk electrode substrate (MnOₓ/GC_RDE). (b) X-ray diffraction (XRD) performed on MnOₓ/AuSi₃N₄ catalyst detected crystallinity corresponding only to the underlying support, Au-Si₃N₄, showing diffraction peaks characteristic to gold and gold oxide. The y-axis of inset (d) is magnified 100 times to observe peaks at lower intensities. Inset (b) shows XRD of GC and MnOₓ/GC, demonstrating alpha-Mn₂O₃ crystallinity of the catalyst.

oxidation state of manganese was probed using *ex-situ* x-ray photoelectron spectroscopy (XPS). *Ex-situ* XPS and XAS characterization of MnOₓ/GC discussed in Chapters 3 and 4 determined that MnOₓ/GC catalyst started out as Mn (III) oxide and remained in a similar oxidation state after exposure to both reaction conditions. The observed differences in the morphology and crystallinity of MnOₓ/GC and MnOₓ/Au-Si₃N₄ suggest that MnOₓ/Au-Si₃N₄ may assume a different surface oxidation state than
Figure 5.4: The variations in Mn 3s splitting distance (a), (b), (c) and in composition of O 1s peak (d), (e), (f) in the freshly prepared MnO$_x$/Au-Si$_3$N$_4$ catalyst, the catalyst exposed to an ORR potential of 0.7 V, and the catalyst exposed to an OER potential of 1.8 V confirm that the oxidation state of Mn in MnO$_x$/Au-Si$_3$N$_4$ increases as the reaction conditions change from oxygen reduction to evolution.

MnO$_x$/GC despite identical preparation conditions. From Figure 5.2 (c) it is seen that the Mn 2p spectra of as prepared MnO$_x$/Au-Si$_3$N$_4$ is different from MnO$_x$/GC and has similarities to features in MnO and MnO$_2$ spectra. Additionally, Figure 5.2 (d)
demonstrates that exposure to an ORR relevant potential of 0.7 V results in a reduction in the distance between Mn 2p$_{1/2}$ peak and its satellite ($\Delta$2p$_{1/2}$) to a value close to that of Mn$_2$O$_3$, while exposure to an OER relevant potential of 1.8 V results in an increase of Mn $\Delta$2p$_{1/2}$ to a value similar to MnO$_2$. Analysis of Mn 3s multiplet splitting, and monitoring of the composition of O 1s peak, shown in Figures 5.4, confirm that the oxidation state of the MnO$_x$/Au-Si$_3$N$_4$ catalyst changes with reaction conditions, first decreasing after exposure to an ORR potential of 0.7 V and then increasing after exposure to an OER potential of 1.8 V. These results provide evidence that unlike the surface of MnO$_x$/GC, which exhibited little or no change in Mn oxidation state after exposure to both reaction conditions, the surface of MnO$_x$/Au-Si$_3$N$_4$ assumes a distinct Mn oxidation state after 0.7 V and 1.8 V holds. To monitor the oxidation state changes in-situ and gain structural information about the catalyst both before and after exposure to reaction conditions, we performed in-situ x-ray absorption spectroscopy (XAS) experiments.

XAS data were collected using a set-up illustrated in Figure 5.1. Prior to collecting in-situ XAS measurements, cyclic voltammetry characterization of the catalyst was performed in air in ORR and OER potential windows of 0.05 V to 1.1 V and 0.05 V to 1.8 V. The resulting cyclic voltammetry behavior shown in Figure 5.5 (a) is similar to the result obtained under standard laboratory conditions in O$_2$ saturated electrolyte (Figure 5.2 (a)). The smaller magnitude of ORR current obtained at beamline 10.3.2 than in the laboratory can be explained by the smaller oxygen concentration in the air saturated electrolyte than O$_2$ saturated electrolyte. The increase in the ORR current after exposure of the catalyst to OER potentials is attributed to the formation of oxygen bubbles on the surface of the catalyst and the resulting increase in oxygen concentration.
Figure 5.5: (a) Cyclic voltammetry characterization of the catalyst performed prior to \textit{in-situ} XAS measurements demonstrates bifunctional activity of the surface for the ORR and the OER; (b) Chronoamperometry at 0.7 V during \textit{in-situ} XAS measurements at an ORR relevant electrochemical conditions in air; (c) Chronoamperometry at 1.8 V during \textit{in-situ} XAS measurements at OER relevant electrochemical conditions in air.

To acquire steady-state \textit{in-situ} XAS data, MnO$_x$/Au-Si$_3$N$_4$ catalyst was held at an ORR relevant potential of 0.7 ± 0.007 V or at an OER relevant potential of 1.8 ± 0.001 V in 0.1 M KOH. The resulting chronoamperometry curves are shown in Figures 5.5 (b)
and (c). The smaller instability in the potential during the OER and the corresponding decreased level of noise in measured current density was due to a smaller ohmic resistance. The occasional drops and recovery observed in the OER chronoamperometry data were likely due to formation and disappearance of oxygen bubbles from the surface.

For comparison, measurements were also performed on a dry catalyst.

Figure 5.6: (a) Comparison of XANES data collected on dry MnOx/Au-Si3N4 film and on MnOx/Au-Si3N4 film after \textit{in-situ} exposure to ORR and OER relevant conditions. (b) MnOx/Au-Si3N4 film poised at 0.7 V overlayed with Mn3O4 and alpha-Mn2O3. (c) MnOx/Au-Si3N4 film poised at 1.8 V overlayed with Mn3O4, alpha-Mn2O3, and H\textsuperscript{+} birnessite and Mg\textsuperscript{+} birnessite.
In-situ XANES measurements, shown Figure 5.6 (a), follow the trend observed with ex-situ XPS characterization. After the dry electrode was introduced into the electrochemical cell and ORR relevant potential of 0.7 V was applied, a negative shift was observed in the XANES spectrum, showing a reduction in Mn oxidation state. On the other hand, subsequent change to OER conditions leads to a shift in the edge position to a higher energy, indicating an increase in Mn oxidation state. Comparison of XANES spectrum obtained under ORR conditions to the spectra of Mn$_3$O$_4$ and alpha-Mn$_2$O$_3$ powder standards in Figure 5.6 (b) demonstrates that at 0.7 V, the Mn valence is less than 3 and is close to 2.7 in Mn$_3$O$_4$ in which the oxidation state is Mn$^{III,II,III}$. Analysis of MnO$_x$/Au-Si$_3$N$_4$ catalyst after exposure to an OER potential of 1.8 V, shown in Figure 5.6 (c), reveals that the MnO$_x$ catalyst is more oxidized than alpha-Mn$_2$O$_3$ phase, and exhibits strong similarity to birnessite phases. Comparison of XANES spectra of Mg$^+$ and H$^+$ birnessite phases to the spectra of various MnO$_x$ standards, shown in Figure 5.7, highlights their unique features and the energy position of the edge between Mn$_3$O$_4$ and MnO$_2$ phases. Consequently, in-situ XANES identifies the oxidation state of the OER
catalyst to be between 3 and 4. The rising edge position of the MnOₓ under OER condition is slightly lower than that of birnessites, suggesting that the OER catalyst has a smaller valency than that of H⁺ or Mg⁺ birnessite. This could be due to the contribution of un-oxidized fraction of Mn₃O₄ that is not accessible electrochemically, or a higher Mn³⁺ sites in the OER catalyst as compared to birnessites.

Figure 5.8: Comparison of in-situ EXAFS data collected under ORR and OER relevant conditions to EXAFS spectra of dry powder standards. (a) MnOₓ/Au-Si₃N₄ film poised at 0.7 V and 1.8 V. (b) MnOₓ/Au-Si₃N₄ film poised at 0.7 V overlayed with Mn₃O₄ and alpha-Mn₂O₃. (c) MnOₓ/Au-Si₃N₄ film poised at 1.8 V overlayed with Mn₃O₄, alpha-Mn₂O₃, and Mg⁺ Birnessite.

The EXAFS spectra of MnOₓ/Au-Si₃N₄ shown in Figure 5.8 provide further information about the relevant phases under reaction conditions. EXAFS of MnOₓ under ORR conditions was compared with those of Mn₃O₄ and alpha-Mn₂O₃ in Figure 5.8 (b).
It shows much weaker EXAFS peak intensity in the ORR catalyst than those of Mn$_3$O$_4$, despite the similarity in XANES region. EXAFS curve fitting, however, demonstrates that the ORR spectrum can be fit well with the Mn$_3$O$_4$ atomic distances with higher Debye-Waller factors as shown in Figure 5.9 and Table 5.2. This suggests that the structure of MnO$_x$ at 0.7 V corresponds to a distorted Mn$_3$O$_4$ phase. A change to the oxidative potential of 1.8 V leads to a structural rearrangement of the MnO$_x$ catalyst, and emergence of similarities in the peak positions between MnO$_x$ OER catalyst and a birnessite phase as shown in Figure 5.8 (c). This result supports the conclusion from XANES analysis, confirming the major OER phase to be similar to birnessite MnO$_x$.

![Figure 5.9: EXAFS Fourier transform (blue line, left) and k-space (blue line, right) with their respective fits (red lines) for (a) Mn$_3$O$_4$ powder standard and (b) MnO$_x$/Au-Si$_3$N$_4$ catalyst held at the ORR potential of 0.7 V.](image-url)
Table 5.2: EXAFS curve fitting parameters for Mn$_3$O$_4$ powder standard and the ORR (0.7 V) relevant surface of MnO$_x$.

<table>
<thead>
<tr>
<th>Path</th>
<th>R (Å)</th>
<th>N</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_3$O$_4$</td>
<td>Mn-O</td>
<td>1.94</td>
<td>4</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Mn-O</td>
<td>2.27</td>
<td>1</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Mn-Mn</td>
<td>2.88</td>
<td>1</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Mn-Mn</td>
<td>3.09</td>
<td>2</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Mn-Mn</td>
<td>3.45</td>
<td>6</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>Mn-Mn</td>
<td>3.79</td>
<td>5</td>
<td>0.006</td>
</tr>
<tr>
<td>0.7 V MnO$_x$</td>
<td>Mn-O</td>
<td>1.90</td>
<td>4</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Mn-O</td>
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<td>0.017</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.012</td>
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<td>Mn-Mn</td>
<td>3.78</td>
<td>5</td>
<td>0.011</td>
</tr>
</tbody>
</table>

The k-range in the fit was 2.9 < k (/Å) < 11.1 (1.0 < R (Å) < 3.8).

Although the valency of birnessite MnO$_x$ differs from the valency of common MnO$_2$ phases as demonstrated in Figure 5.7, XAS spectra available in literature$^{108,110,111}$ show similarities among birnessite, todorokite, hollandite, and psilomelane. The structures of these four MnO$_x$ phases accommodate ions in their tunnels or layers,$^{32}$ which warrants consideration of potassium intercalation into the catalyst during the characterization in potassium hydroxide electrolyte. Previously, potassium intercalation into MnO$_x$ has been reported both under ORR$^{112,113}$ and OER conditions.$^{60,114}$ Using ex-situ XPS measurements we determined the ratio of potassium to Mn in MnO$_x$/Au-Si$_3$N$_4$ catalyst after its exposure to 0.7 V and 1.8 V. Measurements were also performed on as prepared catalyst, in which no potassium cations could be present. Our results, shown in Figure 5.10, indicate that a small amount of potassium, corresponding to one K$^+$ for every 100 surface Mn, intercalates into the catalyst after exposure to the OER conditions, while the intercalation under the ORR conditions is negligible. Therefore, we do not anticipate potassium to play an important role in OER catalysis on MnO$_x$/Au-Si$_3$N$_4$ surface, but its potential contribution to activity cannot be fully discounted.
Figure 5.10: XPS spectra of an MnO$_x$ thin film as deposited and after applying 0.7 V and 1.8 V. Two new peaks appear at ca. 294 eV and 297.5 eV that correspond to K 2$p_{1/2}$ and K 2$p_{3/2}$, respectively. Exposure to an oxygen evolution reaction (OER) relevant potential of 1.8 V results in intercalation of a small amount of K$^+$ ions in MnO$_x$/Au-Si$_3$N$_4$ catalyst.

The in-situ XAS characterization of MnO$_x$/Au-Si$_3$N$_4$ catalyst identified a structural transformation from disordered Mn$_3$O$_4$ phase to a birnessite-like phase as the reaction conditions switched from ORR conditions to OER conditions. These results indicate that different phases are responsible for the ORR and the OER. The presence of close to 100% disordered Mn$_3$O$_4$ phase at 0.7 V links Mn$_3$O$_4$ to the high activity for the ORR. Formation of the Mn$_3$O$_4$ phase at 0.7 V, however, is not entirely expected. Reduction of MnO$_2$ to Mn$_3$O$_4$ has been reported in the past for a number of MnO$_2$ phases, but it was demonstrated only in highly concentrated KOH electrolytes, and was characterized by poor electrochemical reversibility and conductivity. Previous mechanistic studies in low concentration KOH electrolytes, applicable to the present investigation, have identified MnOOH as the final reduction product of MnO$_2$. Additionally, previous ex-situ XPS studies of MnO$_x$ on gold have not shown a reduction of MnO$_x$ below Mn (III) state, although these studies were performed at close to neutral pH conditions. Finally, in-situ XAS characterization of another ORR catalyst, MnO$_x$
dispersed in Vulcan carbon, detected the presence of some Mn$_3$O$_4$ at a similar cathodic potential, but in a mixture with a more oxidized phase of MnOOH.$^{38}$ The scarcity of reports of complete reduction of MnO$_x$ to Mn$_3$O$_4$ under potentials relevant to the ORR warrants further investigation of reductive behavior of MnO$_x$/Au-Si$_3$N$_4$ and identification of precise voltage at which the phase transition to Mn$_3$O$_4$ begins.

Although a few reports suggest that Mn$_3$O$_4$ cannot be electrochemically oxidized,$^{38,87,97,116,117}$ our in-situ results demonstrate that after MnO$_x$ in MnO$_x$/Au-Si$_3$N$_4$ is completely converted to disordered Mn$_3$O$_4$ at 0.7 V, exposure to an OER relevant potential of 1.8 V leads to oxidation of the catalyst to a birnessite-like phase in addition to a possible contribution of minority species with lower valency, likely corresponding to Mn$_3$O$_4$. The presence of a low valence minority species under the OER conditions can be most easily explained by a fairly dense film with only part of the surface accessible to the electrolyte to form a birnessite type phase. To test this hypothesis we prepared a thinner MnO$_x$/Au-Si$_3$N$_4$ catalyst by reducing the number of deposition cycles from nine to one. The thickness of both samples was measured using cross-sectional scanning electron microscopy (SEM). Although the SEM images shown in Figures 5.11 (a) and 5.11 (b) indicate that the samples differ in thickness by a factor of 2, they have similar XANES spectra, under both the ORR and the OER conditions (Figure 5.11 (c)). Comparison of the OER current at 1.8 V, presented in Figure 5.11 (d), reveals about a factor of two higher current for the thicker sample, indicating a direct relationship between the thickness of the catalytic film and the OER activity. This result suggests that the film is porous enough for both samples to have the same proportion of the electrochemically active material and that the OER catalysis occurs throughout the catalytic layer and not at
the top most geometric layer of the film. The less oxidized phase could remain in the interior of the catalytic material in the porous structure. This links the OER activity to the majority component that has a similarity to birnessite.

**Figure 5.11:** (a) Scanning electron microscopy (SEM) image of 200 nm MnOx on Au-Si3N4 after 9 cyclic voltammetry (CV) cycles of deposition. (b) SEM image of 100 nm MnOx on AuSi3N4, demonstrating a 2 fold reduction in the thickness of MnOx after the number of CV deposition cycles is lowered from 9 to 1. (c) Comparison of XANES for 9 (solid lines) and 1 (dashed lines) cycle samples after exposure to ORR (red) and OER (blue) potentials. (d) CV characterization of the ORR and the OER activities, illustrating that the OER activity scales with the thickness of MnOx catalyst deposited on AuSi3N4.
The observed similarity between the catalyst under OER potential of 1.8 V and birnessite phase is consistent with previous literature reports which have demonstrated formation of a disordered birnessite phase (delta-MnO\textsubscript{2}) at high anodic potentials in basic electrolyte.\textsuperscript{87} In-situ XAS study on a homogeneous catalyst prepared in acidic nafion membrane has previously linked this phase to high activity of MnO\textsubscript{x} for OER,\textsuperscript{47} while ex-situ characterization of MnO\textsubscript{x}\textsuperscript{43,44} and calcium MnO\textsubscript{x} catalysts\textsuperscript{42} have also suggested a correlation between the disordered birnessite phase associated with delta-MnO\textsubscript{2} and significant catalytic activity. Our study provides the first in-situ evidence of formation of MnO\textsubscript{x} with a structure similar to birnessite phase on a heterogeneous MnO\textsubscript{x} catalyst during the OER in alkaline environment.

5.5 Conclusions

In-situ X-ray absorption characterization of manganese oxide (MnO\textsubscript{x}) catalyst on Au-Si\textsubscript{3}N\textsubscript{4} (MnO\textsubscript{x}/Au-Si\textsubscript{3}N\textsubscript{4}) identified a disordered Mn\textsubscript{3}O\textsubscript{4} as a phase with high ORR activity and MnO\textsubscript{x}, with a structure similar to birnessite, as a phase with high OER activity. Possible contributions of potassium ions to the OER activity could not be completely discounted but were shown to be unlikely. By studying two catalyst layers of different thicknesses, it was shown that under anodic conditions the majority of the catalyst was oxidized to the OER active phase. Due to previously demonstrated dependence of electrochemical properties of MnO\textsubscript{x} on the electrolyte pH\textsuperscript{118} and the starting MnO\textsubscript{x} phase,\textsuperscript{87,118} it is important to continue in-situ investigation of different MnO\textsubscript{x} catalysts under the ORR and the OER conditions. These investigations will facilitate emergence of design principles for MnO\textsubscript{x} electrocatalysts and accelerate the development of the reversible oxygen electrode.
5.6 Collaborations

Yelena Gorlin, Thomas F. Jaramillo, Benedikt Lassalle-Kaiser, and Junko Yano conceived this study. Yelena performed electrodeposition of MnO\textsubscript{x} catalysts, electrochemical measurements of the ORR and the OER (both \textit{ex-situ} and \textit{in-situ}), XRD characterization, and \textit{ex-situ} XPS. Jesse D. Benck prepared Si\textsubscript{3}N\textsubscript{4} windows for \textit{in-situ} studies by depositing layers of titanium and gold and performed SEM characterization of the MnO\textsubscript{x} catalysts. Benedikt, Sheraz Gul, Junko, and Vittal K. Yachandra designed \textit{in-situ} electrochemistry set-up and carried out XAS measurements on MnO\textsubscript{x} catalysts with assistance from Marcus Matthew, Yelena, and Jesse.
Chapter 6

Interactions between Nanoparticulate Manganese Oxide and Gold in Catalyzing the Oxygen Evolution Reaction

6.1 Abstract

Catalyzing the oxygen evolution reaction (OER), a key energy conversion reaction in a number of clean energy technologies, has been recently shown to depend on the nature of underlying support for a number of transition metal oxides, including manganese oxides (MnO$_x$), cobalt oxides, and nickel oxides. The effect of the support on the oxidation state of the oxide and the corresponding catalytic activity has not yet been determined, and the potential influences of the metal oxide on the properties of the underlying support have not yet been extensively investigated. In this work, we aim to understand the reason for the previously observed high catalytic activity of MnO$_x$ on gold (Au). We prepare catalysts by depositing MnO$_x$ and Au nanoparticles on glassy carbon (GC) and focus on characterization of four samples: MnO$_x$ nanoparticles deposited on GC (MnOx/GC), Au nanoparticles deposited on GC (Au/GC) MnO$_x$ nanoparticles deposited on Au/GC (MnO$_x$/Au) and Au nanoparticles deposited on MnO$_x$/GC (Au/MnO$_x$). Through electrochemical characterization we show that the combination of
MnO\textsubscript{x} and Au leads to high activity for the OER, outperforming electrodes with only a single material deposited on GC. Using \textit{ex-situ} x-ray absorption spectroscopy we correlate the enhancement in OER activity to formation of a mixed valent Mn (III)/Mn (IV) oxide under the OER conditions. Additional electrochemical characterization demonstrates that the combination of MnO\textsubscript{x} and Au results in increased oxidative current in the 0.8 V- 0.9 V potential region, which corresponds to increased adsorption of OH on Au surface and suggests that Au surface may be important to the observed high catalytic activity.

