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# Synthesis, Characterization, and Electrochemical Evaluation of Novel, Highly Active Catalysts for the Oxygen Reduction Reaction in Alkaline Media

Danae Jacquelyne Davis

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**SYNTHESIS, CHARACTERIZATION, AND  
ELECTROCHEMICAL EVALUATION OF NOVEL, HIGHLY  
ACTIVE CATALYSTS FOR THE OXYGEN REDUCTION  
REACTION IN ALKALINE MEDIA**

**by**

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**BACHELOR OF ARTS, CHEMISTRY**

**THESIS**

Submitted in Partial Fulfillment of the  
Requirements for the Degree of

**Master of Science**

**Chemistry**

The University of New Mexico  
Albuquerque, New Mexico

**December, 2013**

## DEDICATION

*This work is lovingly dedicated to my family,  
whose constant encouragement made this possible.*

*Philippians 4:13*

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◆ ◆ ◆

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**ABSTRACT**

Efficient electrocatalysts for the oxygen reduction reaction (ORR) are needed for fuel cells and next generation metal-air batteries, as the overall efficiency of these systems is currently limited by cathode kinetics. While Pt and Pt-based alloys demonstrate excellent electrocatalytic activities, their prohibitive cost and rarity ultimately prevents their widespread utilization. Catalyst materials that are highly active, stable, and cost effective are needed.

Manganese oxide ( $\alpha$ -MnO<sub>2</sub>) catalysts doped with varying amounts of Cu or Ni were synthesized, characterized, and evaluated for their performance as catalysts for the oxygen reduction reaction in alkaline electrolyte. Cu- $\alpha$ -MnO<sub>2</sub> nanowire catalysts consistently attained higher terminal current densities than those achieved with undoped  $\alpha$ -MnO<sub>2</sub>. As the amount of Cu-dopant in the nanowire increases, the kinetic rate constants increase, and the charge transfer resistances decrease. By studying the physicochemical properties of the Cu-doped catalysts, it was discovered that an increase in Cu-content

corresponds to an increase in catalyst surface area, as well as an expansion of the crystalline lattice. The observed improvement in catalytic behavior can also be attributed to an increase in surface  $\text{Mn}^{3+}$  character, as measured by X-ray photoelectron spectroscopy (XPS), that corresponds to an increase in Cu-dopant at the surface. Similarly, an increase in  $\text{Mn}^{3+}$  character is hypothesized to be a significant factor in the activities of Ni- $\alpha$ - $\text{MnO}_2$  catalysts, though the observed catalytic performance of this catalyst series does not trend directly with Ni-content.

In addition, a novel composite containing Ag and graphene nanoribbons (Ag-GNRs) was also studied. Catalytic studies revealed that the Ag-GNR composite outperforms a commercial Ag-Carbon catalyst as determined by comparing terminal current densities,  $n$ -values, kinetic rate constants, onset potentials, and half-wave potentials. In addition, the Ag-GNR composite is more electrocatalytically selective than the benchmark Pt/C catalyst when subjected to simulated methanol crossover effects.

## TABLE OF CONTENTS

<b>Chapter 1</b> The Oxygen Reduction Reaction: Relevance, Mechanisms, and Methods of Electrochemical Analysis.....	1
1.1 Introduction.....	1
1.2 Pathways of ORR.....	3
1.3 Methods for Electrochemical Analysis .....	4
<b>Chapter 2</b> A Brief Overview of Manganese Oxide Electrocatalysts for the Oxygen Reduction Reaction .....	15
2.1 Introduction.....	15
2.2 Diverse Physicochemical Properties of Manganese Oxides and Related Synthetic Techniques .....	15
2.3 Catalytic Performance and Related Rationale .....	20
2.4 The Effect of Dopant Cations and Co-deposited Species .....	24
2.5 Preparation of Manganese Oxide-Carbon Composites .....	26
2.6 Electrochemical Analysis of Composite Catalysts .....	28
2.7 Conclusions .....	33
<b>Chapter 3</b> Elucidating the Role of Cu-dopants in $\alpha$ -MnO <sub>2</sub> Nanowire Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Media .....	34
3.1 Introduction.....	34
3.2 Experimental .....	34
3.2.1 General .....	34
3.2.2 Synthesis .....	35
3.2.3 Materials Characterization .....	35
3.2.4 Electrochemical Studies .....	38
3.3 Results and Discussion .....	39
3.3.1 Synthesis and Characterization .....	39



3.3.2 Electrochemical Analysis.....	52
3.4 Summary and Conclusions .....	67
<b>Chapter 4</b> Efforts to Understand the Role of Ni-dopants in $\alpha$ -MnO <sub>2</sub> Nanowire Catalysts for the Oxygen Reduction Reaction in Alkaline Media.....	69
4.1 Introduction.....	69
4.2 Experimental .....	69
4.2.1 General .....	69
4.2.2 Synthesis .....	70
4.2.3 Materials Characterization .....	70
4.2.4 Electrochemical Studies.....	72
4.3 Results and Discussion .....	73
4.3.1 Synthesis and Characterization .....	73
4.3.2 Electrochemical Analysis.....	83
4.4 Summary and Conclusions .....	90
<b>Chapter 5</b> Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte .....	92
5.1 Introduction.....	92
5.2 Experimental .....	94
5.2.1 General .....	94
5.2.2 Synthesis and Characterization .....	95
5.2.3 Electrochemical Analysis.....	95
5.3 Results and Discussion .....	97
5.4 Summary and Conclusions .....	105
<b>Chapter 6</b> Summary and Conclusions .....	107
<b>References</b> .....	110

## LIST OF FIGURES

### Chapter 1

Figure 1.1: Schematic streamlines for the rotating disk system <sup>14</sup> .....	5
Figure 1.2: Representative LSV obtained at 500 rpm.....	6
Figure 1.3: Representative LSVs demonstrating an increase in observed current as a result of increased rotation rate.....	7
Figure 1.4: A representative LSV with the onset potential, half-wave potential, and terminal current density indicated.....	10

### Chapter 2

Figure 2.1: Various morphologies of nanoscale $\alpha$ -MnO <sub>2</sub> . a) nanowires <sup>19</sup> , b) flower-like nanospheres <sup>19</sup> , and c) nanotubes <sup>26</sup> .....	16
Figure 2.2: The crystal structures for $\alpha$ -, $\beta$ -, $\gamma$ -, $\delta$ -, and $\lambda$ -MnO <sub>2</sub> . <sup>30</sup> .....	19

### Chapter 3

Figure 3.1: Characterization data for the synthesized Cu-doped $\alpha$ -MnO <sub>2</sub> nanowires. a-c) SEM images of the nanowires synthesized at a Mn:Cu ratio of 1:1, 1:0.5, and 1:0.25, respectively. d-f) XRD patterns for Cu- $\alpha$ -MnO <sub>2</sub> nanowires synthesized at a Mn:Cu ratio of 1:1, 1:0.5, and 1:0.25, respectively.....	41
Figure 3.2: EDS spectra obtained by SEM for nanowires prepared at varying precursor ratios a) Mn:Cu ratio of 1:1, b) 1:0.5, and c) 1:0.25. The ratios of the relative intensities of the Cu K $\alpha$ and Mn K $\beta$ peaks are noted. ....	42
Figure 3.3: XPS data showing the splitting of the Mn 3s peaks a) 9.3% Cu, 0.50% Cu at surface, b) 7.8% Cu, 0.42% Cu at surface, c) 7.5 % Cu, 0.31% Cu at surface, and d) undoped $\alpha$ -MnO <sub>2</sub> .....	46
Figure 3.4: The splitting of the Mn 3s peaks ( $\Delta$ BE, eV) plotted as a function of the percent Cu measured at the surface by XPS. ....	47
Figure 3.5: Nitrogen sorption isotherms for a) Cu- $\alpha$ -MnO <sub>2</sub> , 9.3% Cu (81.5 m <sup>2</sup> /g), b) Cu- $\alpha$ -MnO <sub>2</sub> , 7.8% Cu (78.5 m <sup>2</sup> /g), and c) Cu- $\alpha$ -MnO <sub>2</sub> , 7.5% Cu (59.1 m <sup>2</sup> /g).....	49
Figure 3.6: Tetragonal (I4/m) structure; <sup>59</sup> image courtesy of M. Rodriguez (Sandia National Laboratories) .....	51

Figure 3.7: a-c) Averaged linear scanning voltammograms obtained for Cu- $\alpha$ -MnO<sub>2</sub> at 500, 900, 1600, 2500, and 3600 rpm. d) Comparative overlay of averaged LSVs obtained at 2500 rpm, revealing an increase in terminal current density that trends with Cu-content. .... 53

Figure 3.8: Overlay of Koutecky-Levich lines for Cu- $\alpha$ -MnO<sub>2</sub> catalyst samples; 7.5% Cu is shown in red, 7.8% Cu is shown in green, and 9.3% Cu is shown in blue. Idealized slopes for  $n = 2 e^-$  (short dashes) and  $n = 4 e^-$  (long dashes) are included for comparison. .... 55

Figure 3.9: RRDE data for Cu- $\alpha$ -MnO<sub>2</sub> catalysts; data for 9.3% Cu is shown in blue circles, 7.8% Cu is shown in green squares, and 7.5% Cu is shown in red triangles. .... 57

Figure 3.10: The d-orbitals of the Mn<sup>3+</sup> free ion (far left), the Mn<sup>3+</sup> ion in the octahedral complex (center), and the distorted tetragonal high spin state (far right). <sup>63</sup> ..... 64

Figure 3.11: A proposed reaction schematic for the ORR on the cationic transition metal B-site. <sup>63</sup> ..... 65

## Chapter 4

Figure 4.1: Characterization data for the synthesized Ni-doped  $\alpha$ -MnO<sub>2</sub> nanowires. a-c) SEM images of the nanowires synthesized at a Mn:Ni ratio of 1:1, 1:0.5, and 1:0.25, respectively. d-f) XRD patterns for Ni- $\alpha$ -MnO<sub>2</sub> nanowires synthesized at a Mn:Ni ratio of 1:1, 1:0.5, and 1:0.25, respectively. .... 75

Figure 4.2: TEM image of Ni- $\alpha$ -MnO<sub>2</sub> nanowires. .... 77

Figure 4.3: XPS data showing the splitting of the Mn 3s peaks a) 6.1% Ni, 0.57% Ni at surface, b) 4.4% Ni, 0.54% Ni at surface, c) 2.0% Ni, 0.29% Ni at surface, and d) undoped  $\alpha$ -MnO<sub>2</sub>. .... 79

Figure 4.4: The splitting of the Mn 3s peaks ( $\Delta BE$ , eV) plotted as a function of the percent Ni measured at the surface by XPS. .... 80

Figure 4.5: Nitrogen sorption isotherms for a) Ni- $\alpha$ -MnO<sub>2</sub>, 6.1% Ni (60.8 m<sup>2</sup>/g), b) Ni- $\alpha$ -MnO<sub>2</sub>, 4.3% Ni (52.3 m<sup>2</sup>/g), and c) Ni- $\alpha$ -MnO<sub>2</sub>, 2.0% Ni (51.8 m<sup>2</sup>/g). .... 82

Figure 4.6: a-c) Averaged linear scanning voltammograms obtained for Ni- $\alpha$ -MnO<sub>2</sub> at 500, 900, 1600, 2500, and 3600 rpm. d) Comparative overlay of averaged LSVs obtained at 2500 rpm, revealing an increase in terminal current density that does not trend directly with Ni-content. .... 84

Figure 4.7: Overlay of Koutecky-Levich lines for Ni- $\alpha$ -MnO<sub>2</sub> catalyst samples; 2.0% Ni is shown in pink, 4.4% Ni is shown in green, and 6.1% Ni is shown in blue. Idealized slopes for  $n = 2 e^-$  (short dashes) and  $n = 4 e^-$  (long dashes) are included for comparison. .... 86

## Chapter 5

Figure 5.1: A graphene sheet can be formed into fullerene (left), carbon nanotubes (center), and graphite (right). <sup>50</sup>	92
Figure 5.2: Generalized schematic demonstrating the unzipping of a nanotube, forming a nanoribbon. <sup>74</sup>	93
Figure 5.3: Linear scanning voltammograms for GNRs at 500, 900, 1600, 2500, and 3600 rpm.	98
Figure 5.4: Comparison of commercial Vulcan Carbon (gray circles) to GNRs (blue squares) at 2500 rpm.	99
Figure 5.5: Linear scanning voltammograms for Ag-GNR.	100
Figure 5.6: Composite plot for GNRs (blue squares), Ag/C (red diamonds), Ag-GNR (green triangles), and 20% Pt/C (black crossed squares), 2500 rpm.	101
Figure 5.7: RRDE data obtained at 500 rpm for Vulcan Carbon (gray circles), GNR (blue squares), Ag/C (red diamonds), Ag-GNR (green triangles), and 20% Pt/C (black crossed squares).	102
Figure 5.8: RRDE data for Ag-GNR (green squares) and 20% Pt/C (crossed squares), 500 rpm.	103
Figure 5.9: <i>i-t</i> chronoamperometric data for Ag-GNR (green triangles) and 20% Pt/C (crossed squares), 1000 rpm. Electrodes were held at a constant potential of -0.350 V vs. Ag/AgCl. Injection of 2 weight percent methanol occurred at <i>t</i> =250 seconds.	104
Figure 5.10: Percent chronoamperometric response data for Ag-GNR (green triangles) and 20% Pt/C (crossed squares) at -0.350 V upon injection of 2 weight percent methanol at <i>t</i> =250 seconds.	105

## LIST OF EQUATIONS

Equation 1.1: The Koutecky-Levich Equation .....	7
Equation 1.2: Determining $n$ -value using RRDE data.....	9
Equation 1.3: Determining the percent of evolved peroxide using RRDE data .....	10

## LIST OF TABLES

### Chapter 2

Table 2.1: Comparison of ORR Data for $\text{MnO}_x$ -Graphene Composites .....	29
---	----

### Chapter 3

Table 3.1: EDS Measurements of Atomic Percent Content of $\text{Cu-}\alpha\text{-MnO}_2$ , prepared at reactant ratio 1:1, Mn:Cu .....	43
Table 3.2: EDS Measurements of Atomic Percent Content of $\text{Cu-}\alpha\text{-MnO}_2$ , prepared at reactant ratio 1:0.5, Mn:Cu .....	44
Table 3.3: EDS Measurements of Atomic Percent Content of $\text{Cu-}\alpha\text{-MnO}_2$ , prepared at reactant ratio 1:0.25, Mn:Cu .....	44
Table 3.4: Atomic Percentage of Cu as Measured by XPS .....	45
Table 3.5: Splitting of Mn 3s Peaks as Observed by XPS.....	47
Table 3.6: BET Measurements of $\text{Cu-}\alpha\text{-MnO}_2$ Nanowires.....	48
Table 3.7: Unit Cell Parameters.....	51
Table 3.8: Electrocatalytic Data Extracted from Averaged Linear Scanning Voltammograms.....	59

### Chapter 4

Table 4.1: EDS Measurements of Atomic Percent Content of $\text{Ni-}\alpha\text{-MnO}_2$ , prepared at reactant ratio 1:1, Mn:Ni.....	76
Table 4.2: EDS Measurements of Atomic Percent Content of $\text{Ni-}\alpha\text{-MnO}_2$ , prepared at reactant ratio 1:0.5, Mn:Ni.....	76

Table 4.3: EDS Measurements of Atomic Percent Content of Ni- $\alpha$ -MnO <sub>2</sub> , prepared at reactant ratio 1:0.25, Mn:Ni.....	77
Table 4.4: Atomic Percentage of Ni as Measured by XPS .....	78
Table 4.5: Splitting of Mn 3s Peaks as Observed by XPS.....	80
Table 4.6: BET Measurements for Ni- $\alpha$ -MnO <sub>2</sub> Nanowires.....	81
Table 4.7: Electrocatalytic Data Extracted from Averaged Linear Scanning Voltammograms.....	88

## **Chapter 5**

Table 5.1: Electrocatalytic Data for GNRs, Ag/C, Ag-GNR, and 20% Pt/C .....	101
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## **Chapter 1**

### **The Oxygen Reduction Reaction:**

#### **Relevance, Mechanisms, and Methods of Electrochemical Analysis**

##### **1.1 Introduction**

Before many promising advanced technologies, such as optimized portable electronics, electric vehicles, and smart energy grids, can be widely utilized in modern society improved technologies capable of sustaining the necessary capacities for energy storage and conversion must be developed. <sup>1</sup> It is widely acknowledged that the existing supply of natural resources cannot support ever-increasing demands for power, which are expected to total 42 terawatts by 2050. <sup>2</sup> Thus, there is a momentous need for innovative power sources capable of sustaining rapidly evolving technologies.

Environmental compatibility, economic feasibility, and overall performance are crucial criteria that must be considered in the research and development phases of advanced power sources. Currently, metal-air batteries and fuel cells are two electrochemical systems being widely studied for their potential to meet the practical gravimetric energy density of gasoline. <sup>1, 3, 4</sup> The oxygen reduction reaction, commonly referred to as ORR, is a critical electrochemical process that occurs in both fuel cells and metal-air batteries. The factors currently limiting the performance of these promising electrochemical systems are the kinetics and energetics of the reduction reaction occurring at the cathode. Electrocatalysts for ORR must be highly active and durable. Since the kinetics and energetics of the oxygen reduction reaction determine the efficiency of the electrochemical system, sluggish processes will have an adverse impact

on the overall performance. In the past, many development efforts have focused on noble metal catalysts. While noble metals such as platinum, platinum alloys, gold, silver, ruthenium, and palladium demonstrate remarkable catalytic performances, these materials are costly and relatively scarce, thereby preventing widespread implementation of technologies benefitting from improved ORR kinetics.<sup>5-8</sup> Therefore, more economically viable, highly active electrocatalyst materials are needed.

Ultimately, bidirectional catalysts capable of catalyzing not only ORR but also the oxygen evolution reaction (OER) are needed for numerous applications that require reversibility. Bifunctional catalysts are employed in secondary batteries (which, unlike primary batteries, are electrically rechargeable) and regenerative fuel cells.<sup>9</sup> A bifunctional catalyst in a lithium-oxygen battery, for example, enables not only ORR during discharge but also OER upon charging.<sup>2</sup> OER is also integral in applications in which water is electrolyzed to form hydrogen and oxygen, applications which would enable chemical fuels to be derived from solar or electrical energy.<sup>10, 11</sup> The work reported in this thesis focuses exclusively on developing improved catalysts for the ORR in alkaline electrolyte; future work will be directed to developing the bifunctional catalysts necessary for the further development of advanced battery technologies.

Clearly, the path forward to achieving fully optimized electrochemical systems is not immediately apparent. As such, many research efforts are currently dedicated to investigating highly active, durable, cost effective materials in an attempt to enhance the electrochemical capabilities of batteries and fuel cells and thus ultimately enable new technologies to be realized. Numerous affordable materials that have been recently developed offer unique electronic properties and nanoscale structures that can provide



interesting catalytic behaviors, warranting further investigation for future applications in catalysis.

## 1.2 Pathways of ORR

The oxygen reduction reaction is thought to proceed through two possible pathways in alkaline solution, as seen below.<sup>7</sup> The reactions in acidic solution are also provided for comparison; however, the research presented in this thesis will focus exclusively on catalyzing the reaction in alkaline media. The reaction pathways in alkaline solution are either (i) a direct, four-electron process in which O<sub>2</sub> is reduced to OH<sup>-</sup>, or (ii) a less efficient two-step, two-electron pathway that involves the formation of hydrogen peroxide ions as an intermediate, which can then be further reduced by another two-electron process or can decompose catalytically. It is important to note that the catalytic decomposition process forms ½ O<sub>2</sub>, which can be reintroduced into the reduction pathways.<sup>7, 12</sup>

Obviously, the direct reduction pathway, which reduces oxygen to water, is ideal, as the indirect production of reactive peroxide species can corrode various components of electrochemical systems, such as membranes within a fuel cell or carbonaceous additives.

7, 13

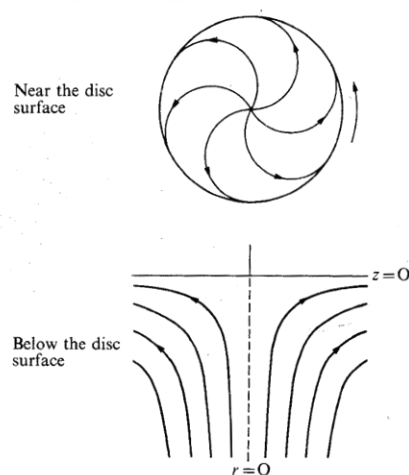
<p><b><u>Alkaline Solution:</u></b></p> <p>(i) Direct four electron pathway:  <math display="block">\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-</math></p> <p>(ii) Indirect (peroxide) pathway:  <math display="block">\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}^- + \text{HO}_2^-</math></p> <p style="text-align: center;">Followed by either</p> <p>(a) The further reduction of peroxide:  <math display="block">\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-</math>  or alternatively,  (b) The catalytic peroxide decomposition  <math display="block">\text{HO}_2^- \rightarrow \frac{1}{2} \text{O}_2 + \text{OH}^-</math></p>	<p><b><u>Acidic Solution:</u></b></p> <p>(i) Direct four electron pathway:  <math display="block">\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}</math></p> <p>(ii) Indirect (peroxide) pathway:  <math display="block">\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2</math></p> <p style="text-align: center;">Followed by either</p> <p>(a) Subsequent reduction:  <math display="block">\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}</math>  or,  (b) Decomposition of peroxide  <math display="block">2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2</math></p>
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It has been acknowledged that, for any catalyst, the direct four-electron process is not the predominant mechanism; rather, a stepwise four-electron process that occurs via two consecutive two-electron reactions in which peroxide is formed and reduced is the probable reduction mechanism.<sup>5</sup> Therefore, the ideal catalyst material must be capable of efficient electron transfer and rapid peroxide decomposition or reduction.<sup>5</sup> A discussion of how electrochemical techniques can be utilized to elucidate the reaction pathway, measure peroxide formation, and compare catalyst materials follows.

### **1.3 Methods for Electrochemical Analysis**

Electrochemical testing of catalysts for the oxygen reduction reaction is typically performed using techniques employing a rotating disk electrode (RDE) or rotating ring disk electrode (RRDE). Rotating electrodes are used because they enable the controlled transport of oxygen ( $O_2$ ) from the bulk of the electrolyte solution to the electrode.<sup>14</sup> By rotating the electrode, the electrolyte solution is continuously mixed, and the solution is drawn to the disk surface.<sup>15</sup> The resulting solution flow patterns in a given system are governed by many equations of hydrodynamics, which have been described extensively in numerous sources.<sup>8, 14</sup> The general principles of a rotating electrode can be understood by considering a disk electrode of a given radius rotating in a liquid at a constant rate. The liquid immediately adjacent to the surface of the disk participates in the rotational motion, while the liquid not immediately adjacent also rotates to some extent due to the viscosity of the solution.<sup>8</sup> As distance from the electrode increases, the rotational motion decreases. The centrifugal forces cause the rotating liquid to be transported to the periphery of the disk; assuming a continuous supply of liquid to the disk surface, this

process is repeated.<sup>14</sup> The limiting current, therefore, is predicted to be proportional to the square root of the rotation rate.<sup>8</sup> Figure 1.1 illustrates the general schematics for the rotating disk system.

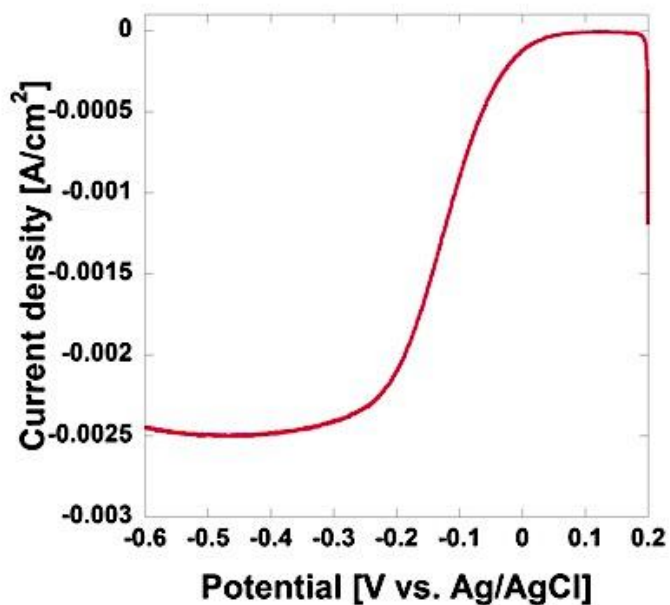


**Figure 1.1:** Schematic streamlines for the rotating disk system<sup>14</sup>

For electrochemical experiments aimed at studying the reduction of  $O_2$ , a thin layer of the electrocatalyst of interest is prepared on the glassy carbon surface of the disk electrode. Typically, this is achieved by drop coating a small aliquot of catalyst suspension, made by dispersing a known amount of catalyst via ultrasonication in an appropriate solvent. A solution of Nafion polymer is commonly included in the catalyst film to act as a binder that improves the adherence of the catalyst to the glassy carbon surface.<sup>6, 15-17</sup> Oxygen is purged through the electrolyte prior to the start of the experiment.

In linear scanning voltammetry, the current density at the working electrode is monitored as a function of the applied potential, which is scanned from a positive

potential to a negative potential, causing oxygen to be reduced. Figure 1.2 illustrates a typical linear scanning voltammogram (LSV) obtained at 500 rpm.

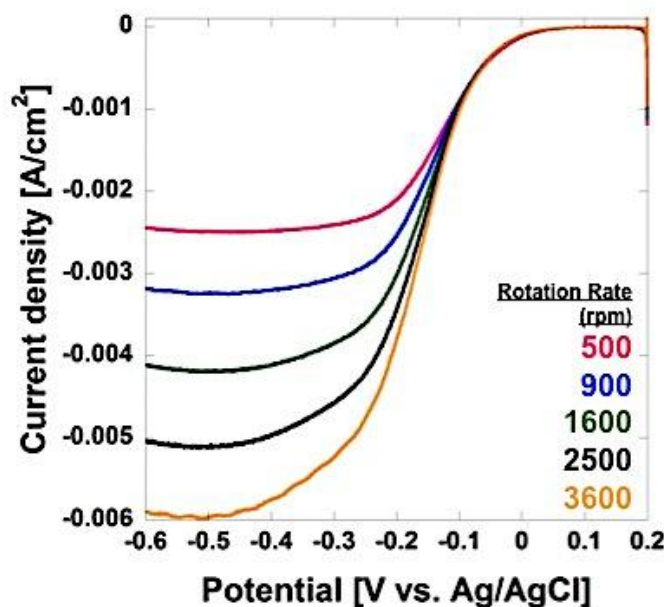


**Figure 1.2:** Representative LSV obtained at 500 rpm

In the curve shown in Figure 1.2, the potential is scanned from a positive potential (0.2 V vs. Ag/AgCl) to a negative potential (-0.6 V vs. Ag/AgCl). As the applied potential becomes increasingly negative, the magnitude of the current increases due the reduction of O<sub>2</sub>. Control experiments performed in a N<sub>2</sub>-purged solution in the same electrochemical window enable the subtraction of the background signal.