6.2 Introduction

As discussed in Chapter 1, the oxygen evolution reaction (OER) is a key energy conversion reaction in a number of clean energy technologies, including rechargeable metal-air batteries, electrolysis cells, and solar fuel synthesis\textsuperscript{4,104} Widespread commercialization of these technologies is limited by the scarcity and high cost of the best known catalysts for OER, ruthenium and iridium oxides\textsuperscript{3} Nickel oxides (NiO\textsubscript{x}) present a viable alternative to precious metal oxides in alkaline environment and are currently used in commercially available alkaline electrolyzers\textsuperscript{119} In search of other active non-precious metal oxide OER catalysts, recent research has focused on the catalytic properties of manganese oxides (MnO\textsubscript{x})\textsuperscript{40,41,82} and cobalt oxides (CoO\textsubscript{x})\textsuperscript{27,120,121}

Interestingly, OER on nickel, cobalt, and manganese oxides has been shown to depend on the nature of the underlying support, with deposition of the metal oxide on gold (Au) resulting in the best OER activity in all three cases\textsuperscript{41,121,122} The observed increased OER activity of sub-monolayer NiO\textsubscript{x} and CoO\textsubscript{x} on Au has been proposed to correspond to high electronegativity of Au and the resulting modification of surface
oxidation state of the metal in the metal oxide,\textsuperscript{122,123} but direct spectroscopic evidence of the change in the oxidation state has not yet been obtained. Previous studies have also shown that sub-monolayer coverage of Au by the metal oxide results in the highest intrinsic activities for the OER, while full coverage of Au leads to a drop in catalytic activity.\textsuperscript{121,122,124} These results suggest that the Au surface may participate in the reaction directly.

Au electrodes are not generally known to have high activity for the OER, due to a requirement of high anodic potentials for the formation of an oxidized surface necessary to drive the reaction.\textsuperscript{9,125} The OER activity of Au is not negligible in basic electrolyte,\textsuperscript{125} however, and although Au is likely to modify the properties of the metal oxide, it is also possible that the metal oxide has an effect on the surface properties of Au. El-deab and co-workers have considered the possibility that MnO\textsubscript{x} modifies the electronic structure of Au and measured x-ray photoelectron spectra of Au before and after deposition of MnO\textsubscript{x}. Because they observed no differences in the positions of Au 4f peaks, they concluded that MnO\textsubscript{x} is unlikely to modify the electronic properties of Au and proposed that the enhanced OER activity of MnO\textsubscript{x} modified electrodes occurs at the spots of the exposed Au via mediation of charge transfer by MnO\textsubscript{x}.\textsuperscript{41,124} An alternative possibility which has not previously been explored is that the metal oxide catalysts could influence the oxidation of the Au surface.

In our work, we investigate the reason for the previously observed high catalytic activity of MnO\textsubscript{x} on Au. We deposit MnO\textsubscript{x} and Au nanoparticles on glassy carbon (GC) support and show that electrodes consisting of both MnO\textsubscript{x} and Au have significantly higher OER activity than electrodes prepared from either MnO\textsubscript{x} or Au alone. Using ex-
situ x-ray absorption spectroscopy and electrochemical characterization, we correlate the enhancement in OER activity to changes in the properties of both the MnOx and gold. We observe the formation of a mixed valent Mn (III)/Mn (IV) oxide under the OER conditions and increased adsorption of OH on Au surface. Although the precise contributions of MnOx and Au to the observed catalytic activity for the OER are not yet understood, these results highlight the importance of Au in OER activity of MnOx/Au electrodes and warrant investigation of other metal oxides’ influence on oxidation of Au surface and corresponding OER activity.

6.3 Experimental Methods

6.3.1 Preparation of Electrode Substrates

Rotating disk electrode substrates were prepared from 200 mm long glassy carbon (GC) rods (dia 5 mm, Sigradur G HTW Hochtemperatur-Werkstoffe GmbH). Before deposition of MnOx or Au nanoparticles, the rods were processed by Stanford crystal shop to produce 4 mm long pieces with one side lapped and chamfered and the other side polished to a surface RMS roughness of less than 50 nm. A subset of substrates was also sputter coated with a 10 nm binding layer of titanium and a 100 nm layer of gold to produce electrodes consisting of Au_{film} on GC.

6.3.2 Synthesis of Catalytic Materials

MnOx nanoparticles were produced with a sputtering system (Nanosys500, Mantis Deposition Ltd.) using the inert gas condensation technique.\textsuperscript{126,127} The deposition chamber consisted of the nanoparticle source and the quadrupole mass filter, which \textit{in-situ} filtered sputtered nanoparticles by mass. Selected nanoparticles were then deposited
directly on the GC substrates in the main chamber, where the pressure was maintained at 0.3 mTorr with continuous Ar and He flow rates of 100 sccm and 2 sccm. Mn nanoparticles were size selected at approximately 10 nm and deposited at a pressure of 0.3 mTorr with a rate of 0.16 Å·s⁻¹, monitored by a quartz crystal microbalance (QCM). When necessary, the concentration of sputtered MnOₓ nanoparticles was varied by adjusting the position of the substrates inside the system. After deposition, samples were transferred to the load lock chamber, which was vented with Ar. Gold nanoparticles were prepared using an electron beam evaporator to deposit 8 Å gold at a rate of 0.1 – 0.2 Å·s⁻¹ monitored by a QCM.

6.3.3 Physical and Chemical Characterization of Nanoparticles

Size and morphology of the catalytic materials were monitored using scanning electron microscopy (SEM, FEI Magellan 400XHR). The images were obtained using a secondary electron detector, a beam current of 25 pA, and beam voltage of 5 kV. The oxidation state of the MnOₓ nanoparticles was characterized using ex-situ x-ray absorption spectroscopy (XAS, Stanford Synchrotron Radiation Lightsource). The measurements were performed on the 31-pole wiggler beamline 10-1 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 350 mA and a 1000 L·mm⁻¹ spherical grating monochromator with 40 μm entrance and exit slits, providing ~10¹¹ ph·s⁻¹ at 0.3 eV resolution in a 1 mm² beam spot. All data were acquired in a single load at room temperature and under ultra-high vacuum (10⁻⁹ torr) in total electron yield (TEY) mode. The measurements were performed on MnOₓ nanoparticles and four powder standards (MnF₂, Mn₃O₄, Mn₂O₃, and alpha-MnO₂) attached to an aluminum sample holder using conductive carbon. Alpha-MnO₂ powder was prepared by dissolving
0.5 g of KMnO₄ in 30 mL of Millipore water, followed by drop-wise addition of ethanol under stirring, drying the resulting powder at 60 °C overnight, and calcining the powder at 400°C for 3 hours. MnF₂, Mn₃O₄, and Mn₂O₃ powders were purchased from Sigma-Aldrich and used as received. MnF₂ powder was selected as a Mn (II) reference instead of MnO powder due to known surface oxidation of MnO during sample preparation.⁶⁵

The energy was carefully calibrated in two steps, as described previously in Chapter 4 (4.3.7. Normalization of XAS Spectra). Briefly, we first corrected the energy scale for the drift in the beam energy and then aligned the energy of the first peak of the Mn₃O₄ powder control with a literature value of 639.6 eV.⁶⁵ To normalize all data, we fit a linear background to the spectra of the samples using the following two constraints: the area from 636 eV to 660 eV was specified to be the same in every spectrum and the edge jump in the 660 eV to 665 eV region of each spectrum was fixed to match the edge jump of MnO₂ powder standard.

6.3.4 Electrochemical Characterization

The oxygen evolution reaction (OER) activity of nanoparticulate samples was characterized using cyclic voltammetry (CV) in a three electrode electrochemical cell in a rotating disk electrode (RDE) configuration. Characterization was performed in 0.1 M KOH electrolyte using a scan rate of 20 mV·s⁻¹, at room temperature. Carbon rod was used as a counter electrode, while Ag/AgCl was used as a reference electrode. The potential scale was calibrated to a reversible hydrogen electrode (RHE), and all the potentials were iR-compensated to 85% and reported vs. RHE. The average measured resistance between working and reference electrodes was ~40 Ω for all samples. The OER activity was determined by scanning the potential from 0.05 V to 1.7-1.8 V in N₂.
saturated environment. To prepare surfaces for ex-situ XAS characterization, the potential was scanned from 0.05 V to vertex potentials 1.65 V and held at 1.65 V for 30 min. To investigate the effect of manganese oxide on oxidation of the gold surface, we performed additional CV experiments in the potential region between 0.05 V and 1.1 V in N$_2$ saturated electrolyte.

### 6.4 Results and Discussion

Manganese oxide (MnO$_x$) and gold (Au) nanoparticles were deposited on glassy carbon (GC) support to produce four samples shown in Figure 6.1: (a) MnO$_x$ on GC (MnO$_x$/GC), (b) Au on GC (Au/GC), (c) MnO$_x$ on Au/GC (MnO$_x$/Au), and (d) Au on MnO$_x$/GC (Au/MnO$_x$). Oxygen evolution reaction (OER) activity of the four catalysts was characterized electrochemically in N$_2$ saturated 0.1 M KOH electrolyte and is shown in Figure 6.2. Both composite structures consisting of MnO$_x$ and Au nanoparticles have

![Figure 6.1: Scanning electron microscopy images showing morphology and coverage of (a) manganese oxide (MnO$_x$) nanoparticles on glassy carbon (GC) support (MnO$_x$/GC), (b) gold (Au) nanoparticles on GC (Au/GC), (c) MnO$_x$ nanoparticles on Au/GC (MnO$_x$/Au), and (d) Au nanoparticles on MnO$_x$/GC (Au/MnO$_x$).](image)
significant OER activity, outperforming OER activity of each individual nanoparticulate catalysts on GC: MnO\textsubscript{x}/GC and Au/GC. This result demonstrates that combination of Au and MnO\textsubscript{x} leads to an increase in catalytic activity for the OER.

![Figure 6.2: Cyclic voltammetry (CV) characterization demonstrating oxygen evolution reaction (OER) activities of composite structures, MnO\textsubscript{x}/ Au and Au\textsubscript{nanos}/MnO\textsubscript{x}, and nanoparticulate controls on GC support, MnO\textsubscript{x}/GC and Au/GC. CVs were collected in N\textsubscript{2} saturated 0.1 M KOH electrolyte, using 20 mV/s sweep rate, and 1600 rpm rotation rate.](image)

Previous theoretical calculations and experimental results have indicated that the OER activity may depend on the deposited phase of MnO\textsubscript{x}\textsuperscript{11,39,40,43,44}. To determine if a difference in Mn oxidation state is associated with the observed difference in the OER activity, we investigated the Mn oxidation state in the three catalytic samples containing manganese, MnO\textsubscript{x}/GC, MnO\textsubscript{x}/Au, and Au/MnO\textsubscript{x}, using ex-situ soft x-ray absorption spectroscopy (XAS) in total electron yield (TEY) mode. In the experiments we obtained spectra in the Mn L-edge region both after initial deposition of the nanoparticles and after subsequent exposure of the catalysts to an OER relevant potential of 1.65 V for 30 minutes. The chronoamperometry curves of the samples held at 1.65 V are shown in Figure 6.3.
Figure 6.3: Chronoamperometry curves demonstrating oxygen evolution reaction (OER) current for four catalytic samples at 1.65 V over a period of 30 minutes.

Figure 6.4 shows Mn L-edge XAS characterization of (a) four powder standards, (b) samples after deposition, and (c) samples after exposure to OER potential of 1.65 V. The spectra of powder standards in Figure 6.4 (a) demonstrate different edge positions and shapes for Mn (II), Mn (II)/Mn (III), Mn (III), and Mn (IV) oxides and allow for straightforward differentiation of Mn oxidation state in the samples of interest. Inspection of spectra corresponding to as-prepared samples in Figure 6.4 (b) reveals that MnOₓ deposits on GC in Mn (II) oxidation state, corresponding to MnO. The small differences between the spectra of MnOₓ/GC and MnF₂, the Mn (II) powder standard used in this study, are due to the expected differences in the spectra of various Mn (II) compounds. Addition of Au to MnOₓ/GC catalyst or deposition of MnOₓ on Au/GC leads to oxidation of MnO to a mixed oxide, indicating that the presence of Au results in a higher oxidation state of Mn. Subsequent exposure of the catalysts to an OER relevant potential of 1.65 V leads to oxidation of MnOₓ in MnOₓ/GC to MnO₂, and only partial oxidation of MnOₓ to a mixed valent Mn (III)/Mn (IV) oxide in the two composite structures containing Au, as shown in Figure 6.4 (c). In this case, the presence of Au leads to a more reduced state of
Figure 6.4: Mn L-edge x-ray absorption spectra measured in total electron yield (TEY) mode of (a) four powder controls, (b) catalytic samples after deposition, and (c) catalytic samples after exposure to an oxygen evolution reaction (OER) relevant potential of 1.65 V for 30 minutes. For clarity, the spectra of Mn$_3$O$_4$ and MnO$_2$ powders are included as dotted lines with as-deposited and OER samples, respectively.

Mn than in a MnO$_x$/GC sample. There is some evidence in literature that mixed valent MnO$_x$ catalysts have superior OER activity than pure MnO$_2$,\textsuperscript{42-44,47} with the effect explained by their higher level of disorder.\textsuperscript{43} Therefore, it is possible that Au contributes
indirectly to the high OER activity of composite structures consisting of both materials by favoring formation of the more active phase of MnO$_x$.

![Scanning electron microscopy (SEM) image of samples](image)

**Figure 6.5**: (a) Scanning electron microscopy (SEM) image of a sample with low concentration of manganese oxide (MnO$_x$) nanoparticles on a gold film (Au$_\text{film}$), (b) SEM image of a sample with high concentration of MnO$_x$ nanoparticles on Au$_\text{film}$, (c) cyclic voltammetry (CV) characterization comparing the oxygen evolution reaction (OER) activity of the samples with low and high concentration of MnO$_x$ on Au$_\text{film}$. CVs were collected in N$_2$ saturated 0.1 M KOH electrolyte, using 20 mV/s sweep rate, and 1600 rpm rotation rate.

To explore the role of MnO$_x$ in OER activity of composite catalysts consisting of MnO$_x$ and Au, we investigated the OER activity as a function of MnO$_x$ concentration. For this part of study, we prepared thin film Au substrates (Au$_\text{film}$) by sputter coating GC electrodes with a binding layer of titanium and 100 nm of Au. Two samples with different amount of MnO$_x$ nanoparticles were prepared on Au$_\text{film}$, forming MnO$_x$/Au$_\text{film}$ catalysts. The difference in concentration was confirmed using SEM characterization shown in Figure 6.5 (a) and (b). Although MnO$_x$ concentration in the two samples differs by more than two-fold, electrochemical characterization of the two samples depicted in
Figure 6.5 (c) reveals that they have the same OER activity on geometric basis. The catalytic performance of MnO$_x$/Au$^{\text{film}}$ catalysts is thus independent of MnO$_x$ concentration, suggesting that the phase of MnO$_x$ nanoparticles in the presence of Au does not solely determine the OER activity of composite samples consisting of both MnO$_x$ and Au.

In addition to possible influence of Au on the oxidation state of Mn, it is also possible that MnO$_x$ nanoparticles have an effect on the oxidation of the Au surface and its corresponding OER activity. Theoretical calculations of Nørskov and co-workers have proposed that on a gold surface, OER can only proceed after a sufficient potential has been applied to form 1/3 monolayer (ML) of adsorbed OH. Previous electrochemical characterization of gold surface identified two regions of gold oxidation: an initial oxidation in the region below 1 V vs. RHE$^{109,128-131}$ and a complete surface oxidation in the potential region beginning from 1.2 V vs. RHE. $^{109,125,129,130}$ The presence of OH atoms in the 0.8-1.2 V region has been confirmed by in-situ Raman spectroscopy$^{131}$ and the OH surface coverage has been quantified by Lecoeur and co-workers to be in the range of 10-20%. Therefore, if deposition of MnO$_x$ increases OH coverage on Au surfaces in the 0.8-1.2 V region, this could lead to an earlier onset of OER activity on Au surface.$^9$

Since sufficient surface oxidation is critical to the onset of OER on gold,$^9,125$ we electrochemically characterized the composite samples and the two controls in the potential region from 0.05 to 1.1 V to probe the effect of MnO$_x$ on the initial OH adsorption on Au surfaces. The CVs for the two composite structures, MnO$_x$/Au and Au/MnO$_x$, and the two control samples, MnO$_x$/GC and Au/GC, are shown in Figure 6.6.
Interestingly, the presence of MnO\textsubscript{x} in MnO\textsubscript{x}/Au and Au/MnO\textsubscript{x} samples is associated with an increase in the oxidation peak at 0.8-0.9 V, which has been previously linked to OH adsorption on Au surface by in-situ Raman experiments\textsuperscript{131}. Comparison to CVs of MnO\textsubscript{x}/GC and Au/GC, 10-fold magnification of which is shown in the inset of Figure 6.6, confirms that the observed peak is characteristic of Au and not MnO\textsubscript{x} surface. This result indicates that MnO\textsubscript{x} has an influence on the oxidation properties of Au surface and therefore may indirectly affect OER activity of composite catalysts consisting of MnO\textsubscript{x} and Au nanoparticles by changing the catalytic properties of Au.

![Figure 6.6: Cyclic voltammetry (CV) characterization in 0.05 to 1.1 V potential region of manganese oxide (MnO\textsubscript{x}) and gold (Au) nanoparticles deposited on glassy carbon (GC) support and composite structures consisting of both MnO\textsubscript{x} and Au on GC. CVs were performed in N\textsubscript{2} saturated environment in a potential region prior to onset of oxygen evolution reaction and bulk gold oxidation.](image)

Through a combination of ex-situ Mn L-edge XAS experiments and electrochemical characterization of OH adsorption on Au surface, we have shown that the superior OER activity of the composite electrodes consisting of MnO\textsubscript{x} and Au nanoparticles is associated both with formation of a mixed valent Mn (III)/Mn (IV) oxide under OER relevant potentials and an increase in initial Au surface oxidation in the region between 0.8-0.9 V. Future studies, which will combine DFT calculations with
spectroscopic characterization of Au surface, will focus on clarifying the precise contributions of MnO\textsubscript{x} and Au to the enhanced catalytic activity for the OER and on understanding the mechanism of the reaction.