Rotation of the disk electrode at discrete rates changes the flux, or mass transport, of O<sub>2</sub> to the surface; as the rate of rotation increases, the flux of O<sub>2</sub> to the electrocatalyst increases, and the limiting current becomes increasingly negative, which is indicative of more oxygen arriving at the disk surface, resulting in increasingly more cathodic

(reduction) current being generated by the ORR.<sup>14, 15, 18</sup> The effect of rotation rate is illustrated in Figure 1.3.



**Figure 1.3:** Representative LSVs demonstrating an increase in observed current as a result of increased rotation rate.

The curves obtained in RDE experiments can be analyzed using the Koutecky-Levich equation, which is as follows:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = -\frac{1}{nFAkC^0} - \frac{1}{0.62nFAD_{O_2}^{2/3}v^{-1/6}C^0\omega^{1/2}}$$

**Equation 1.1:** The Koutecky-Levich Equation

where  $i$ ,  $i_k$ , and  $i_d$  represent the measured, kinetic, and diffusion-limiting current, respectively,  $n$  corresponds to the number of electrons transferred in the reduction,  $F$  is the Faraday constant,  $A$  is the geometric area of the electrode ( $\text{cm}^2$ ),  $k$  is the rate constant

for oxygen reduction,  $C^o$  is the saturated concentration of oxygen in electrolyte (0.1 M KOH,  $1.14 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $D_{O_2}$  is the diffusion coefficient of oxygen ( $1.73 \times 10^{-5} \text{ cm}^2/\text{s}$ ),  $\nu$  is the kinetic viscosity of solution ( $0.01 \text{ cm}^2/\text{s}$ ), and  $\omega$  is the rotation rate (rad/s).

18, 19

Applying the Koutecky-Levich equation to RDE data enables the extraction of several important catalytic criteria. The first is termed  $n$ -value, which is the number of electrons involved in the reduction process ( $n$ ); the  $n$ -value is calculated using the slope of the Koutecky-Levich line, which is obtained when the inverse of the current is plotted as a function of the inverse square root of the rotation rate.<sup>18</sup> Referencing the reaction schemes previously discussed and shown on page 3, it is apparent that the nominal value is equal to four. An  $n$ -value of four electrons indicates that the either a) the direct four electron reduction pathway or b) the competing apparent four electron process involving the formation and rapid reduction of peroxide are the predominant mechanisms. However, because there are numerous reactions occurring simultaneously, with complex electron-transfer processes involving O, OH,  $O_2^-$ , and  $HO_2^-$ , the  $n$ -value can actually be any value between two and four.<sup>1, 9, 13, 20</sup>

In addition, the kinetic rate constant ( $k$ ) can also be calculated from the y-intercept of the Koutecky-Levich line, and it is a useful metric of comparison when studying catalysts.<sup>18</sup> Since the rates of electrocatalytic reactions are affected by rates of varied adsorption processes for both initial-state reactants and intermediates, the value of  $k$  is most relevant when employed as a means to compare the relative rates of the entire process, as opposed to a single step of the complex mechanism.<sup>12</sup>

When a bipotentiostat is utilized, a rotating ring disk electrode can be used to monitor two electrochemical processes concurrently. In the context of oxygen reduction, rotating ring disk electrode studies allow for measurement of the amount of peroxide being generated in the system, in addition to the aforementioned metrics obtained from RDE studies. The solution flow patterns of a rotating disk electrode cause the product generated at the disk, peroxide, to be swept radially outward. Because the ring electrode surrounds the disk electrode and is isolated electrochemically, the ring electrode can detect the amount of peroxide present.<sup>15</sup> By using the currents generated at both the disk (reduction of O<sub>2</sub>) and the ring (oxidation of peroxide), hypotheses regarding the ORR mechanism can be formed. While the Koutecky-Levich equation can be used to analyze RRDE data, the equation that follows is also commonly applied, which yields an *n*-value for the process:

$$n = 4 \times \frac{|I_d|}{|I_d| + \frac{I_r}{N}}$$

**Equation 1.2:** Determining *n*-value using RRDE data

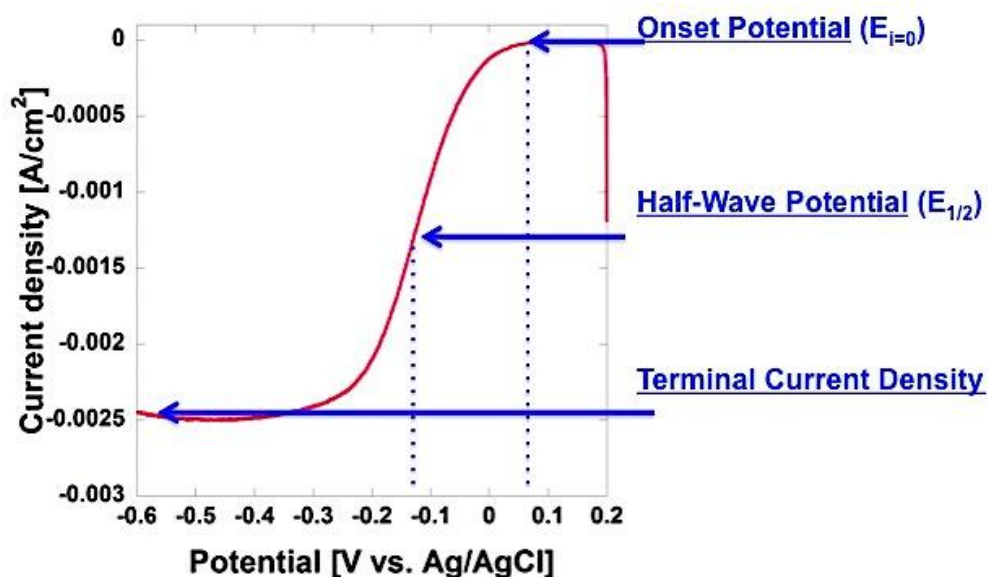
where *I<sub>d</sub>* is the disk current, *I<sub>r</sub>* is the current at the ring electrode, and *N* is the measured collection efficiency for the specific RRDE employed for the experiment.<sup>14, 21-23</sup> It should be emphasized that *N* is exclusively used to denote collection efficiency, a specific parameter for the ring electrode, whereas *n* consistently refers to the *n*-value.

Also, the following equation can be used to determine the percent peroxide generated.<sup>14, 21, 22</sup>

$$\% (\text{HO}_2^-) = 200 \times \frac{\frac{Ir}{N}}{\left( Id + \frac{Ir}{N} \right)}$$

**Equation 1.3:** Determining the percent of evolved peroxide using RRDE data

The linear scanning voltammograms contain a wealth of information that can be used to effectively assess catalyst performance and compare various catalysts. The obtained LSV curves are typically examined for onset potential, half-wave potential, and terminal current density (which can be further utilized to calculate mass activity, mA/mg). Several key criteria used for catalyst comparisons are outlined in Figure 1.4.



**Figure 1.4:** A representative LSV with the onset potential, half-wave potential, and terminal current density indicated

The onset potential ( $E_{i=0}$ ) can be conceptualized as the energy investment that must be made before the system begins to generate reductive current; clearly, the more



positive the onset potential, the lower the overpotential required for reduction. The defined reduction potential for the ORR is 0.401V vs. NHE at 25 °C.<sup>7</sup> Therefore, the overpotential is the difference between the theoretical reduction potential and the experimentally observed value. Many researchers assert that the onset potential is the first potential at which the current is a negative value;<sup>19</sup> therefore, this potential can be easily obtained by examining the numerical data from a LSV curve. However, it has been our assertion that since the first negative current density value is often negligible in magnitude, a more effective means of determining the true onset potential is needed. Also, the negligible negative current density often does not correspond to the potential at which the LSV visibly changes slope. Therefore, we calculate the onset potential by fitting two tangential lines to the LSV and finding the potential value that corresponds to their intersection. The first tangential line is fit to the sloped region (mass transport regime) of the LSV; the second tangential line is fit to the linear region that exists before negative current density predominates. Thus, these lines intersect where the slope of the LSV visibly changes slope, yielding a value that could be considered a more representative onset potential for oxygen reduction.

The half-wave potential ( $E_{1/2}$ ) is defined as the point half-way between zero current and the terminal current density plateau<sup>19</sup> - the more positive the half-wave potential, the more effective the catalyst, as it does not require high overpotentials to generate reductive current. The half-wave region is of particular interest because it is a potential range that is most realistic for the operation of electrochemical systems such as fuel cells in which ORR catalysts are commonly employed.<sup>24</sup>

Also relevant to any study of a novel catalyst material is a comparison to the commercial benchmark, typically regarded to be 20% Pt on Vulcan XC-72 Carbon (termed Pt/C).<sup>1</sup> The inclusion of an internal metric of comparison enables both the researcher and the scientific community to assess whether a not a novel material has the potential to attain or possibly exceed the catalytic activity routinely attained by Pt/C benchmarks.

While Pt-containing catalysts are known to demonstrate remarkable catalytic behavior, they are not electrocatalytically selective, meaning that these catalysts are subject to deactivation. For example, methanol crossover, a process that can occur in direct methanol fuel cells (DMFC), renders Pt catalysts relatively inactive. To show this, previous reports have demonstrated the drastic change (50 to 60% decrease) in current density that results upon injection of two weight percent methanol into an electrochemical cell in which Pt/C is the catalyst.<sup>24</sup> Also, Pt/C is sensitive to CO, a poison which originates from the H<sub>2</sub> fuel generation in conventional fuel cells. Carbon monoxide will strongly adsorb onto Pt surfaces, causing a decrease in the performance of the catalyst.<sup>3</sup> Therefore, another key criteria for catalysts to be employed in fuel cells is that they are electrocatalytically selective, not susceptible to possible deactivation or poisoning.

The research presented in this thesis describes the synthesis, characterization, and electrochemical evaluation of highly active, novel electrocatalysts for the oxygen reduction reaction. Chapter 2 outlines recent work in the development of manganese oxide catalysts, as well as recent syntheses of composite catalysts that augment the performance and conductivity of manganese oxides with graphene. Chapter 3 describes

the synthesis, characterization, and electrochemical evaluation of Cu-doped  $\alpha$ -MnO<sub>2</sub> nanowires, performed with the goal of determining the role of the Cu-dopant species in electrocatalysis. In a similar fashion, Chapter 4 describes the synthesis, characterization, and electrochemical evaluation of Ni-doped  $\alpha$ -MnO<sub>2</sub> nanowires; preliminary results regarding the specific electrocatalytic role of Ni-dopants are presented. Finally, Chapter 5 presents the electrocatalytic performance of a composite material comprised of silver nanoparticles on graphene nanoribbons. Chapter 6 provides a brief summary and overall conclusions of this research.



## **Chapter 2**

# **A Brief Overview of Manganese Oxide Electrocatalysts for the Oxygen Reduction Reaction**

### **2.1 Introduction**

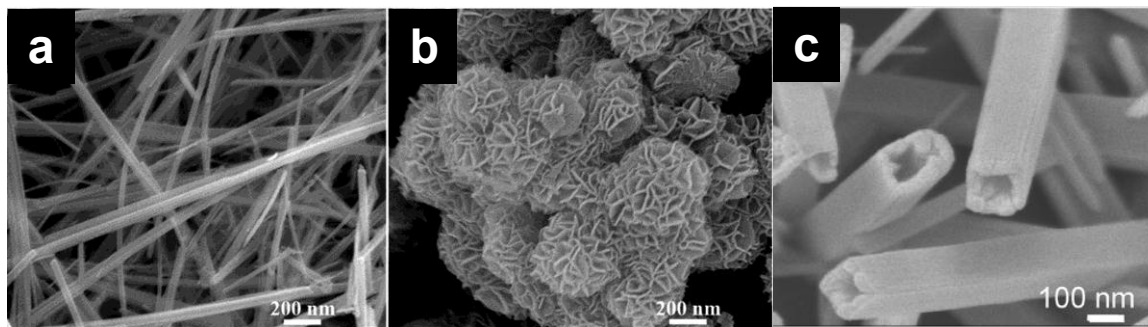
Manganese oxides have been utilized extensively as catalysts for the oxygen reduction reaction in alkaline electrolytes. First investigated in the early 1970s, manganese oxide was demonstrated to improve the performance of carbon-air electrodes when added in small amounts, generally less than 10% by weight.<sup>25</sup> Since then, numerous newly developed manganese oxide ( $\text{MnO}_x$ ) catalysts have been investigated extensively for applications as ORR catalysts and have consistently demonstrated promising catalytic behavior.<sup>19, 26, 27</sup> In addition to favorable catalytic performance, manganese oxides offer additional benefits of being environmentally benign, abundant, and relatively inexpensive, making them compelling alternatives to costly Pt and Pt-based alloys.

### **2.2 Diverse Physicochemical Properties of Manganese Oxides and Related Synthetic Techniques**

This overview will focus on various manganese oxides that have been synthesized on the nanoscale. Nanomaterials have typically demonstrated more promising electrochemical activities as compared to bulk materials due to their unique properties and reactivity.<sup>19, 28</sup> Manganese oxides are structurally versatile, and have been shown to exist in a number of diverse morphologies with varied particle sizes, stoichiometries, and crystalline phases. Many research efforts have focused on elucidating the effects of these

physicochemical factors on the electrochemical performance. As a result, changing the reaction parameters, such as duration, temperature, and reagents, often enables control of the shapes, sizes, and phases of the synthesized nanomaterials.<sup>28</sup>

A number of nanostructured morphologies have been synthesized, including plates, urchin-structures, spheres, flowers, cubes, wires, rods, belts, tubes, sheets, core-corona particles, stars, and dendritic hierarchical structures.<sup>19, 26, 28-34</sup> Uniquely shaped reaction products of various crystalline phases are commonly obtained by hydrothermal syntheses<sup>19, 26, 30-34</sup> or microwave-assisted hydrothermal processes,<sup>29</sup> but microemulsion techniques and sol-gel procedures have also been demonstrated.<sup>28</sup> Examples of the morphological diversity that exist in manganese oxide materials are shown in Figure 2.1.



**Figure 2.1:** Various morphologies of nanoscale  $\alpha$ -MnO<sub>2</sub>.  
a) nanowires<sup>19</sup>, b) flower-like nanospheres<sup>19</sup>, and c) nanotubes<sup>26</sup>

Xiao *et al.* demonstrated control of the product morphology by varying the reaction temperature of a hydrothermal synthesis using KMnO<sub>4</sub> (0.45 g) and HCl (1.0 mL, 37 wt. %) as reagents.<sup>29</sup> Lower temperatures (100 °C) yielded  $\delta$ -MnO<sub>2</sub> nanosheets, whereas tetragonal  $\alpha$ -MnO<sub>2</sub> nanorods and  $\alpha$ -MnO<sub>2</sub> nanotubes were observed at higher temperatures (120 °C and 140 °C, respectively).<sup>26</sup> This work also proposed a mechanism for the transition from  $\delta$ -MnO<sub>2</sub> nanosheets to  $\alpha$ -MnO<sub>2</sub> nanostructures; initially, unstable  $\delta$ -MnO<sub>2</sub> domains form, which are highly sensitive to both temperature and reaction

acidity. Diffusion of the  $\delta$ -MnO<sub>2</sub> domains to the stable  $\alpha$ -MnO<sub>2</sub> domains leads to a phase transition, ultimately forming  $\alpha$ -MnO<sub>2</sub> exclusively.<sup>26, 29</sup>

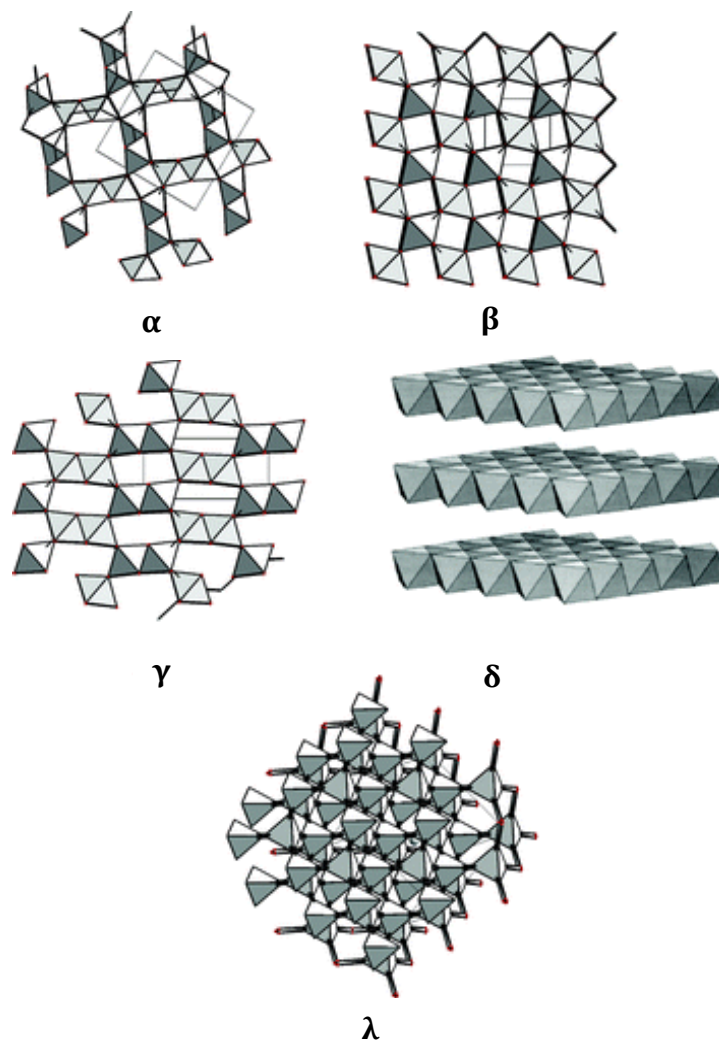
Other efforts have focused on determining how the morphology changes as a function of reaction time. The work of Truong *et al.* revealed that  $\delta$ -MnO<sub>2</sub> microflowers comprised of smaller nanosheets began to form after a mere two minutes of heating an aqueous solution of KMnO<sub>4</sub> and HCl within a microwave reactor. After five minutes,  $\alpha$ -MnO<sub>2</sub> nanowires begin to form, and after six hours pure  $\alpha$ -MnO<sub>2</sub> nanotubes are obtained.<sup>29</sup> For the hydrothermal syntheses performed by Cheng *et al.*, variations in the duration of the hydrothermal reaction between MnSO<sub>4</sub>·H<sub>2</sub>O and KMnO<sub>4</sub> caused significant changes in product morphology. Flower-like  $\alpha$ -MnO<sub>2</sub> nanospheres were obtained after two hours of heating, whereas  $\alpha$ -MnO<sub>2</sub> nanowires could be obtained after twelve hours.<sup>19</sup> In this synthesis, KMnO<sub>4</sub> is used to oxidize Mn<sup>2+</sup>.

A recent report by Sun *et al.* demonstrated the syntheses of  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub>,  $\gamma$ -MnO<sub>2</sub>, MnOOH, Mn<sub>3</sub>O<sub>4</sub>, and several mixed phases via hydrothermal processes.<sup>32</sup> By changing the concentrations of acetic acid (AcOH) and potassium acetate (AcOK) in the reaction while maintaining constant concentrations of MnSO<sub>4</sub> and KClO<sub>3</sub> at a standard reaction time (12 hours) and temperature (160 °C), the mechanism of crystal evolution for  $\beta$ -MnO<sub>2</sub> or MnOOH to  $\alpha$ -MnO<sub>2</sub> could be studied in detail. Through the precise control of the concentration of H<sup>+</sup> and K<sup>+</sup> ions, the attained product can be tailored, since these ions can affect the reaction acidity, stabilize crystal structures by occupying tunnel sites, or promote phase transformations.<sup>32</sup>

MnO<sub>2</sub> is of particular interest because it exists in a number of crystalline forms, which are denoted as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\lambda$  phases. The various possible arrangements of the

basic structural unit of  $\text{MnO}_2$ , the  $[\text{MnO}_6]$  octahedron, gives rise to the different crystalline forms in which the  $[\text{MnO}_6]$  octahedra are connected by sharing either corners or edges.<sup>19</sup> The resulting polymorphic structures can be divided into the three following classes: the one-dimensional chain-like tunnel structure ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases), the two-dimensional layered sheet structure ( $\delta$ - $\text{MnO}_2$ ), or the three-dimensional spinel structure ( $\lambda$ - $\text{MnO}_2$ ).<sup>19, 28</sup> The one-dimensional structures of  $\alpha$ -,  $\beta$ -, and  $\gamma$ - $\text{MnO}_2$  vary in the arrangement and sizes of the tunnels within the lattice. The  $\alpha$ - $\text{MnO}_2$  lattice contains both (2 x 2) and (1 x 1) tunnels;  $\beta$ - $\text{MnO}_2$  contains only (1 x 1) tunnels;  $\gamma$ - $\text{MnO}_2$  contains (1 x 2) tunnels, as well as (1 x 1) tunnels.<sup>19</sup> A defective structure based on  $\gamma$ - $\text{MnO}_2$  is also known to exist and is called  $\epsilon$ - $\text{MnO}_2$ .<sup>35</sup> Schematics of these  $\text{MnO}_2$  crystal structures are shown in Figure 2.2.





**Figure 2.2:** The crystal structures for  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ - $\text{MnO}_2$ .<sup>30</sup>

## 2.3 Catalytic Performance and Related Rationale

It is generally accepted that phase and morphology have significant impacts on the performance of manganese oxides for various applications, which include electrochemical capacitors,<sup>28, 30, 33</sup> molecular sieves,<sup>33, 36</sup> and catalysts for the combustion of volatile organic compounds.<sup>32, 37</sup> However, the discussion to follow will focus solely on the demonstrated performance of manganese oxides as catalysts for the oxygen reduction reaction. Nanostructured catalyst materials are of particular interest in the field of catalyst development because these materials possess higher surface areas than bulk counterparts, causing the adsorption, diffusion, and transport of small molecules ( $O_2$ ) to be more readily accommodated.<sup>19</sup> In addition, the porosity of nanostructures provides for improved interactions between  $O_2$  and the catalyst. Surface defects present in nanostructures could also influence their catalytic performance. Electrochemical data clearly reveals that the catalytic behavior of nanostructures outperforms that of bulk structures and microstructures.<sup>19</sup>

The activities of  $MnO_2$  phases employed as catalysts for the ORR have been demonstrated to be in the following order:  $\alpha\text{-}MnO_2 \approx \delta\text{-}MnO_2 > \gamma\text{-}MnO_2 > \lambda\text{-}MnO_2 > \beta\text{-}MnO_2$ .<sup>38</sup> This order of ORR activities was determined by examining the reduction currents generated by air cathodes in air-saturated 6M KOH solution. However, another study found  $\alpha\text{-}MnO_2 > \beta\text{-}MnO_2 > \gamma\text{-}MnO_2$  for both attained current density and the calculated n-value.<sup>19</sup> These experimental findings were correlated to the physical parameters of the crystal structures. Specifically, the  $\alpha\text{-}MnO_2$  structure possesses (2 x 2) tunnels of approximately 4.6 Å, which are larger than the (1 x 1) and (1 x 2) tunnels

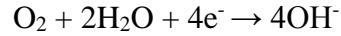
observed in the  $\beta$ - and  $\gamma$ -phases (1.89 Å and 2.3 Å, respectively).<sup>19,30</sup> Larger tunnels could promote the insertion and transfer of ions throughout the lattice.<sup>19</sup>

A recent study rigorously examined the  $\alpha$ - and  $\delta$ -MnO<sub>2</sub> phases and determined that  $\alpha$ -MnO<sub>2</sub> nanorods and nanotubes are more catalytically active than mixed microsphere/nanosheet  $\delta$ -MnO<sub>2</sub>,<sup>26</sup> a difference that was attributed to the Mn-O bond strength, channel structure, and the adsorption mechanism of O<sub>2</sub>. For  $\delta$ -MnO<sub>2</sub>, the average Mn-O bond length is 1.94 Å, as compared to the Mn-O bond length of 1.98 Å in the  $\alpha$ -phase. Therefore, the stronger Mn-O bond length in  $\delta$ -MnO<sub>2</sub> can be correlated to lower electrocatalytic activity. Also, the sheet-like structure of  $\delta$ -MnO<sub>2</sub> is dense, so although O<sub>2</sub> can be adsorbed in the interlayer region the tunneled structure of  $\alpha$ -MnO<sub>2</sub> is more favorable for the reversible adsorption and desorption processes required for electrocatalysis.<sup>26</sup> Finally, the O-O bond length of dioxygen, approximated to be 0.12 nm, is considered to be comparable to the size of the (1 x 1) tunnels present in  $\alpha$ -MnO<sub>2</sub>. Therefore, it is hypothesized that the O<sub>2</sub> molecule can bind in such a way that favors the cleavage of the O-O bond, promoting the four-electron pathway.<sup>26</sup>

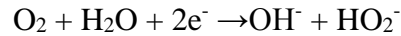
It is important to note that, for each of the aforementioned electrochemical studies of various phases of MnO<sub>2</sub>,  $\alpha$ -MnO<sub>2</sub> is consistently identified as the most active species. Cheng *et al.* synthesized this phase in two different morphologies. This work further demonstrated the effect that catalyst morphology has on activities of  $\alpha$ -MnO<sub>2</sub> catalysts;  $\alpha$ -MnO<sub>2</sub> nanowires were more catalytically active than nanospheres of the same crystalline phase.<sup>19</sup> The surface areas of the nanowires (32.9 m<sup>2</sup>/g) and nanospheres (40.1 m<sup>2</sup>/g) were comparable.

Revisiting the possible pathways for oxygen reduction in alkaline electrolyte, the reader will recall that there are competing reduction processes occurring. The various pathways for ORR in alkaline solution are outlined as follows: <sup>7</sup>

(i) Direct four electron pathway:



(ii) Indirect (peroxide) pathway:

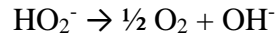


Followed by either

(a) The further reduction of peroxide:



(b) The catalytic peroxide decomposition:



With respect to manganese oxides ( $\text{MnO}_2$ ), the following equations have been presented to demonstrate how the Mn species mediates the charge transfer processes in the oxygen reduction reaction. <sup>19</sup>

Four-electron pathway	Two-electron pathway
$\text{MnO}_2 + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{MnOOH} + \text{OH}^-$	$\text{MnO}_2 + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{MnOOH} + \text{OH}^-$
$2\text{MnOOH} + \text{O}_2 \leftrightarrow 2(\text{MnOOH} \bullet \bullet \bullet \text{O})$	$\text{MnOOH} + \text{O}_2 \leftrightarrow \text{MnOOH} \bullet \bullet \bullet \text{O}_2$
$(\text{MnOOH} \bullet \bullet \bullet \text{O}) + \text{e}^- \leftrightarrow \text{MnO}_2 + \text{OH}^-$	$\text{MnOOH} \bullet \bullet \bullet \text{O}_2 + \text{e}^- \leftrightarrow \text{MnO}_2 + \text{HO}_2^-$
<hr/>	<hr/>
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{OH}^- + \text{HO}_2^-$

For both possible pathways, the first proposed step is the same – a charge is transferred, generating MnOOH. The primary difference between the apparent four-electron pathway and the indirect two-electron pathway is the manner in which O<sub>2</sub> is adsorbed. For the adsorption necessary for a four-electron process, the O<sub>2</sub> must adsorb onto two MnOOH neighboring sites and the O-O bond is cleaved. In contrast, to achieve a two-electron process, the O<sub>2</sub> can adsorb onto a single MnOOH site. Then, the bond between O atoms is not broken, thus generating HO<sub>2</sub><sup>-</sup>. It has been shown that  $\alpha$ -MnO<sub>2</sub> catalyzes the ORR through an apparent four-electron process ( $n = 4\text{ e}^-$ ) in which the peroxide intermediate is rapidly reduced upon its formation.<sup>23, 26, 38</sup> Other crystalline phases ( $\delta$ -MnO<sub>2</sub>, for example) give  $n \approx 3\text{ e}^-$ , indicating that both the apparent four-electron process and the two-electron process are occurring simultaneously.<sup>26</sup>

Manganese can exist in numerous oxidation states (+2, +3, +4, +6, and +7), a property that has been hypothesized to be a key factor in the catalytic activity of a transition metal-containing species. Because Mn-containing catalysts can be mixed-valent, it is possible that the redox reactions that occur simultaneously with the electron transfer to oxygen, as well as the storage of surface charges, are factors that enhance catalysis.<sup>39</sup> For  $\alpha$ -MnO<sub>2</sub>, the oxidation state is typically considered to be +4; however, it has been suggested that the presence of accessible Mn<sup>3+</sup> ions at the surface of MnO<sub>2</sub> electrocatalysts can account for the differences in demonstrated electrocatalytic activities.<sup>38</sup> Similarly, catalytic performance has been correlated to the Mn<sup>3+</sup>/Mn<sup>4+</sup> redox couple and the resulting average valence. The existence of this redox couple permits moderate bond strength between the catalyst and the reactant and/or product and facilitates rapid

charge transfer.<sup>39</sup> The role of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couple as it pertains to  $\alpha\text{-MnO}_2$  is discussed further in Chapter 3.

## 2.4 The Effect of Dopant Cations and Co-deposited Species

In order to further augment the catalytic activities demonstrated by nanoscale manganese oxides, numerous efforts have been focused on doping the crystalline lattice with various cations that are conductive and, ideally, affordable.<sup>23, 24, 40-42</sup> Roche *et al.* prepared  $\text{MnO}_x$ /carbon composites doped with Ni (~ 5 wt.%) or Mg (~ 2 wt. %) and found the doped catalysts to yield higher  $n$ -values as compared to the undoped catalyst, indicating an improvement in the ORR catalysis. The Ni-doped species was shown to give a significant decrease in the production of peroxide intermediate; the Ni was hypothesized to be stabilizing the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couple, thereby promoting the apparent four-electron reduction process.<sup>23</sup> Similarly, a Ni-doped/ $\text{MnO}_x$  catalyst prepared by Garcia *et al.* demonstrated enhanced ORR kinetics.<sup>41</sup> Benbow *et al.* synthesized Ni-doped  $\alpha\text{-MnO}_2$  nanorods that were shown to be more catalytically active than the undoped species in both aqueous and organic electrolytes.<sup>42</sup> In addition to studying Ni-doped  $\alpha\text{-MnO}_2$ , in recent work from our own group, Lambert *et al.* prepared a Cu-doped  $\alpha\text{-MnO}_2$  and demonstrated that both the Ni- and Cu-doped species were improved ORR catalysts relative to undoped  $\alpha\text{-MnO}_2$  in terms of calculated  $n$ -value, current density, onset potential, and peroxide formation.<sup>24</sup> Interestingly,  $\text{CaMnO}_3$  and  $\text{CaMn}_3\text{O}_6$  microspheres have also been studied as ORR electrocatalysts; calculated  $n$ -values were 3.95 and 3.86, respectively, and the average amount of peroxide generated was 2.2% for  $\text{CaMnO}_3$ .<sup>39</sup> In addition, the Ca-Mn-O species were shown to have slightly

better activity retention during durability studies conducted over 60,000 seconds as compared to the Pt/C benchmark.<sup>39</sup>

Other efforts have demonstrated improved catalysis by co-depositing nanoparticles of other metals (such as Ni, Au, and Ag) onto a manganese oxide template.<sup>19, 43, 44</sup> By utilizing  $\alpha$ -MnO<sub>2</sub> nanowires as a template material for the deposition of conductive Ni-nanoparticles, Cheng *et al.* were able to increase the conductivity of the catalyst by an order of magnitude as measured by a four-probe instrument, subsequently improving the half-wave potential, terminal current density, and calculated *n*-value.<sup>19</sup> The inclusion of nano-Au species on a nano-MnO<sub>x</sub> electrode was shown to decrease the amount of peroxide that was generated, indicating the promotion of the apparent four-electron reduction.<sup>43</sup> A composite of Ag/Mn<sub>3</sub>O<sub>4</sub> obtained via pyrolysis yielded a calculated *n*-value of 3.97 e<sup>-</sup>, and was determined to be more stable than Pt/C when subjected to accelerated aging studies.<sup>44</sup>

Alternatively, catalytic activities can be enhanced through facile post-treatment processes that induce oxygen vacancies in a given material. Recently, it was shown that the performance of  $\beta$ -MnO<sub>2</sub> could be improved through controlled calcination processes, which introduced oxygen defects to the surface. When O<sub>2</sub> is bound to the surface defect, the O-O bond is elongated and activated, and the kinetic barriers are lowered.<sup>45</sup> Also, the inclusion of conductive additives, such as commercially available carbons or graphene, is another technique proven to achieve enhancement of the catalytic character.<sup>19, 23, 24, 41, 46-</sup>

## 2.5 Preparation of Manganese Oxide-Carbon Composites

Commercially available conductive carbons have been utilized in composite catalysts for some time, including catalysts in which these carbons are paired with manganese oxides.<sup>23, 28, 41, 49</sup> However, while these investigations did demonstrate the fact that the conductivity of the composite is improved upon the addition of commercial carbonaceous species, graphene, a network of  $sp^2$  hybridized carbons, is also garnering significant attention in electrochemical applications. The high surface area, superior electron mobility, and tailorable surface properties of graphene make this material of interest for catalytic applications.<sup>50</sup> In order to achieve a true synergistic effect from a composite catalyst, the interactions between the ceramic material and graphene must be maximized so as to ensure that the entirety of the ceramic material is rendered electrochemically active while still being augmented by the conductive graphene component. Studies investigating  $MnO_x$ -graphene composite materials have addressed this through varied synthetic routes aimed at attaining optimized interactions between the active ceramic component and the conductive graphene.

Several groups have demonstrated an *in situ* preparation in which nanostructured  $MnO_x$  is grown directly on reduced graphene oxide (RGO). RGO commonly finds application as the graphene component of composite or hybrid catalyst materials due to its surface area (100-400  $m^2/g$ ) and conductivity. The primary synthetic route that is utilized to obtain RGO is a modified Hummers method<sup>51, 52</sup> in which graphite powder is oxidized, yielding graphene oxide (GO), which is then chemically reduced.<sup>53</sup> The commonly used Mn-containing precursors are  $KMnO_4$  or  $MnSO_4 \cdot H_2O$ , and are typically introduced after the graphene has been dispersed in solution.<sup>46, 54, 55</sup> Modified routes to



activated graphene-ceramic composites have also been employed - specifically, calcination of GO under N<sub>2</sub> to yield graphene nanosheets with KMnO<sub>4</sub> as ceramic precursor,<sup>54</sup> polymer-assisted chemical reduction of GO with MnSO<sub>4</sub>•H<sub>2</sub>O,<sup>55</sup> and ionic-liquid functionalization of GO followed by hydrazine reduction with NaMnO<sub>4</sub> as precursor.<sup>47</sup>

For each *in situ* preparation, the formation of the hybrid material is dependent upon certain interactions between the graphene and the Mn-containing precursor. Feng *et al.* report the preparation of a hybrid catalyst comprised of Mn<sub>3</sub>O<sub>4</sub> grown on GO coupled with mildly oxidized multi-walled carbon nanotubes.<sup>46</sup> As demonstrated by SEM, the Mn<sub>3</sub>O<sub>4</sub> nanoparticles are clearly coupled to the GO as a result of the *in situ* technique; the functional groups residing on the GO promote nucleation and a distinctly controlled formation of nanoparticles that are approximately 11 nm in size.<sup>46</sup>

The polymer-assisted route, yielding ceramic nanoparticles that are approximately 10-20 nm in size in the obtained composite MnO<sub>2</sub>/RGO, obtains similar results. In this synthesis, poly(sodium 4-styrene sulfonate (PSS), functions to promote the solubility of the graphene and improves the interactions between the Mn<sup>2+</sup> and the graphene, ultimately enabling the growth of MnO<sub>2</sub>.<sup>55</sup> The synthetic procedure involving the ionic liquid (IL) functionalized graphene material relies upon a reaction at the carboxylic acid groups on GO to obtain the functionalized species. This process demonstrates improved electronic conductivity for the GO-IL material, and later promotes the favorable electrostatic interactions with the Mn-containing precursor.<sup>47</sup> Cao *et al.* has shown the growth of  $\alpha$ -MnO<sub>2</sub> nanorods approximately 50-80 nm long and ~10 nm in diameter on

graphene nanosheets. The growth is facilitated by the electrostatic interactions between the  $\text{Mn}^{2+}$  and the oxygen-containing groups on the oxidized graphene nanosheets.<sup>54</sup>

*In situ* techniques are often selected in order to attain optimum, synergistic interactions between the ceramic and graphene that are considered unachievable by simple mixing techniques. While some groups do demonstrate that their hybrid composites are preferable to simple mixtures,<sup>46, 54</sup> it has also been shown that highly active, uniform blends can be attained through straightforward preparations. Previous work done in our laboratories in the Lambert group demonstrated that a simple sonication protocol performed with a graphene-like carbon scaffold (termed GLC) and  $\alpha\text{-MnO}_2$  nanowires doped with nickel or copper afforded a highly active catalyst material in which the doped  $\alpha\text{-MnO}_2$  nanowires appear by SEM to be uniformly dispersed throughout the GLC.<sup>24</sup> One such advantage of such a preparation is the ease with which multiple blends may be prepared and subsequently assessed; therefore, the optimal blend composition yielding the greatest current density could be determined (20% Ni- $\alpha\text{-MnO}_2$  and 80% GLC).<sup>24</sup>

## 2.6 Electrochemical Analysis of Composite Catalysts

In addition to enhancing the conductivity of the catalyst, graphene also improves the efficiency of ORR catalysis as suggested by the calculated  $n$ -value, though the exact mechanism of oxygen reduction on composite materials has yet to be elucidated. The majority of efforts reporting an  $n$ -value claim a value of approximately four electrons, which is the nominal value. A summary of notable data for  $\text{MnO}_x$ -graphene composites is given in Table 2.1.

**Table 2.1:** Comparison of ORR Data for MnO<sub>x</sub>-Graphene Composites

Author Ref.	Preparation of Composite	Composite Description	Electrolyte	n-value (Potential Range)  <i>Technique</i>	Onset Potential  <i>Half-Wave Potential</i>	Other Data of Interest
Feng  46	<i>in situ</i>	Mn <sub>3</sub> O <sub>4</sub> /Nano-C	1 M KOH	3.9 (-0.151 to -0.301 V)  3.7 (-0.601 V)  <i>RRDE</i>	Onset not presented  <i>-0.191 V (Pt/C -0.171 V)</i>	Reduction Peak Potential = -0.181 V at 5 mV/s  (Pt/C -0.151 V)
Lambert  24	simple mixing protocol	Cu- $\alpha$ -MnO <sub>2</sub> / GLC and Ni- $\alpha$ -MnO <sub>2</sub> / GLC	0.1 M KOH	3.9 $\pm$ 0.2 (avg. -0.280 to -0.530 V)  <i>RDE</i>	-0.042 V  <i>- 0.189 V (Comparable to Pt/C)</i>	Kinetic rate constant = 3.50 x 10 <sup>-2</sup> cm s <sup>-1</sup> compared to 3.24 x 10 <sup>-2</sup> cm s <sup>-1</sup> for Pt/C; Blend is tolerant to MeOH crossover
Lee  47	<i>in situ</i>	rGO-IL/Mn <sub>3</sub> O <sub>4</sub> (10:1)  rGO-IL/Mn <sub>3</sub> O <sub>4</sub> (2:1)	0.1 M KOH	3.50 (avg. -0.330 to -0.530 V)  2.75 (avg. -0.330 to -0.530 V)  <i>RDE</i>	estimated at -0.030 V  estimated at -0.070 V  <i>Approximated to be -0.180 V from LSV</i>	rGO-IL/Mn <sub>3</sub> O <sub>4</sub> (10:1) has comparable power density to commercial cathode when implemented in Zn-air cell
Wu  56	layered on electrode surface	$\alpha$ -MnO <sub>2</sub> on graphene	0.1 M KOH	K-L slope $\sim$ 4 (- 0.455 V)  <i>RDE</i>	Data not presented	Catalytic durability: 3.2 mA/cm <sup>2</sup> = current density for composite electrode after 10Ks of running time

*Reference potentials have been converted to V vs. Standard Calomel Electrode.*

*Relevant comparisons to Pt/C are provided for studies that presented this data.*

In addition to the well-established fact that  $\text{MnO}_x$  catalysts are capable of efficient peroxide decomposition,<sup>23</sup> it is also known that  $n$  is highly dependent upon the applied overpotential,<sup>46</sup> and this conclusion appears to be true for composite electrodes as well. Wu *et al.*, who prepared a layered electrode of  $\text{MnO}_2$  on GO, corroborates that the four-electron reduction can be achieved at lower overpotentials.<sup>56</sup> Results obtained by Lee *et al.* with  $\text{Mn}_3\text{O}_4$  grown on functionalized rGO (rGO-IL/ $\text{Mn}_3\text{O}_4$ ) show that, by applying the Koutecky-Levich equation to RDE data,  $n = 3.5$  could be obtained with a composite containing more rGO (prepared in a 10:1 weight ratio of rGO-IL to Mn precursor). Conversely, a composite that contains more  $\text{Mn}_3\text{O}_4$  (2:1 reactant ratio rGO-IL to Mn precursor) gives  $n = 2.75$ .<sup>47</sup> The authors attribute this to the two possible reaction pathways (a quasi-four-electron transfer and the two-step, two-electron path), and speculate that the reaction mechanism (and thus, the  $n$  value) can be tuned by the amount of ceramic in the composite. The  $\text{Mn}_3\text{O}_4$ /Nano-C hybrid containing GO and mildly oxidized multi-walled carbon nanotubes as prepared by Feng *et al.* is 67%  $\text{Mn}_3\text{O}_4$ , and gave  $n = 3.9$  at low overpotentials and 3.7 at higher overpotentials, as determined by the RRDE method. This technique also revealed that the peroxide produced by this hybrid varies from 5% at low overpotentials to ~15% at a high overpotential.<sup>46</sup> The manually blended Cu- $\alpha$ - $\text{MnO}_2$  (20%) / GLC (80%) catalyst prepared by Lambert *et al.* yielded  $n = 3.9 \pm 0.2$ , and corroborated that more peroxide is generated at higher overpotentials.<sup>24</sup>

For the papers that describe  $\text{MnO}_x$ -graphene composite materials, only two authors (Lambert and Lee) present onset potentials for their novel hybrids.<sup>24, 47</sup> For the sake of comparison, all potentials have been converted to the standard calomel electrode (SCE). The rGO-IL/ $\text{Mn}_3\text{O}_4$  composites prepared by Lee *et al.* at the ratios of rGO-IL:Mn

equal to 10:1 and 2:1 give onsets of approximately -0.030 V and -0.070 V, respectively.<sup>47</sup> Clearly, the 10:1 composite (determined to be 19.2% Mn) possesses an evident synergistic effect with respect to the onset potential, as the onset of rGO-IL is determined to be roughly equivalent to the 2:1 composite (52.5% Mn). Despite the higher carbon content of the 10:1 composite, the onset is 40 mV more positive, indicating that less energy has to be invested in the system to generate reductive current. Similarly, Lambert *et al.* show that the onset potential for the Ni- $\alpha$ -MnO<sub>2</sub> / GLC blend is -0.042 V, which is a value within the range obtained with Lee's composites.<sup>24</sup> In addition, they demonstrate that the onset is a tunable parameter that can be adjusted with the amount of Ni- $\alpha$ -MnO<sub>2</sub> incorporated into the blend.

Half-wave potentials for composite catalysts are provided for only two composites: Mn<sub>3</sub>O<sub>4</sub>/Nano-C (-0.191 V)<sup>46</sup> and the Cu- $\alpha$ -MnO<sub>2</sub> / GLC blend (-0.189 V).<sup>24</sup> A half-wave potential can be approximated from LSV curves for rGO-IL/Mn<sub>3</sub>O<sub>4</sub> 10:1 composite (-0.180 V).<sup>47</sup> For an extensive comparison of half-wave potentials of manganese oxides and manganese oxides blended with commercial conductive carbons, see the electronic supplementary material from Feng *et al.*<sup>46</sup>

Feng *et al.* performed a thorough assessment of reduction-peak potentials by CV for the Mn<sub>3</sub>O<sub>4</sub>/Nano-C hybrid as compared to the Mn<sub>3</sub>O<sub>4</sub> and Nano-C alone, as well as their physical mixture.<sup>46</sup> Also insightful is the comparison they present for 20% Pt on Vulcan from E-Tek. The hybrid material affords a peak potential of -0.181 V, which is more positive than the ORR peak potentials observed when the Mn<sub>3</sub>O<sub>4</sub> and Nano-C materials are tested alone, or when they are manually blended together. However, the demonstrated peak potential for the hybrid material is less positive than Pt/C, for which

the observed peak potential was -0.151 V. Similarly, the current densities obtained at 5 mV/s and 1600 rpm at varied catalyst loadings do not exceed -3 mA/cm<sup>2</sup>, while Pt/C yields a current density of nearly -4 mA/cm<sup>2</sup>.

Results presented by Lambert *et al.* demonstrate a remarkable tolerance to methanol crossover by the 20% Ni- $\alpha$ -MnO<sub>2</sub> / 80% GLC composite catalyst as compared to Pt/C. Specifically, the addition of 2 weight percent methanol into the electrochemical cell triggered a 60% decrease in current for Pt/C; conversely, the blended composite demonstrated a stable amperometric response with a mere 5% decrease in current. In addition, the kinetic rate constants for the 20% Ni- $\alpha$ -MnO<sub>2</sub> / 80% GLC composite and Pt/C are shown to be comparable ( $3.50 \times 10^{-2}$  cm/s and  $3.24 \times 10^{-2}$  cm/s, respectively).<sup>24</sup>

Two studies employed their composite catalysts in battery applications. The rGO-IL/Mn<sub>3</sub>O<sub>4</sub> (10:1) composite prepared by Lee *et al.* was employed in a Zn-air full cell and was shown to perform better than the commercial air cathode under the current density range from 0 to 200 mA/cm<sup>2</sup>.<sup>47</sup> The catalytic activities of the hybrid material comprised of  $\alpha$ -MnO<sub>2</sub> nanorods and graphene nanosheets ( $\alpha$ -MnO<sub>2</sub>/GN hybrid) prepared by Cao *et al.* was tested in LiO<sub>2</sub> batteries. The hybrid material delivered a higher reversible capacity under galvanostatic charge/discharge experiments than the mixtures of  $\alpha$ -MnO<sub>2</sub> and graphene nanosheets prepared via ball milling. In addition, the hybrid also demonstrated stable reversible capacities when the cycling stability was assessed.<sup>54</sup>

## 2.7 Conclusions

Ultimately, much of the work done thus far to investigate catalysts based on manganese oxide, both as independent catalyst materials and in hybrid composites with graphene, demonstrates the promise that these materials hold for effective implementation as oxygen reduction catalysts. Considering that manganese oxide based catalysts are affordable, environmentally friendly, and catalytically active, continued investigations in this regime of research are warranted. Continued advances toward optimizing these catalyst systems could lead to the development and widespread utilization of improved electrochemical devices that employ highly active manganese oxides as a catalyst material. One technique proven to enhance the catalytic performance of  $\alpha$ -MnO<sub>2</sub> is the addition of transition metal dopant species, such as Ni and Cu.<sup>24</sup> Chapters 3 and 4 will discuss my efforts to synthesize and characterize Cu- and Ni-doped  $\alpha$ -MnO<sub>2</sub> nanowires to gain a more thorough understanding of the role of the dopant species in ORR catalysis.

## Chapter 3

### Elucidating the Role of Cu-dopants in $\alpha$ -MnO<sub>2</sub> Nanowire

### Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Media

#### 3.1 Introduction

The synthesis of transition metal oxides is of interest for applications in energy storage and conversion.<sup>1, 28</sup> Manganese oxides have been extensively studied for their performance to catalyze the ORR, a critical reaction that occurs in fuel cells and metal air batteries. While our previous study of Cu- $\alpha$ -MnO<sub>2</sub> nanowires demonstrated improved catalytic performance relative to undoped  $\alpha$ -MnO<sub>2</sub>, a more thorough understanding of the role of Cu-dopants in catalysis was desired.<sup>24</sup> This study consisted of the synthesis, characterization, and electrochemical evaluation of Cu- $\alpha$ -MnO<sub>2</sub> nanowire catalysts containing varied levels of Cu-dopant. To our knowledge, this is the first study that correlates the physicochemical properties of Cu- $\alpha$ -MnO<sub>2</sub> nanowires to the demonstrated electrocatalytic behavior.

#### 3.2 Experimental

##### 3.2.1 General

All chemicals were obtained commercially and used as received, without further purification. MnSO<sub>4</sub>·H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were purchased from Alfa Aesar. KMnO<sub>4</sub>, isopropanol, and Nafion solution (5 wt. % solution in water and lower aliphatic alcohols) were used as received from Sigma-Aldrich.



### 3.2.2 Synthesis

The synthesis of Cu- $\alpha$ -MnO<sub>2</sub> nanowires was performed via a modified hydrothermal reaction in an acid digestion bomb (PTFE liner, 45 mL capacity, Parr™ reactor), adapted from a previously published synthesis for  $\alpha$ -MnO<sub>2</sub> and described in our previous studies.<sup>19, 24</sup> Solutions of MnSO<sub>4</sub>·H<sub>2</sub>O (0.2 g, 1.18 mmol), KMnO<sub>4</sub> (0.5 g, 3.16 mmol) and a specified amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in deionized water were heated in the acid digestion bomb at 140 °C for 120 hours to ensure nanowire morphology. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was added in specific molar ratios to the manganese-containing precursor of 1:1, 1:0.5 and 1:0.25 (Mn:Cu) to achieve different copper doping levels. Undoped  $\alpha$ -MnO<sub>2</sub> was obtained by a hydrothermal reaction that excluded the copper precursor.<sup>19, 24</sup> Following heating for 120 hours at 140 °C, all reactions were cooled to room temperature, and the solids were isolated by centrifugation (3000 rpm). The solids were washed with deionized H<sub>2</sub>O (4x, 10 mL) and ethanol (4x, 10 mL), isolated via centrifugation, and dried in a vacuum oven overnight at 65 °C.

### 3.2.3 Materials Characterization

**Powder X-ray Diffraction (PXRD).** Catalyst powders were mounted directly onto a zero background holder purchased from The Gem Dugout. Samples were scanned at a rate of 0.02°/2 s in the 2 $\theta$  range of 10-80° on a Bruker D8 Advance Diffractometer in Bragg-Brentano geometry with Cu K $\alpha$  radiation and a diffracted beam graphite monochromator; extended scans (12 hour scan time) were performed at a rate of 0.0240°/15 s in the range of 10-80°. Phase identification was achieved through use of the Jade 9.0 software suite and the Joint Committee on Powder Diffraction Standards (JCPDS). Diffraction peak positions were determined by profile fitting of peak profiles

within the program Jade 9.0 using a pseudo-Voigt profile function. Using these peak positions, lattice parameters were then derived using a least-squares refinement procedure embedded within the Jade 9.0 software. Initial values of the unit cell were input based on the  $\alpha$ -MnO<sub>2</sub> structure (JCPDS file number 00-44-0141).

***Transmission Electron Microscopy (TEM).*** TEM analysis was carried out on a JEOL 2010F electron microscope at 200kV acceleration voltage. Energy Dispersive Spectroscopy was collected using its attachment of Oxford Instruments ISIS/Inca System with Oxford Pentafet Ultrathin Window Detector (UTW).

***Scanning Electron Microscopy (SEM).*** The samples were dispersed onto carbon tape and imaged using a Zeiss Supra 55VP field emitter gun scanning electron microscope (FEGSEM). Samples were sputter coated with gold-palladium prior to analysis. A Noran Energy Dispersive X-Ray Spectroscopy (EDS) detector and Noran System Six software were used for the acquisition of the EDS spectra. EDS data were plotted with Kaleidagraph software for presentation purposes. Samples were sputter coated with gold-palladium prior to analysis.

***Brunauer-Emmett-Teller (BET) Surface Area Analysis.*** Gas sorption experiments were performed on an Autosorb iQ2-Chemi instrument (Quantachrome Instruments, Boynton Beach FL, USA) at 77 K (liquid nitrogen temperature) using ultra-high purity (UHP) nitrogen as adsorbate. Specimens were degassed at 140 °C for between 2 and 3 hours (the exact degas time was determined automatically based upon periodic evaluation of rate of gas evolution from each specimen). The specimen cells were quartz glass with a 9 mm outer diameter, and filler rods were inserted to reduce

dead volume above the sample. Cell volumes were determined prior to each run using ultra-high purity helium.