6.5 Conclusions

In this study we investigated oxygen evolution reaction (OER) activity of catalysts consisting of manganese oxide (MnO\textsubscript{x}) and gold (Au) nanoparticles deposited on glassy carbon (GC) support using cyclic voltammetry in alkaline electrolyte. We found that the OER activity of composite catalysts consisting of both MnO\textsubscript{x} and Au is significantly higher than the OER activity of MnO\textsubscript{x} or Au alone. X-ray absorption spectroscopy characterization of the Mn L-edge indicated that the presence of Au has an effect both on the initial Mn oxidation state and the Mn oxidation state after exposure of the samples to OER conditions. Both composite structures were shown to be of mixed valent Mn (III)/Mn (IV) state after exposure to OER potentials, thereby linking the phase to high electrochemical activity for the reaction. Electrochemical characterization of catalysts with two different concentrations of MnO\textsubscript{x} deposited on a thin film of gold revealed little difference in geometric OER, shedding doubt on direct contributions of MnO\textsubscript{x} to the observed OER activity. Additional cyclic voltammetry characterization revealed that in composite catalysts consisting of MnO\textsubscript{x} and Au nanoparticles, MnO\textsubscript{x} influences OH adsorption properties of Au surfaces, resulting in greater initial OH adsorption in the 0.8-0.9 V potential region. This indirect effect of MnO\textsubscript{x} on Au properties may influence the OER activity of Au surface and result in enhanced catalytic turnover. Although future work is necessary to determine precise contributions of MnO\textsubscript{x} and Au to OER catalysis, these results warrant investigation of the effect of other metal
oxides on gold oxidation properties and highlight the importance of the support in catalytic activity of nanoparticulate electrodes.

6.6 Collaborations

Yelena Gorlin, Thomas F. Jaramillo, Chia-Jung Chung, and Bruce M. Clemens (BMC) conceived this study. Yelena performed scanning electron microscopy, x-ray absorption spectroscopy (XAS), and electrochemical measurements. Chia-Jung deposited MnO$_x$ nanoparticles. Jesse D. Benck prepared gold modified glassy carbon support and gold nanoparticles. Dennis Nordlund assisted with XAS data acquisition and was instrumental to XAS data normalization and interpretation.
Chapter 7

Mn$_3$O$_4$ Supported on Glassy Carbon: An Active Non-Precious Metal Catalyst for the Oxygen Reduction Reaction

7.1 Abstract

In this work, we explore the interplay between manganese oxide (MnO$_x$) nanomaterials and a glassy carbon (GC) support in catalyzing the oxygen reduction reaction (ORR) in an alkaline environment. Initially, we characterize the ORR activity of bare GC electrodes as a function of heat treatments in air, and find that ORR activity increases with increasing temperature up to 500°C. Modification of GC with size-selected 1 nm MnO$_x$ nanoparticles prior to the 500°C heat treatment yields a highly porous glassy carbon (pGC) structure, devoid of MnO$_x$. This pGC sample exhibits the highest ORR performance of the bare carbon electrodes reaching an onset potential of 0.75 V vs. the reversible hydrogen electrode (RHE) and a complete 2-electron reduction of oxygen to peroxide. Having established ORR activity of bare GC electrodes, we deposit size-selected 14 nm MnO nanoparticles onto the GC and pGC electrodes and then incite phase changes in MnO through heat treatments in air. Electrochemical characterization of the resulting electrodes reveals that MnO nanoparticles offer no
improvement in the ORR onset potential over bare GC or pGC and only slightly increase the number of electrons transferred. In contrast, thermal oxidation of MnO nanoparticles to Mn$_3$O$_4$ at 500°C, confirmed by Mn L-edge x-ray absorption spectroscopy, results in an improved ORR onset potential of 0.80 V and a complete 4-electron reduction of oxygen at higher overpotentials. Koutecky-Levich analysis reveals that the Mn$_3$O$_4$/pGC catalyst goes beyond the standard 2-electron oxygen reduction at 0.75 V, a potential at which bare GC or bare pGC do not display any appreciable ORR current. This result conclusively determines that at low overpotentials, MnO$_x$ sites contribute both to initial 2-electron reduction of oxygen to peroxide and subsequent peroxide disproportionation or further 2-electron reduction. The catalyst’s estimated specific activity of 3700 μA·cm$^{-2}$$_{\text{cat}}$ at 0.75 V compares favorably with specific activities of Pt/C as well as the best non-precious metal catalysts. This establishes Mn$_3$O$_4$ as another MnO$_x$ phase with high activity for the ORR.

### 7.2 Introduction

Chapter 1 has identified the oxygen reduction reaction (ORR) as an important reaction in the cathodes of fuel cells and metal-air batteries and manganese oxides (MnO$_x$) as promising catalysts for these applications. Out of the MnO$_x$ characterized for the ORR, gamma-MnOOH, alpha-Mn$_2$O$_3$, alpha-MnO$_2$, birnessite-MnO$_2$, and beta-MnO$_2$ have all been identified as high performing catalysts. Although the precise ORR mechanism on these MnO$_x$ catalysts is not yet known, the high activity of MnO$_x$ for peroxide disproportionation reaction may play a role in the observed MnO$_x$ activity for 4-electron reduction of oxygen. The ability of MnO$_x$ to catalyze peroxide disproportionation reaction is especially important if MnO$_x$ is combined with another material that is active for 2-electron reduction of oxygen to peroxide.
Carbon electrodes, the most common supports for the ORR catalysts in the cathodes of fuels and metal-air batteries,\textsuperscript{104} have long been recognized as materials with high intrinsic activity for the electro-reduction of oxygen to peroxide.\textsuperscript{104,134} Thus for MnO\textsubscript{x} catalysts supported on carbon, it is important to understand the roles of each material in catalyzing the ORR and the mechanistic pathways involved. Previous studies have linked the efficiency of the 2-electron reduction of oxygen on carbon both to the structure of the electrode and the various types of surface modifications.\textsuperscript{135-137} Among the various forms of carbon, glassy carbon (GC) electrodes are known to have higher ORR activity than ordered carbon surfaces such as highly oriented pyrolitic graphite, likely due to a higher concentration of undercoordinated sites or oxidized carbon sites on the surface of the GC.\textsuperscript{137} Modifications of the carbon surface through cleaning,\textsuperscript{135,138,139} anodic polarization,\textsuperscript{137,140,141} fracturing,\textsuperscript{137} and heat treatment at reduced pressure\textsuperscript{99,137} is associated with a further improvement in the overpotential for the ORR, while exposure to atmosphere and electrolyte solutions leads to a gradual deactivation of the carbon surface.\textsuperscript{135,138,142}

In our work, we explored the ORR activity of bare glassy carbon and glassy carbon supported MnO\textsubscript{x} electrodes as a function of heat treatments in air over a range of temperatures. Since previous studies have linked improvements in ORR activity of GC to heat treatment of the electrode at reduced pressure,\textsuperscript{99,138} but identified exposure of GC to air as a contributing factor in deactivation of the electrode,\textsuperscript{135,142} we initially focused on understanding the effect of thermal oxidation on the electrochemical activity of bare GC. After establishing the background ORR activity of thermally oxidized bare GC electrodes, we deposited MnO\textsubscript{x} nanoparticles onto various GC electrodes, manipulated
the MnOx oxidation state through heat treatments in air, and then studied their activity for
the ORR. Aiming to correlate the oxidation state of Mn in MnOx on GC with the ORR
activity of the electrodes, we investigated the Mn valency using ex-situ Mn L-edge x-ray
absorption spectroscopy in addition to conventional ex-situ x-ray photoelectron
spectroscopy characterization. Our experiments identified Mn3O4 as a MnOx phase with
4-electron oxygen reduction activity for the ORR and an estimated specific activity of
3700 μA·cm⁻² at 0.75 V vs. the reversible hydrogen electrode, a value that is extremely
competitive with the best precious metal and non-precious metal catalysts for the ORR in
base.

7.3 Experimental Section

7.3.1 Preparation of Glassy Carbon Supports

Glassy carbon (GC) electrodes, polished to a surface roughness of less than 50
nm (0.196 cm², SigradurG), were purchased from HTW Hochtemperatur-Werkstoffe
GmbH and subsequently heated in a quartz tube furnace (Mellen Company SC13) for 10
hours at temperatures ranging from 250°C to 500°C. Five different types GC electrodes
were subsequently characterized: polished GC and GC after heat treatment at 250°C,
350°C, 450°C, and 500°C.

7.3.2 Synthesis of Nanoparticles

MnOx nanoparticles were produced with a sputtering system (Nanosys500, Mantis
Deposition Ltd.) using the inert gas condensation technique. The details of the
deposition chamber are presented in Chapter 6 (6.3.2 Synthesis of Catalytic Materials). In
this study, Mn nanoparticles were size selected at approximately 10 nm and 1 nm and
deposited with a rate of either 0.16 Å·sec\(^{-1}\) or less than 0.01 Å·sec\(^{-1}\), monitored by a Quartz Crystal Microbalance (QCM). After deposition, samples were transferred to the load lock chamber and vented with Ar. To modify the oxidation state of the nanoparticles, a subset of manganese oxide nanoparticles was heat treated for 10 hours in air at 500°C in a quartz tube furnace (Mellen Company SC13).

7.3.3 Physical and Chemical Characterization of Nanoparticles

Size and morphology of the MnO\(_x\) nanoparticles and GC support were determined using scanning electron microscopy (SEM, FEI Magellan 400XHR). The images were obtained using a secondary electron detector, a beam current of 25 pA, and beam voltage of 5 kV. The oxidation state of the MnO\(_x\) nanoparticles was characterized using ex-situ x-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) and ex-situ x-ray absorption spectroscopy (XAS, Stanford Synchrotron Radiation Lightsource). Monochromatized Al Ka 1486.6 eV x-rays were used to collect high resolution Mn 3s and C 1s x-ray photoelectron spectra on the samples and four MnO\(_x\) powder standards (MnO, Mn\(_3\)O\(_4\), Mn\(_2\)O\(_3\), MnO\(_2\); Sigma-Aldrich). Prior to collecting spectra on MnO, the powder was sputtered to remove the oxidized surface known to form on MnO in air.\(^{65}\) All spectra were calibrated to 285.0 eV, the line position of adventitious carbon.\(^{86}\) To acquire the spectra, a pass energy of 23.5 eV, an energy step of 0.1 eV, and a time of 20 ms per step were used; the corresponding resolution of the XPS measurement was 0.6 eV. Oxidation state of the MnO\(_x\) nanoparticles was monitored using the relative the magnitude of the 3s multiplet splitting (\(\Delta E_{3s}\)), previously shown to provide information on the oxidation state of Mn.\(^{55,56}\) If necessary, XPS survey scan was performed from 0 to 1400 eV, using a pass energy of 117.4 eV, an energy step of 1 eV, and a time of 20 ms per step.
Ex-situ XAS measurements were performed on the 31-pole wiggler beamline 10-1 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 350 mA and a 1000 l·mm⁻¹ spherical grating monochromator with 40 μm entrance and exit slits, providing ~10¹¹ ph·s⁻¹ at 0.3 eV resolution in a 1 mm² beam spot. All data were acquired in a single load at room temperature and under ultra-high vacuum (10⁻⁹ torr) in total electron yield (TEY) mode, where the sample drain current was normalized by the current from freshly evaporated gold on a thin grid positioned upstream of the sample chamber. The measurements were performed on MnOₓ nanoparticles and three powder standards (Mn₃O₄, Mn₂O₃, MnO₂; Sigma-Aldrich) attached to an aluminum sample holder using conductive carbon. XAS spectra were not collected on the MnO powder because of surface oxidation in air during sample preparation. The energy was carefully calibrated in two steps, as described previously in Chapter 4 (4.3.7. Normalization of XAS Spectra). Briefly, we first corrected the energy scale for the drift in the beam energy and then aligned the energy of the first peak of the Mn₃O₄ powder control with a literature value of 639.6 eV. To normalize all data, we fit a linear background to the spectra of the samples using the following two constraints: the area from 636 eV to 660 eV was specified to be the same in every spectrum and the edge jump in the 660 eV to 665 eV region of each spectrum was fixed to match the edge jump of MnO₂ powder standard.

7.3.4 Electrochemical characterization

The electrochemical activities for the ORR of GC supports and MnOₓ nanoparticles were evaluated using cyclic voltammetry (CV) in a three electrode electrochemical cell in a rotating disk electrode configuration. CVs were collected in 0.1
119

M potassium hydroxide (KOH) electrolyte using a carbon rod counter electrode and Ag|AgCl reference electrode. The electrolyte was prepared from high purity KOH pellets (Sigma-Aldrich, 99.99%) and Millipore water. All CVs were iR-compensated to 85% during the measurements and performed at room temperature (25°C), 1600 revolutions per minute (rpm) rotation rate, and a sweep rate of 20 mV·s⁻¹. The potential scale was calibrated to a reversible hydrogen electrode (RHE), and all potentials are reported vs. RHE. RHE calibration was performed at the end of each characterization in a hydrogen saturated electrolyte with platinum catalyst at the working electrode. The potential at which the current crossed zero, which was approximately 0.960 V in all of the experiments, was taken to be the thermodynamic potential for the hydrogen electrode reactions. Oxygen reduction reaction activities were measured in oxygen saturated electrolyte in the potential region between 0.05 V and 1.1 V. Multiple cycles of cyclic voltamograms were recorded for each catalytic material and a representative CV is shown for each catalyst.

The ORR activities of GC electrodes and MnOₓ nanoparticles were compared to ORR activity of platinum nanoparticles supported on a high surface area carbon (46 wt% Pt/C, Tanaka Kikinzoku Kogyo). Pt/C catalyst inks were prepared using a standard procedure for fuel cell catalyst testing. Briefly, 11.9 μg of Pt/C was ultrasonically dispersed in 6 ml of Millipore water, 4 ml of isopropanol, and 40μl of nafion solution (5 wt%, Sigma-Aldrich), to achieve a concentration of 1.2 mgpt·μl⁻¹. 10 μl of the catalyst ink was dropcast onto a GC disk mounted into inverted RDE system, as recommended by Garsany and co-authors, and dried for 45 min at 700 rpm to achieve a high quality Pt/C film on GC with a platinum loading of 28 μg·cm⁻² on geometric surface area basis. The
ORR activity of the resulting catalyst was characterized using the procedure described above.

To determine the number of electrons transferred during the ORR on MnO$_x$ catalyst heat treated at 500°C, Koutecky-Levich analysis was carried out. For the analysis, CVs were performed in an oxygen saturated environment under experimental conditions described above at 400, 900, and 1600 rpm rotation rates. The inverse of the measured current was plotted versus the inverse square root of the rotation rate at three potential values: 0.6 V, 0.70 V, and 0.75 V. The number of electrons, n, transferred during the reaction was extracted from the slope of the resulting plots using equation 7.1

\[
slope = \frac{1}{0.62nFD_O^2v^{-1/6}C_O^2}
\]

where F is Faraday's constant in mA·s·mol$^{-1}$, $D_O$ is the diffusion coefficient of oxygen in cm$^2$·s$^{-1}$, $v$ is the kinematic viscosity in cm$^2$·s$^{-1}$, $C_O$ is the solubility of oxygen in mol·cm$^{-3}$, and $w$ is the rotation rate of the rotating disk electrode in rad·s$^{-1}$. In 0.1 M KOH electrolyte at room temperature (25°C), $D_O$, $v$, and $C_O$ are 1.85·10$^{-5}$ cm$^2$·s$^{-1}$, 1.21·10$^{-6}$ mol·cm$^{-3}$. 7.4 Results and Discussion

To investigate the effect of thermal oxidation on the electrochemical activity of bare glassy carbon (GC) electrodes, we heat treated GCs at 250°C, 350°C, 450°C, and 500°C in air. The morphology of the disks prior to heat treatment and after these heat treatments is shown in Figures 7.1 (a)–(e). Only subtle changes in the surface morphology are observed up to and including 450°C. After heat-treatment at 500°C the
surface visibly roughens to form craters in the GC due to corrosion of carbon and evolution of CO and CO$_2$ gases.$^{99,100}$ We found that addition of catalytic material onto GC prior to heat treatment resulted in even greater corrosion of the electrode. Specifically, deposition of ~1 nm manganese oxide (MnO$_x$) nanoparticles and subsequent heat treatment at 500°C produced significant gas evolution from the surface, forming a highly porous carbon morphology shown in Figure 7.1 (f). X-ray photoelectron spectroscopy (XPS) characterization of this particular surface revealed that no MnO$_x$ was left on the surface, as shown in Figure 7.2. We will refer to this particular form of heat-treated carbon, as porous GC (pGC).

![Figure 7.1: SEM images demonstrating morphologies of polished glassy carbon (GC) disks subjected to different heat treatments: (a) no heat treatment, (b) 250°C, (c) 350°C, (d) 450°C, (e) 500°C, (f) GC heat treated at 500°C after having deposited 1 nm MnO$_x$ nanoparticles to form porous GC (pGC).](image)

Electrochemical activity of the bare GC supports for the oxygen reduction reaction (ORR) measured in an oxygen-saturated 0.1 M KOH electrolyte at 1600 rpm is shown in Figures 7.3 (a) and 7.3 (b). Figure 7.3 (a) shows that the catalytic activity
improved with increasing heat treatment temperature up to 450°C, as noted by the decrease in overpotential required for the electro-reduction of oxygen to peroxide. For the sample heat treated at 450°C, the electrode demonstrated close to complete 2-electron reduction to OOH$^-$. by reaching the expected diffusion limited current of 2.9 mA/cm$^2$ (see Appendix G for the calculation of the theoretical diffusion limited current). GC surfaces with visibly roughened morphologies due to heat treatment at 500°C, both with and without the addition of a small amount of MnO$_x$ prior to heating, exhibit similar activities to the catalyst heat treated at 450°C, as observed in Figure 7.3 (b). At about 0.35 V, all carbon surfaces show an onset of another reduction process, likely corresponding to subsequent 2 e$^-$ conversion of peroxide to water.$^{35}$ The favorable effect of thermal oxidation on the ORR activity of GCs was consistent with previous studies that had reported an improvement in both the onset potential and the number of electrons transferred on electrochemically oxidized GCs.$^{137,140,141}$

![Survey X-ray photoelectron spectroscopy scan of a porous glassy carbon (pGC) substrate, illustrating the absence of MnO$_x$ by means of negligible intensity in Mn 2p region. The pGC surface was generated by the deposition of 1 nm MnO$_x$ nanoparticles on a polished GC followed by heat treatment in air at 500°C.](image)

**Figure 7.2:** Survey X-ray photoelectron spectroscopy scan of a porous glassy carbon (pGC) substrate, illustrating the absence of MnO$_x$ by means of negligible intensity in Mn 2p region. The pGC surface was generated by the deposition of 1 nm MnO$_x$ nanoparticles on a polished GC followed by heat treatment in air at 500°C.