Isotherms were typically measured using 40 adsorption points and 40 desorption points, with an optional 30 additional adsorption points in the micropore range. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method using seven adsorption points in the range  $P/P_0 = 0.05$  to 0.3. Total pore volumes were calculated based on the total gas adsorbed at  $P/P_0$  values of 0.996. Pore sizes were determined using the Barrett-Joyner-Halenda (BJH) method during the desorption branch of the isotherm, ignoring  $P/P_0$  points below 0.35.

***X-ray Photoelectron Spectroscopy (XPS).*** X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra Delay-Line Detector (DLD) instrument with base pressures less than  $5 \times 10^{-9}$  Torr. Powder samples were pressed into carbon tape for analyses. No interferences from the carbon tape were observed. Charge neutralization was not required; however, the neutralizer was used for all samples to ensure that differential charging did not influence the spectral lineshapes. XPS was performed with a monochromatic Al-K $\alpha$  (1486.7 eV) source operated at 150 W with an elliptical spot size of 300x700 microns. Survey spectra were taken with a pass energy of 80 eV, 600 meV step, and 100 ms dwell times. With Al-K $\alpha$  X-rays, the Mn LMM Auger transition overlaps with the Cu 2p core-level peaks, so XPS was also performed with a non-monochromatic Mg X-ray source (1253.6 eV) operated at 180 W. The energy resolution is lower with the non-monochromatic source, so step sizes were 800-1000 meV for survey spectra. XPS with the Mg source was helpful for resolving the Cu 2p peaks on a relatively flat background. High resolution spectra were recorded with a 20

eV pass energy, 200 ms dwell time, and step sizes ranging from 30-50 meV (100 meV for Mg X-ray XPS). Data processing was performed with CasaXPS. Quantifications were performed using the built-in relative sensitivity factors. Mn 3s peak fitting was performed with a linear background and two unconstrained Gaussian/Lorentzian (70/30) peaks.

### 3.2.4 Electrochemical Studies

Oxygen reduction studies were performed using rotating disk electrode and rotating ring disk electrode assemblies. Catalyst inks consisting of 5.0 mg of catalyst material, 200  $\mu\text{L}$  isopropanol, and 300  $\mu\text{L}$  Nafion solution were sonicated for approximately 20 minutes. For RDE, a 5  $\mu\text{L}$  aliquot was drop-cast on a glassy carbon RDE electrode (BASi, active area = 0.0788  $\text{cm}^2$ ). For RRDE, 10  $\mu\text{L}$  of the prepared ink was drop-cast onto the glassy carbon disk, surrounded by a platinum ring electrode (Pine, disk area = 0.2475  $\text{cm}^2$ , ring area = 0.1866  $\text{cm}^2$ ). Prior to each drop-coating process, the RDE or RRDE glassy carbon electrode surface was polished with 0.05  $\mu\text{m}$  alumina slurry and rinsed with deionized water and ethanol.

Linear Scanning Voltammograms were executed in a potential window from 0.2 V to -0.6 V (V vs. Ag/AgCl) at a scan rate of 1 mV/s. For RDE, LSVs were run at rotation rates of 500, 900, 1600, 2500, and 3600 rpm. For RRDE, LSVs were obtained at 500 and 2500 rpm in a potential window from 0.2 V to -0.6 V, and the reference was Hg/HgO. The collection efficiency of the ring electrode ( $N$ ) was determined to be 37%.<sup>6,</sup>

<sup>14</sup> All experiments were run in 0.1 M KOH electrolyte that had been thoroughly purged with ultra-high purity oxygen (or ultra-high purity nitrogen for background

measurements) prior to each run. The appropriate gaseous atmosphere was preserved via blanketing for the duration of the experiment.

RDE experiments were performed in a three-electrode cell, manufactured by Bioanalytical Systems, Inc. connected to a Versastat 4 potentiostat operated by VersaStudio software. Electrodes (BASi) included the glassy carbon working electrode prepared as previously described, a Pt coil counter electrode, and a Ag/AgCl reference electrode (3 M NaCl, potential = 0.209 V vs. NHE). RRDE experiments were performed in a three-electrode cell, manufactured by Gamry Instruments connected to a Gamry Series G 750 Test System Bipotentiostat. Electrodes included the Gamry RDE710 rotating working electrode prepared as described, Pt foil as the counter electrode, and a Hg/HgO reference electrode (Hach, 0.1 M KOH, potential = 0.171 V vs. NHE).

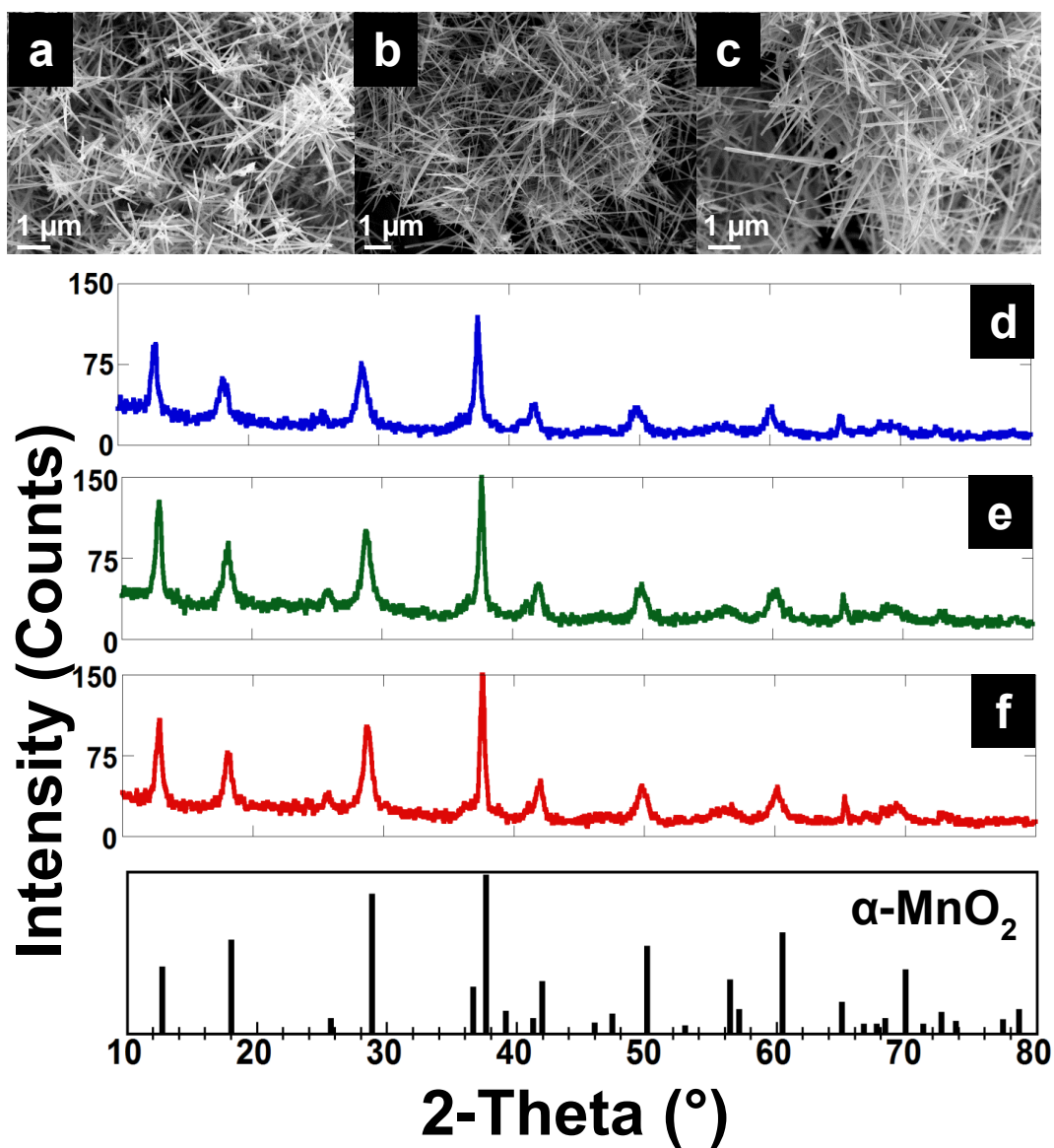
### **3.3 Results and Discussion**

#### **3.3.1 Synthesis and Characterization**

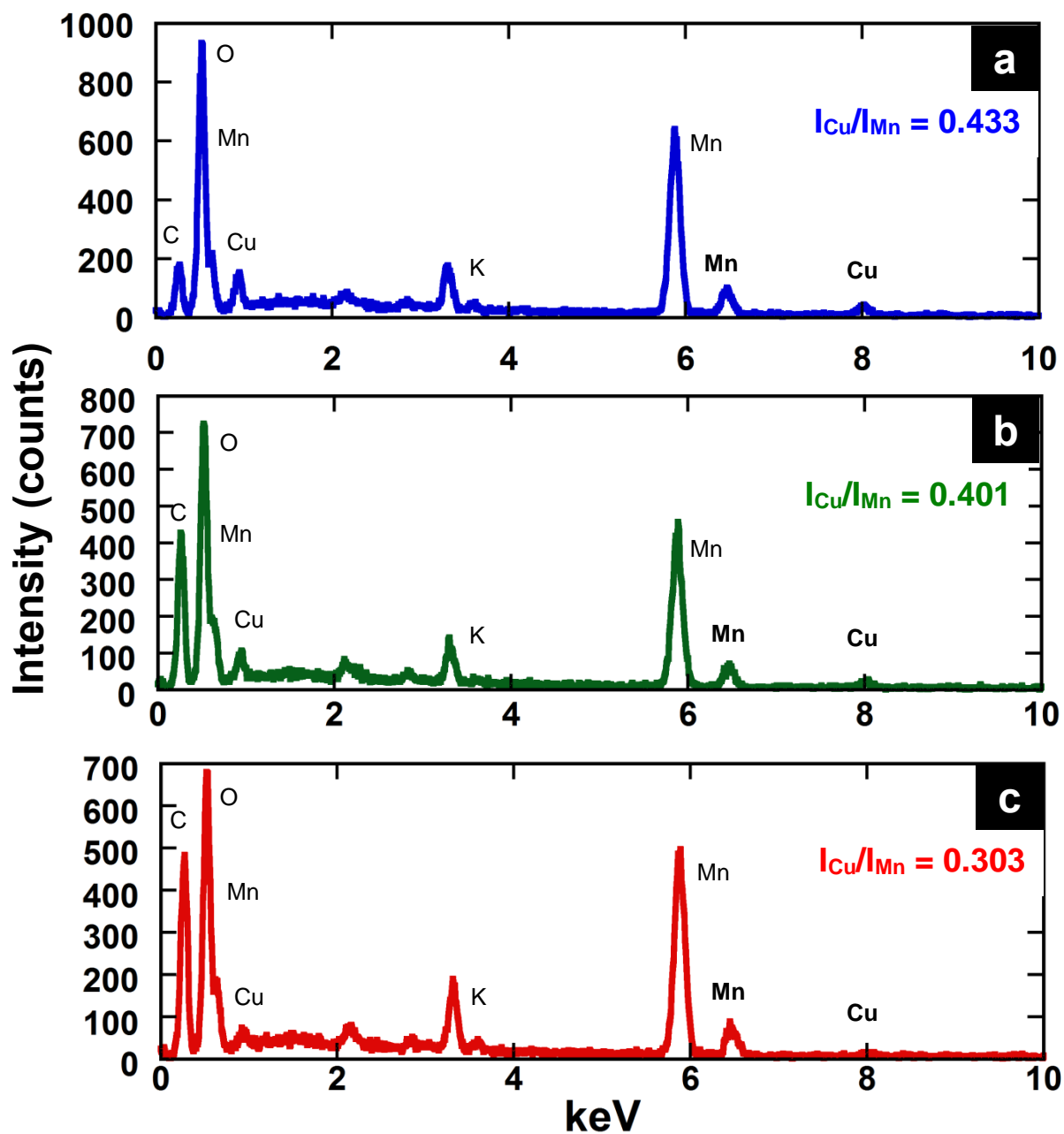
It has been previously demonstrated that  $\alpha$ -MnO<sub>2</sub> nanowires contain the most active crystalline phase and morphology, respectively, for manganese oxide nanostructures utilized for the ORR in alkaline electrolyte.<sup>19, 24</sup> The modified hydrothermal method utilized in this study was selected with the goal of synthesizing Cu-doped  $\alpha$ -MnO<sub>2</sub> nanowires. Therefore, the first characterization techniques utilized in this study were scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD). The hydrothermal syntheses previously described yielded nanowires at all reactant ratios, as shown in the SEM images in Figure 3.1 a-c. The crystalline phase was determined by

PXRD to be exclusively  $\alpha$ -MnO<sub>2</sub> (JCPDS file number 00-44-0141), Figure 3.1 d-f, indicating that the phase was retained upon attempted doping with Cu.

Initially, the presence of copper in the samples was confirmed and qualitatively approximated by energy-dispersive X-ray spectroscopy (EDS) obtained via scanning electron microscopy (SEM), Figure 3.2 a-c. As a preliminary comparison, a ratio of the intensities of the Mn K $\beta$  line at ~6.49 keV and the Cu K $\alpha$  line at 8.04 eV revealed that an increased amount of Cu precursor in the reaction correlated to an increased amount of Cu in the sample. Ratios trended from  $I_{\text{Cu}}:I_{\text{Mn}} = 0.433, 0.401$  to  $0.303$  for the 1:1, 1:0.5 and 1:0.25 (Mn:Cu) reactions, respectively.



**Figure 3.1:** Characterization data for the synthesized Cu-doped  $\alpha$ - $\text{MnO}_2$  nanowires. a-c) SEM images of the nanowires synthesized at a Mn:Cu ratio of 1:1, 1:0.5, and 1:0.25, respectively. d-f) XRD patterns for Cu- $\alpha$ - $\text{MnO}_2$  nanowires synthesized at a Mn:Cu ratio of 1:1, 1:0.5, and 1:0.25, respectively.



**Figure 3.2:** EDS spectra obtained by SEM for nanowires prepared at varying precursor ratios a) Mn:Cu ratio of 1:1, b) 1:0.5, and c) 1:0.25. The ratios of the relative intensities of the Cu  $K_{\alpha}$  and Mn  $K_{\beta}$  peaks (labeled in bold) are noted.



Quantitative measurement of the copper content of each sample was obtained by EDS performed via transmission electron microscopy (TEM), as shown in Tables 3.1, 3.2, and 3.3; average atomic percentages and the corresponding standard deviations are included as well. The sample synthesized at the initial reactant ratio of 1:1 (Mn:Cu) contained  $9.31 \pm 2.35\%$  Cu. The sample prepared at the reactant ratio of 1:0.5 (Mn:Cu) contained  $7.79 \pm 0.92\%$  Cu, and the sample prepared at the reactant ratio of 1:0.25 (Mn:Cu) contained  $7.55 \pm 1.52\%$  Cu.

**Table 3.1:** EDS Measurements of Atomic Percent Content of Cu- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:1, Mn:Cu

<b>Cu-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Cu</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	11.44	37.08	49.51	1.98
	7.72	39.84	49.19	3.25
	7.79	39.77	49.19	3.25
	8.02	39.73	49.25	3.01
	13.62	36.34	49.98	0.06
	13.25	36.71	49.99	0.05
	7.52	40.16	49.23	3.09
	8.3	39.84	49.38	2.48
	8.39	39.73	49.37	2.5
	7.06	40.51	49.19	3.25
<b>AVERAGE</b>	9.31	38.97	48.43	2.29
<b>STD. DEV.</b>	2.35	1.51	0.29	1.19

**Table 3.2:** EDS Measurements of Atomic Percent Content of Cu- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:0.5, Mn:Cu

<b>Cu-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Cu</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	8.38	39.19	49.19	3.24
	8.22	39.96	49.39	2.43
	7.49	40.46	49.32	2.74
	8.02	39.99	49.34	2.64
	9.82	37.51	49.11	3.56
	6.93	40.28	49.07	3.72
	6.13	40.62	48.92	4.33
	7.88	39.57	49.15	3.4
	7.36	39.83	49.06	3.74
	7.62	39.94	49.19	3.25
<b>AVERAGE</b>	7.79	39.74	49.17	3.31
<b>STD. DEV.</b>	0.92	0.84	0.14	0.55

**Table 3.3:** EDS Measurements of Atomic Percent Content of Cu- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:0.25, Mn:Cu

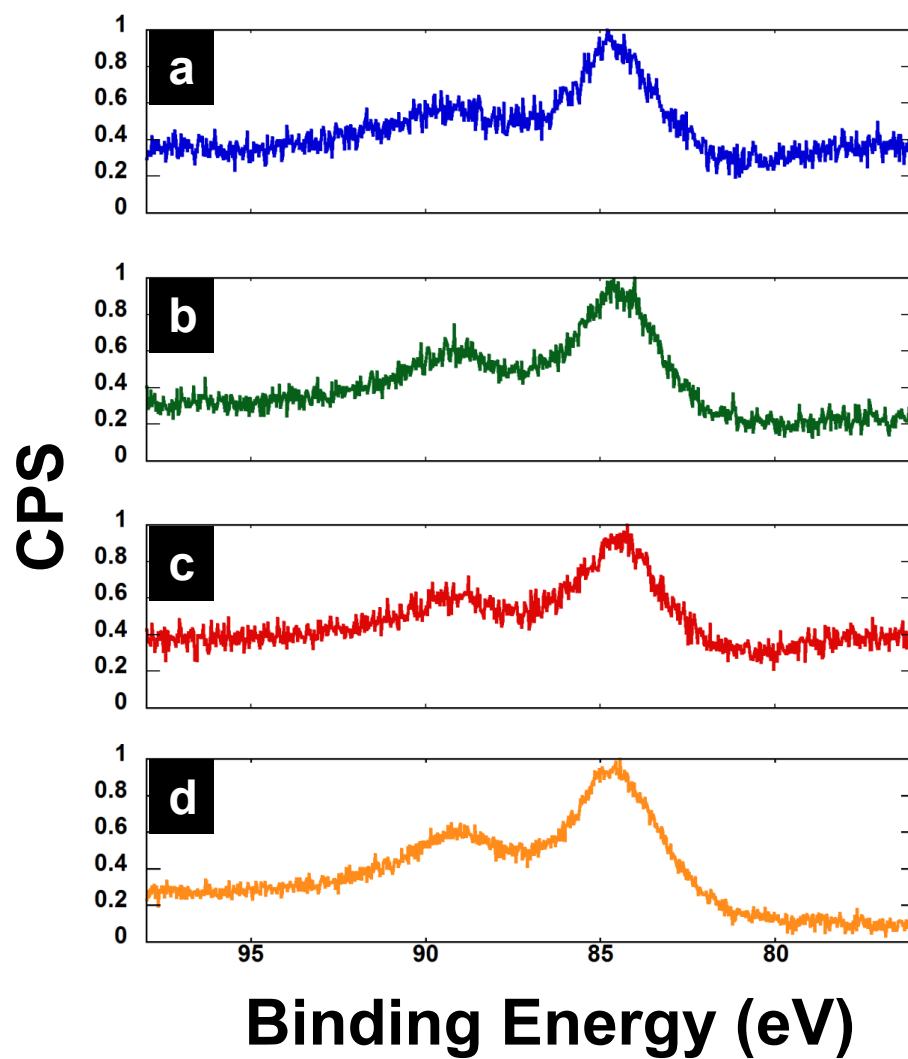
<b>Cu-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Cu</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	5.32	41.02	48.78	4.87
	6.54	41.42	49.32	2.71
	7.76	42.14	49.97	0.14
	7.43	42.48	49.97	0.12
	7.93	41.96	49.96	0.16
	8.45	41.45	49.97	0.13
	4.61	41.59	48.73	5.08
	9.2	40.28	49.83	0.68
	9.26	40.21	49.82	0.71
	8.95	37.73	48.9	4.41
<b>AVERAGE</b>	7.55	41.03	49.53	1.90
<b>STD. DEV.</b>	1.52	1.30	0.51	2.03

X-ray photoelectron spectroscopy (XPS) was used to analyze the percent composition at the surface of the nanowires. The Cu atomic concentration at the surface was found to be much lower than the Cu content of the nanowires measured by EDS, as demonstrated in the XPS data shown in Table 3.4. Because XPS is a surface-sensitive technique that probes a sample depth of approximately 10 nm whereas EDS analyzes the bulk, the notable differences between the EDS and XPS data can be rationalized.

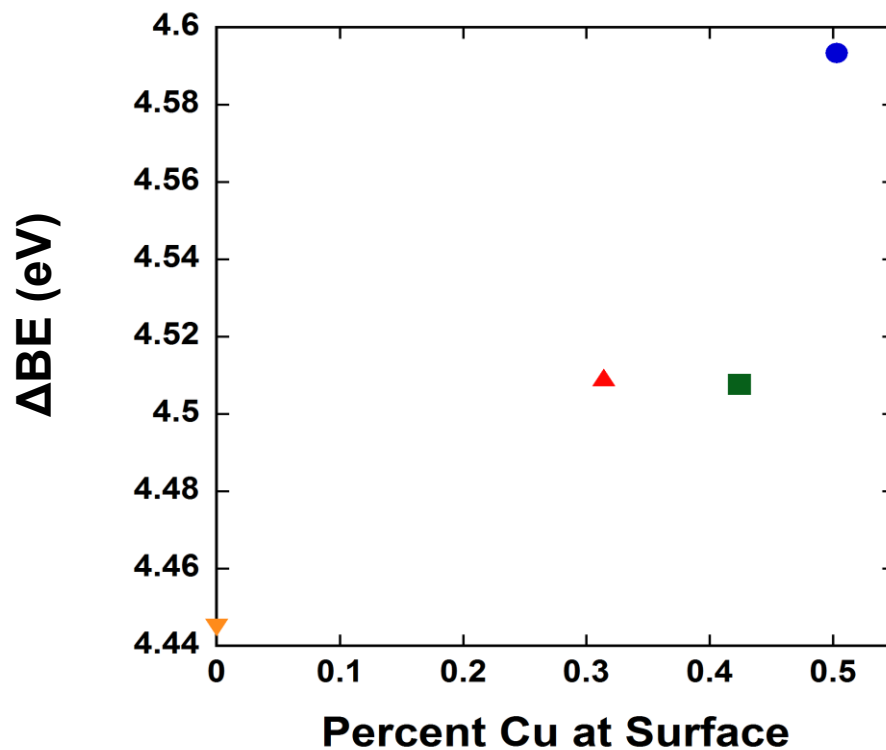
**Table 3.4:** Atomic Percentage of Cu as Measured by XPS  
*Percentages obtained by EDS are included for comparison.*

Sample (Mn:Cu Ratio)	Atomic % Cu (XPS)	Atomic % Cu (EDS)
$\alpha$ -MnO <sub>2</sub>	0%	0%
Cu- $\alpha$ -MnO <sub>2</sub> (1:0.25)	0.31%	7.5%
Cu- $\alpha$ -MnO <sub>2</sub> (1:0.5)	0.42%	7.8%
Cu- $\alpha$ -MnO <sub>2</sub> (1:1)	0.50%	9.3%

XPS was also utilized to gain a more thorough understanding of the oxidation states of the Mn ions within the Cu- $\alpha$ -MnO<sub>2</sub> catalysts; the data is presented in Figure 3.3. The difference in binding energies between the Mn 3s peaks can be used to approximate the oxidation state, as shown in Figures 3.3 and 3.4. As the amount of Cu in the sample increases, the extent of splitting between the Mn 3s peaks becomes greater, indicating that more Mn<sup>3+</sup> is present.<sup>57, 58</sup> The greatest splitting value (4.589 eV) was observed for the Cu- $\alpha$ -MnO<sub>2</sub> sample determined to contain 0.5% Cu at the surface; in comparison, the observed Mn 3s splitting for the undoped  $\alpha$ -MnO<sub>2</sub> sample was determined to be 4.445 eV. Figure 3.4 and accompanying data in Table 3.5 show that as the amount of surface Cu-dopant increases, the splitting between the Mn 3s peaks ( $\Delta$ BE) increases slightly.



**Figure 3.3:** XPS data showing the splitting of the Mn 3s peaks a) 9.3% Cu, 0.50% Cu at surface, b) 7.8% Cu, 0.42% Cu at surface, c) 7.5 % Cu, 0.31% Cu at surface, and d) undoped  $\alpha$ -MnO<sub>2</sub>.



**Figure 3.4:** The splitting of the Mn 3s peaks ( $\Delta BE$ , eV) plotted as a function of the percent Cu measured at the surface by XPS.

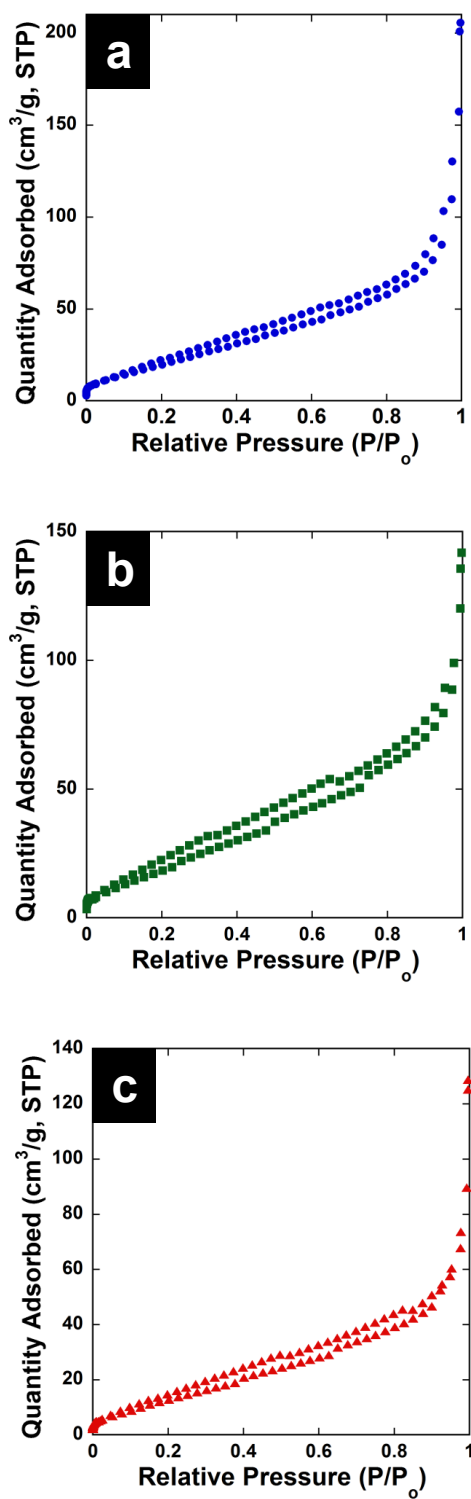
**Table 3.5:** Splitting of Mn 3s Peaks as Observed by XPS

Sample (Symbol)	Atomic % Cu (XPS)	$\Delta BE$ (eV)
$\alpha$ -MnO <sub>2</sub> ( <span style="color: orange;">▼</span> )	0%	4.445
Cu- $\alpha$ -MnO <sub>2</sub> ( <span style="color: red;">▲</span> )	0.31%	4.523
Cu- $\alpha$ -MnO <sub>2</sub> ( <span style="color: green;">■</span> )	0.42%	4.495
Cu- $\alpha$ -MnO <sub>2</sub> ( <span style="color: blue;">●</span> )	0.50%	4.589

The surface areas, average pore diameters, and pore volumes of the Cu- $\alpha$ -MnO<sub>2</sub> powders were analyzed using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method. The results of these studies are shown in Table 3.6, and corresponding isotherm plots are provided in Figure 3.5 a-c. The sample containing 9.3% Cu was determined to have a surface area of 81.5 m<sup>2</sup>/g, an average pore diameter of 5.9 nm, and a pore volume of 0.24 cm<sup>3</sup>/g. The sample containing 7.8% Cu was determined to have a surface area of 78.5 m<sup>2</sup>/g, an average pore diameter of 4.7 nm, and a pore volume of 0.18 cm<sup>3</sup>/g. Finally, the sample containing 7.5% Cu was determined to have a surface area of 59.1 m<sup>2</sup>/g, an average pore diameter of 4.7 nm, and a pore volume of 0.14 cm<sup>3</sup>/g. Clearly, as more Cu is introduced into the  $\alpha$ -MnO<sub>2</sub> structure, the surface area, pore size, and pore volume increase as well.

**Table 3.6:** BET Measurements of Cu- $\alpha$ -MnO<sub>2</sub> Nanowires

<b>Cu-content (avg. atomic %)</b>	<b>BET Surface Area (m<sup>2</sup>/g)</b>	<b>Average Pore Diameter (nm)</b>	<b>Pore Volume (cm<sup>3</sup>/g)</b>
7.5%	59.1	4.7	0.14
7.8%	78.5	4.7	0.18
9.3%	81.5	5.9	0.24



**Figure 3.5:** Nitrogen sorption isotherms for a) Cu- $\alpha$ -MnO<sub>2</sub>, 9.3% Cu (81.5 m<sup>2</sup>/g), b) Cu- $\alpha$ -MnO<sub>2</sub>, 7.8% Cu (78.5 m<sup>2</sup>/g), and c) Cu- $\alpha$ -MnO<sub>2</sub>, 7.5% Cu (59.1 m<sup>2</sup>/g).

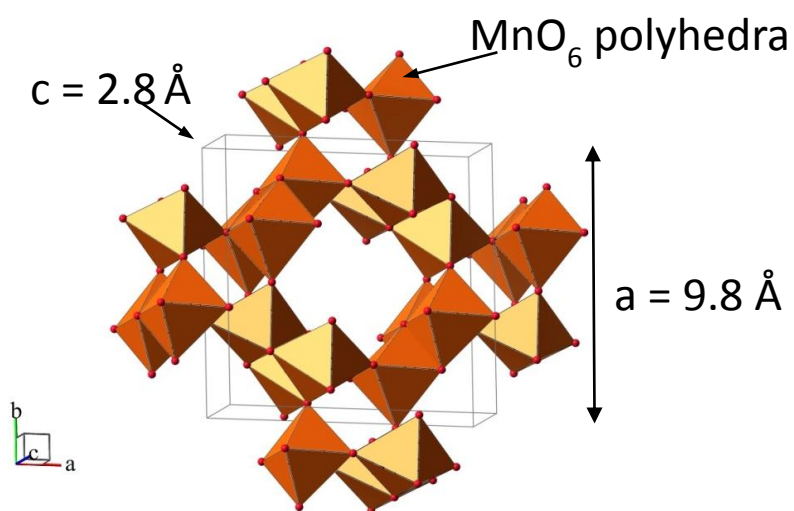
Further analyses of PXRD data were pursued to determine the effects of the Cu dopant on the unit cell parameters of the  $\alpha$ -MnO<sub>2</sub> lattice, Table 3.7. For the as-synthesized, undoped  $\alpha$ -MnO<sub>2</sub> sample, the dimensions of the a-axis (9.836 Å), c-axis (2.858 Å), and unit cell volume (276.45 Å<sup>3</sup>) were greater than the dimensions documented in JCPDS file 00-044-0141 (9.785 Å, 2.863 Å, and 274.1 Å<sup>3</sup>, respectively). Further expansions of the a-axis and cell volume were observed upon additional incorporation of Cu. For the sample containing 7.5% Cu, the a-axis was determined to be 9.838 Å and the c-axis was determined to be 2.859 Å, giving an overall cell volume of 276.74 Å<sup>3</sup>. For the sample containing 7.8% Cu, the a-axis was determined to be 9.84 Å and the c-axis was determined to be 2.857 Å, giving an overall cell volume of 276.5 Å<sup>3</sup>. For the sample containing 9.3% Cu, the a-axis was determined to be 9.866 Å, the c-axis was determined to be 2.857 Å, giving an overall cell volume of 278.12 Å<sup>3</sup>. The tetragonal unit cell structure for  $\alpha$ -MnO<sub>2</sub> is depicted in Figure 3.6.

Rietveld refinements for Cu- $\alpha$ -MnO<sub>2</sub> (9.3% Cu) and undoped  $\alpha$ -MnO<sub>2</sub> provided information about the average Mn-O bond lengths in the [MnO<sub>6</sub>] octahedra. The average Mn-O bond lengths in the Cu- $\alpha$ -MnO<sub>2</sub> sample (9.3% Cu) are  $1.900 \pm 0.010$  Å. This stands in comparison to the average bond lengths in the undoped  $\alpha$ -MnO<sub>2</sub>, which were determined to be  $1.915 \pm 0.035$  Å. It is hypothesized that the convergence of the Mn-O bond length on an average value of 1.9 Å can be partially attributed to Cu<sup>2+</sup> ions occupying some of the metal sites.



**Table 3.7:** Unit Cell Parameters

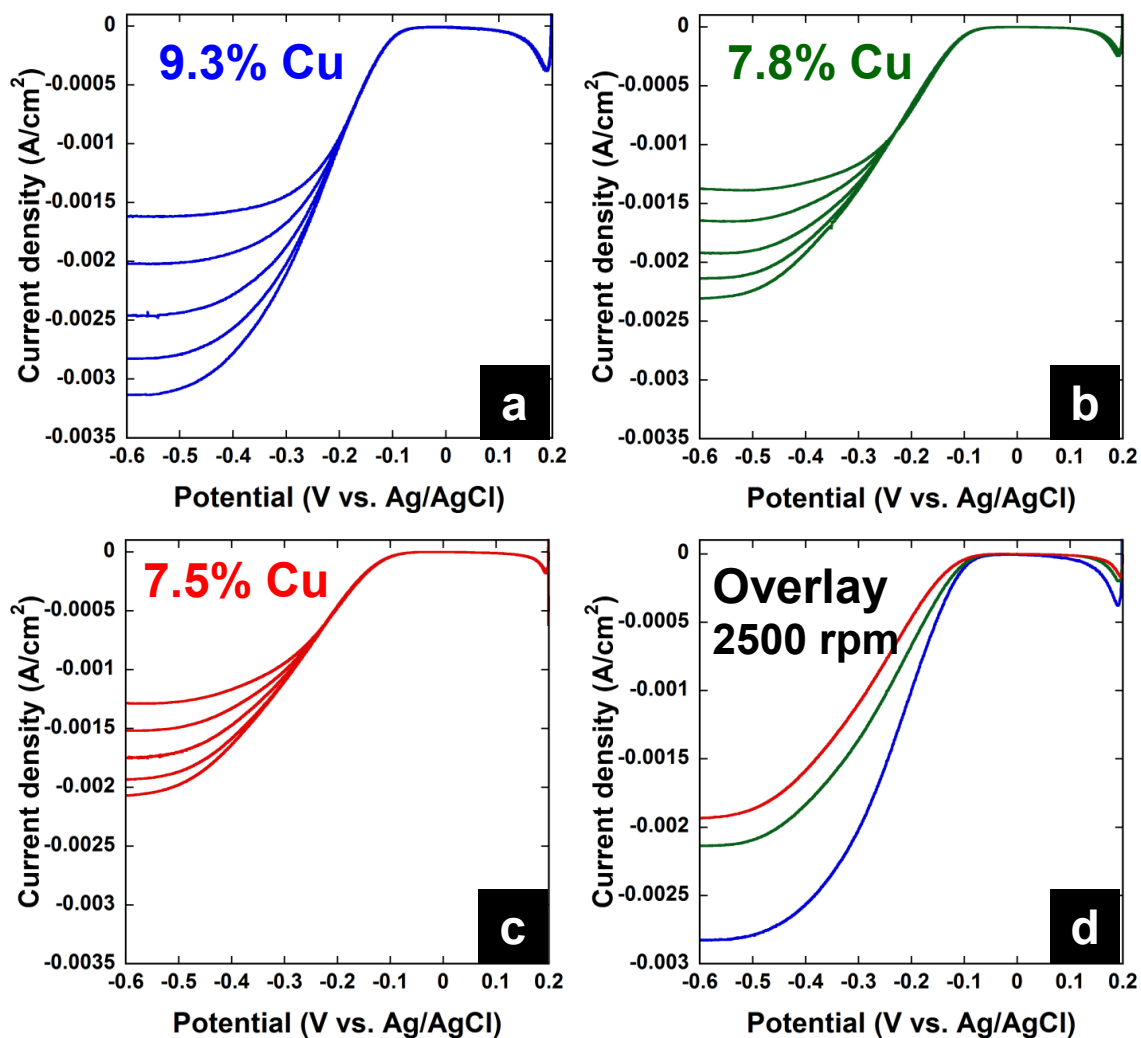
Sample	Cu %	a (Å)	c (Å)	Volume (Å <sup>3</sup> )
JCPDS 00-044-0141	0%	9.785	2.863	274.1
$\alpha$ -MnO <sub>2</sub> as synthesized	0%	9.836 (3)	2.858 (1)	276.45
Cu- $\alpha$ -MnO <sub>2</sub>	7.5%	9.838 (3)	2.859 (1)	276.74
Cu- $\alpha$ -MnO <sub>2</sub>	7.8%	9.84 (1)	2.857 (2)	276.5
Cu- $\alpha$ -MnO <sub>2</sub>	9.3%	9.866 (5)	2.857 (1)	278.12



**Figure 3.6:** Tetragonal (I4/m) structure; <sup>59</sup> image courtesy of M. Rodriguez (Sandia National Laboratories)

### 3.3.2 Electrochemical Analysis

Films of the as-synthesized Cu- $\alpha$ -MnO<sub>2</sub> powders were prepared via a drop-cast technique in which an aliquot of the catalyst ink was deposited onto rotating disk electrodes as previously described. The electrodes were utilized for RDE studies, which enable the observation of kinetically controlled processes in the absence of mass-transfer phenomena. Figure 3.7 shows averaged linear scanning voltammograms (obtained for Cu- $\alpha$ -MnO<sub>2</sub> at 9.3% Cu (Figure 3.7 a), 7.8% Cu (Figure 3.7 b), and 7.5% Cu (Figure 3.7 c). For each individual set of data, there is an increase in the terminal current density that corresponds to an increase in the rotation rate of the working electrode. This is attributed to the change in flux of O<sub>2</sub> to the electrode surface that occurs as the rotation rate increases. As demonstrated by the composite plot of LSVs obtained at 2500 rpm (Figure 3.7 d), there is an observed increase in the terminal current density attained that correlates to increasing Cu-content of the catalyst. The terminal current density (-0.6 V vs. Ag/AgCl) attained by the catalyst containing 7.5% Cu was -1.93 mA/cm<sup>2</sup>; for the catalyst containing 7.8% Cu, the terminal current density was -2.14 mA/cm<sup>2</sup>. Finally, for the catalyst containing 9.3% Cu, the terminal current density attained was -2.82 mA/cm<sup>2</sup>. When compared to the average terminal current density of for undoped  $\alpha$ -MnO<sub>2</sub> of -1.62 mA/cm<sup>2</sup>, it is apparent that the addition of Cu causes an increase in the terminal current density.

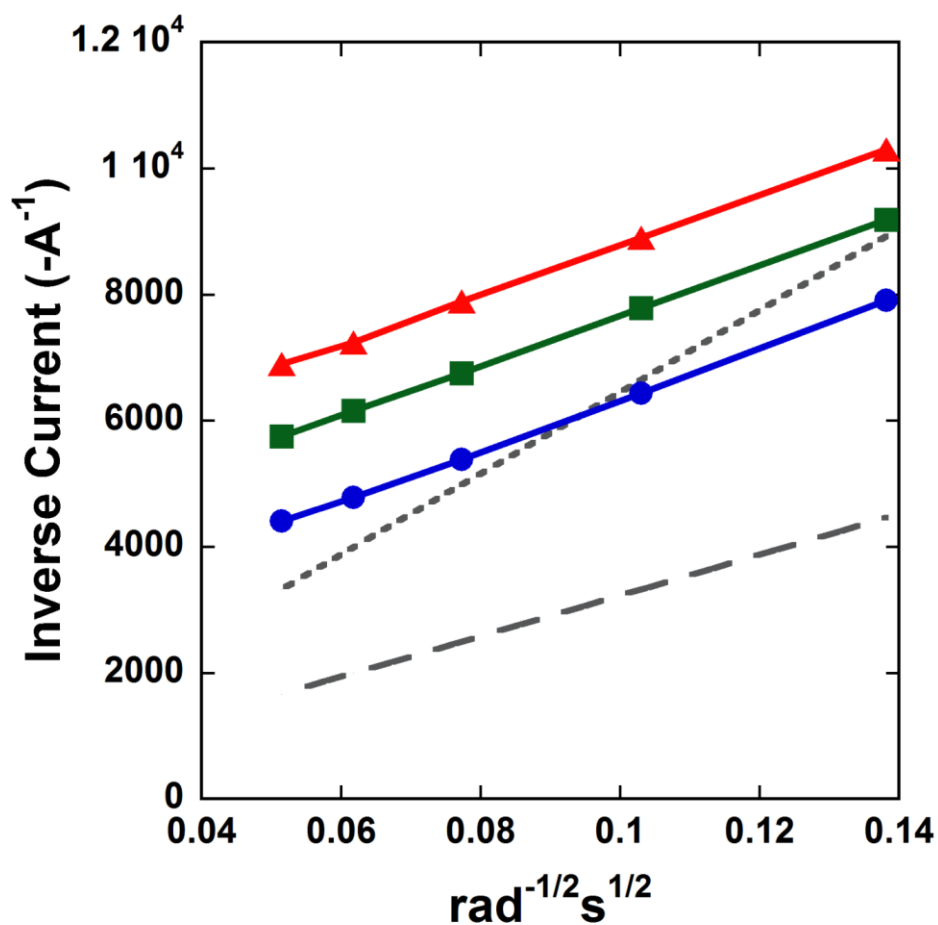


**Figure 3.7:** a-c) Averaged linear scanning voltammograms obtained for Cu- $\alpha$ -MnO<sub>2</sub> at 500, 900, 1600, 2500, and 3600 rpm. d) Comparative overlay of averaged LSVs obtained at 2500 rpm, revealing an increase in terminal current density that trends with Cu-content.

The linear scanning voltammograms contain a wealth of information that is useful in the comparison of various catalysts. As previously outlined in Chapter 1, the  $n$ -value, which is indicative of the reaction pathway that is predominant for a given catalyst, can be calculated by employing the Koutecky-Levich equation. Surprisingly, the average  $n$ -values calculated using the Koutecky-Levich equation revealed little difference between samples of varying Cu content. The calculated  $n$ -value for the Cu- $\alpha$ -MnO<sub>2</sub> sample containing 9.3% Cu was 3.20 e<sup>-</sup>, the calculated  $n$ -value for the Cu- $\alpha$ -MnO<sub>2</sub> sample containing 7.8% Cu was 3.31 e<sup>-</sup>, and finally, the calculated  $n$ -value for the Cu- $\alpha$ -MnO<sub>2</sub> containing 7.5% Cu was 3.28 e<sup>-</sup>. The  $n$ -value for undoped  $\alpha$ -MnO<sub>2</sub> of 3.1 e<sup>-</sup> has been calculated in previous studies by Cheng *et al.* and our own group.<sup>19, 24</sup> Our data suggests that the presence of Cu-dopants in  $\alpha$ -MnO<sub>2</sub> does cause a slight improvement in the attained  $n$ -value relative to undoped  $\alpha$ -MnO<sub>2</sub>, though there is not a significant difference in  $n$ -value that can be detected between Cu-doping levels ranging from 7.5% to 9.3%.

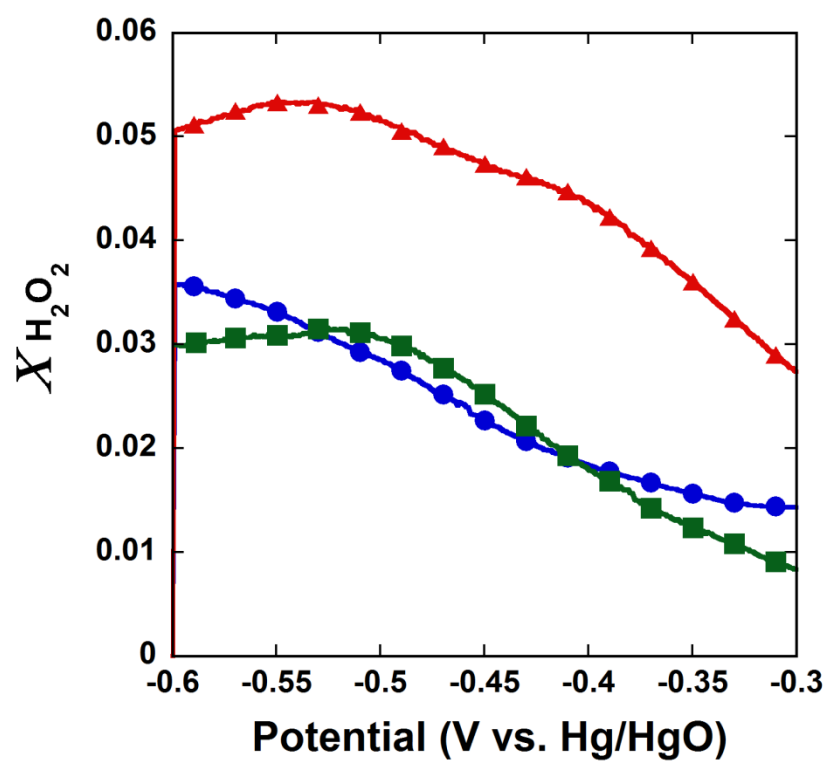
The kinetic rate constants, extracted from the y-intercept of the Koutecky-Levich plots, do indicate an increase in reaction rate that correlates with an increase in the Cu-content. This is clearly shown in Figure 3.8, which shows an overlay of the averaged Koutecky-Levich lines for each sample. The two factors of average  $n$ -value and reaction rate, when considered together, suggest that while the ORR mechanism is not highly influenced by the Cu-content of the  $\alpha$ -MnO<sub>2</sub> catalyst, the kinetic rate constant of the reaction increases as more Cu-dopant is added. When employed as a catalyst, the Cu- $\alpha$ -MnO<sub>2</sub> containing 9.3% Cu was shown to have an average kinetic rate constant of  $1.9 \times 10^{-2}$  cm/s, the sample containing 7.8% Cu gave an average rate constant of  $9.7 \times 10^{-3}$  cm/s, and the rate constant for the sample containing 7.5% Cu gave an average rate

constant of  $7.8 \times 10^{-3} \text{ cm/s}$ . When the kinetic rate constant obtained under identical conditions for  $\alpha\text{-MnO}_2$  is considered ( $7.5 \times 10^{-3} \text{ cm/s}$ ), it is evident that Cu enhances the ORR kinetics.



**Figure 3.8:** Overlay of Koutecky-Levich lines for Cu- $\alpha\text{-MnO}_2$  catalyst samples; 7.5% Cu is shown in red, 7.8% Cu is shown in green, and 9.3% Cu is shown in blue. Idealized slopes for  $n = 2 \text{ e}^-$  (short dashes) and  $n = 4 \text{ e}^-$  (long dashes) are included for comparison.

The assertion that Cu-dopants enhance the kinetics of the ORR appears to be true for the reactions in which peroxide is reduced or catalytically decomposed. Manganese oxides are acknowledged to promote the disproportionation and decomposition of peroxide intermediates.<sup>19, 23</sup> To study peroxide formation on our Cu- $\alpha$ -MnO<sub>2</sub> catalysts, RRDE experiments were performed. The amount of evolved peroxide was calculated by  $X_{H_2O_2} = 2(I_R/N) / [(I_R/N)+(I_D)]$  where  $I_R$  is the ring current,  $N$  is the collection efficiency of the ring electrode, and  $I_D$  is the disk current. The percentage of evolved peroxide can be easily obtained by  $X_{H_2O_2} \times 100\%$ .<sup>14, 21, 22</sup> Figure 3.9 illustrates the data extracted from RRDE experiments at 500 rpm from the approximate half-wave potential (-300 mV) to the terminal potential (-600 mV) and demonstrates that while the percentage of evolved peroxide is low (< 6%) for all samples, an increasing amount of Cu does appear to correlate to a decrease in the amount of peroxide that is generated.



**Figure 3.9:** RRDE data for Cu- $\alpha$ -MnO<sub>2</sub> catalysts; data for 9.3% Cu is shown in blue circles, 7.8% Cu is shown in green squares, and 7.5% Cu is shown in red triangles.

The onset potential is typically defined as the potential at which the current first becomes negative, as outlined in Chapter 1. An alternative approach to determining the onset potential in this study utilized the intersection of tangential lines fit to the curved portion of the LSV (half-wave region) and the region in which negligible current is generated. This point defines the onset potential as the point at which the slope of the LSV visibly changes. As shown in Table 3.8, Cu- $\alpha$ -MnO<sub>2</sub> catalysts have onset potentials ranging from -100.3 mV vs. Ag/AgCl for the highest Cu-content (9.3%) to -107.7 mV vs. Ag/AgCl for the lowest Cu-content (7.3%). However, the average onset potential for  $\alpha$ -MnO<sub>2</sub> in this study was determined to be -85 mV vs. Ag/AgCl. The average onset potential obtained in the same fashion for the benchmark catalyst, 20% Pt on Vulcan XC-72 Carbon (E-Tek), was found to be -51 mV vs. Ag/AgCl. Our previous study indicated that the addition of Cu-dopants improved the onset potential relative to  $\alpha$ -MnO<sub>2</sub>.<sup>24</sup> Therefore, the work performed thus far has not determined there to be a definitive effect of Cu-dopants on the onset potential of  $\alpha$ -MnO<sub>2</sub> nanowire catalysts. As stated in Chapter 1, the standard reduction potential for oxygen is 401 mV vs. SHE, or 192 mV vs. Ag/AgCl.<sup>1, 7</sup> The onset potentials measured in this study, including those for the Pt/C benchmark, are at higher (more negative) overpotentials than the ideal standard value, indicating that the thermodynamic potentials of the reduction reactions at the catalyst surfaces are less than the maximum potential.

The effect of Cu-dopants on the average half-wave potential is not conclusive. The average half-wave potentials of the Cu- $\alpha$ -MnO<sub>2</sub> samples do become increasingly positive as more Cu-dopant is introduced. However, when compared to the undoped  $\alpha$ -MnO<sub>2</sub> sample ( $E_{1/2}$  = -302 mV), only the Cu- $\alpha$ -MnO<sub>2</sub> catalyst containing 9.3% Cu



demonstrates only a slight favorable increase of +10 mV ( $E_{1/2} = -292$  mV). The half-wave potential for the catalyst containing 7.8% Cu was determined to be -303 mV, which is essentially equivalent to that of  $\alpha$ -MnO<sub>2</sub>. For the 7.5% Cu sample,  $E_{1/2}$  was determined to be -312 mV.

Charge transfer resistances were calculated from the slope of the linear portion of the current-potential curve at low overpotentials ( $\pm 10$  mV of the onset). When the amount of Cu-dopant reaches 9.3%, the average charge transfer resistance ( $3430 \pm 1391 \Omega$ ) has decreased by  $\sim 1800 \Omega$  relative to that of  $\alpha$ -MnO<sub>2</sub> ( $5229 \pm 1010 \Omega$ ). These data indicate that the electronic resistance posed to the charge transfer steps of the reduction reaction is decreased most significantly for the catalyst with the greatest Cu content, Table 3.8. Interestingly, one trial with Cu- $\alpha$ -MnO<sub>2</sub> (9.3% Cu) gave a charge transfer resistance of 2089  $\Omega$ , which is comparable to the average charge transfer resistance of 2040  $\Omega$  obtained with 20% Pt/C. The calculated resistances for samples containing 7.5% Cu ( $5744 \pm 2357 \Omega$ ) and 7.8% Cu ( $4380 \pm 974 \Omega$ ) were roughly equivalent to that of  $\alpha$ -MnO<sub>2</sub>.

**Table 3.8:** Electrocatalytic Data Extracted from Averaged Linear Scanning Voltammograms

<b>Cu-content (atomic %)</b>	<b>terminal current density (mA cm<sup>-2</sup>)</b>	<b>n (e<sup>-</sup>)</b>	<b>onset potential (V)</b>	<b><math>E_{1/2}</math> (V)</b>	<b><math>k</math> (cm/s)</b>	<b><math>R_{CT}</math> (<math>\Omega</math>)</b>
0% $\alpha$ -MnO <sub>2</sub>	-1.62	3.1	-0.085	-0.302	$7.5 \times 10^{-3}$	5229.3
7.5%	-1.93	3.28	-0.107	-0.312	$7.8 \times 10^{-3}$	5743.7
7.8%	-2.14	3.31	-0.097	-0.303	$9.7 \times 10^{-3}$	4379.7
9.3%	-2.82	3.20	-0.100	-0.292	$1.9 \times 10^{-2}$	3430.3

The electrochemical data presented in Table 3.8 suggest that doping  $\alpha$ -MnO<sub>2</sub> nanowires with Cu can result in improved electrocatalytic performance relative to the undoped  $\alpha$ -MnO<sub>2</sub>, especially for the catalyst containing the highest level of Cu. When compared to the undoped  $\alpha$ -MnO<sub>2</sub> catalyst, the most notable improvements for the Cu-doped species are in terminal current densities,  $n$ -values, and kinetic rate constants. The goal of this research is to elucidate the role of Cu-dopant ions in  $\alpha$ -MnO<sub>2</sub> electrocatalysts. Therefore, a more thorough understanding of the relationship between the physicochemical properties of the Cu-doped  $\alpha$ -MnO<sub>2</sub> nanowires and the observed electrochemical performance is needed.