After characterization of the baseline ORR activity of the various GC electrodes, size-selected MnO$_x$ nanoparticles of approximately 14 nm in diameter were deposited
Figure 7.3: Cyclic voltammograms of various GC electrodes and Pt/C nanoparticles obtained in oxygen saturated 0.1 M KOH electrolyte, at 20 mV·s⁻¹ sweep rate, and 1600 rpm rotation rate. (a) Comparison of ORR activities of GC electrodes as a function of heat-treatment temperature demonstrates an increase in ORR activity as the temperature increases to 450°C. (b) Further increase in temperature to 500°C and the formation of the porous GC (pGC) morphology results in little change in ORR activities with GCs showing significantly lower onset potential and diffusion limited current than Pt/C nanoparticles.

Figure 7.4: SEM images demonstrating the morphologies of MnOₓ on GC and pGC disks: (a) as-deposited size-selected 14 nm MnOₓ nanoparticles on GC, (b) as-deposited 14 nm MnOₓ nanoparticles on pGC, (c) agglomerated MnOₓ nanoparticles on pGC after a heat treatment at 500°C. onto either GC or pGC and further processed to form the following set of samples: (1) as deposited MnOₓ catalyst on GC, (2) as-deposited MnOₓ catalyst on pGC and (3) an MnOₓ catalyst deposited onto GC and subsequently heat treated at 500°C. The 500°C heat treatment was expected to induce a phase change in the MnOₓ catalyst as well as a morphological change in the carbon support to form pGC. SEM images of these three samples are shown in Figures 7.4 (a), (b), and (c), respectively. Figures 7.4 (a) and 7.3 (b) show that with no heat treatment the MnOₓ nanoparticles were well dispersed (i.e.
minimal agglomeration) on both the GC and the pGC supports, respectively. A surface coverage of approximately 12% was determined for these two samples. For the third sample, which underwent the 500°C heat treatment, the MnO\textsubscript{x} nanoparticles had agglomerated substantially, forming thin-film like particles several hundred nm wide as observed in Figure 7.4 (c). Since a sample with smaller MnO\textsubscript{x} nanoparticles of 1 nm diameter resulted in a structure devoid of all manganese oxide after the same heat treatment, it is likely that some MnO\textsubscript{x} material of the 14 nm size-selected clusters was lost during the heating step.

The oxidation state of Mn in the three samples was first studied using \textit{ex-situ} XPS. Mn 3s XPS spectra of four well-defined powder standards (MnO, Mn\textsubscript{3}O\textsubscript{4}, Mn\textsubscript{2}O\textsubscript{3}, and MnO\textsubscript{2}) as well as the three MnO\textsubscript{x}/GC samples are shown in Figures 7.5 (a) and 7.5 (b), respectively, plotted on a binding energy scale relative to the low binding energy multiplet. The magnitude of the 3s multiplet splitting (\(\Delta E_{3s}\)) in the Mn XPS spectra of powder standards decreased from 6.0 eV to 4.5 eV as the oxidation state increased from Mn(II) of MnO to Mn(IV) of MnO\textsubscript{2}, in agreement with the reported \(\Delta E_{3s}\) splitting as a function of formal valence.\textsuperscript{55,56} Both the as-deposited MnO\textsubscript{x}/GC sample and the as-deposited MnO\textsubscript{x}/pGC sample exhibited \(\Delta E_{3s}\) multiplet splittings of 6.2 eV, consistent with MnO. This suggests that MnO is the native form of MnO\textsubscript{x} produced by the cluster source in the 14 nm size regime. Heat-treatment of the MnO nanoparticles resulted in a decrease in the splitting value from about 6.2 eV to about 5.5 eV, indicating an increase in the oxidation state from Mn (II) to a valency closer to 3+,\textsuperscript{147} but detailed information on the oxidation state and coordination could not be extracted using XPS results. To better understand the catalyst structure, we turned to synchrotron methods, specifically XAS.
Mn L-edge XAS is a sensitive probe of Mn oxidation state and coordination. In Figure 7.5 (c) we show Mn L-edge XAS spectra of the three reference powder samples (MnO₂, Mn₂O₃, and Mn₃O₄) measured in our study as well as that of MnO, a sputtered sample without any oxidized surface contribution, reproduced from Gilbert et al. (shifted by 0.5 eV). The four different types of MnOₓ have distinct L-edge spectra, allowing for a straightforward differentiation between possible oxidation
states of MnOx. As observed in Figure 7.5 (d), the spectrum of the heat treated sample is in excellent agreement with the spectrum of Mn3O4 powder, while the spectra of the as-deposited nanoparticles on GC and pGC are nearly identical to the spectrum of MnO by Gilbert et al.,22 revealing a Mn (II) oxidation state with a very small surface oxidation contribution. Ex-situ XAS measurements thus confirm the oxidation of the nanoparticles during the heat treatment at 500°C and elucidate the specific starting and ending phases as MnO and Mn3O4, respectively. It is worthy to note that for bulk MnOx, the expected phase at 500°C in air is alpha-Mn2O3 and not Mn3O4.56,150 MnOx phase behavior, however, has been previously shown to be size-dependent, with smaller particles favoring the formation of Mn3O4, the phase with a lower surface energy.151 Thus, the observed formation of Mn3O4 at 500°C can be explained in part the nanoparticulate nature of the sample.

The ORR activities of the three carbon-supported MnOx samples are shown in Figure 7.6 (a) along with ORR activities of bare GC, bare pGC, and the Tanaka Pt/C catalyst for comparison. The MnO/GC and MnO/pGC samples offer little, if any, improvement in the ORR activity over the baseline activities of their respective bare carbon surfaces. More specifically, in the kinetic region the ORR current densities of the MnO/GC and MnO/pGC samples overlap those of their respective bare carbon surfaces, while in the diffusion limited region only a slight enhancement in the ORR current is observed. This result is consistent with previous literature studies that have not observed greater than 2-electron reduction of oxygen on MnO.38,152 Thermal oxidation of MnO nanoparticles to Mn3O4 and concomitant conversion in carbon morphology to pGC results in a significant improvement in ORR activity, as measured by a 50 mV decrease
in the overpotential for O₂ reduction and an increase in diffusion limited current to 5.7 mA/cm², the theoretical diffusion limited current for 4-electron reduction of oxygen (see Appendix G for calculation details).

Figure 7.6: (a) Cyclic voltammograms of six samples: MnO/GC, MnO/pGC, Mn₃O₄/pGC, bare GC, bare pGC, and nanoparticulate Pt/C, all measured in oxygen saturated 0.1 M KOH electrolyte, at a 20 mV·s⁻¹ sweep rate and 1600 rpm rotation rate. (b) Koutecky-Levich analysis of Mn₃O₄/pGC catalyst demonstrates an increase in the number of electrons transferred with an increase in applied potential. (c) Tafel plots of kinetic current density for MnO/pGC, Mn₃O₄/pGC, and Pt/C constructed after correcting the potential for uncompensated ohmic losses and capacitive current obtained in N₂ scans and removing mass-transport losses from the measured current. (d) Normalization of Tafel plots by estimated surface areas of Mn₃O₄ and Pt to determine specific activities of the catalysts as a function of applied potential.

Koutecky-Levich analysis of ORR on Mn₃O₄/pGC, shown in Figure 7.6 (b), demonstrates that initially, the reaction proceeds predominantly through 2-electron reduction of O₂ to OOH⁻, involving approximately 2.9 electrons at 0.75 V. As the overpotential increases, the number of electrons involved in the reduction of oxygen also
increases, until it reaches the theoretical limit of 4. The significant improvement both in
the onset potential and the number of electrons transferred displayed by Mn$_3$O$_4$/pGC over
the bare pGC substrate demonstrates that the Mn$_3$O$_4$ phase has high activity for the ORR.
Several research groups have previously investigated the activity of Mn$_3$O$_4$ for the
ORR, demonstrating that the catalyst is capable of reaching between 2
and 3-electron reduction of oxygen both on gold$^{76}$ and carbon$^{38,46,123}$ supports, with onset
potentials of 0.75-0.85 V$^{35,38,46,76,123,155}$. A recent theoretical study, detailed in Appendix
C, has also predicted Mn$_3$O$_4$ to be among active MnO$_x$ phases for the 4-electron
reduction of oxygen with ORR activity similar to that of beta-MnO$_2$ and alpha-Mn$_2$O$_3$.
Our Mn$_3$O$_4$/pGC catalyst matches the previously reported onset potentials for the ORR
and, for the first time, demonstrates a complete 4-electron reduction of oxygen on a
Mn$_3$O$_4$ phase.

To gain a better understanding of the kinetics of the ORR on MnO/pGC and
Mn$_3$O$_4$/pGC, Tafel plots were constructed by plotting the logarithm of the kinetic current
vs. the iR-corrected potential for the two MnO$_x$ catalysts and Pt/C nanoparticles. To
extract kinetic current of the catalytic materials, several corrections were applied to the
ORR CVs. First, the potential was compensated for the remaining 15% of ohmic
resistance of the electrolyte, which was approximately 40 Ω for all samples. Second, the
ORR CVs were adjusted for capacitive contributions using N$_2$ scans, shown in Figure 7.7,
obtained in the same potential window and under the same conditions as the ORR CVs.
The kinetic current was then calculated by correcting for mass transport losses using
equation 7.2,

$$\frac{1}{i_m} = \frac{1}{i_k} + \frac{1}{i_d}$$

(7.2)
where $i_m$ refers to the measured current in the ORR CV in anodic direction corrected for ohmic resistance and capacitance current, $i_k$ refers to the kinetic current, and $i_d$ refers to the diffusion limited current obtained experimentally. As seen in Figure 7.6 (c), the Mn$_3$O$_4$/pGC catalyst has the same Tafel slope of 80 mV·decade$^{-1}$ as Pt/C nanoparticles, while MnO/pGC has a slightly larger Tafel slope of 90 mV·decade$^{-1}$. The calculated kinetic current was normalized by the estimated surface areas of Mn$_3$O$_4$ and Pt to calculate specific activities of the two catalysts. The upper bound value of the surface area of Mn$_3$O$_4$ catalyst was estimated to be 0.1 cm$^2$ from SEM images of the nanoparticles prior to heat treatment. We stress that this value is an upper bound, as after the heat treatment the particles have agglomerated and will likely have substantially lower surface area than the starting nanoparticles.

![Cyclic voltammograms (CVs) obtained in nitrogen saturated 0.1 M KOH electrolyte, at 20 mV·s$^{-1}$ sweep rate, and 1600 rpm rotation rate.](#)

**Figure 7.7**: Cyclic voltammograms (CVs) obtained in nitrogen saturated 0.1 M KOH electrolyte, at 20 mV·s$^{-1}$ sweep rate, and 1600 rpm rotation rate.

The surface area of Pt/C nanoparticles was calculated to be 2.65 cm$^2$ using an established procedure which involves the measurement of the charge from the electrochemical hydrogen underpotential deposition (HUPD) and then determining the electrochemically active surface area based on 210 μC·cm$^{-2}$ Pt.$^{1,156}$ The details of the
surface area calculations are provided in Appendix H. The resulting specific activity, shown in Figure 7.6 (d), and the corresponding mass activity plots, presented in Appendix H, demonstrate that the ORR activity of Mn₃O₄/pGC catalyst, with a loading of 0.1 μg·cm⁻² (1.4 nmol·cm⁻²), compares favorably with the ORR activity of the Pt/C catalyst, despite the later ORR onset potential of Mn₃O₄/pGC. Considering that a higher loading of 3.5 μg·cm⁻² (17.9 nmol·cm⁻²) is necessary for platinum in nanoparticulate Pt/C catalysts to achieve 4-electron reduction of oxygen in a RDE configuration,¹⁵⁷ the ability of the Mn₃O₄/pGC to catalyze the 4-electron reduction of oxygen is exceptional. The outstanding ORR performance of the Mn₃O₄/pGC catalyst is further evidenced by comparing its specific activity of 3700 μA·cm⁻²_cat and the corresponding mass activity of 3100 A·g⁻¹_cat, both measured at 0.75 V, to the best reported MnOₓ catalysts (Table 7.1)³⁶⁻³⁸,⁴⁶,⁷⁶,⁸²,¹³² and the best non-noble metal catalysts reported in literature.¹⁸ The specific activity of the Mn₃O₄/pGC catalyst at 0.75 V vs. RHE is 1-2 orders of magnitude higher than the specific activities of the majority of high-performance manganese oxide and perovskite ORR catalysts and is of the same order of magnitude as the best reported non-precious metal catalysts in alkaline media, LaMnO₃⁺δ and LaNiO₃.¹⁸

<table>
<thead>
<tr>
<th>Catalytic phase</th>
<th>Specific Activity (μA·cm⁻²_cat)</th>
<th>Mass activity (A·g⁻¹_cat)</th>
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</thead>
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<tr>
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<td>3100</td>
</tr>
<tr>
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<td>N/A</td>
<td>2</td>
</tr>
<tr>
<td>alpha-Mn₂O₃ on GC⁸²</td>
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<td>N/A</td>
</tr>
<tr>
<td>alpha-MnO₂ on GC¹³²</td>
<td>N/A</td>
<td>4</td>
</tr>
<tr>
<td>birnessite-MnO₂/graphite⁷⁷</td>
<td>N/A</td>
<td>2</td>
</tr>
<tr>
<td>beta-MnO₂/C on GC²⁸</td>
<td>N/A</td>
<td>3000</td>
</tr>
</tbody>
</table>

Having established the outstanding ORR activity of the Mn₃O₄/pGC catalyst, we turn our attention to mechanistic possibilities for oxygen reduction on this electrode. The
overall 4-electron oxygen reduction reaction in basic electrolyte is shown in equation 7.3. This can be achieved by a direct pathway or a series pathway involving a peroxide intermediate.\textsuperscript{104} The direct pathway proceeds through a sequence of steps such that all four electron transfers of Equation 7.3 occur on the same catalytic site. In the series pathway, there is an initial 2-electron reduction of oxygen to peroxide (equation 7.4), likely proceeding in two distinct electron transfer steps (not shown), followed by one of two possibilities: either a 2-electron reduction step of peroxide to water (equation 7.5a) or the peroxide disproportionation reaction (equation 7.5b) that produces O\textsubscript{2} in half the original amount via a chemical and not electrochemical step. This $\frac{1}{2}$O\textsubscript{2} is subsequently reduced back to peroxide with equations 7.4 and 7.5b cycled repeatedly until reaching a theoretical limit of an overall 4-electron process [(2 + $\frac{1}{2}$ + $\frac{1}{4}$ + · · · $\approx$ 4)] e\textsuperscript{−} as the number of cycles tends to infinity.\textsuperscript{104} In the series pathway, it is plausible that two completely different catalytic sites can participate in the reactions 7.4 and 7.5a/5b.

\begin{align*}
O_2 + 2H_2O + 4e^- &\rightarrow 4OH^- \\
O_2 + H_2O + 2e^- &\rightarrow OO^- + OH^- \\
OOH^- + H_2O + 2e^- &\rightarrow 3OH^- \\
OOH^- &\rightarrow \frac{1}{2}O_2 + OH^-
\end{align*}

While the subject of ORR mechanisms on MnO\textsubscript{x} based catalysts is still being explored, several research groups have proposed a series pathway consisting of reactions 7.4 and 7.5b as the likely mechanism.\textsuperscript{35,36,38,46,76,104} In this particular pathway, reaction 7.4 has been shown to occur either on the electrode support onto which MnO\textsubscript{x} is deposited, such as carbon or gold,\textsuperscript{35,76,133} or on Mn (IV)/Mn (III) sites of MnO\textsubscript{x},\textsuperscript{38,158} while the catalytic activity for reaction 7.5b has been attributed to MnO\textsubscript{x}.\textsuperscript{1,4,6,9,38,39} In our work on
the Mn$_3$O$_4$/pGC catalyst, we recognize that at potential cathodic of 0.75 V, the exposed bare sites of the pGC support will likely contribute catalytically to the initial 2-electron reduction since a bare porous GC electrode demonstrated high activity for 2-electron reduction of oxygen at these potentials. At potential of 0.75 V, where no appreciable current is yet observed on a bare pGC electrode, the confirmed 2.9 electron oxygen reduction on the Mn$_3$O$_4$/pGC catalyst indicates that in this potential region MnO$_x$ sites must be involved in all steps of the reaction, irrespective of the pathway. We note, however, that the pGC support could still be contributing to the observed catalytic activity in other, indirect ways, for instance by tuning the electronic or geometric structure of the MnO$_x$, or perhaps through a bi-functional mechanism where atomically adjacent MnO$_x$ and C sites participate in turning over an adsorbed molecule at that particular interface. Further experiments, which investigate the effect of surface coverage by Mn$_3$O$_4$, could provide information on the role of pGC in producing high catalytic activity.

The morphology of the GC support could also play a critical role in producing the exceptional catalytic activity observed on this Mn$_3$O$_4$/pGC catalyst. For example, the porous electrode may trap peroxide intermediates and thus, facilitate the disproportionation pathway.$^{159,160}$ This could potentially be probed in a future study by quantifying the amount of peroxide formed as a function of the porosity of the GC support, assuming that the same Mn$_3$O$_4$ phase and morphology can be maintained. As porous carbon is a common support material both in fuel cells and metal-air batteries,$^{104}$ further study of the contribution of pGC to the ORR activity of Mn$_3$O$_4$ phase could aid in the design of active electrodes for energy storage and energy conversion technologies.
7.5 Conclusions

In this work, we investigated the interplay between manganese oxide (MnO₅) and glassy carbon (GC) supports in catalyzing the oxygen reduction reaction (ORR) in alkaline media. We studied the ORR activity of thermally oxidized bare GC electrodes, which formed a highly porous structure (pGC) under certain preparation conditions, as well as that of MnO₅/GC and MnO₅/pGC electrodes to probe the effects of MnO₅ phase and GC morphology. We demonstrated that heat treatment of bare glassy carbon in air at 500°C resulted in an improvement in ORR onset potential from 0.70 V to 0.75 V and a complete 2-electron reduction of oxygen to peroxide. Among the various MnO₅/GC and MnO₅/pGC catalysts studied, we found that size-selected MnO nanoparticles of 14 nm diameter did not improve the onset potential for the reaction beyond that of what was expected from the bare carbon supports, and only slightly increased the number of electrons transferred in the diffusion limited current region. However, upon thermal oxidation the MnO nanoparticles were converted to Mn₃O₄, confirmed by L-edge x-ray Absorption Spectroscopy (XAS), along with concomitant conversion of the carbon support to pGC. The resulting Mn₃O₄/pGC electrode exhibited a significant enhancement in catalytic activity. The onset potential improved to 0.80 V and a complete 4-electron reduction of oxygen was observed. At 0.75 V, the Mn₃O₄/pGC catalyst’s measured specific and mass activities of 3700 μA·cm⁻²cat and 3100 A·g⁻¹cat represent an extremely high performing catalyst; these values compare favorably to those of the best non-noble metal catalysts and even to that of a state-of-the-art nanoparticulate Pt/C catalyst. To understand the ORR pathway on Mn₃O₄/pGC we employed Koutecky-Levich analysis. Our analysis revealed that the Mn₃O₄/pGC catalyst achieves 2.9 electron oxygen
reduction at 0.75 V, a potential at which the bare GC electrode did not display any appreciable ORR current. This indicates that at low overpotentials, MnO\textsubscript{x} sites must participate in all steps of the reaction. Our electrochemical results in combination with ex-situ L-edge x-ray absorption spectroscopy characterization establish Mn\textsubscript{3}O\textsubscript{4} as MnO\textsubscript{x} phase with high activity for the ORR.