In 1979, Brenet considered possible relationships between the physicochemical properties of metallic and mixed metallic oxides used as electrocatalysts and the demonstrated electrochemical reactivity.<sup>60</sup> One physicochemical property of interest in electrochemical applications is the surface area. An increase in surface area can generally be correlated to enhanced electrochemical performance.<sup>60</sup> This was demonstrated by studies of the electrochemical capacitance of  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\lambda$ -MnO<sub>2</sub> conducted by Devaraj *et al.*<sup>30</sup> The two samples of  $\alpha$ -MnO<sub>2</sub> nanoparticles (surface areas of 17.29 m<sup>2</sup>/g and 123.39 m<sup>2</sup>/g) studied were found to demonstrate specific capacitances that correlated to the respective surface area.<sup>30</sup> While the crystalline phase of MnO<sub>2</sub> is known to have a significant impact on the electrochemical performance, a comparison of varied surface areas for a given phase is also relevant. For  $\alpha$ -MnO<sub>2</sub> species utilized as catalysts for ORR, higher surface areas are hypothesized to facilitate increased interactions between the Mn-species and O<sub>2</sub> and improve the adsorption and diffusion processes pertaining to O<sub>2</sub>.<sup>19</sup>

Therefore, the analysis of the surface areas, average pore diameters, and pore volumes of the synthesized Cu- $\alpha$ -MnO<sub>2</sub> can provide some insight for relative catalytic behaviors observed in this study.

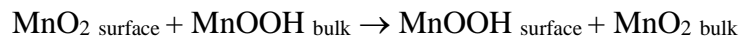
As demonstrated in the linear scanning voltammograms of the Cu- $\alpha$ -MnO<sub>2</sub> nanowires, a trend of increasing surface area correlates to an increase in the reductive current that is generated in the LSVs. The surface area, average pore diameter, and pore volume of the most active Cu- $\alpha$ -MnO<sub>2</sub> sample (9.3% Cu) were measured as being 81.5 m<sup>2</sup>/g, 5.9 nm, and 0.24 cm<sup>3</sup>/g, respectively. In contrast, the surface area, average pore diameter, and pore volume of the least active Cu- $\alpha$ -MnO<sub>2</sub> sample (7.5% Cu) were measured as being 59.1 m<sup>2</sup>/g, 4.7 nm, and 0.14 cm<sup>3</sup>/g, respectively (Table 3.6). These results indicate that as the surface area, average pore diameter, and pore volume of the doped  $\alpha$ -MnO<sub>2</sub> catalyst increase, there is an increased capacity for the adsorption and sequential reduction of O<sub>2</sub>.

While surface area measurements can provide some insight to rationalize demonstrated electrocatalytic performance, previous work by our group has demonstrated that the surface area of a catalyst is not a sole indicator of catalytic behavior. Preliminary studies of previously synthesized  $\alpha$ -MnO<sub>2</sub> and Cu- $\alpha$ -MnO<sub>2</sub> (~10% Cu) nanowires revealed that the Cu-doped sample (43.7 m<sup>2</sup>/g) demonstrated improved electrocatalytic behavior relative to the undoped  $\alpha$ -MnO<sub>2</sub> (73.6 m<sup>2</sup>/g).<sup>24</sup> Therefore, developing optimized synthetic procedures that enable precise control of both the amount of dopant and the catalyst surface area would be an objective of future studies.

Possible correlations between structural properties and catalytic activity are also of interest. As demonstrated through further analysis of the PXRD data, the a-axis and

cell volume increase upon addition of Cu-dopants. The open structure of  $\alpha$ -MnO<sub>2</sub> facilitates the adsorption and diffusion of O<sub>2</sub>, thereby promoting its reduction at the surface of the catalyst. Therefore, it stands to reason that even a slight increase in the unit cell parameters would increase this effect and improve the catalytic performance. As Cheng *et al.* demonstrated with  $\beta$ -MnO<sub>2</sub>, even a slight increase of approximately 0.2% in the lattice parameters corresponds to an enhanced ORR process.<sup>45</sup> The observed increase in lattice parameters in  $\beta$ -MnO<sub>2</sub> was attributed to induced oxygen vacancies in the structure, as well as an increasing presence of Mn<sup>3+</sup>. In our structure, the substitution of a Cu<sup>2+</sup> ion (ionic radii = 0.73 Å) in a metal site previously occupied by a Mn<sup>4+</sup> ion (ionic radii = 0.530 Å) would account for some degree of expansion in the lattice. It is also possible that an increase in Mn<sup>3+</sup> (ionic radii = 0.645 Å, high spin) could be responsible for the observed increase in the crystalline lattice.<sup>61</sup>

Catalytic activity for the ORR can be related to the oxidation state of the Mn species.<sup>23, 38-40</sup> The presence of the Mn<sup>3+</sup>/Mn<sup>4+</sup> redox couple enhances the electron mobility between the bulk sample and the surface, thereby enhancing the redox processes of the ORR by facilitating the rapid conversion between Mn<sup>3+</sup>OOH and Mn<sup>4+</sup>O<sub>2</sub>.<sup>62</sup> This reversible conversion was described by Cao *et al.* as follows:<sup>38</sup>



The Mn<sup>3+</sup>/Mn<sup>4+</sup> couple (present in MnOOH and MnO<sub>2</sub> species) has been demonstrated to act as a mediator that assists in charge transfer to adsorbed oxygen during ORR.<sup>23, 38</sup> Considering the Mn-ion center and one O<sup>2-</sup> ligand, the following equations involving Mn<sup>3+</sup>/Mn<sup>4+</sup> can be proposed:<sup>1, 63</sup>

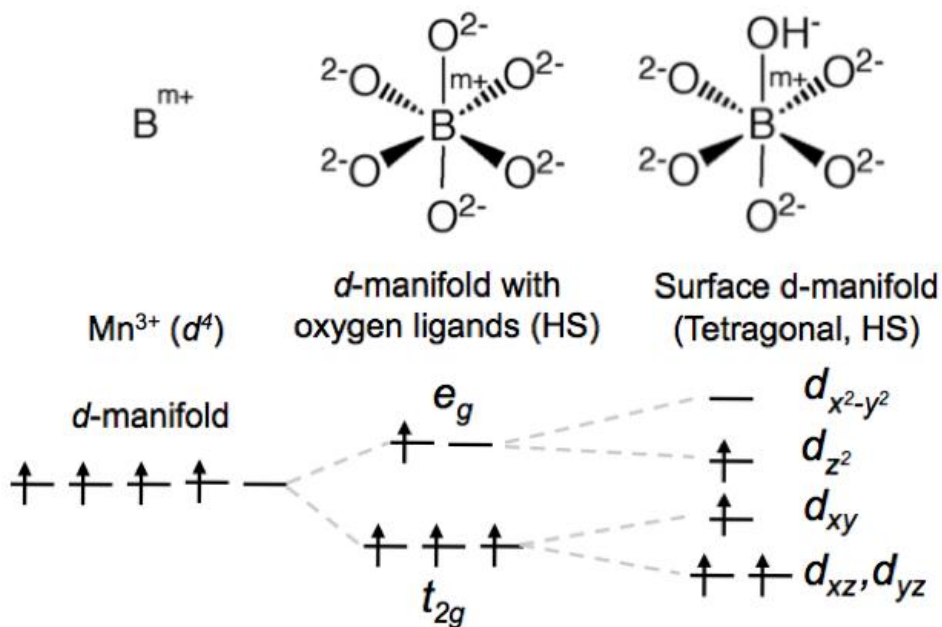
Formation of surface hydroxide	$\text{Mn}^{4+}\text{O}^{2-} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Mn}^{3+}\text{-OH}^- + \text{OH}^-$
Displacement of surface hydroxide	$\text{Mn}^{3+}\text{-OH}^- + \text{O}_2^- (\text{adsorbed}) + \text{e}^- \rightarrow \text{Mn}^{4+}\text{-O-O}^{2-} + \text{OH}^-$
Formation of surface peroxide	$\text{Mn}^{4+}\text{-O-O}^{2-} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Mn}^{3+}\text{-O-OH}^- + \text{OH}^-$
Formation of surface oxide	$\text{Mn}^{3+}\text{-O-OH}^- + \text{e}^- \rightarrow \text{Mn}^{4+}\text{O}^{2-} + \text{OH}^-$
(followed by regeneration of surface hydroxide)	

X-ray photoelectron spectroscopy (XPS) revealed that there was some correlation between Cu-content at the surface and a slight increase in  $\text{Mn}^{3+}$  character. Because the amount of Cu detected at the surface was approximately 0.5% for the most highly Cu-doped sample, the observed difference in  $\text{Mn}^{3+}$  content is very subtle. However, other reports have cited  $\text{Mn}^{3+}$  content increasing as the amount of Cu-dopant in the  $\text{Mn}_x\text{O}_y$  species increases<sup>40, 64</sup> Despite the fact that the atomic percentages of Cu obtained by EDS (Tables 3.1-3.3) were much greater, it is likely that the amount of Cu at the surface is closely related to the observed catalytic behavior. When the peak separation ( $\Delta\text{BE}$ , eV) for the Mn 3s peaks is plotted against the amount of Cu detected by XPS at the surface, a linear relationship is observed as shown in Figure 3.4. This indicates that an increase in the Cu-dopant at the surface could be consistent with a decrease in the average oxidation state of Mn in the catalyst. Many sources have cited the importance of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  couple of the oxygen reduction reaction; however, the majority of these discussions simply claim that this redox pair facilitates the charge transfer processes involved in ORR. While this is supported by the data, it provides only a limited explanation of the role of  $\text{Mn}^{3+}$  in the catalyst.

In 2011, Suntivich *et al.* presented design principles for perovskite oxide oxygen reduction catalysts for fuel cells and metal-air batteries.<sup>63</sup> These discussions focused primarily upon the *d*-orbital occupancies of the B-site cation, which resides at the center

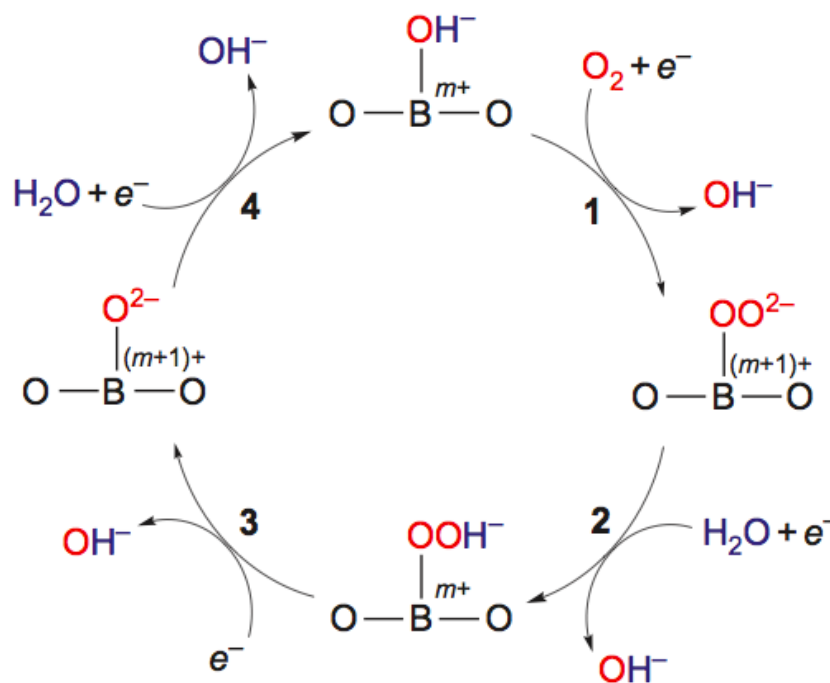
of the octahedral complex in the perovskite structure. Therefore, their findings are relevant in this study as well due to the fact that  $\text{MnO}_2$  is made of  $[\text{MnO}_6]$  octahedra with the B-site cation analogous to the Mn center. Suntivich's study reported correlations between  $d$ -electron number of the B-site cation and ORR activity, and found that the catalytic activity reaches a maximum for cations that are  $d^4$  or  $d^7$ .<sup>63</sup> Interestingly,  $\text{Mn}^{3+}$  is a  $d^4$  species with an electronic configuration that promotes the reduction of oxygen.

Figure 3.10, originally presented by Suntivich *et al.*, illustrates the  $d$ -electron configuration for a B-site cation ( $\text{Mn}^{3+}$ ). When the cation is in the octahedral complex with six oxygen ligands, the  $d$ -orbitals split into the  $t_{2g}$  and  $e_g$  sets, leaving the degenerate  $e_g$  orbitals asymmetrically filled in the high-spin state. This degeneracy is removed upon a geometric distortion to tetragonal symmetry. The  $e_g$  electron resides in the  $d_{z^2}$  orbital, which is oriented toward the surface  $\text{OH}^-$  group and is slightly lower energetically than the  $d_{x^2-y^2}$  orbital.<sup>63</sup>



**Figure 3.10:** The  $d$ -orbitals of the  $\text{Mn}^{3+}$  free ion (far left), the  $\text{Mn}^{3+}$  ion in the octahedral complex (center), and the distorted tetragonal high spin state (far right).<sup>63</sup>

As seen in step one of the reaction schematic below (Figure 3.11), there is an exchange that must occur between  $\text{O}_2^{2-}$  and  $\text{OH}^-$  on the transition metal site. It is proposed that the rate-limiting step of the ORR is the displacement of the surface hydroxide species, which is driven by the transfer of the unpaired  $e_g$  electron to the O-O  $\pi^2$  orbital. The presence of the  $e_g$  electron destabilizes the B-OH $^-$  bond, thereby enabling the formation of B-O $_2^{2-}$ .<sup>63</sup>



**Figure 3.11:** A proposed reaction schematic for the ORR on the cationic transition metal B-site.<sup>63</sup>

Step two of the cycle is the formation of surface peroxide, which is reduced to the surface oxide in step three. Finally, step four involves the regeneration of the surface hydroxide. It is evident that the redox of the Mn center between the 3+ and 4+ states is involved, but this mechanism provides a basis for understanding how the electronic configuration of the  $\text{Mn}^{3+}$  ion contributes to the reaction.<sup>63</sup>

Since the majority of the Cu-dopant species resides within the nanowire, it is currently hypothesized that the conductivity of the nanowires would demonstrate a trend that correlates to the Cu-content observed by EDS. Performing a series of measurements in which the conductivity of a single nanowire, or even a small cluster of nanowires, for  $\alpha$ -MnO<sub>2</sub> samples of varying Cu-content could potentially provide additional insight into the underlying role of Cu-dopants in  $\alpha$ -MnO<sub>2</sub> nanowire electrocatalysts. While obtaining this data via conductive tip atomic force microscopy (AFM) is a future objective of this study, some insight can be drawn from recent literature that will support the hypothesis of Cu-doping enhancing the conductivity of  $\alpha$ -MnO<sub>2</sub>.

A previous report has stated that the measured conductivity of  $\alpha$ -MnO<sub>2</sub> nanowires synthesized by a hydrothermal route to be 0.086 S/cm.<sup>19</sup> Manganese oxide (MnO<sub>2</sub>) has been cited as being a semiconductor at ambient temperatures,<sup>65</sup> but it is acknowledged that manganese oxides inherently possess low conductivities.<sup>28</sup> As a result, conductive carbon additives are commonly utilized in composite electrode materials to enhance the overall conductivity. However, some recent reports have demonstrated an enhanced electrical conductivity for manganese oxides achieved by Cu-doping. Li *et al.* demonstrated the synthesis of Cu-doped Mn<sub>2</sub>O<sub>3</sub> mesocrystals with charge transfer abilities that are more favorable than the un-doped Mn<sub>2</sub>O<sub>3</sub> mesocrystals.<sup>66</sup> Similarly, a Cu-doped MnO<sub>2</sub> sample prepared by cyclic voltammetry also demonstrated improved charge transfer relative to the undoped film.<sup>67</sup> A study of Cu<sub>1+x</sub>Mn<sub>1-x</sub>O<sub>2</sub> (0 ≤ x ≤ 0.2) solid solutions revealed that as the Cu-content increased, the activation energy related to electrical conductivity decreased, which is indicative of a correlation between increased Cu-content and improved charge carrier mobility.<sup>68</sup>



### 3.4 Summary and Conclusions

The synthesis of Cu-doped  $\alpha$ -MnO<sub>2</sub> was achieved by the addition of Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O into the hydrothermal reaction previously used to prepare  $\alpha$ -MnO<sub>2</sub> nanowires.<sup>19, 24</sup> By varying the amount of Cu-precursor in discrete molar ratios of 1:1, 1:0.5, and 1:0.25 (Mn:Cu), varying atomic percentages of Cu were attained, 9.3%, 7.8%, and 7.3%, respectively. The  $\alpha$ -MnO<sub>2</sub> crystalline phase and the nanowire morphology were retained upon doping, both factors known to be critical to the overall catalytic performance. The inclusion of Cu was demonstrated to increase the lattice parameters of  $\alpha$ -MnO<sub>2</sub> that trended with Cu content. In addition, the BET surface areas, average pore diameters, and pore volumes demonstrated increases that correlated with Cu content.

Doping  $\alpha$ -MnO<sub>2</sub> nanowires with Cu improves their performance as catalysts for the ORR in alkaline electrolyte. Specifically, the inclusion of this dopant species provides for not only a higher terminal current density, but also enhanced kinetic rate constants that exceed rates attained by  $\alpha$ -MnO<sub>2</sub> alone. Data obtained through RRDE studies indicates that the production of peroxide decreases as the amount of Cu increases. The charge transfer resistances demonstrate similar trends; the average resistance decreases as the amount of Cu in the catalyst increases.

The inclusion of Cu also has an effect on the oxidation state of Mn, and more specifically, the Mn<sup>3+</sup>/Mn<sup>4+</sup> couple. The oxidation state of surface Mn was estimated by examining the splitting of the Mn 3s peaks by XPS, which revealed that as the amount of Cu in the sample increased, the concentration of Mn<sup>3+</sup> increased as well. Mn<sup>3+</sup> has a *d*-electron count of four (*d*<sup>4</sup>), which indicates the presence of an unpaired electron in the degenerate e<sub>g</sub> set in octahedral geometry. Through a distortion to the tetragonal geometry,

the  $e_g$  orbitals split, leaving the unpaired electron in the  $d_z^2$  orbital at a lower energy, oriented toward the surface  $\text{OH}^-$ . This electron destabilizes the bond between the  $\text{Mn}^{3+}$  ion and the surface hydroxide, promoting the formation and subsequent reduction of  $\text{O}_2^{2=}$  on the surface.<sup>63</sup>

The presence of the Cu-dopant ions in  $\alpha\text{-MnO}_2$  nanowires increases the  $\text{Mn}^{3+}$  content at the catalyst surface, thereby promoting the reduction of oxygen. In addition, it is likely that the Cu-species enhance the conductivity of the  $\alpha\text{-MnO}_2$  electrocatalyst. Future research efforts will attempt to measure the conductivity of the Cu- $\alpha\text{-MnO}_2$ . Also, the development of optimized synthetic procedures that enable the precise control of Cu-content and Mn oxidation state is of interest.

## Chapter 4

### Efforts to Understand the Role of Ni-dopants in $\alpha$ -MnO<sub>2</sub> Nanowire Catalysts for the Oxygen Reduction Reaction in Alkaline Media

#### 4.1 Introduction

Doping manganese oxide electrocatalysts with nickel has been demonstrated to enhance the catalytic performance in several electrochemical studies.<sup>23, 24, 41, 42</sup> These doped species have demonstrated catalytic activities reported to be comparable to that of Pt/C commercial benchmarks, indicating their potential to serve as cost-effective alternatives to precious metal catalysts.<sup>23, 24</sup> Other studies have noted demonstrated abilities to efficiently decompose peroxide<sup>36, 41</sup> and operate in both aqueous and organic electrolytes,<sup>42</sup> as well as exhibit tolerance to methanol crossover.<sup>24</sup> Ongoing efforts to gain insight into the role of the Ni-dopants in  $\alpha$ -MnO<sub>2</sub> nanowire electrocatalysts are presented.

#### 4.2 Experimental

##### 4.2.1 General

All chemicals were obtained commercially and used as received, without further purification. MnSO<sub>4</sub>·H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were purchased from Alfa Aesar. KMnO<sub>4</sub>, isopropanol, and Nafion solution (5 wt. % solution in water and lower aliphatic alcohols) were used as received from Sigma-Aldrich.

### 4.2.2 Synthesis

The synthesis of Ni- $\alpha$ -MnO<sub>2</sub> nanowires was performed via a modified hydrothermal reaction in an acid digestion bomb (PTFE liner, 45 mL capacity, Parr™ reactor), adapted from a previously published synthesis for  $\alpha$ -MnO<sub>2</sub> and introduced in our previous studies.<sup>19, 24</sup> Solutions of MnSO<sub>4</sub>·H<sub>2</sub>O (0.2 g, 1.18 mmol), KMnO<sub>4</sub> (0.5 g, 3.16 mmol) and a specified amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in deionized water were heated in the acid digestion bomb at 140 °C for 120 hours to ensure nanowire morphology. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added in specific molar ratios to the manganese-containing precursor of 1:1, 1:0.5 and 1:0.25 (Mn:Ni) to achieve different copper doping levels. Phase-pure  $\alpha$ -MnO<sub>2</sub> was obtained by a hydrothermal reaction that excluded the copper precursor.<sup>19, 24</sup> Following heating for 120 hours at 140 °C, all reactions were cooled to room temperature, and the solids were isolated by centrifugation (3000 rpm). The solids were washed with deionized H<sub>2</sub>O (4x, 10 mL) and ethanol (4x, 10 mL), isolated via centrifugation, and dried in a vacuum oven overnight at 65 °C.

### 4.2.3 Materials Characterization

***Powder X-ray Diffraction (PXRD).*** Catalyst powders were mounted directly onto a zero background holder purchased from The Gem Dugout. Samples were scanned at a rate of 0.02°/2 s in the 2 $\theta$  range of 10-80° on a Bruker D8 Advance Diffractometer in Bragg-Brentano geometry with Cu K $\alpha$  radiation and a diffracted beam graphite monochromator. Phase identification was achieved through use of the Jade 9.0 software suite and the Joint Committee on Powder Diffraction Standards (JCPDS).

***Transmission Electron Microscopy (TEM).*** TEM analysis was carried out on a JEOL 2010F electron microscope at 200kV acceleration voltage. Energy Dispersive

Spectroscopy (EDS) was collected using its attachment of Oxford Instruments ISIS/Inca System with Oxford Pentafet Ultrathin Window Detector (UTW).

**Scanning Electron Microscopy (SEM).** The samples were dispersed onto carbon tape and imaged using a Zeiss Supra 55VP field emitter gun scanning electron microscope (FEGSEM). Samples were sputter coated with gold-palladium prior to analysis. A Noran EDS detector and Noran System Six software were used for the acquisition of the EDS spectra. EDS data were plotted with Kaleidagraph software for presentation purposes.

**Brunauer-Emmett-Teller (BET) Surface Area Analysis.** Gas sorption experiments were performed on an Autosorb iQ2-Chemi instrument (Quantachrome Instruments, Boynton Beach FL, USA) at 77 K (liquid nitrogen temperature) using ultra-high purity (UHP) nitrogen as adsorbate. Specimens were degassed at 140 °C for between 2 and 3 hours (the exact degas time was determined automatically based upon periodic evaluation of rate of gas evolution from each specimen). The specimen cells were quartz glass with a 9 mm outer diameter, and filler rods were inserted to reduce dead volume above the sample. Cell volumes were determined prior to each run using UHP helium.

Isotherms were typically measured using 40 adsorption points and 40 desorption points, with an optional 30 additional adsorption points in the micropore range. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) method using seven adsorption points in the range  $P/P_0 = 0.05$  to  $0.3$ . Total pore volumes were calculated based on the total gas adsorbed at  $P/P_0$  values of  $0.996$ . Pore sizes were determined using the Barrett-Joyner-Halenda (BJH) method during the desorption branch of the isotherm, ignoring  $P/P_0$  points below  $0.35$ .

***X-ray Photoelectron Spectroscopy (XPS).*** X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD instrument with base pressures less than  $5 \times 10^{-9}$  Torr. Powder samples were pressed into carbon tape for analyses. No interferences from the carbon tape were observed. Charge neutralization was not required; however, the neutralizer was used for all samples to ensure that differential charging did not influence the spectral lineshapes. XPS was performed with a monochromatic Al-K $\alpha$  (1486.7 eV) source operated at 150 W with an elliptical spot size of 300x700 microns. Survey spectra were taken with an 80 eV pass energy, 600 meV step, and 100 ms dwell times. With Al-K $\alpha$  X-rays the Ni 2p 3/2 appears as a relatively sharp peak on a much broader Mn LMM Auger peak. XPS was also performed with a non-monochromatic Mg X-ray source (1253.6 eV) operated at 180 W to confirm the presence of nickel. The energy resolution is lower with the non-monochromatic source, so step sizes were 800-1000 meV for survey spectra. XPS with the Mg source was helpful for resolving the Ni 2p peaks on a relatively flat background. High resolution spectra were recorded with a 20 eV pass energy, 200 ms dwell time, and step sizes ranging from 30-50 meV (100 meV for Mg X-ray XPS). Data processing was performed with CasaXPS. Quantifications were performed using the built-in relative sensitivity factors. Mn 3s peak fitting was performed with a linear background and two unconstrained Gaussian/Lorentzian (70/30) peaks.

#### **4.2.4 Electrochemical Studies**

Oxygen reduction studies were performed using rotating disk electrode assembly. Catalyst inks consisting of 5.0 mg of catalyst material, 200  $\mu$ L isopropanol, and 300  $\mu$ L Nafion solution were sonicated for approximately 20 minutes. For RDE, a 5  $\mu$ L aliquot

was drop-cast on a glassy carbon RDE electrode (BASi, active area= 0.0788 cm<sup>2</sup>). Prior to each drop-coating process, the RDE glassy carbon electrode surface was polished with 0.05  $\mu$ m alumina slurry and rinsed with deionized water and ethanol.

Linear Scanning Voltammograms were executed in a potential window from 0.2 V to -0.6 V (V vs. Ag/AgCl) at a scan rate of 1 mV/s. For RDE, LSVs were run at rotation rates of 500, 900, 1600, 2500, and 3600 rpm. All experiments were run in 0.1 M KOH electrolyte that had been thoroughly purged with UHP oxygen (or UHP nitrogen for background measurements) prior to each run. The appropriate gaseous atmosphere was preserved by blanketing for the extent of the experiment.

RDE experiments were performed in a three electrode cell, manufactured by Bioanalytical Systems, Inc. connected to a Versastat 4 potentiostat operated by VersaStudio software. Electrodes (from BASi) included the glassy carbon working electrode prepared as previously described, a Pt coil counter electrode, and a Ag/AgCl reference electrode (3 M NaCl, potential= 0.209 V vs. NHE).

## **4.3 Results and Discussion**

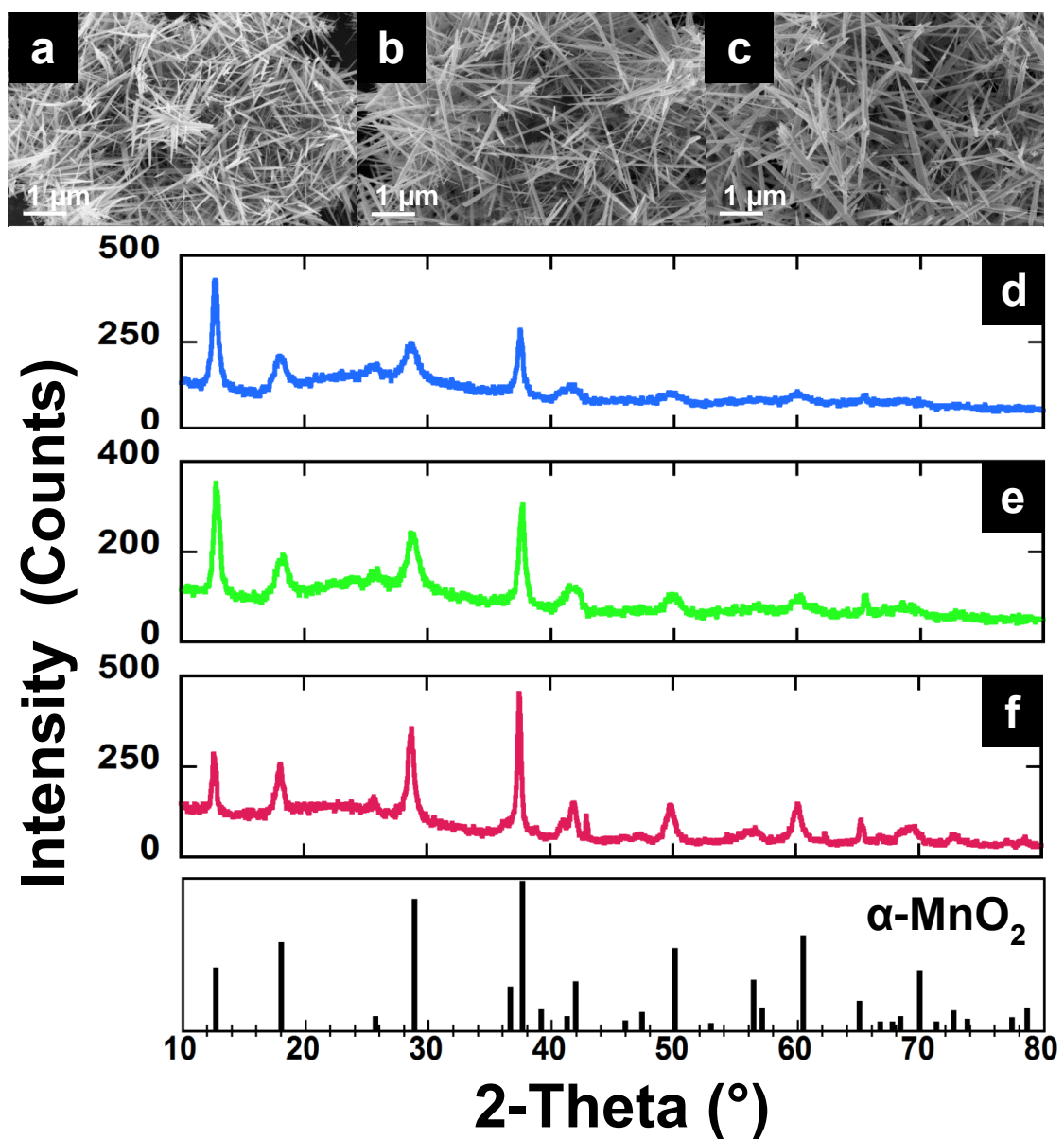
### **4.3.1 Synthesis and Characterization**

Initially, the synthesized materials were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Previous studies have established that  $\alpha$ -MnO<sub>2</sub> nanowires contain the most active phase and morphology for manganese oxide catalysts for the ORR in alkaline electrolyte. Therefore, upon attempted doping with Ni, it was critical that the  $\alpha$ -MnO<sub>2</sub> phase and

nanowire morphology be retained. As shown in Figure 4.1 a-c, SEM imaging confirmed that the reaction products were of the nanowire morphology. The obtained XRD patterns in Figure 4.1 d-f indexed to JCPDS number 00-044-0141, serving as a clear indication that the crystalline phase of  $\alpha$ -MnO<sub>2</sub> was retained.

EDS obtained in conjunction with SEM imaging served as preliminary confirmation of the presence of Ni in the nanowires; however, further data were desired in order to quantify the amount of Ni in the synthesized samples. Therefore, EDS measurements were obtained via transmission electron microscopy (TEM). The complete set of data is provided in Tables 4.1, 4.2, and 4.3; corresponding averages and standard deviations are also included. EDS of the sample prepared at the 1:1 Mn:Ni ratio contained  $6.13 \pm 1.55\%$  Ni; the sample prepared at the 1:0.5 Mn:Ni ratio contained  $4.43 \pm 0.60\%$  Ni, and the sample prepared at 1:0.25 Mn:Ni ratio contained  $2.02 \pm 0.43\%$  Ni. A TEM image (Figure 4.2) of a Ni- $\alpha$ -MnO<sub>2</sub> nanowire ( $\sim 100$  nm wide) reveals that it is actually comprised of many small, very thin wires ( $\sim 10$  nm wide) bundled together.





**Figure 4.1:** Characterization data for the synthesized Ni-doped  $\alpha$ -MnO<sub>2</sub> nanowires. a-c) SEM images of the nanowires synthesized at a Mn:Ni ratio of 1:1, 1:0.5, and 1:0.25, respectively. d-f) XRD patterns for Ni- $\alpha$ -MnO<sub>2</sub> nanowires synthesized at a Mn:Ni ratio of 1:1, 1:0.5, and 1:0.25, respectively.

**Table 4.1:** EDS Measurements of Atomic Percent Content of Ni- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:1, Mn:Ni

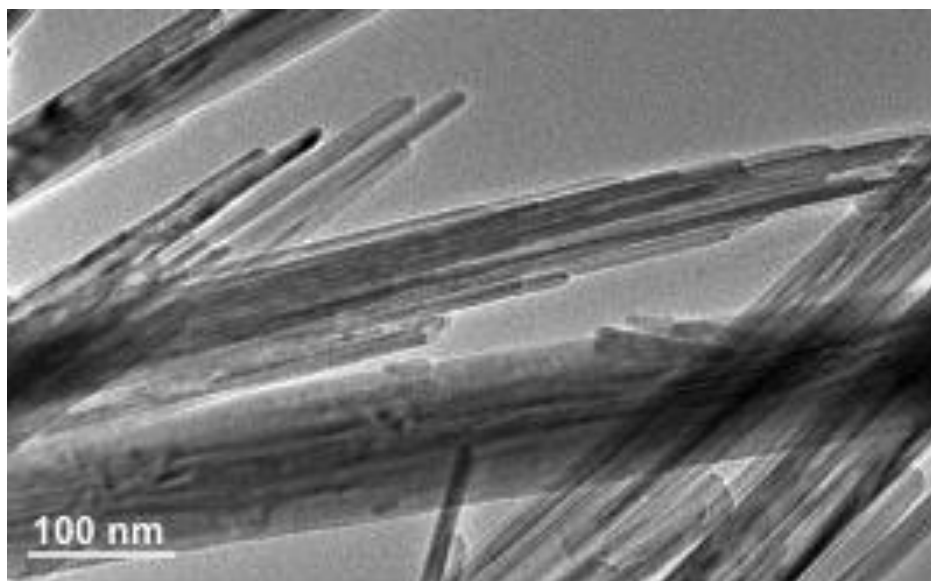
<b>Ni-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Ni</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	6.13	43.55	49.89	0.43
	6.41	43.56	49.99	0.04
	7.42	42.38	49.93	0.26
	10.1	39.85	49.98	0.06
	5.54	43.29	49.61	1.56
	5.93	42.78	49.57	1.72
	5.5	43.17	49.56	1.78
	4.96	42.11	49.02	3.91
	4.75	42.46	49.07	3.72
	4.53	42.45	48.99	4.02
<b>AVERAGE</b>	<b>6.13</b>	<b>42.56</b>	<b>49.56</b>	<b>1.75</b>
<b>STD. DEV.</b>	1.55	1.03	0.38	1.53

**Table 4.2:** EDS Measurements of Atomic Percent Content of Ni- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:0.5, Mn:Ni

<b>Ni-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Ni</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	3.94	42.82	48.92	4.32
	3.92	42.84	48.92	4.32
	4.02	43.48	49.16	3.34
	3.52	43.78	49.1	3.6
	4.13	43.14	49.09	3.65
	4.79	42.54	49.11	3.56
	3.99	43.34	49.11	3.56
	5.37	44.44	49.93	0.26
	4.84	44.96	49.93	0.28
	5.14	44.65	49.93	0.28
	5.09	44.65	49.93	0.27
<b>AVERAGE</b>	<b>4.43</b>	<b>43.70</b>	<b>49.38</b>	<b>2.49</b>
<b>STD. DEV.</b>	0.60	0.82	0.43	1.71

**Table 4.3:** EDS Measurements of Atomic Percent Content of Ni- $\alpha$ -MnO<sub>2</sub>, prepared at reactant ratio 1:0.25, Mn:Ni

<b>Ni-<math>\alpha</math>-MnO<sub>2</sub></b>	<b>Ni</b>	<b>Mn</b>	<b>O</b>	<b>K</b>
	1.84	44.35	48.73	5.08
	1.46	44.76	48.74	5.04
	1.93	44.24	48.72	5.11
	2.78	43.33	48.7	5.18
	1.79	44.42	48.74	5.05
	2.14	44.11	48.75	5.00
	1.61	44.55	48.72	5.13
	1.84	44.29	48.71	5.16
	1.83	44.42	48.75	5.00
	2.07	44.2	48.76	4.97
	2.93	43.49	48.81	4.78
<b>AVERAGE</b>	<b>2.02</b>	<b>44.20</b>	<b>43.74</b>	<b>5.05</b>
<b>STD. DEV.</b>	0.43	0.41	0.03	0.11



**Figure 4.2:** TEM image of Ni- $\alpha$ -MnO<sub>2</sub> nanowires.

X-ray photoelectron spectroscopy (XPS) was utilized to analyze the content at the surface of the nanowires. As expected, the Ni content at the surface was much lower than the atomic percentages measured with EDS. The data are presented in Table 4.4.

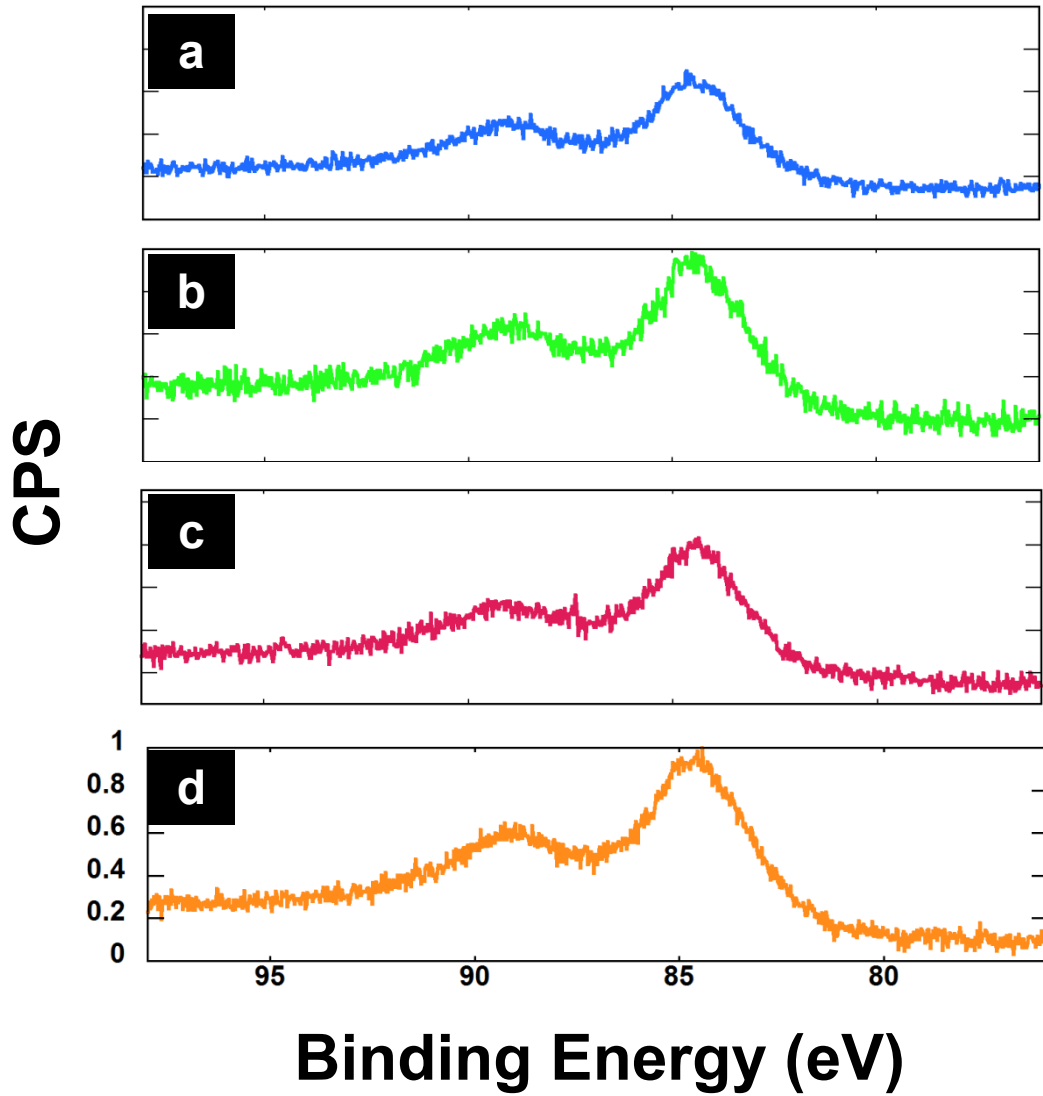
**Table 4.4:** Atomic Percentage of Ni as Measured by XPS

*Percentages obtained by EDS are included for comparison.*

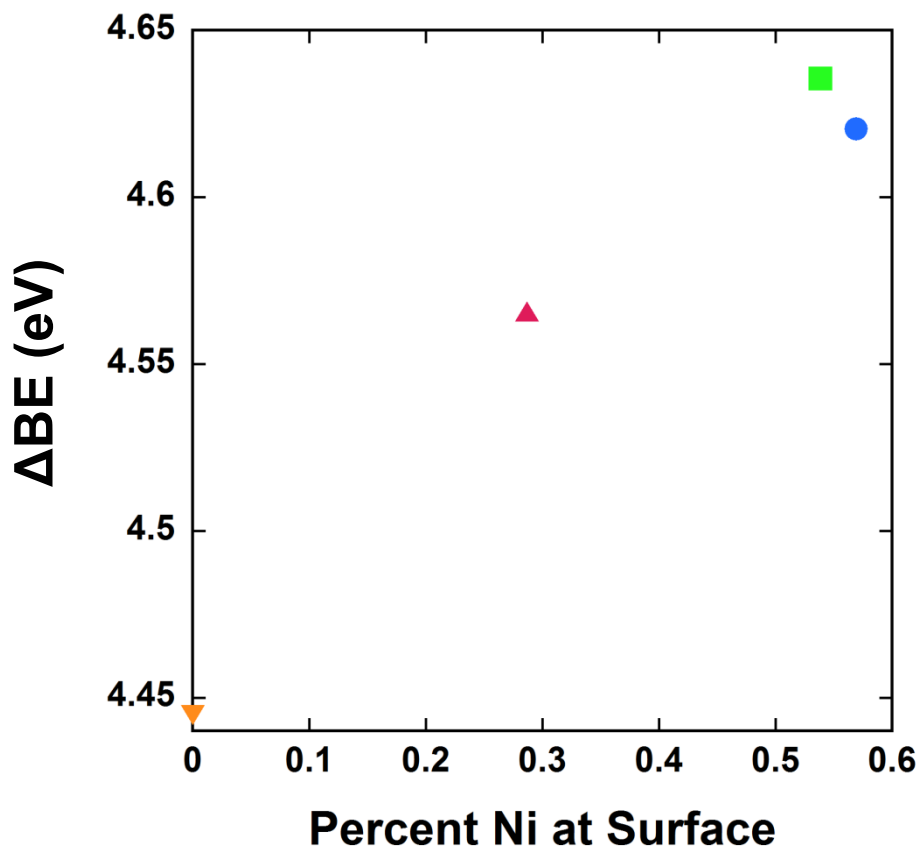
Sample (Mn:Ni Ratio)	Atomic % Ni (XPS)	Atomic % Ni (EDS)
$\alpha$ -MnO <sub>2</sub>	0%	0%
Ni- $\alpha$ -MnO <sub>2</sub> (1:0.25)	0.29%	2.0%
Ni- $\alpha$ -MnO <sub>2</sub> (1:0.5)	0.54%	4.4%
Ni- $\alpha$ -MnO <sub>2</sub> (1:1)	0.57%	6.1%

XPS was also utilized to gain a more thorough understanding of the oxidation states of the Mn ions within the Ni- $\alpha$ -MnO<sub>2</sub> catalysts. The difference in binding energy between the Mn 3s peaks can be used to approximate the oxidation state, as shown in Figures 4.3 and 4.4. As the amount of Ni in the sample increases, the extent of splitting between the Mn 3s peaks becomes greater, indicating that more Mn<sup>3+</sup> is present.<sup>57, 58</sup> Interestingly, the greatest Mn 3s splitting (4.6356 eV) was observed for the sample synthesized at the Mn:Ni ratio of 1:0.5 (0.54% Ni at surface, 4.4% Ni by EDS). The Mn 3s splitting obtained for the sample synthesized at the Mn:Ni ratio of 1:1 was only slightly lower (4.6205 eV). The Mn 3s spectra are shown in Figure 4.3. Figure 4.4 shows the

relationship between Ni-content at the surface and the splitting between the Mn 3s peaks ( $\Delta$  BE, eV). The splitting values are presented in Table 4.5.



**Figure 4.3:** XPS data showing the splitting of the Mn 3s peaks a) 6.1% Ni, 0.57% Ni at surface, b) 4.4% Ni, 0.54% Ni at surface, c) 2.0% Ni, 0.29% Ni at surface, and d) undoped  $\alpha$ -MnO<sub>2</sub>.



**Figure 4.4:** The splitting of the Mn 3s peaks ( $\Delta BE$ , eV) plotted as a function of the percent Ni measured at the surface by XPS.

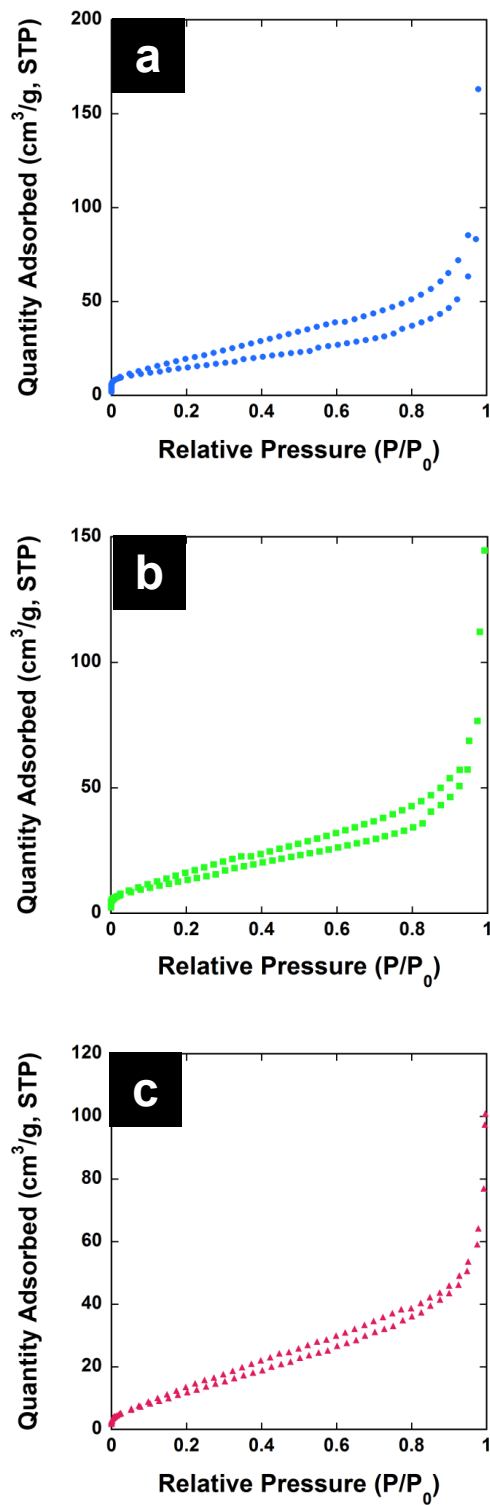
**Table 4.5:** Splitting of Mn 3s Peaks as Observed by XPS

Sample (Symbol)	Atomic % Ni (XPS)	$\Delta BE$ (eV)
$\alpha$ -MnO <sub>2</sub> ( <span style="color: orange;">▼</span> )	0%	4.4448
Ni- $\alpha$ -MnO <sub>2</sub> ( <span style="color: magenta;">▲</span> )	0.29%	4.5657
Ni- $\alpha$ -MnO <sub>2</sub> ( <span style="color: green;">■</span> )	0.54%	4.6356
Ni- $\alpha$ -MnO <sub>2</sub> ( <span style="color: blue;">●</span> )	0.57%	4.6205

The surface areas, average pore diameters, and pore volumes of the Ni- $\alpha$ -MnO<sub>2</sub> powders were analyzed using the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method. The results of these studies are shown in Table 4.6; corresponding isotherm plots are provided in Figure 4.5 a-c. The sample containing 6.1% Ni was determined to have a surface area of 60.8 m<sup>2</sup>/g, an average pore diameter of 12.42 nm, and a pore volume of 0.35 cm<sup>3</sup>/g. The sample containing 4.4% Ni was determined to have a surface area of 52.3 m<sup>2</sup>/g, an average pore diameter of 8.65 nm, and a pore volume of 0.22 cm<sup>3</sup>/g. Finally, the sample containing 2.0% Ni was determined to have a surface area of 51.8 m<sup>2</sup>/g, an average pore diameter of 4.6 nm, and a pore volume of 0.12 cm<sup>3</sup>/g. Clearly, as more Ni is introduced into the  $\alpha$ -MnO<sub>2</sub> structure, the surface area, average pore diameter, and pore volume increase as well.

**Table 4.6:** BET Measurements for Ni- $\alpha$ -MnO<sub>2</sub> Nanowires

<b>Ni-content (avg. atomic %)</b>	<b>BET Surface Area (m<sup>2</sup>/g)</b>	<b>Average Pore Diameter (nm)</b>	<b>Pore Volume (cm<sup>3</sup>/g)</b>
2.0%	51.8	4.6	0.12
4.4%	52.3	8.65	0.22
6.1%	60.8	12.42	0.35

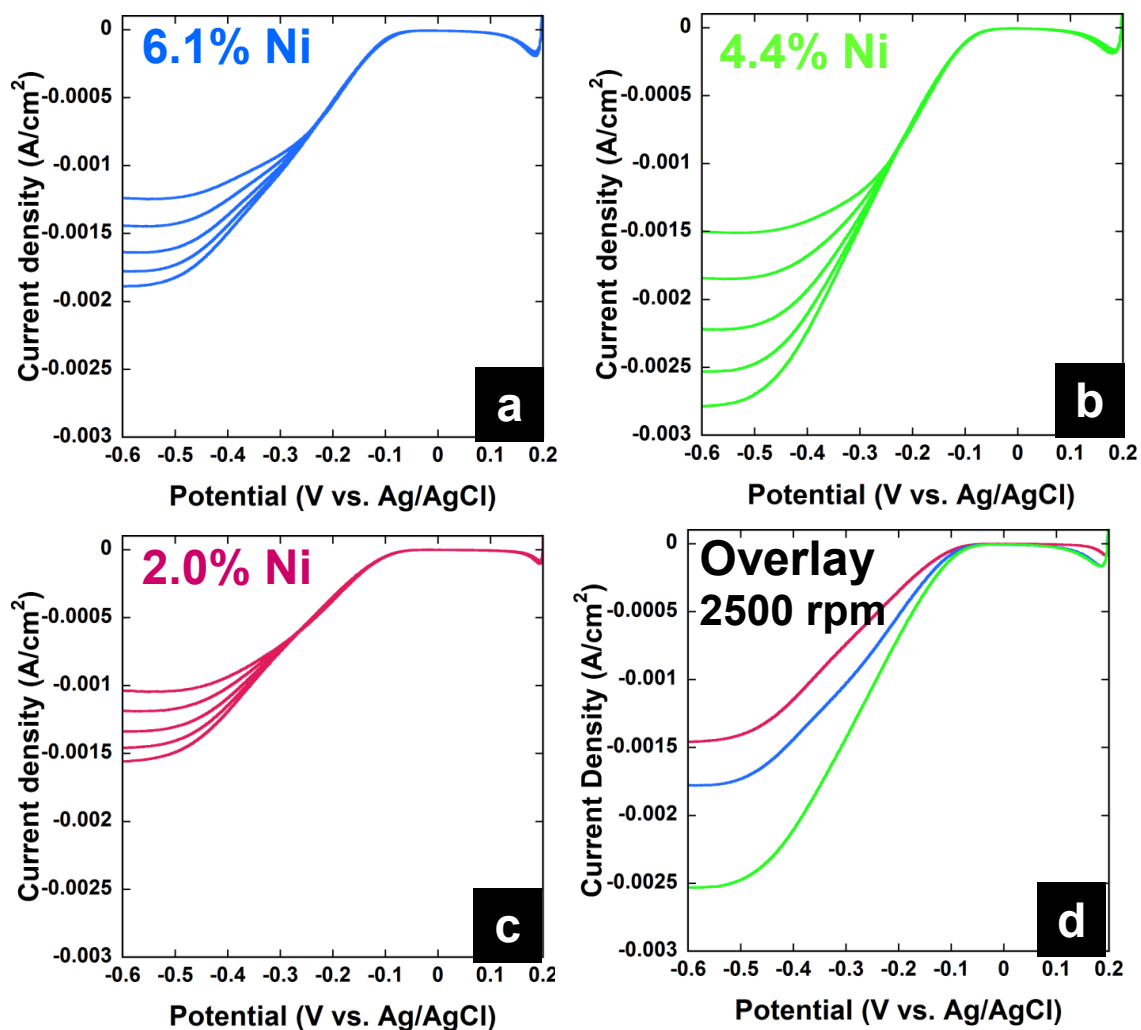


**Figure 4.5:** Nitrogen sorption isotherms for a) Ni- $\alpha$ -MnO<sub>2</sub>, 6.1% Ni (60.8 m²/g), b) Ni- $\alpha$ -MnO<sub>2</sub>, 4.3% Ni (52.3 m²/g), and c) Ni- $\alpha$ -MnO<sub>2</sub>, 2.0% Ni (51.8 m²/g).