### 7.6 Collaborations

Yelena Gorlin, Thomas F. Jaramillo, Chia-Jung Chung, and Bruce M. Clemens conceived this study. Yelena performed electrochemical measurements, scanning electron microscopy, x-ray photoelectron spectroscopy, and x-ray absorption spectroscopy characterization. Chia-Jung deposited MnO\textsubscript{x} nanoparticles and assisted with XAS measurements and data interpretation. Dennis Nordlund assisted with XAS data acquisition and was instrumental to data normalization and interpretation.
Chapter 8

Conclusions

This dissertation discussed synthesis of manganese oxide (MnO\textsubscript{x}) catalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) on glassy carbon and gold supports. The surfaces of the resulting catalysts were characterized using spectroscopic techniques, including \textit{ex-situ} X-ray photoelectron spectroscopy (XPS), \textit{ex-situ} Mn L-edge X-ray absorption spectroscopy (XAS), and \textit{in-situ} Mn K-edge XAS to find that both the underlying support and the preparation route of MnO\textsubscript{x} have an influence on the starting surface oxidation state of Mn in MnO\textsubscript{x} and the surface oxidation state at reaction conditions.

In the case of MnO\textsubscript{x} electrodeposited on glassy carbon, we found an increase in heat treatment temperature corresponded to eventual formation of Mn (III) oxide at temperatures above 450°C. The catalyst maintained the Mn (III) state at both the ORR and the OER potentials and exhibited high catalytic activity for both reactions. MnO\textsubscript{x} heat treated at lower temperatures, however, showed changes in Mn oxidation state as a function of potential and had a much lower catalytic activity for the two reactions.

Electrodeposition of MnO\textsubscript{x} on gold deposited on silicon nitride window and subsequent heat treatment at temperatures above 450°C resulted in formation of a different phase than on glassy carbon – a mixture of Mn\textsubscript{3}O\textsubscript{4} and MnO\textsubscript{2}. Furthermore, the oxidation state of Mn changed significantly with changes in reaction conditions, first reducing to Mn\textsubscript{3}O\textsubscript{4} at an ORR potential of 0.7 V vs. the reversible hydrogen electrode.
(RHE) and then oxidizing to a 3:2 mixture of MnO₂ to Mn₃O₄ at an OER relevant potential of 1.8 V vs. RHE, while displaying high catalytic activity for both reactions.

Synthesis of composite structures consisting from MnOₓ and gold nanoparticles on glassy carbon electrode demonstrated that both MnOₓ and gold have an effect on the surface oxidation properties of the other component. Investigation of the OER activity to as a function of MnOₓ coverage showed that the OER current was independent of MnOₓ concentration, indicating that MnOₓ alone is not responsible for the observed high OER activity.

Deposition of MnOₓ nanoparticles on glassy carbon followed by heat treatment at 500°C revealed formation of Mn₃O₄ phase with high geometric activity for the ORR, despite the low loading of MnOₓ. Investigation of the ORR activity of the bare glassy carbon electrodes before and after a series of heat treatment conditions confirmed that the observed activity was associated with formation of Mn₃O₄ phase and could not be explained by the changes in the activity of the bare support alone.

These results identify important areas for future research. Demonstration of bifunctional activity of MnOₓ for the ORR and the OER makes them interesting catalytic systems. Future investigation of MnOₓ surfaces with and without bifunctional activity for the two reactions will deepen the understanding of the particular structural properties that are involved in oxygen electrocatalysis and contribute to the eventual development of catalysts which approach the behavior of an ideal reversible oxygen electrode. The demonstration of the influence of the support and the preparation route on the oxidation state under reaction conditions highlights the complexity of the catalyst design in the search of an ideal reversible oxygen electrode. When correlating a specific phase to
electrocatalytic activity of the surface, special attention should be paid to the preparation history of the electrode and the influence of the underlying support to the catalytic activity. It is also important to not only understand the active surfaces under reaction conditions, but also study the mechanism of the ORR and the OER on MnO$_x$ based catalysts. These studies will aid in understanding of the specific contributions of MnO$_x$ and other components, such as glassy carbon or gold, to catalytic activity for the ORR and the OER and lead to rational design of active catalytic materials.
Appendix A

Relevance of the Oxygen Evolution Reaction Activity Metric

In the area of solar fuels, the energy of solar radiation is utilized to drive red-ox reactions for the synthesis of fuels. For example:

\[ 2H^+ + 2e^- \rightarrow H_2 \ (E^0 = 0.00 \text{ V/RHE}), \text{ or} \]
\[ CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \ (E^0 = +0.05 \text{ V/RHE}) \]

For large scale solar fuel synthesis, it has been suggested that water oxidation is the ideal source of the protons and electrons needed for the fuel-synthesis (reduction) reactions above, as water is inexpensive and abundant.\textsuperscript{4,27}

\[ 2H_2O \rightarrow 2O_2 + 4H^+ + 4e^- \ (E^0 = +1.23 \text{ V/RHE}) \]

The challenge is to minimize the overpotentials required to drive these red-ox reactions, i.e. the development of improved catalysts. One reason why we suggest the OER catalyst metric of the E(V) required to reach 10 mA·cm\(^{-2}\) of water oxidation is that this current density roughly matches the solar spectrum for a 10 % efficient solar-to-fuel device. Here, we show how we arrived at this value:

1. In a collaborative effort, the photovoltaics (PV) industry, government laboratories, and the American Society for Testing and Materials (ASTM) defined the standard terrestrial solar spectrum: AM1.5G.\textsuperscript{161} Integration of this spectrum yields a value of
1000 W·m⁻² = 100 mW·m⁻², an illumination intensity which is typically referred to as “1 sun”.

2. Note that the red-ox potentials above for fuel synthesis and water oxidation are approximately 1.2 V apart. If 1 sun = 100 mW·cm⁻² = 100 (mA·V)·cm⁻², then a 100 % efficient solar-to-fuel device would draw \( \frac{100 \text{ (mA·V)·cm}^{-2}}{1.2 \text{ V}} \) = 83 mA·cm⁻² under AM1.5G.

3. A 10 % efficient solar-to-fuel device would draw 1/10th the current, at 8.3 mA·cm⁻².

4. Thus, the voltage required to drive water oxidation at 10 mA·cm⁻² is a relevant value in ranking OER catalysts for a 10 % solar-to-fuel device under AM1.5G illumination. The lower this voltage, the better the catalyst is for this application.
Appendix B

Comparison of the Oxygen Reduction and Evolution Activities of Manganese Oxides

Direct comparisons to literature results are not straightforward as experimental conditions are rarely identical; one example is the potential scale. In our work, we calibrated the reference electrode to a true Reversible Hydrogen Electrode (RHE) after each experiment, and we present our voltammetry vs. RHE, the most convenient scale for the readers to interpret. If published literature reported voltammetry vs. a commercial reference electrode, such as Ag|AgCl and Hg|HgO, we converted their data to a mathematically derived RHE. To do so, we shifted their potential scale to NHE using tabulated standard electrode potentials and adjusted their scale to pH=0 based on the Nernst Equation, which yields 59 mV/pH unit. The resulting overall shifts for Hg|HgO and Ag|AgCl reference electrodes in common alkaline electrolytes are listed in Table B.1. Using values in Table B.1, we estimated the potentials at which manganese oxide materials reach an ORR current of 3 mA·cm⁻² at a rotation rate of 1600 rpm and an OER current of 10 mA·cm⁻² for a number of previously published catalysts, see Tables B.2 and B.3, respectively. As seen in Table B.2, beta-MnO₂ studied by Lima et al. has the highest ORR activity out of the manganese oxide catalysts studied in literature and as seen in Table B.3, alpha-Mn₂O₃ reported by Morita et al. demonstrates the highest OER activity. Interestingly, beta-MnO₂ has been shown to...
have only moderate activity for the OER,\textsuperscript{39} while alpha-Mn$_2$O$_3$ has been shown to have only moderate activity for the ORR.\textsuperscript{36,38} The ORR activity of our Mn (III) oxide matches the activity of Lima’s beta-MnO$_2$ and is comparable (although not directly) to an extremely high surface area massive alpha-Mn$_2$O$_3$ prepared by Morita et al.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Reference Electrode & Electrolyte & Shift to RHE \\
\hline
Hg|$\text{HgO}$ & 1.0 M KOH & 0.93 V \\
Hg|$\text{HgO}$ & 0.1 M KOH & 0.87 V \\
Ag|$\text{AgCl}$ & 1.0 M KOH & 1.02 V \\
Ag|$\text{AgCl}$ & 0.5 M KOH & 1.00 V \\
Ag|$\text{AgCl}$ & 0.1 M KOH & 0.96 V \\
\hline
\end{tabular}
\caption{Potential of reference electrodes vs. RHE}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Literature Citation & Type of material & ORR: E(V), I=$-3$ mA·cm$^{-2}$ \\
\hline
Gorlin and Jaramillo 2010 (this work) & Nanostructured Mn (III) oxide & 0.73 (0.74*) \\
Lima, F. H. B. et al. \textit{Electrochimica Acta} 2007, 52, 3732. & beta-MnO$_2$; Mn$_2$O$_3$, Mn$_3$O$_4$ & 0.74; fails to reach 3 mA·cm$^{-2}$; fails to reach 3 mA·cm$^{-2}$ \\
Cheng, F. Y. et al. \textit{Chemistry of Materials} 2010, 22, 898. & alpha-MnO$_2$; beta-MnO$_2$; gamma-MnO$_2$ & All fail to reach 3 mA·cm$^{-2}$ \\
Roche, I. et al. \textit{Journal of Physical Chemistry C} 2007, 111, 1434. & MnO$_x$/C & no CV provided \\
Mao, L. et al. \textit{Electrochimica Acta} 2003, 48, 1015. & Mn$_5$O$_8$, Mn$_3$O$_4$, Mn$_2$O$_3$, MnOOH & Highest activity: MnOOH – 0.65 \\
Xiao, W. et al. \textit{Journal of Physical Chemistry C}, 2010, 114, 1694 & alpha-MnO$_2$; delta-MnO$_2$; & 0.5; fails to reach 3 mA·cm$^{-2}$ \\
Raj, A et al. \textit{International Journal of Hydrogen Energy}, 1990, 15, 751. & Electrolytic manganese dioxide & Fails to reach 3 mA·cm$^{-2}$ \\
\hline
\end{tabular}
\caption{Summary of ORR activities on manganese oxides published in literature.}
\end{table}

A direct comparison to massive alpha-Mn$_2$O$_3$ cannot be made because the metric of 10 mA·cm$^{-2}$ is normalized to geometric and not electrochemical surface area. However, when Morita et al. compare their “massive” alpha-Mn$_2$O$_3$ to similarly high
surface area Ru and Ir based DSA electrodes, they find that at 10 mA·cm⁻² the catalyst is 0.18V and 0.12V worse than Ru and Ir, respectively. This compares favorably with our catalyst, as we found it to be 0.16V and 0.15V worse than Ru and Ir nanoparticles, respectively. To verify that the noble metal nanoparticles utilized in our work had a surface area of at least the same order of magnitude as the nano-structured Mn (III) oxide thin film, we had to estimate the electrochemically active surface areas (ECSA) of our samples. To estimate the ECSA of noble metal nanoparticles we utilized the hydrogen underpotential deposition method (HUPD) for the platinum catalyst and assumed that ruthenium and iridium catalysts would have similar surface areas due to identical method of preparation. This yielded $ECSA_{\text{precious metals}} = 3.0 \text{ cm}^2$ for the precious metal nanoparticles.

**Table B.3:** Summary of OER activities on manganese oxides published in literature.

<table>
<thead>
<tr>
<th>Literature Citation</th>
<th>Type of material</th>
<th>OER: E(V), I=10 mA·cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gorlin and Jaramillo, 2010 (this work)</td>
<td>Nanostructured Mn (III) oxide</td>
<td>1.77</td>
</tr>
<tr>
<td>Jiao, F.; Frei, H. <em>Chemical Communications</em> 2010, 46, 2920.</td>
<td>Mn₃O₄, Mn₂O₃, MnO₂</td>
<td>Visible light driven OER using Ru(bpy)₃: Mn₂O₃ is most active.</td>
</tr>
</tbody>
</table>
To estimate the ECSA of nano-structured Mn (III) oxide thin film, we performed cyclic voltammetry in a nitrogen saturated environment on an identically prepared sample to the one reported in the manuscript and integrated the amount of charge passed in an oxidation feature around 0.9-1.0 V vs RHE. This feature corresponds to a transition from Mn$^{3+}$ to Mn$^{4+}$. To convert the amount of charge passed to an estimate of the ECSA$_{\text{MnOx}}$, we assumed an alpha-Mn$_2$O$_3$ lattice with an oxidation that penetrates only one monolayer deep. This yielded ECSA$_{\text{MnOx}} = 2.8$ cm$^2$. This value is nearly identical to that of ECSA$_{\text{precious metals}}$. Note, however, that the ECSA$_{\text{MnOx}}$ value of 2.8 cm$^2$ is actually an upper bound as the oxidation feature likely penetrates deeper than one monolayer; i.e. not all of the redox active Mn cations are at the surface.
Appendix C

Identifying Active Surface Phases for Metal Oxide Electrocatalysts: A Study of Manganese Oxide Bifunctional Catalysts for Oxygen Reduction and Water Oxidation Catalysis

C.1 Abstract

Progress in the field of electrocatalysis is often hampered by the difficulty in identifying the active site on an electrode surface. Herein we combine theoretical analysis and electrochemical methods to identify the active surfaces in a manganese oxide bifunctional catalyst for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). First, we electrochemically characterize the nanostructured alpha-Mn$_2$O$_3$ and find that it undergoes oxidation in two potential regions: initially, between 0.5 V and 0.8 V, a potential region relevant to the ORR and subsequently, between 0.8 V and 1.0 V, a potential region between the ORR and the OER relevant conditions. Next, we perform density function theory (DFT) calculations to understand the changes in the MnO$_x$
surface as a function of potential and to elucidate reaction mechanisms that lead to high activities observed in the experiments. Using DFT, we construct surface Pourbaix and free energy diagrams of three different MnO\textsubscript{x} surfaces and identify ½ ML HO* covered Mn\textsubscript{2}O\textsubscript{3} and O* covered MnO\textsubscript{2}, as the active surfaces for the ORR and the OER, respectively. Additionally, we find that the ORR occurs through an associative mechanism and that its overpotential is highly dependent on the stabilization of intermediates through hydrogen bonds with water molecules. We also determine that OER occurs through direct recombination mechanism and that its major source of overpotential is the scaling relationship between HOO* and HO* surface intermediates. Using a previously developed Sabatier model we show that the theoretical predictions of catalytic activities match the experimentally determined onset potentials for the ORR and the OER, both qualitatively and quantitatively. Consequently, the combination of first-principles theoretical analysis and experimental methods offers an understanding of manganese oxide oxygen electrocatalysis at the atomic level, achieving fundamental insight that can potentially be used to design and develop improved electrocatalysts for the ORR and the OER and other important reactions of technological interest.

C.2 Introduction

Fundamental understanding of electrochemical reactions on surfaces has improved significantly in recent years, yet many microscopic processes occurring during electrochemical reactions are still poorly understood due to difficulties in simulating electrochemical reactions computationally and in pinpointing active sites experimentally. The ultimate challenge in electrocatalyst development is to identify the active sites on a given catalytic surface and determine the reaction mechanisms on those sites. If one can
achieve such level of fundamental understanding, one could accelerate the design and development of improved electrocatalysts.\textsuperscript{27,168-171}

The electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are of great interest as they are processes involved in energy conversion between fuel and electricity and vice versa. The development of a bifunctional catalyst for both reactions is an important challenge in electrochemistry; such a catalyst could be particularly useful for energy storage applications. For example, the catalyst could be employed in a unitized regenerative fuel cell (URFC), which is an energy storage device that can utilize intermittent renewable energy such as wind or solar. During operation, a URFC splits water into H\textsubscript{2} and O\textsubscript{2}, in the electrolysis mode and consumes H\textsubscript{2} to produce electricity, in the fuel cell mode.\textsuperscript{4,68} Both the fuel cell reaction and the water electrolysis reaction require large overpotentials at the oxygen electrode – no current catalyst material operates near the equilibrium potential for either the ORR or the OER. Consequently, improved oxygen electrode catalysts will increase the efficiency of the full conversion cycle from electricity to hydrogen and back to electricity in an URFC.\textsuperscript{172,173} Furthermore, it is desirable to develop highly active catalysts from cheap and abundant materials, i.e. alternatives to IrO\textsubscript{2}/Pt or IrO\textsubscript{2}-RuO\textsubscript{2}/Pt, the best catalysts for these reactions.\textsuperscript{174-176}

In this study, we investigate ORR/OER catalytic activity of manganese oxides (MnO\textsubscript{x}) surfaces. Several characteristics of MnO\textsubscript{x} motivate our study: (1) Mn changes oxidation states from +2 to +3 to +4 near the equilibrium potential for the ORR and the OER,\textsuperscript{88} suggesting that Mn can exchange oxygen atoms with the electrolyte at relevant potentials – a property that could potentially facilitate ORR and OER chemistry, (2) Manganese is an inexpensive, earth-abundant element, and thus is scalable for large-scale
energy applications, and (3) There is precedent for Mn oxides effectively catalyzing the OER: the Oxygen-Evolving Complex (OEC) in Photosystem II is a Mn-oxo cluster that catalyzes the OER during photosynthesis.\textsuperscript{45,71,177,178} Historically, a number of manganese oxides have shown promising electrocatalytic activity for either the ORR or the OER, but not for both.\textsuperscript{35-38,40,46,76,93,124,163,179-181} Recently, it was shown that a nanostructured alpha-Mn\textsubscript{2}O\textsubscript{3} exhibited excellent bifunctional ORR and OER activity similar to that of the best known precious metal nanoparticle catalysts: Pt, Ru, and Ir.\textsuperscript{82} However, the bifunctional ORR/OER activities of the nanostructured alpha-Mn\textsubscript{2}O\textsubscript{3} and precious metal nanoparticles are still short of an ideal reversible oxygen electrode.

In principle, it should be possible to develop an ideal reversible oxygen electrode – a material that effectively catalyzes both the ORR and the OER. With such a catalyst, one would be able to obtain a high reduction current at potentials just cathodic of the equilibrium potential and a high anodic current at potentials just anodic of the equilibrium potential. Such a catalyst would likely undergo minimal changes in surface structure swinging from one reaction to the other as it would always operate near the equilibrium potential. For imperfect catalysts, there are large overpotentials associated with both the ORR and the OER, which means that the two reactions operate at significantly different potentials away from equilibrium in opposite directions. The different operating conditions will likely result in different surface conditions within each potential window of activity and likely different oxidation states of the catalyst surface at the relevant potentials for the ORR and the OER.

To understand surface conditions of imperfect catalysts under ORR/OER relevant potentials, a variety of \textit{in-situ} and \textit{ex-situ} spectroscopic techniques have been
employed.\textsuperscript{38,94,121,182,183} We believe that density functional theory (DFT) calculations can also be used to help elucidate active catalyst surfaces. While DFT methods have problems describing transition metal oxides accurately, they have been shown recently to describe trends in reactivity of metals and metal oxides for the OER and the ORR quite well.\textsuperscript{6,8,10,184,185} Due to the complexity of the systems of interest in describing these processes, DFT calculations are the only methods available to us at the moment. The calculations can be used to construct surface Pourbaix diagrams, which describe surface oxidation and dissolution processes at a given pH and potential\textsuperscript{186} making it possible to identify thermodynamically stable surface phases during reaction conditions (as a function of pH and potential), the catalytic activity of those surfaces, and the associated mechanistic pathways for the reactions of interest. The knowledge of active surfaces and reaction mechanisms gained from DFT studies will shed light onto the surface chemistry of catalyst materials in ways that are extremely difficult to obtain with modern experimental tools. DFT can thus play a unique role in contributing to the design and development of improved materials.

In the work described herein, we present DFT calculations in combination with electrochemical characterization to elucidate the active surfaces and reaction mechanisms for the ORR and the OER on a bifunctional Mn oxide catalyst. First, the electrochemical characterization of a recently developed nano-structured manganese oxide catalyst demonstrates excellent ORR and OER activity, but suggests that the catalyst undergoes a change in the oxidation state in the onset region of ORR activity as well as in the potential region between ORR and OER activity. Attempts to characterize the surface oxidation state under operating conditions using ex-situ x-ray photoelectron spectroscopy
have yielded some information on the active surfaces involved. To gain greater insight into the surface chemistry of this catalyst during reaction conditions, we turn to DFT calculations to identify the precise surface structures involved as well as associated reaction mechanisms for both oxygen reduction and oxygen evolution.

Our study involves the following elements: The first step is to determine which surface structures of manganese oxide are present as a function of pH and applied potential versus the reversible hydrogen electrode (RHE). We obtain this information by employing DFT calculations to generate surface Pourbaix diagrams for different adsorbate (e.g. O* and HO*) covered surfaces. To link the calculated surface structures of manganese oxide to ORR or OER conditions, we then use DFT to calculate binding energies for all reaction intermediates involved in the ORR and the OER and predict ORR and OER overpotentials for each surface structure. These overpotentials are then inserted into the previously developed Sabatier model to produce a computationally derived linear sweep voltammogram (LSV). The computationally derived LSV reveals activity as a function of applied potential for manganese oxide surfaces in a self-consistent manner, meaning that reaction turnover can only occur on surface phases that are identified to be present at a given potential. Our results indicate that the active surface for the ORR is ½ ML HO* covered Mn$_2$O$_3$ and for the OER, O* covered MnO$_2$. Having identified the active surfaces involved in these reactions, our DFT calculations can offer further insight into mechanistic pathways: the associative mechanism is the expected pathway for the ORR pathway on ½ ML HO* covered Mn$_2$O$_3$ and the direct recombination mechanism is the most likely OER pathway on O* covered MnO$_2$. 
When the computationally derived LSV is compared to the experimental LSV measured on a recently developed nano-structured manganese oxide catalyst, the theoretical predictions closely match experimental onsets for ORR and OER catalytic activities. The close match between theory and experiment validates the application of a first-principles theoretical analysis to the electrochemical oxygen reduction and oxygen evolution reactions on surfaces at the atomic level. By focusing our analysis on reaction energetics, namely the binding energies of reactive intermediates, we expect our approach to be robust and not very dependent on the computational setup and the exchange and correlation functional applied in the DFT simulations.

C.3 Methods

C.3.1 Computational Methods

The spin-polarized DFT calculations are performed at the generalized gradient approximation (GGA) RPBE level\textsuperscript{188} using the plane wave implementation in Dacapo and the Atomic Simulation Environment Ultra-soft pseudo-potentials are used to deal with the ion cores\textsuperscript{189}. Therefore the electronic wave-functions can be represented well by plane wave basis set with a cutoff energy of 350 eV. The electron density is treated on a grid corresponding to a plane wave cutoff at 500 eV. A Fermi smearing of 0.1 eV and Pulay mixing is used to ensure the fast convergence of the self-consistent electron density. Atomic positions are relaxed until the sum of the absolute forces is less than 0.05 eV/Å. For reference, the calculated equilibrium lattice constants of MnO\textsubscript{x} are 4.5 Å/MnO, 5.78 Å(a), 9.59 Å(c) /Mn\textsubscript{3}O\textsubscript{4}, 9.51 Å/alpha-Mn\textsubscript{2}O\textsubscript{3} and 4.43 Å(a), 2.86 Å(c)/beta-MnO\textsubscript{2}, in good agreement with the experimental measurements and previous DFT studies\textsuperscript{190-198}. 

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Figure C.1: The schematic structures (top view) of different manganese oxide phases, Mn atoms in blue, O atoms in red. (a) Mn$_3$O$_4$ (001) – white rectangle indicates the (2x1) unit cell with the equivalent five-fold coordinated active sites 1, 2, 3, 4 (b) Mn$_2$O$_3$ (110) white rectangle indicates the (1x1) unit cell with four types of sites: 1- five-fold coordinated (with four oxygen atoms in the same plane), 4 – five-fold coordinated (three oxygen atoms in the same plane and two in the second layer), 2 – four-fold coordinated (three oxygen atoms in the same plane and one in the second layer) and 3 – four-fold coordinated (two oxygen atoms in the same plane and two in the second layer), and (c) MnO$_2$ (110) surfaces – a rutile type stoichiometric surface. The dashed line indicates a (1x2) unit cell. Positions 1 and 2 are equivalent and represent the active sites (cus). Sites 3 and 4 are equivalent six-fold coordinated and are so called the bridge sites d) MnO(100) with (1x1) unit cell. 1 and 2 are equivalent five-fold coordinated active sites.

The starting point for this analysis is calculations on four well-defined manganese oxide surfaces, Figure C.1. For the OER and the ORR it is likely the facets control surface activity rather than surface defects since defects are expected to be covered by oxygen at the very oxidizing conditions relevant for OER and ORR. In this work, we specifically consider four close packed MnO$_x$ surfaces$^{199}$ and examine their trends in behavior: MnO (001), beta-MnO$_2$ (110), Mn$_3$O$_4$ (100) and alpha-Mn$_2$O$_3$
The surface structures with the most stable terminations are shown in Figure C.1. For Mn$_3$O$_4$ (in Figure C.1 (a)) all the surface Mn atoms are equivalent and each Mn atom coordinates with four oxygen atoms in the same plane and one oxygen in the second layer (see Figure C.1 (a)). The alpha-Mn$_2$O$_3$ (110) surface has four different types of Mn atoms (Figure C.1 (b)): two Mn atoms coordinate with five oxygen atoms: four oxygen atoms in the same plane and one in the second layer (site 1), and three oxygen atoms in the same plane and two in the second layer (site 4). The other two atoms coordinate with four oxygen atoms: three oxygen atoms in the same plane and one oxygen in the second layer (site 2), and two oxygen atoms in the same plane and two in the second layer (site 3). beta-MnO$_2$ has a rutile phase$^{200,201}$ and two types of Mn atoms on the surface: five-coordinated Mn (coordinated unsaturated site, site 1 in Figure C.1 (c)), with four oxygen in the same plane and one in the second layer, and six-coordinated Mn (bridge site, site 3 in Figure C.1 (c)) that is considered to be the inactive sites. Our calculations show that the MnO (001) surface (Figure C.1 (d)) reconstructs immediately in the presence of oxygen, and thus this oxide phase is not considered any further.

A periodically repeating 4–8 layer slab is employed in the model to determine the most stable MnO$_x$ surfaces in our calculations (see Figure C.1). A vacuum of at least 20 Å is used to separate the slab from its periodic images. Supercells with periodicity (2×1) have been employed to simulate adsorption and electrochemical reaction, with Monkhorst-Pack type of k-point sampling of 4×4×1 for MnO (100) and beta-MnO$_2$ (110), and 2×4×1 for Mn$_3$O$_4$ (001). For the complex crystal structure of alpha-Mn$_2$O$_3$ (110), only (1×1) unit cell and 2×3×1 Monkhorst-Pack type of k-point
sampling are used. The 2–4 top layers as well as possible adsorbates are fully relaxed. We apply a previously developed method, the computational standard hydrogen electrode (CSHE) for modeling the thermochemistry of electrochemical reactions.\textsuperscript{6,10}

In this method the only way the potential affects the relative free energy is through the chemical potential of the electrons in the electrode. This "first order" inclusion of the potential has been used to predict the activity trends for the ORR on metal and metal alloys and in the design of electrocatalysts.\textsuperscript{6,202} Furthermore, we have shown that thermochemical features such as phase diagrams in water are also well described by this method.\textsuperscript{203} The only effect of the pH is the change of chemical potential of the solvated protons. At standard conditions (pH = 0), H\textsuperscript{+}(aq) + e\textsuperscript{-} is in equilibrium with ½ H\textsubscript{2}(g) at zero potential vs. the SHE. At finite pH and potential vs. SHE (U\textsubscript{SHE}) the chemical potential of a proton and an electron is:

\[
(\text{H}^+(\text{aq})) + (\text{e}^-) = \frac{1}{2} \text{H}_2(\text{g}) - e\text{U}_{\text{SHE}} + k\text{B}T \ln 10 \text{ pH}
\] (C.1)

### C.3.2 Pourbaix Diagrams

To construct the surface Pourbaix diagram for MnO\textsubscript{x} system, we first generate a calculated bulk Pourbaix diagram by considering the equilibrium between different bulk oxide phases and bulk manganese metal. In the same diagram we also include the equilibrium between different soluble products and solid substances. As we start by exploring phase behaviour in the bulk, all these values can be adapted from the Pourbaix atlas, the reference system is the bulk metallic phase.\textsuperscript{88} After constructing bulk Pourbaix diagrams which are equivalent to the diagrams found in the Pourbaix atlas, we go one step further and identify the adsorbates (e.g. O\textsuperscript{*} or HO\textsuperscript{*}) that are present and their coverage (e.g. \(\frac{1}{4}\)ML, \(\frac{1}{2}\) ML, etc.). We thus identify the most stable
surface structures for each oxide phase at respective pH and potential, key information that is not found in the Pourbaix atlas. The calculations employed to determine the stable surfaces as a function of pH and potential employ a previously developed model. In short, the surface is in equilibrium with protons and liquid water at 298K so that oxygen and hydroxyl may be exchanged between the surface and a reference electrolyte.

Consider a clean surface with a quantity of $X^*$ available sites onto which oxygen or hydroxyl can potentially adsorb. At a given pH and potential, the surface will interact with the interfacial water layer such that some of the $H_2O$ molecules at the interface will dissociate onto available sites, producing adsorbed $O$ or $HO$ and releasing protons and electrons in the process. We introduce the variables $N_{O^*}$ and $N_{HO^*}$ to reflect the number of adsorbed $O$ and $HO$ species, respectively, and the variable $N^*$ which represents the number of remaining free sites at the given pH and potential after the adsorption processes have occurred. Thus, the total number of available sites to begin with, $X^* = N_{O^*} + N_{HO^*} + N^*$, i.e. after adsorption sites either contain $O$, $HO$, or remain free sites. The stoichiometric equation reflecting this process is as follows:

$$X^* + (N_{O^*} + N_{HO^*})H_2O(l) \rightarrow (N_{O^*} + N_{HO^*} + N^*)_{ads} + (2N_{O^*} + N_{HO^*})H^+ + (2N_{O^*} + N_{HO^*})e^-$$

We can thus calculate the free energy change of the surface covered with adsorbates relative to the clean surface, on the DFT scale as follows:

$$G_{surf} = E_{(N_{O^*} + N_{HO^*} + N^*)_{ads}}^{DFT} - E_{X^*}^{DFT} - (N_{O^*} + N_{HO^*})\epsilon_{H_2O^{(g)}}^{DFT} + \frac{(2N_{O^*} + N_{HO^*})}{2} \epsilon_{H_2^{(g)}}^{DFT} + \Delta ZPE - T\Delta S - (2N_{O^*} + N_{HO^*})k_B T \ln(a_{H^+})$$

$$(C.3)$$
where $E_{\text{DFT}}^{(N_{\text{ads}},N_{\text{sur}})}$, $E_{\text{DFT}}^{(N_{\text{ads}},N_{\text{sur}})}$, $E_{\text{DFT}}^{(N_{\text{ads}},N_{\text{sur}})}$ are the calculated ground state energies of the surface with the adsorbates, of the clean surface and of the references molecules in the gas phase. Zero point energies (ZPE) corrections are calculated using DFT calculations of the vibrational frequencies and standard tables of molecules. The change in entropy ($S^0$, $T = 298$ K) are calculated from the standard tables for gas phase molecules. Detailed description about how to perform all corrections can be found in references.  

C.3.3 Experimental Methods

The electrochemical characterization was performed on alpha-Mn$_2$O$_3$ nanostructured thin films electrodeposited onto polished glassy carbon disks (GC, 0.196 cm$^2$, SigradurG HTW Hochtemperatur-Werkstoffe GmbH) as described previously. The films were characterized using cyclic voltammetry (CV) in a three electrode electrochemical cell in a rotating disk electrode (RDE, Pine Instruments) configuration. All CVs were iR-compensated and measured using a Bio-Logic potentiostat (VMP3) in 0.1 M KOH electrolyte, in nitrogen or oxygen saturated environments, with a scan rate of 5 mV·s$^{-1}$ and a rotation rate of 1600 rpm. Platinum wire was used as a counter electrode and Hg/HgO electrode was used as a reference electrode. The potential scale was calibrated to a reversible hydrogen electrode (RHE) and all potentials are reported vs RHE. CVs in nitrogen were used to identify oxidation state changes in an inert environment, while CVs in oxygen identified potentials relevant for the ORR and the OER. Base CVs in nitrogen and ORR CVs in oxygen were performed from 0.05 V to 1.1 V vs RHE, while OER linear sweep voltammograms (LSV) were performed from 0.05 V to 1.9 V vs RHE.
To compare ORR and OER activities of the nanostructured alpha-Mn$_2$O$_3$ to active precious metals and metal oxides, electrochemical characterization was also performed on commercial carbon-supported Platinum (20wt.% Pt/C, Etek) and Ruthenium (20wt.% Ru/C, Premetek) nanoparticles which were previously shown to have a comparable surface area to the nanostructured alpha-Mn$_2$O$_3$.\textsuperscript{82} Catalyst dispersions of precious metal nanoparticles were prepared by adopting a known literature procedure.\textsuperscript{51} For characterization, 10 μl of the dispersed catalyst was drop-casted onto a polished glassy carbon electrode and allowed to dry in room air. To capture both ORR and OER activities in one linear sweep, characterization was performed between 0.05 V and 1.7 V for Ru/C, 1.9 V for alpha-Mn$_2$O$_3$, and 2.2 V for Pt/C. Different anodic potentials were used in different catalytic systems to reach an OER current of 10-20 mA·cm$^{-2}$ in each case; the highest value of 2.2 V used in Pt/C system was not applied to all other catalysts to mitigate carbon oxidation. Although the nanoparticles are prepared as metals, at the anodic potentials relevant to OER, the surface of the nanoparticles is converted to a metal oxide. Consequently, while the ORR is observed on metal or on partially oxidized metal surfaces, the OER is observed on the electrochemically formed metal oxide surfaces.

C.4 The Oxygen Reduction and Oxygen Evolution Reactions

In an acid environment the ORR and the OER can be written as:

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O} \quad (C.4)$$

We consider two possible ORR/OER reaction mechanisms: an associative mechanism
that involves a HOO* species, where * represents the active site on the metal surface, and a direct O₂ dissociation/recombination mechanism.

In acid, the associative mechanism goes through the following elementary steps (the ORR proceeds top to bottom, Eqn 3.2 → Eqn 3.5, where the OER proceeds bottom to top, Eqn 3.5 → Eqn 3.2):

\[
\begin{align*}
O_2 + H^+ + e^- & \leftrightarrow HOO^* \\
HOO^* + H^+ + e^- & \leftrightarrow O^* + H_2O \\
O^* + H^+ + e^- & \leftrightarrow HO^* \\
HO^* + H^+ + e^- & \leftrightarrow H_2O
\end{align*}
\]  

In an alkaline electrolyte H₂O rather than H₃O⁺ may act as the proton donor, resulting in the overall ORR and OER equation:

\[O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-\]  

The analogous associative mechanism in base is as follows:

\[
\begin{align*}
O_2 + H_2O + e^- & \leftrightarrow HOO^* + OH^- \\
HOO^* + e^- & \leftrightarrow O^* + OH^- \\
O^* + H_2O + e^- & \leftrightarrow HO^* + OH^- \\
HO^* + e^- & \leftrightarrow OH^-
\end{align*}
\]  

Notice that the surface intermediates (HOO*, O*, HO*) are the same in both environments and that they all contain at least one oxygen atom. It is through this oxygen that the intermediates bind to a Mn ion at the surface.

The mechanism via direct O₂ dissociation/recombination mechanism consists of the following elementary steps (for simplicity, only the steps in acid are shown):

\[1/2O_2 \leftrightarrow O^*\]
\[ O^* + H^+ + e^- \leftrightarrow HO^* \quad (C.15) \]

\[ HO^* + H^+ + e^- \leftrightarrow H_2O \quad (C.16) \]

The ORR and OER mechanisms considered in this study neglect the effect of the electric field in the double layer and do not treat barriers which may depend on whether the proton donor is \( H_2O \) or \( H_3O^+ \). Thus, at a fixed potential on the RHE scale, there is no difference in the free energy of the ORR/OER intermediates calculated in acid versus in base for the following reasons: (1) All reactions involve the same intermediates and the same number of protons and electrons and (2) \( a_{H^+} \) and \( a_{OH^-} \) are directly related by means of a pH/pOH scale since water is in equilibrium with \( H^+ \) and \( OH^- \). 10 As such, we will use the equations derived for the acid solution and apply them to a basic environment to be commensurate with the experimental data in base presented herein. Although this method cannot accurately model absolute kinetic rates, the consistent set of assumptions will allow for direct comparison of relative trends in activity. We note that for a number of catalyst systems the ORR activity has been found experimentally to be a function of pH. This could arise for a number of reasons, for instance the possibility of an \( O_2^- \) reaction pathway in which the step producing \( O_2^- \) does not involve binding to the catalyst surface. 205 Nevertheless, for the most active catalysts like Pt and Ru, the ORR/OER overpotentials are not particularly sensitive to pH and do not proceed through \( O_2^- \) reaction pathway.

**C.5 Results**

**C.5.1 Electrochemical Characterization**

Figure C.2 shows experimental results from our electrochemical characterization of a nanostructured alpha-Mn_2O_3 electrode performed in nitrogen and
oxygen saturated 0.1M KOH. Three different data sets are presented in the figure: (1) a base CV in a nitrogen-saturated environment, (2) a CV in an oxygen saturated environment of the same potential window, and (3) a linear sweep voltammogram (LSV) in a wide potential window in an oxygen saturated solution. The base CV performed in the nitrogen saturated environment was used to identify oxidation/reduction features on the nanostructured alpha-Mn$_2$O$_3$ surface. As seen in the inset of the figure, two oxidation features are observed in the anodic sweep – one between 0.5 and 0.8 V and another between 0.8 and 1.0 V. These features likely correspond to the oxidation of Mn$_3$O$_4$ to Mn$_2$O$_3$ and Mn$_2$O$_3$ to MnO$_2$, consistent with the thermodynamic standard potentials for these processes, which are 0.69 V and 1.01 V, respectively. The reductive feature occurring between 0.90 and 0.65 V in the cathodic sweep of the nitrogen saturated CV pertains to the discharge reaction of MnO$_2$ to Mn$_2$O$_3$, as assigned in the literature.

**Figure C.2:** Electrochemical characterization of an alpha-Mn$_2$O$_3$ nanostructured thin film, showing a direct comparison of a base CV in nitrogen (also shown in the inset) to a LSV in oxygen. Later in this paper the DFT-produced surface Pourbaix diagram of Figure C.8 shows that the relevant surface for the ORR is Mn$_2$O$_3$ and the relevant surface for the OER is MnO$_2$. 

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The CV in the oxygen saturated environment was used to identify the onset potential for the ORR. The catalyst first draws ORR current at approximately 0.83 V in the cathodic direction (0.80 V in the anodic direction) and reaches a diffusion limited current at 0.60 V. The onset potential of 0.83 V corresponds to overpotential of 0.4 V, which indicates a highly active non-precious metal ORR catalyst. The experimental LSV reveals that the onset potential for the OER occurs at 1.5 V, which corresponds to overpotential of 0.27 V and provides evidence of high catalytic activity for the OER. The location of the second oxidation feature between 0.8 V and 1.0 V, suggests that during the anodic sweep, the catalyst changes its oxidation state in the potential region between ORR and OER activity. Additionally, since the ORR region is located at the end of the reduction feature seen in the cathodic sweep of the base CV (0.90 V to 0.65 V) and overlaps with an oxidation feature in the anodic sweep of the base CV (0.50 V to 0.80 V), the active surface may undergo changes at different potentials of ORR activity. Spectroscopic methods have been used to study oxidation state changes in MnO\textsubscript{x}, however specific identification of the surface phases has remained elusive.\textsuperscript{94} To identify these phases, we employ theory.

C.5.2 DFT Studies of Stable Surface Structures of MnO\textsubscript{x} as a Function of pH, Applied Potential, and Starting Bulk Material

We aim to understand how MnO\textsubscript{x} bulk and surface structures change across the pH-potential window, and how these changes impact ORR and OER activity. To do so, we first investigate the relative stability of different adsorbate surface structures for each of three different bulk oxide phases: (a) Mn\textsubscript{3}O\textsubscript{4} (001), (b) Mn\textsubscript{2}O\textsubscript{3} (110) and (c) MnO\textsubscript{2} (110). The MnO\textsubscript{x} phase, crystal structure, and the surface
adsorbates present during reaction conditions (pH and applied potential) will likely depend on how the material was synthesized in the first place, e.g. starting MnOₓ.

Figure C.3: The phase-diagram of the (a) Mn₃O₄ (001), (b) Mn₂O₃ (110), and (c) MnO₂ (110) surfaces calculated as function of the potential at pH=0. The notations *, b and c within the figure legends represent the stoichiometric surfaces (Mn₃O₄ (001) and Mn₂O₃ (110)) or reduced surface (MnO₂ (110)), the adsorbates at the bridge sites and coordinated unsaturated sites, respectively. The dissolution process is not included here.

Figure C.3: The phase-diagram of the (a) Mn₃O₄ (001), (b) Mn₂O₃ (110), and (c) MnO₂ (110) surfaces calculated as function of the potential at pH=0. The notations *, b and c within the figure legends represent the stoichiometric surfaces (Mn₃O₄ (001) and Mn₂O₃ (110)) or reduced surface (MnO₂ (110)), the adsorbates at the bridge sites and coordinated unsaturated sites, respectively. The dissolution process is not included here.

crystal structure and nanoparticle size. Here we present a thermodynamic analysis for all possible bulk and surface structures. Though only one combination of a bulk

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and surface structure can be the most thermodynamically stable at a given pH, temperature, and applied potential, it is possible that other structures might be present due to kinetic control. Those structures could also contribute to OER and ORR activities.\textsuperscript{88}

\textbf{Figure C.4:} Surface Pourbaix diagram on (a) Mn$_3$O$_4$ (001), (b) Mn$_2$O$_3$ (110), and (c) MnO$_2$ (110). Lines a and b represent the reversible hydrogen electrode (RHE) line and the O$_2$/H$_2$O equilibrium line. The notation "b" within the Figure C.4 (c) legend represents the adsorbates at the bridge sites and coordinated unsaturated sites.
The calculated free energies for all possible surface adsorbate structures on each of the three bulk structures (Mn$_3$O$_4$, Mn$_2$O$_3$, and MnO$_2$) are plotted versus potential at pH = 0, shown in Figure C.3. The structure with the lowest free energy at a given potential determines the most likely surface structure as it is the most thermodynamically stable. Figure C.4 then incorporates the effect of pH to produce three surface Pourbaix diagrams in which the most stable surface for each bulk oxide is constructed as a function of pH and the electrode potential vs. SHE ($U_{SHE}$). Later in Section C.6, we ultimately combine this information along with thermodynamic data for the bulk oxide phases construct a single General Surface Pourbaix diagram that allows for phase changes both at the surface as well as deeper within the bulk of oxide. We first discuss details of the surface changes for each of the bulk MnO$_x$ phases, as shown in Figure C.4.

Figure C.4 shows that at low potentials in acidic solutions, dissolution to Mn$^{2+}$ is spontaneous for all MnO$_x$ bulk phases. In alkaline solutions this process is suppressed, and instability is not as problematic as it is in acidic solutions. In both types of electrolytes, corrosion is most severe at potentials higher than 1.46 V (RHE) where the MnO$_x$ can be oxidized and dissolved into MnO$_4^-$. We thus focus our discussion on the alkaline environment and within that region identify the most stable surface structures as a function of potential on (a) Mn$_3$O$_4$, (b) Mn$_2$O$_3$, and (c) MnO$_2$. Note that in Figure C.4 the potential versus RHE at any pH, can be read off as the vertical distance from line 'a' to the region of interest.

For the case of Mn$_3$O$_4$ (001), presented in Figure C.4 (a), at low potentials (0.46 V < $U_{RHE}$ < 0.95 V) the clean surface (i.e. no adsorbates) is the most stable
As the potential increases ($0.95 < U_{RHE} < 1.29$ V), water dissociation begins, leading to the presence of HO* with increasing coverage, e.g. $\frac{1}{4}$ ML HO/Mn$_3$O$_4$ and 1 ML HO/Mn$_3$O$_4$. At potentials $U_{RHE} > 1.29$ V the adsorbed hydroxyls are oxidized further to O* to form 1ML O/Mn$_3$O$_4$. For the case of Mn$_2$O$_3$ (110), presented in Figure C.4 (b), water will dissociate to HO* at potentials $U_{RHE} > 0.53$ V, with HO* coverage increasing from $\frac{1}{4}$-1ML HO/Mn$_2$O$_3$ all the way to 1 ML HO/Mn$_2$O$_3$ by $U_{RHE} = 1.23$ V. At this point, the hydroxyls are oxidized further to produce 1 ML O/Mn$_2$O$_3$. For the case of MnO$_2$ (110), presented Figure C.4 (c), at low potentials ($0.78$ V < $U_{RHE}$ < 1.1 V) the surface Pourbaix diagram shows that the bridge sites of MnO$_2$ (110) are occupied by HO* (2OH$_b$/MnO$_2$). The bridge HO* then gradually dissociates into O* within the potential region of 1.1 V < $U_{RHE}$ < 1.38 V (O$_b$+OH$_b$/MnO$_2$ and 2O$_b$/MnO$_2$). At higher potentials O* adsorbs at the coordinated-unsaturated sites to form 3O/MnO$_2$ and 4O/MnO$_2$.

**C.5.3 Activity of Stable MnO$_x$ Surface Structures for the OER/ORR.**

Having identified the most thermodynamically stable surface structures as a function of pH and potential for each of the bulk phases of MnO$_x$, we now look to identify which of those surfaces are likely to be present during OER/ORR operating conditions. To accomplish this goal, we first use ORR/OER free energy diagrams generated by DFT to calculate the theoretical overpotentials for OER/ORR on all the relevant MnO$_x$ surfaces. The “theoretical overpotential” to which we are referring is the overpotential beyond which all reaction steps become thermodynamically downhill. The "theoretical overpotential" is related to, but not identical to, the “onset”
potential that is often used as a figure of merit in experimental LSVs. Previously
described kinetic models of electrocatalytic reactions show that the experimental
“onset” potential is expected to occur approximately 0.15 V prior to the “theoretical
overpotential.” Our calculations of the reaction energetics for the OER/ORR are
not shown for every possible surface configuration in Figure C.3, but rather only for
the 'self-consistent' catalytic surfaces; that is, the surfaces that are thermodynamically
stable, according to the Pourbaix diagrams of Figure C.4, at the overpotential at which
catalyst is operating.

At the high potentials required to drive the OER, the self-consistent surfaces
for each of the three MnOₓ bulk phases are quite similar – they are all completely
covered by oxygen. This is in agreement with our previous work investigating the
OER on rutile oxide surfaces. Since the oxide surfaces are covered with oxygen at
OER relevant potentials, no active sites are available for water adsorption, and thus
the effect of water and its interactions with adsorbed reaction intermediates can be
neglected. This simplifies the analysis of OER reaction energetics substantially.

At ORR potentials, however, the effect of water cannot be neglected as there
are available sites for water to adsorb and potentially dissociate into HO* and O*.
This leads to considerably different MnOₓ adsorbate surface structures for each of the
three bulk structures, namely clean Mn₃O₄ (001), ½ ML HO* covered Mn₂O₃ (110)
and MnO₂ (110) with HO* at bridge sites as spectators. Notice that for all of these
surfaces, there are empty sites where water can adsorb and impact the adsorption
energies of ORR intermediates, particularly with HO* and HOO* as these adsorbates
can form H bonds to adjacent water molecules. Therefore, the effect of water is
included in the free energy diagram for intermediates involved in the ORR. Detailed studies on metals\textsuperscript{9} have shown that water stabilizes surrounding HO* and HOO* species by -0.3 eV. In our preliminary studies of this effect for metal oxide surfaces, we investigated a single neighboring water molecule interacting with HO* and HOO* adsorption on a MnO\textsubscript{2} (110) surface. We obtained similar stabilization effects of -0.5 eV and -0.35 eV, respectively. For the purposes of this work, we choose to use -0.3 eV for the stabilization effect of water on both HO* and HOO* intermediates and note that more detailed studies of the effects of water at metal oxide interfaces will be considered in future studies.

We note that in this work we identify surface structures based solely on static equilibrium considerations. Under reaction conditions the local coverage of reaction intermediates is in a very dynamic state, and these dynamics could very well play a role on the reaction chemistry. For low rates of reaction, however (i.e. near the experimental 'onset' potential, which occurs before the theoretical overpotential), the surface Pourbaix diagram is a good model for determining the self-consistent surface.

Free energy diagrams constructed for the self-consistent surfaces, shown in Figure C.4, provide insight into the mechanistic pathways involved in oxygen reduction and oxygen evolution. They also point out the source of reaction overpotentials for each surface, exactly the kind of information needed to facilitate the development of improved catalysts.

The free energy calculations for the OER indicate that for O* covered Mn\textsubscript{3}O\textsubscript{4} (001) and O* covered Mn\textsubscript{2}O\textsubscript{3} (110), the associative pathway is energetically favorable compared to the direct mechanism. For the O* covered MnO\textsubscript{2} (110) surface, however,
the direct pathway is slightly favored. Previous studies have shown that the OER activity of metal oxides follow a 'volcano' relationship based on scaling relations that correlate binding energies for the different reaction intermediates. The O* covered MnO$_2$ (110) surface is close to the top of the volcano where the intermediates have a better compromise in interaction strength, which results in a more flexible reaction mechanism. In this case, the direct mechanism by recombination of oxygen atoms has a slightly lower free energy than associative mechanism by only 0.08 eV, as described in Figure C.5.

![Free-energy diagram for oxygen evolution on MnO$_2$ (110) with O as spectator species at the bridge sites and coordinated unsaturated site by associative mechanism and direct mechanism at $U = 0$, pH = 0, $T = 298$ K.](image)

**Figure C.5:** Free-energy diagram for oxygen evolution on MnO$_2$ (110) with O as spectator species at the bridge sites and coordinated unsaturated site by associative mechanism and direct mechanism at $U = 0$, pH = 0, $T = 298$ K.

To gain more information about the sources of overpotential on the self-consistent MnO$_x$ surfaces, we compared those free energy diagrams with that of an ideal oxygen evolution/reduction catalyst, shown in Figure C.6 (a). The ideal catalyst is defined by a free energy reaction diagram in which the four charge transfer steps have identical reaction free energies of $1.23$ eV = $4.92$ eV/4 for an electrode held at $U_{SHE} = 0$. If one is able to tune the binding energy of each intermediate on a surface to achieve this optimal situation, that catalyst surface would approach the activity of an ideal oxygen electrode. However, as illustrated in recent work, there is a
universal scaling relationship on a wide range of metals and oxides that governs the binding energy of the HOO* intermediate with respect to HO*, resulting in an approximately constant difference between the two energy levels ($\Delta G_{\text{HOO}*} - \Delta G_{\text{HO}^*} \approx 3.2$ eV). This is far off of an optimal catalyst which would exhibit an energy difference of 2.46 eV ($2e \times 1.23V$) between those two particular energy levels. Thus, the 'universal' 3.2 eV energy difference between HOO* and HO* levels can be used to define the lowest possible “theoretical overpotential” for the OER and the ORR $[(3.2\text{eV} - 2.46\text{eV})/2e \approx 0.37 \text{ V}]$ on a wide variety of materials. The scaling relationship between HOO* and HO* holds for MnO_x just as well, as shown in Figure C.6 (b), (c) and (d), with values of 3.18 eV, 3.1 eV and 3.12 eV. The slight deviation of $\Delta G_{\text{HOO}^*} - \Delta G_{\text{HO}^*}$ from 3.2 eV can be attributed to adsorbate coverage effects.

Indeed, the scaling relationship between the HOO* and HO* binding energies explains one major source of reaction overpotential, however additional sources of overpotential can also arise from sub-optimal O* binding. It has been previously shown that the potential-determining step for the OER is either the second water dissociation step (Eqn C.5) or the HO* oxidation step (Eqn C.6).^{10} Both steps involve O* and either HOO* or HO*; as the latter two species scale linearly with one another, the expression ($\Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*}$) contains information regarding the binding energies for all three species and is introduced as the universal descriptor of oxygen evolution activities.

We can see from Figure C.6 (b) and C.4 (c) that for the OER, the O* covered Mn_3O_4 (001) and Mn_2O_3 (110) have the same potential-determining step, the second water dissociation step (Eqn C.5) in which the third (of four) H^+ and e^- are
transferred. The O* covered Mn$_3$O$_4$ (001) surface exhibits a lower “theoretical overpotential” than the O* covered Mn$_2$O$_3$ (110) surface (0.6 V vs. 0.79 V). This originates from the placement of the O* energy level with respect to the energy levels of the intermediates, specifically below HO* intermediate and above HOO* intermediate. The closer the placement of the O* energy level is to the half-way point between the energy levels HO* and HOO* intermediates the smaller the “theoretical overpotential” will be. For the O* covered MnO$_2$ surface, the second water dissociation (Eqn C.5) is the potential-determining step when the associative mechanism is considered. The mechanism is shown in Figure C.6 (d) and leads to a “theoretical overpotential” of 0.6 V.

\[ \Delta G_{\text{HOO}^*} - \Delta G_{\text{HO}^*} \]

Values of the three manganese oxides in (b), (c), and (d), are close to 3.2 eV, the average value found on a wide range of metals and oxides. The optimum value is 2.46 eV.

**Figure C.6** Free-energy diagram for the oxygen evolution reaction on (a) the perfect catalyst, and O covered (b) Mn$_3$O$_4$ (001), (c) Mn$_2$O$_3$ (110) and (d) MnO$_2$ (110) at U = 0, pH = 0 and T = 298 K. $\Delta G_{\text{HOO}^*}$-$\Delta G_{\text{HO}^*}$ (vertical solid lines) values of the three manganese oxides in (b), (c), and (d), are close to 3.2 eV, the average value found on a wide range of metals and oxides. The optimum value is 2.46 eV.
Figure C.7: Free-energy diagram for oxygen reduction on (a) Mn$_3$O$_4$ (001), (b) ½ ML HO* covered Mn$_2$O$_3$ (110) and (c) MnO$_2$ (110) with spectator HO* at bridge sites at U = 0, pH = 0 and T = 298K.

For the ORR, the same scaling relationship holds between HOO* and HO*.

Thus, much like the OER, one part of the ORR overpotential originates from this
correlation while the other part arises from sub-optimal O* binding. The free energy diagrams of the intermediates for the ORR on the self-consistent MnOx surfaces are shown in Figure C.7. Our previous studies have shown that the potential-determining ORR step is either the formation of HOO* (Eqn C.4) or the reduction of HO* (Eqn C.7). As HO* and HOO* scale linearly with one another, ΔG_{HO*} can be introduced as a universal descriptor of oxygen reduction activities. We can see that all three self-consistent MnOx surfaces – clean Mn3O4 (001), ½ ML HO* covered Mn2O3 (110) and ½ ML HO* (bridge) MnO2 (110) – are active for the ORR. The potential-determining step is HO* reduction for Mn3O4 and Mn2O3 and HOO* formation for MnO2. Calculated “theoretical overpotentials” are 0.55-0.57 V for all cases. As mentioned above, water can stabilize ORR intermediates during reaction, and changes in water coverage and the number of hydrogen bonds could influence the calculated overpotentials. A more detailed study of water adsorption would provide a more accurate estimate of “theoretical overpotentials.”

C.6 Discussion

The Pourbaix diagrams generated in Figure C.4 describe changes in adsorbate surface structure as a function of pH and potential for the three different MnOx bulk structures, ignoring the changes in the bulk of the material with respect to pH and potential. In Figure C.8, we present a general MnOx Pourbaix diagram that accounts for phase transitions in both the bulk (e.g. in the near-surface region) and at the very surface of the catalyst. As seen in Figure C.6, from 0.46 V < U_{RHE} < 0.69 V, the most stable MnOx bulk/surface is a clean (adsorbate-free) Mn3O4 (001) surface. From 0.69 V < U_{RHE} < 0.98 V, the material is oxidized into ½ ML HO* covered Mn2O3 (110),
assuming no kinetic difficulties. From 0.98 V < \( U_{\text{RHE}} \) < 1.01 V the Mn\(_2\)O\(_3\) (110) surface remains, while HO* coverage increases to \( \frac{3}{4} \) ML. From 1.01 V to 1.21 V, the bulk is oxidized to MnO\(_2\) (110) and the surface bridge sites become covered with HO*. As the potential increases above 1.21 V, the surface is further oxidized until it is completely covered by O*. At even higher potentials the MnO\(_4^-\) dissolution becomes thermodynamically favorable at any pH.

In combination with the “theoretical overpotentials” for the ORR and the OER on relevant surface structures of Mn\(_3\)O\(_4\) (001), Mn\(_2\)O\(_3\) (110), MnO\(_2\) (110) as described in Figure C.6 and Figure C.7, we can use the DFT-calculated general MnO\(_x\) Pourbaix diagram to identify the active surfaces during operating conditions. We find that for the ORR, the active surface in the onset region is a \( \frac{1}{2} \) ML HO* covered Mn\(_2\)O\(_3\) (110), while for the OER, the active surface is O* covered MnO\(_2\) (110). The predicted change in the oxidation state from Mn (III) in Mn\(_2\)O\(_3\) to Mn (IV) in MnO\(_2\) in the potential region between the ORR and the OER is supported by the oxidation feature between 0.8 V and 1.0 V seen in the anodic sweep of the base CV, Figure C.2. "Theoretical onset potentials" for the ORR and OER were calculated for these two surfaces by subtracting 0.15 V from the "theoretical overpotentials" based on the kinetic models described earlier, resulting in calculated values of 0.40 V and 0.45 V, respectively. These values are in good agreement with the experimentally observed onset potentials of 0.4 for the ORR and 0.27 for the OER measured on the nanostructured alpha-Mn\(_2\)O\(_3\) electrocatalyst.

To visually relate theoretical predictions of ORR/OER activities to experimental results, we used the Sabatier model\(^{187}\) to create theoretical LSVs for the
ORR and the OER, Figure C.9. Constructing the theoretical LSVs could only be possible by having first identified the most thermodynamically stable bulk and surface structures present during reaction conditions. In producing these theoretical LSVs, diffusion limitations for the ORR are included by invoking the Koutecky-Levich equation for a rotating disk at 1600 RPM. Figure C.9 (a) shows theoretical LSVs for the self-consistent surface structures pertaining to bulk Mn$_3$O$_4$ (001), Mn$_2$O$_3$ (110) and MnO$_2$ (110), constructed as if no changes in bulk MnO$_x$ stoichiometry were induced by the electrochemical potential. In other words, the bulk structure was fixed throughout the entire potential window – only the surface was allowed to change as shown in Figure C.4. Figure C.9 (a) thus reveals the intrinsic catalytic activities of bulk Mn$_3$O$_4$ (001), Mn$_2$O$_3$ (110) and MnO$_2$ (110) structures. All three bulk MnO$_x$ structures are shown to be active ORR catalysts, but only O$^*$ covered MnO$_2$ (110) and O$^*$ covered Mn$_3$O$_4$ (001) are active OER catalysts.

Figure C.8: General surface Pourbaix diagram for MnO$_x$ catalysts. The oxidation state of the surface and the ORR and OER potential are constant versus the reversible hydrogen electrode (RHE). Line a and b represent the RHE line and the O$_2$/H$_2$O equilibrium line.

Figure C.9 (b) shows a theoretical LSV in which both the bulk structure and the surface structure are allowed to change with applied potential. Figure C.9 (b) is
most relevant for MnOₓ catalysts with negligible kinetic barriers to phase changes in the near surface region, thus allowing both the bulk and the surface to reach their

![Graphs](image)

**Figure C.9** Calculated current density for (a) Mn₃O₄, Mn₂O₃ and MnO₂ (b) self-consistent curves from DFT calculation for MnOₓ, Ru and Pt (c) experimental curves for MnOₓ, Ru and Pt.
thermodynamically stable structures. For such a catalyst, the ORR has two relevant active surfaces. At the ORR onset potential of 0.83 V, the active surface is a ½ ML HO* covered Mn$_2$O$_3$ (110). However, as the potential decreases below 0.69 V and the current approaches diffusion-limited values, the ½ ML HO* covered Mn$_2$O$_3$ (110) is predicted to be reduced to clean Mn$_3$O$_4$ (001) surface. This DFT-predicted change in the oxidation state of MnO$_x$ is supported by the oxidation feature between 0.5 V and 0.8 V seen in the anodic sweep of the base CV, Figure C.2.

![Figure C.10](image)

**Figure C.10:** The free energy of HO* (ΔG$_{HO^*}$, solid circle) and the free energy difference between O* and HO* (ΔG$_{O^*-HO^*}$, open circle) plot against the number of O (N$_O$) coordinated with Mn on Mn$_2$O$_3$ (110) and MnO$_2$ (110). I, II and III represent three different type of Mn atoms on the Mn$_2$O$_3$ (110) surface respectively.

In the OER region of Figure C.9 (b), the theoretical OER activity of the self-consistent MnO$_x$ surface is also shown. At the high potentials of the OER, O* covered MnO$_2$ is the expected bulk-surface combination. Figure C.9 (b) also compares the theoretical LSVs of MnO$_x$ in both the ORR and OER regions to those of self-consistent Ru and Pt, in which phase transitions to RuO$_2$ and PtO$_2$ at oxidative potentials were taken into account. According to theoretical LSVs shown in Figure C.9 (b), the predicted activity order for the OER is RuO$_2$ > MnO$_2$ > PtO$_2$, and for the
ORR is Pt > Mn₂O₃ > Ru. We note that this same model has previously been successful in predicting the trends in ORR activity for metal-alloy catalysts.¹⁸⁴,²⁰²

Next, we compare theoretical predictions with experimental measurements.

Figure C.9 (c) shows experimental LSVs for the nanostructured alpha-Mn₂O₃, Ru/C and Pt/C. Pt/C demonstrates the best ORR activity, while the oxidized Ru/C demonstrates the best OER activity. The nanostructured alpha-Mn₂O₃ shows high activity for both reactions. Under reductive potentials relevant to the ORR, the Mn₂O₃ surface outperforms Ru/C and approaches activity of Pt/C, while under oxidative potentials relevant to the OER, the MnO₂ surface outperforms the oxidized Pt/C and approaches the activity of the oxidized Ru/C. For both the ORR and the OER, the experimental activity trends are identical to those predicted by the DFT models. There is also excellent quantitative agreement between theory and experiment.

Only minor discrepancies are observed between the theoretically-predicted and the experimentally-observed onset potentials for MnOₓ. One possible source of the discrepancies could be due the assumptions made about the number of oxygen atoms, N₀, coordinated to each Mn atom at the MnOₓ surface in the DFT calculations. This theoretical study focuses solely on beta-MnO₂ amongst the MnO₂ family as this is the most stable of its phases. However, the presence of alpha-MnO₂ and gamma-MnO₂ phases can be expected in experimental MnO₂ electrodes,³⁵,³⁷,⁹³,¹²⁴,¹⁸⁰ and the coordination environment of these phases will exhibit different values of N₀. Furthermore, the theoretical calculations of the catalyst surface structure as a function of electrochemical potential, Figure C.4, examined the changes in the MnOₓ structure only in the top-most layer. During the experiments, however, it is quite possible that
complete or incomplete stoichiometric changes could penetrate deeper into the material and impact $N_O$, which can lead to significant variation in electrochemical activity. Some, but not all of the possibilities are accounted for in Figure C.8, the general Pourbaix diagram. Figure C.10 shows the origin of this particular effect, exhibiting the relationships among (1) the free energy of $HO^*$ ($\Delta G_{HO^*}$, descriptor for ORR activity), (2) the free energy difference between $O^*$ and $HO^*$ ($\Delta G_{O^*} - \Delta G_{HO^*}$, descriptor for OER activity), and (3) $N_O$, the number of oxygen atoms coordinated to surface Mn. For the case of $Mn_2O_3$ surfaces, as the oxygen coordination number increases, $\Delta G_{HO^*}$ changes only marginally, while $\Delta G_{O^*} - \Delta G_{HO^*}$ changes by 0.7 eV, which means that the catalytic activities of manganese oxides can sometimes, but not always, be sensitive to oxygen coordination at the surface.

The close match between theoretical predictions and experimental results suggests that we have successfully modelled the surface structure of MnOx catalysts, and in particular how metal oxide surfaces change with pH and applied electrochemical potential. We have also successfully simulated the catalytic activity of those surfaces for the ORR and the OER, having identified the active surface structure as well as the reaction pathways involved. This insight gained from DFT calculations can now be used to improve the design principles for OER/ORR catalysts. For example, our theoretical calculations have identified that the stabilization of intermediates through hydrogen bonds with water is an important contributor to ORR overpotential on MnO$x$ catalysts. Therefore, a rational design of more hydrophobic catalyst structures, resulting in a reduced number of water molecules adsorbed on the surface, can lead to a significant improvement in ORR
activity of MnOₓ catalysts. Our calculations have also demonstrated that O* covered
MnO₂ surface is close to the top of OER volcano. Therefore, to improve the activity
of O* covered MnO₂ for OER, it will be necessary to modify the catalyst surface in
such a way as to break the scaling relationship between the energies of HOO* and
HO* intermediates. Finally, our finding that the number of oxygen atoms coordinated
to each Mn atom at the MnOₓ surface has a significant impact on the binding energy
of reaction intermediates suggests that manipulation of the surface coordination
environment, through approaches such as nanostructuring, doping, and alloying, can
also lead to an improved manganese oxide electrocatalysts for the ORR and the OER.

C.7 Conclusions

The surface electrochemistry of metal oxide catalysts is complex. Phase
changes are prevalent both at the surface and in the near-surface region that depend
greatly on pH and applied potential. And the structure of the material, both at the
surface and within the bulk, has a significant influence on catalyst activity. In this
work, we combine theory and experiment to understand this chemistry for the specific
case of MnOₓ materials that catalyze the ORR and the OER. The theoretical models
developed in this work, however, are more broadly applicable to other metal oxides as
well as to other electrocatalytic reactions.

Experimentally, we have shown that a nanostructured alpha-Mn₂O₃ is an
excellent bifunctional catalyst for the ORR and the OER, and that the catalyst likely
undergoes phase changes at the surface as a function of applied potential, in particular
at ORR potentials and in the potential window between the ORR and the OER. In an
effort to understand surface changes under reaction conditions, as well as how they
impact catalytic activity and reaction pathways for both reactions, we developed theoretical models using density functional theory (DFT). DFT calculations were employed to construct surface Pourbaix diagrams for MnO$_x$ and then to identify “theoretical overpotentials” for the surfaces present during reaction conditions across the pH and potential window. Our calculations reveal that the active surfaces for the ORR and the OER are ½ ML HO* covered Mn$_2$O$_3$ and O* covered MnO$_2$, respectively. As shown in Figure C.7 (b), this phase transition between the two operating conditions is beneficial in that MnO$_2$ is a better catalytic surface for the OER than Mn$_2$O$_3$. Thus an active catalyst phase is formed under each of the two reaction conditions.

The calculations also suggest mechanistic pathways for the ORR and the OER on the relevant surface structures: the ORR proceeds by the associative pathway, while for the OER, the direct pathway is favored slightly. Using these calculations we constructed theoretical LSVs for MnO$_x$ and predicted catalytic activity of the surfaces for the ORR and the OER. The theoretical LSVs agreed well with the experimental LSVs measured on a bifunctional MnO$_x$ catalyst; the close match between theory and experiment suggests that the theoretical model is accurate and robust.

By combining first-principles theoretical analysis and experimental methods, atomic-level insight into the catalyst chemistry can be achieved. This allows one to determine principles for improving catalyst design. For the ORR, our DFT model predicts that decreasing the surface's affinity for water adsorption should significantly increase catalytic activity, as it is desirable to destabilize the reaction intermediates HOO* and HO*. For the OER, our calculations show that to improve the activity of
MnO$_x$, it is necessary to design a surface structure that can break the scaling relationship between the energies of HOO* and HO* intermediates. If future ORR and OER catalysts are developed with these design principles in mind, superior activity for both reactions can be achieved.

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**C.9 Collaborations**

Hai-Yan Su, Isabela C. Man, Federico Calle-Vallejo, and Jan Rossmeisl performed DFT. Yelena Gorlin performed all electrochemical measurements.

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Appendix D

Deposition of Manganese Oxide Catalyst

Figure D.1: Representative cyclic voltammetry curves showing cycles 1 through 9 of manganese oxide thin film deposition from an aqueous solution of manganese acetate tetrahydrate (0.1 M) and sodium sulfate (0.1 M).
Appendix E

X-ray Diffraction of Manganese Oxide

Powder Standards

Figure E.1: X-ray diffraction data confirming (a) gamma-MnOOH, (b) alpha-MnO₂, beta-MnO₂, gamma-MnO₂, and lambda-MnO₂, and (c) alpha-Mn₂O₃ phases of powders used as standards in x-ray absorption spectroscopy (XAS) characterization.
Appendix F

X-ray Absorption Spectra of MnO₂ Polymorphs

Figure F.1: X-ray absorption spectra of four MnO₂ polymorphs (alpha-MnO₂, beta-MnO₂, gamma-MnO₂, and lambda-MnO₂) are compared to the spectrum of commercial MnO₂ powder purchased from Sigma-Aldrich (Aldrich).
Appendix G

Calculation of the Theoretical Diffusion Limited Current

According to Levich equation, the limiting current is given by\textsuperscript{144}

\[ i_d = 0.62nFD_0^{2/3}v^{-1/6}C_{O_2}w^{1/2} \]  \hspace{1cm} \text{(G.1)}

where \( i_d \) is the diffusion limited current in mA·cm\(^{-2}\), \( n \) is the number of electrons transferred during the reaction, \( F \) is the Faradays constant in mA·s·mol\(^{-1}\), \( D_{O_2} \) is the diffusion coefficient of oxygen in cm\(^2\)·s\(^{-1}\), \( v \) is the kinematic viscosity in cm\(^2\)·s\(^{-1}\), \( C_{O_2} \) is the solubility of oxygen in mol·cm\(^{-3}\), and \( w \) is the rotation rate of the rotating disk electrode in rad·s\(^{-1}\). In 0.1 M KOH electrolyte at 25°C, \( D_{O_2} \), \( v \), and \( C_{O_2} \) are 1.85·10\(^{-5}\) cm\(^2\)·s\(^{-1}\),\textsuperscript{145} 0.89·10\(^{-2}\) cm\(^2\)·s\(^{-1}\),\textsuperscript{146} and 1.21·10\(^{-6}\) mol·cm\(^{-3}\).\textsuperscript{145} For 2-electron and 4-electron oxygen reduction, the theoretical diffusion limited current at 1600 revolution per minute (rpm) rotation rate can be calculated to be 2.9 mA·cm\(^{-2}\) and 5.7 mA·cm\(^{-2}\), as shown in equations D.1 and D.2.

\[ i_{d2} = 0.62 \cdot 2 \cdot 9.65 \cdot 10^7 (1.85 \cdot 10^{-5})^{2/3} (0.89 \cdot 10^{-2})^{1/2} (1.21 \cdot 10^{-6}) \left( \frac{2\pi 1600}{60} \right)^{1/2} = 2.9 \text{ mA cm}^{-2} \]  \hspace{1cm} \text{(G.2)}

\[ i_{d4} = 0.62 \cdot 4 \cdot 9.65 \cdot 10^7 (1.85 \cdot 10^{-5})^{2/3} (0.89 \cdot 10^{-2})^{1/2} (1.21 \cdot 10^{-6}) \left( \frac{2\pi 1600}{60} \right)^{1/2} = 5.7 \text{ mA cm}^{-2} \]  \hspace{1cm} \text{(G.3)}
Appendix H

Determination of the Surface Area and Mass Activity of Catalytic Materials

Calculation of the surface area of Mn$_3$O$_4$ catalyst deposited on porous glassy carbon (Mn$_3$O$_4$/pGC) was challenging due its extremely low loading and irregular coverage of the pGC surface. Therefore, we estimated the surface area of the catalyst using the average diameter of MnO nanoparticles and the surface coverage of GC by MnO nanoparticles prior to heat treatment. The estimate is expected to be an upper bound of the actual surface area due to agglomeration and possible loss of nanoparticles during the heat treatment at 500°C, resulting in a decreased surface area of the catalyst. A representative SEM image of MnO on GC prior to heat treatment is shown in Figure H.1. Using information from four SEM images, we calculated 12% coverage of the surface with 14 nm diameter ($\sigma=3$ nm) of the nanoparticles. The corresponding surface area, calculated assuming a spherical geometry of the nanoparticles, was 0.10 cm$^2$.

The hydrogen Underpotential deposition (HUPD) charge from hydrogen adsorption and desorption on Pt/C was calculated in the region between 0.05 V and 0.5 V from a CV measured in the 0.05 V to 0.6 V potential window, shown in Figure H.2. As observed in the figure, the extension of the potential window to 1.1 V results in formation of platinum oxide during the anodic sweep, which is then reduced during the cathodic sweep in the region immediately prior to HUPD. Restriction of the anodic potential to 0.6
V avoids formation of platinum oxide and facilitates a more accurate estimation of the current due to double layer capacitance.\textsuperscript{156} After subtracting the charge of the double layer capacitance from the total HUPD charge, half of the resulting value, corresponding to the average of hydrogen adsorption and desorption processes, was divided by the expected deposition charge per platinum surface area of 210 $\mu$A·cm$^{-2}$ to obtain electrochemically active surface area of Pt/C.

![Figure H.1: SEM image of MnO nanoparticles prior to heat treatment at 500°C.](image)

**Figure H.1:** SEM image of MnO nanoparticles prior to heat treatment at 500°C.

![Figure H.2: Comparison of cyclic voltammetry (CV) of Pt/C from 0.05 V to 1.1 V to a CV restricted to 0.6 V to avoid formation of platinum oxide. CVs were obtained in nitrogen saturated 0.1 M KOH electrolyte, at 20 mV·s$^{-1}$ sweep rate, and 1600 rpm rotation rate.](image)

**Figure H.2:** Comparison of cyclic voltammetry (CV) of Pt/C from 0.05 V to 1.1 V to a CV restricted to 0.6 V to avoid formation of platinum oxide. CVs were obtained in nitrogen saturated 0.1 M KOH electrolyte, at 20 mV·s$^{-1}$ sweep rate, and 1600 rpm rotation rate.
The mass activity of Pt/C nanoparticles and Mn$_3$O$_4$/pGC catalyst was calculated by normalizing the kinetic current of the two catalysts to the estimated mass loading. The mass loading of Pt was determined from the concentration and volume of the dropcast catalyst ink to be 5.5 μg of Pt on the surface of GC. The mass loading of Mn$_3$O$_4$ in Mn$_3$O$_4$/pGC catalyst was estimated as 0.12 μg from the volume of MnO nanoparticles deposited prior to the thermal treatment which agglomerated the particles and converted the MnO to Mn$_3$O$_4$. A density of 5.28 g·cm$^{-3}$ was used for the MnO in this calculation. Attempts to estimate the mass loading using ICP-OES were not successful due to the low concentration of Mn. The plot showing iR-corrected potential vs. the mass activity on a logarithmic scale is shown in Figure H.3. From the figure, it is evident that Mn$_3$O$_4$/pGC has a high mass activity despite a lower onset potential than Pt/C nanoparticles.

![Figure H.3: Estimated mass activity of Pt/C nanoparticles and Mn$_3$O$_4$ on GC catalyst.](image-url)
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