### 4.3.2 Electrochemical Analysis

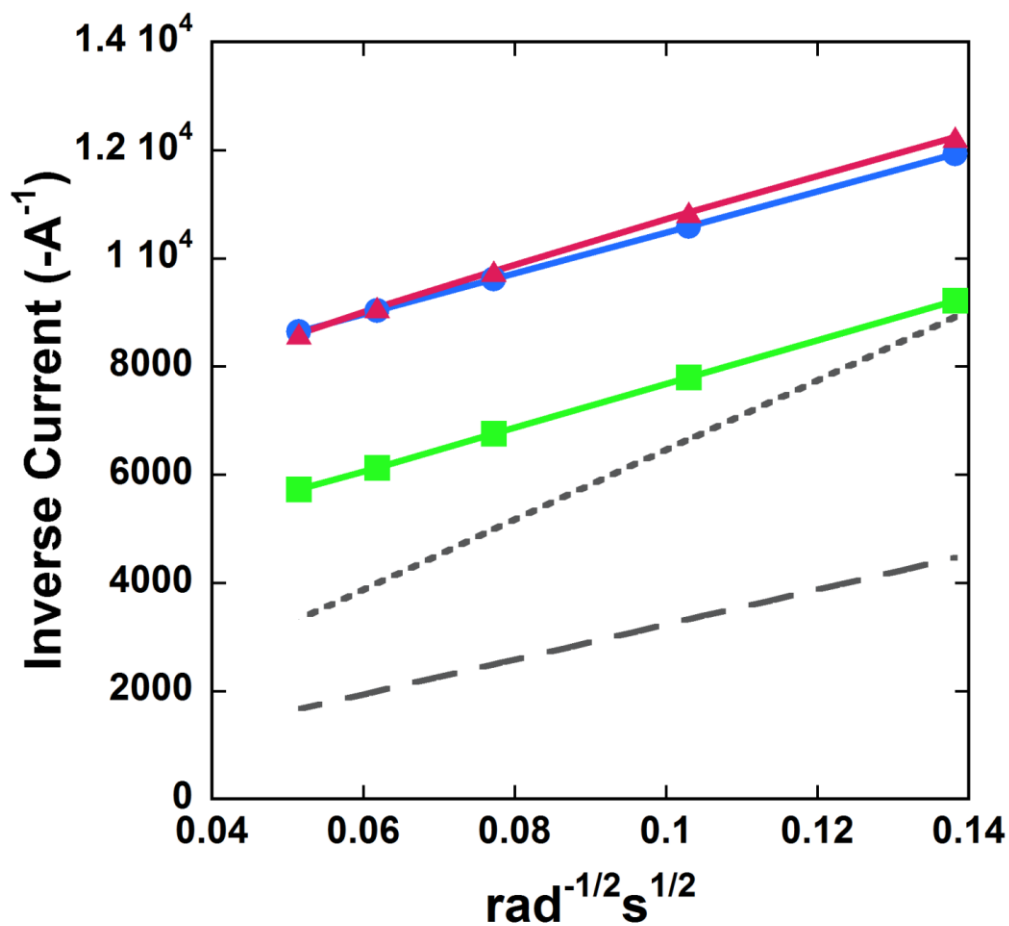
Films of the as-synthesized Ni- $\alpha$ -MnO<sub>2</sub> powders were prepared via a drop-cast technique in which an aliquot of the catalyst ink was deposited onto rotating disk electrodes as previously described. The electrodes were utilized for RDE studies, which enable the observation of kinetically controlled processes in the absence of mass-transfer phenomena. Figure 4.6 shows averaged linear scanning voltammograms obtained for Ni- $\alpha$ -MnO<sub>2</sub> at 6.0% Ni (Figure 4.6 a), 4.4% Ni (Figure 4.6 b), and 2.0% Ni (Figure 4.6 c). For each individual set of data, there is an increase in the terminal current density that corresponds to an increase in the rotation rate of the working electrode; this is attributed to the change in flux of O<sub>2</sub> to the electrode surface that occurs as the rotation rate increases. The terminal current density (-0.6 V vs. Ag/AgCl) attained by the catalyst containing 2.0% Ni was -1.46 mA/cm<sup>2</sup>; and for the catalyst containing 4.4% Ni the terminal current density was -2.53 mA/cm<sup>2</sup>. Finally, for the catalyst containing 6.1% Ni, the terminal current density attained was -1.78 mA/cm<sup>2</sup>. When compared to the average terminal current density for undoped  $\alpha$ -MnO<sub>2</sub> of -1.62 mA/cm<sup>2</sup>, only the Ni- $\alpha$ -MnO<sub>2</sub> samples containing 4.4% Ni and 6.1% Ni demonstrate improvements relative to the undoped sample. The terminal current density for the sample containing 2.0% Ni was less than that attained by the undoped  $\alpha$ -MnO<sub>2</sub>. Figure 4.6 d shows an overlay of averaged LSVs obtained at 2500 rpm for each Ni- $\alpha$ -MnO<sub>2</sub> catalyst sample. The terminal current densities do not trend in accordance with the Ni-content of the nanowires as the sample containing 4.4% Ni attains the highest current density.



**Figure 4.6:** a-c) Averaged linear scanning voltammograms obtained for Ni- $\alpha$ -MnO<sub>2</sub> at 500, 900, 1600, 2500, and 3600 rpm. d) Comparative overlay of averaged LSVs obtained at 2500 rpm, revealing an increase in terminal current density that does not trend directly with Ni-content.

Further analysis of the linear scanning voltammograms provides a number of metrics of comparison for Ni- $\alpha$ -MnO<sub>2</sub> catalysts. As stated in Chapter 1, applying the Koutecky-Levich equation to the LSV data enables the  $n$ -value to be calculated. The  $n$ -value can provide some insight into the predominant reaction pathway. The calculated  $n$ -value for the Ni- $\alpha$ -MnO<sub>2</sub> sample containing 6.1% Ni was 3.45 e<sup>-</sup>, the calculated  $n$ -value for the sample containing 4.4% Ni was 3.29 e<sup>-</sup>, and the calculated  $n$ -value for the sample containing 2.0% Ni was 3.26 e<sup>-</sup>. Clearly, there is a demonstrated improvement relative to the undoped  $\alpha$ -MnO<sub>2</sub> ( $n = 3.1$  e<sup>-</sup>).<sup>19, 24</sup> These data suggest that the  $n$ -value increases as the amount of Ni-dopant increases, though the most significant improvement is attained with the catalyst containing 6.0% Ni.

The kinetic rate constants, calculated using the y-intercept of the Koutecky-Levich lines, demonstrate a trend that is similar to the trend observed for terminal current density. Specifically, the sample containing 4.4% Ni was shown to give a kinetic rate constant of  $1.4 \times 10^{-2}$  cm/s. In contrast, the calculated kinetic rate constants for the samples containing 6.1% Ni and 2.0% Ni were  $6.50 \times 10^{-3}$  cm/s and  $5.75 \times 10^{-3}$  cm/s, respectively. Therefore, only the sample containing 4.4% Ni yielded an improved kinetic rate constant relative to that of the undoped  $\alpha$ -MnO<sub>2</sub> ( $7.5 \times 10^{-3}$  cm/s). An overlay of the Koutecky-Levich lines for the Ni- $\alpha$ -MnO<sub>2</sub> catalyst series is shown in Figure 4.7.



**Figure 4.7:** Overlay of Koutecky-Levich lines for Ni- $\alpha$ -MnO<sub>2</sub> catalyst samples; 2.0% Ni is shown in pink, 4.4% Ni is shown in green, and 6.1% Ni is shown in blue. Idealized slopes for  $n = 2 \text{ e}^-$  (short dashes) and  $n = 4 \text{ e}^-$  (long dashes) are included for comparison.

As described in Chapter 1, the onset potential is typically defined as the potential at which the current first becomes negative. An alternative approach to determining the onset potential in this study utilized the intersection of tangential lines fit to the curved portion of the LSV (half-wave region) and the region in which negligible current is generated. This point defines the onset potential as the point at which the slope of the LSV visibly changes. The onset potentials of the Ni- $\alpha$ -MnO<sub>2</sub> catalysts are all within 5 mV of each other, only ranging from -0.093 V (4.4% Ni) to -0.098 V (6.1% Ni). These are slightly more negative than the onset potential for the undoped  $\alpha$ -MnO<sub>2</sub> (-0.085 V). Therefore, this study did not reveal that Ni-doping has a significant effect on exhibited onset potentials.

An increase in catalyst Ni-content from 2.0% to 6.1% gives a slight improvement in half-wave potential (+ 0.013 V). As compared to undoped  $\alpha$ -MnO<sub>2</sub> ( $E_{1/2}$ = -0.301 V), the half-wave potentials of the 4.4% Ni and 6.1% Ni catalysts are roughly equivalent ( $E_{1/2}$ =-0.297 V). Therefore, the data indicate that there is not a significant effect on the half-wave potential that correlates to Ni-content.

Charge transfer resistances were calculated from the slope of the linear portion of the current-potential curve at low overpotentials ( $\pm$  10 mV of the onset). The charge transfer resistance for the catalyst containing 6.1% Ni ( $5252.5 \pm 595 \Omega$ ) was roughly equivalent to that of the undoped  $\alpha$ -MnO<sub>2</sub> ( $5229 \pm 1010 \Omega$ ). While the calculated charge transfer resistance for the catalyst containing 4.4% Ni ( $4839.8 \pm 2670 \Omega$ ) was slightly less than that of the undoped material, the inclusion of the significant standard deviation does not allow any definitive conclusions to be drawn. The catalyst containing the least amount of Ni-dopant (2.0% Ni) was found to have a higher charge transfer resistance

( $7918.7 \pm 1982 \Omega$ ) than that of the undoped sample. The electrocatalytic data for the Ni- $\alpha$ -MnO<sub>2</sub> catalyst series are summarized in Table 4.7.

**Table 4.7:** Electrocatalytic Data Extracted from Averaged Linear Scanning Voltammograms

Ni-content (atomic %)	terminal current density (mA cm <sup>-2</sup> )	n (e <sup>-</sup> )	onset potential (V)	E <sub>1/2</sub> (V)	k (cm/s)	R <sub>CT</sub> ( $\Omega$ )
2.0%	-1.46	3.26	-0.095	-0.310	$5.75 \times 10^{-3}$	7918.7
4.4%	-2.53	3.29	-0.093	-0.297	$1.42 \times 10^{-2}$	4839.8
6.0%	-1.78	3.45	-0.098	-0.297	$6.50 \times 10^{-3}$	5252.5

The data do not definitively demonstrate trends of improved catalytic performance that correlate directly with the Ni-content of the catalyst. The catalyst containing 4.4% Ni outperforms the catalyst containing 6.1% Ni in terminal current density, onset potential, and kinetic rate constant, most notably. However, the catalyst containing 6.1% Ni has the highest calculated *n*-value.

As previously stated, data obtained by XPS indicated that the sample containing 4.4% Ni contained slightly more Mn<sup>3+</sup> than the sample which contained 6.1% Ni. Chapter 3 extensively outlined the role of Mn<sup>3+</sup> in the ORR. Because Mn<sup>3+</sup> is *d*<sup>4</sup>, the unpaired electron in the e<sub>g</sub> orbital set promotes a geometric distortion. The presence of this unpaired electron also destabilizes the bond between the Mn and the surface OH<sup>-</sup>, thereby promoting its displacement and the reduction of oxygen that follows. Previously, it has been hypothesized that Ni-dopants stabilize the formation of Mn<sup>3+</sup> ions.<sup>23</sup> Therefore, it would be expected that Ni-content could serve as a fairly accurate basis for predicting the relative amounts of Mn<sup>3+</sup> in the catalyst. However, our data do not indicate that this is the

case. While Ni-content is a factor that influences the catalytic performance, the trends in our electrocatalytic data do not directly coincide with the amount of Ni in the catalyst. A previous study by Garcia *et al.* also demonstrated that although the addition of Ni to  $\text{MnO}_x/\text{C}$  does enhance ORR catalysis initially, adding more Ni to the composite does not correspond to a linear increase in performance.<sup>41</sup>

The electrochemical data also demonstrate that catalyst surface area is not a sole predictor of catalytic performance. Despite the 6.1% Ni catalyst having the highest surface area in the series, it only outperforms the 4.4% Ni catalyst in  $n$ -value. In the future, RRDE studies should provide further insight regarding the predominant ORR pathway that occurs on Ni- $\alpha$ - $\text{MnO}_2$  catalysts. Ni-dopants in  $\text{MnO}_x$  catalysts have been cited as promoting the two-electron reduction and catalytic decomposition of peroxide.<sup>23</sup> Therefore, RRDE studies with these catalyst materials are expected to reveal if the formation of peroxide is decreased for the catalyst containing 6.1% Ni catalyst, indicating that the greater Ni-content corresponds to a more rapid reduction of the intermediate species.

This study demonstrates that the catalysis of the ORR is a complex process that is influenced by multiple physicochemical factors of the catalyst, such as surface area and Mn oxidation state. Further studies of Ni- $\alpha$ - $\text{MnO}_2$  nanowire catalysts are of interest, as the puzzling catalytic performance of these materials is not entirely explained by the physicochemical data collected thus far.

#### 4.4 Summary and Conclusions

The synthesis of Ni-doped  $\alpha$ -MnO<sub>2</sub> nanowires was achieved by the addition of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O into the hydrothermal reaction previously used to prepare  $\alpha$ -MnO<sub>2</sub> nanowires.<sup>19, 24</sup> By varying the amount of Ni-precursor in discrete molar ratios of 1:1, 1:0.5, and 1:0.25 (Mn:Ni), varying atomic percentages of Ni were attained in the reaction product – 6.1%, 4.4%, and 2.0%, respectively. The  $\alpha$ -MnO<sub>2</sub> crystalline phase and the nanowire morphology were retained upon doping, factors known to be critical to the overall catalytic performance. The BET surface areas, average pore diameters, and pore volumes demonstrated an increase that correlated with Ni content.

There is some experimental evidence that doping  $\alpha$ -MnO<sub>2</sub> nanowires with Ni improves their performance as catalysts for the ORR in alkaline electrolyte relative to the undoped  $\alpha$ -MnO<sub>2</sub>. Catalysts containing 4.4% and 6.1% Ni demonstrated higher terminal current densities than the undoped species. Also, the kinetic rate constant for the sample containing 4.4% Ni was greater than that of the undoped  $\alpha$ -MnO<sub>2</sub> catalyst.

The addition of Ni-dopants in  $\alpha$ -MnO<sub>2</sub> has some impact on the oxidation state of Mn, and specifically, the Mn<sup>3+</sup>/Mn<sup>4+</sup> redox couple. The oxidation state of Mn was approximated by examining the splitting of the Mn 3s peaks in the x-ray photoelectron spectra, which revealed that the greatest Mn<sup>3+</sup> character exists in the sample containing 4.4% Ni (0.54% Ni at the surface). Mn<sup>3+</sup> has a d-electron count of four ( $d^4$ ), which indicates the presence of an unpaired electron in the degenerate e<sub>g</sub> set in octahedral geometry. Through a distortion to the tetragonal geometry, the e<sub>g</sub> orbitals split, leaving the unpaired electron in the d<sub>z</sub><sup>2</sup> orbital at a lower energy, oriented toward the surface OH<sup>-</sup>. This electron destabilizes the bond between the Mn<sup>3+</sup> ion and the surface hydroxide,



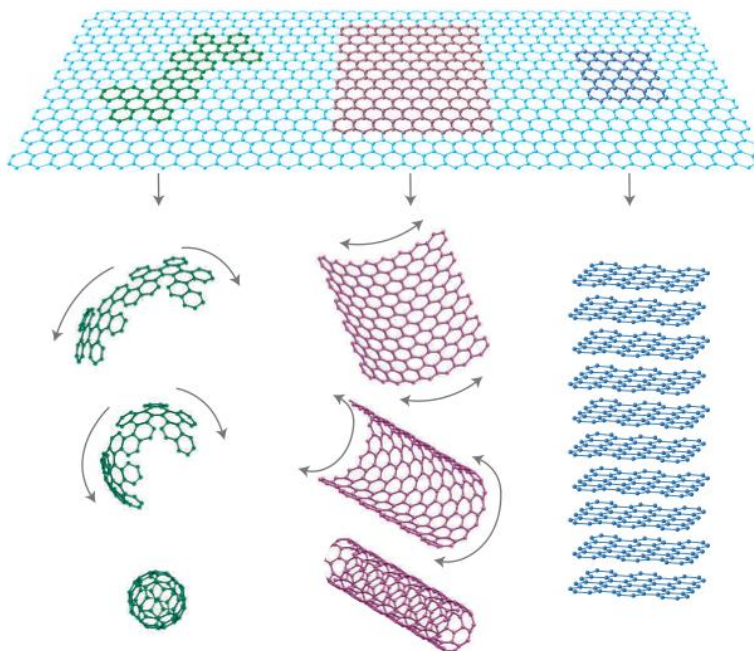
promoting the formation and subsequent reduction of  $\text{O}_2^{2-}$  on the surface.<sup>63</sup> Future studies will measure the amounts of peroxide formed for each Ni- $\alpha$ - $\text{MnO}_2$  catalyst, providing some additional insight into the predominant reaction pathway. Also, conductivity studies would enable further comparison to undoped  $\alpha$ - $\text{MnO}_2$  and other catalytic species.

## Chapter 5

### Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte

#### 5.1 Introduction

Graphene has been described as the basic building block for all graphitic materials.<sup>50</sup> Graphite, fullerenes, and carbon nanotubes are graphitic materials of varying dimensionalities that are made of graphene, as illustrated in Figure 5.1.



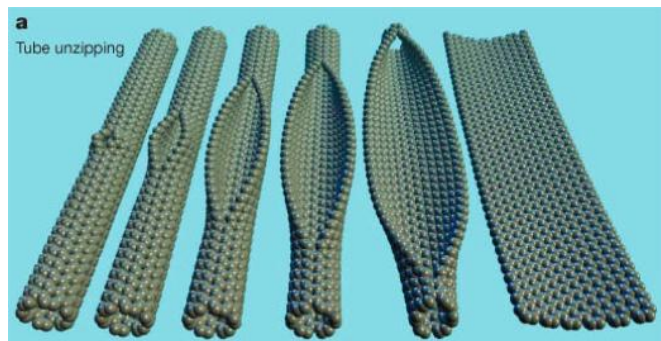
**Figure 5.1:** A graphene sheet can be formed into fullerene (left), carbon nanotubes (center), and graphite (right).<sup>50</sup>

Comprised of a network of  $sp^2$  hybridized carbons arranged in a honeycomb structure, graphene is widely acknowledged for its unique electronic properties and high surface area, theoretically  $2630 \text{ m}^2/\text{g}$  for single-layer graphene.<sup>50, 69</sup> This unique material is often

utilized for applications in energy storage and conversion and has been employed in composite catalysts for the ORR.<sup>70-73</sup> Composite catalysts containing graphene are obtained through *in situ* syntheses or simple blending techniques.<sup>70, 71</sup> In a composite, the graphene component can offer enhanced conductivity and promote the apparent four-electron reduction pathway. Though graphene alone catalyzes the ORR via the less preferred two-electron process generating peroxide, the apparent four-electron process is favored when graphene is employed in a composite, preventing the accumulation of corrosive peroxide species.<sup>24</sup>

Graphenes utilized in composite catalysts have been obtained through chemical vapor deposition (CVD) methods and other synthetic techniques that yield chemically modified graphenes (CMGs).<sup>71</sup> CMGs include heteroatom-doped graphene, chemically reduced graphene oxide (RGO), and functionalized graphene.<sup>71</sup> Carbon nanotubes have also been used in composite catalysts. However, the electrocatalytic properties of graphene nanoribbons (GNRs) and related composites have not been fully investigated.

Graphene nanoribbons are thin, elongated strips of graphene obtained by the splitting of carbon nanotubes.<sup>74, 75</sup> A schematic of a gradual unzipping process is illustrated in Figure 5.2.



**Figure 5.2:** Generalized schematic demonstrating the unzipping of a nanotube, forming a nanoribbon.<sup>74</sup>

The edges of graphene nanoribbons have been reported to be uniquely reactive, both chemically and electronically.<sup>76, 77</sup> Density functional calculations have suggested that the nature of the nanoribbon edge lowers the barrier posed to oxygen adsorption and the first electron transfer of the ORR.<sup>78</sup> Therefore, the properties of graphene nanoribbons could provide for enhanced electrocatalytic performance.

Numerous studies have shown Ag and related composites to be active ORR catalysts. A recent report describes a reduced graphene oxide (RGO)-Ag composite with catalytic activities surpassing that of a commercial Ag/Vulcan Carbon composite (referred to as Ag/C) with similar Ag content.<sup>79</sup> The enhanced catalytic behavior was attributed to Ag nanoparticles that were smaller and more disperse than what existed on the Vulcan Carbon. Ag-MWCNTs (multi-walled carbon nanotubes) composites have also been reported to operate by a four-electron process.<sup>20, 80</sup> Another composite catalyst containing Ag was reported to achieve mass activities on the same order of magnitude as Pt/C catalysts.<sup>81</sup> Considering the demonstrated synergistic effects achieved by Ag and graphene-based materials, novel composite catalysts containing both Ag and GNRs are of interest.

## **5.2 Experimental**

### **5.2.1 General**

Full descriptions of the syntheses of the graphene nanoribbons and silver-graphene nanoribbon (Ag-GNR) composite catalyst are available in the recent publication that corresponds to this chapter.<sup>82</sup> Isopropanol and Nafion solution (5 wt. % solution in water and lower aliphatic alcohols) were used as received from Sigma-Aldrich. The

commercial benchmark used in this study, 20% Pt on Vulcan XC-72, was used as received from E-Tek. A commercial Ag/C composite, 60% Ag on Vulcan XC-72, was used as received from Premetek.

### 5.2.2 Synthesis and Characterization

A detailed description of the synthesis and characterization of Ag-GNRs is provided in Davis *et al.*<sup>82</sup> Briefly, Ag-GNRs were obtained by the unzipping of multi-walled carbon nanotubes (MWCNTs) achieved through the intercalation of Na/K alloy. Treating the partially split nanotubes with Ag(O<sub>2</sub>CCH<sub>3</sub>) in the presence of Na/K causes reduction of the Ag ions, and Ag nanocrystals form on the carbon scaffold. Quenching the reaction with methanol completes the unzipping of the nanotubes. Transmission electron microscopy (TEM) revealed the Ag nanocrystals to range in size from 5 to 25 nm. TEM imaging and X-ray diffraction (XRD) confirmed the nanocrystallinity of the Ag species. Thermogravimetric analysis (TGA) revealed the Ag-GNR composite to be 70% percent Ag by weight.<sup>82</sup>

### 5.2.3 Electrochemical Analysis

To prepare the catalyst ink, the Ag-GNR composite (5.0 mg) was combined with isopropanol (200  $\mu$ L) and Nafion solution (300  $\mu$ L) in a small vial and thoroughly dispersed via ultrasonication for 20 minutes. Immediately following, 5.0  $\mu$ L of the ink solution was deposited by micropipette onto the surface of a glassy carbon rotating disk electrode (RDE, BASi, active area = 0.0788 cm<sup>2</sup>). The electrode was then allowed to dry at ambient temperature overnight. For rotating ring disk electrode studies, 10.0  $\mu$ L of the prepared ink was drop-cast onto the glassy carbon disk, surrounded by a platinum ring electrode (Pine, disk area = 0.2475 cm<sup>2</sup>, ring area = 0.1866 cm<sup>2</sup>). Prior to each drop-

coating process, the RDE or RRDE glassy carbon electrode surface was polished with 0.05  $\mu\text{m}$  alumina slurry and rinsed with deionized water and ethanol. The films were dried overnight at ambient temperature.

Linear Scanning Voltammograms were executed in a potential window from 0.2 V to -0.6 V (V vs. Ag/AgCl) at a scan rate of 1 mV/s. For RDE studies, a preliminary break-in scan at 500 rpm was conducted, followed by LSVs run at rotation rates of 500, 900, 1600, 2500, and 3600 rpm. For RRDE, LSVs were obtained at 500 and 2500 rpm in a potential window from 0.2 V to -0.6 V, and the reference was Hg/HgO. The collection efficiency of the ring electrode ( $N$ ) was determined to be 37%. All experiments were run in 0.1 M KOH electrolyte that had been thoroughly purged with UHP oxygen (or UHP nitrogen for background measurements) prior to each run. The appropriate gaseous atmosphere was preserved via blanketing for the duration of the experiment.

RDE experiments were performed in a three-electrode cell, manufactured by Bioanalytical Systems, Inc. connected to a Versastat 4 potentiostat operated by VersaStudio software. Electrodes (from BASi) included the glassy carbon working electrode prepared as previously described, a Pt coil counter electrode, and a Ag/AgCl reference electrode (3 M NaCl, potential= 0.209 V vs. NHE). RRDE experiments were performed in a three-electrode cell, manufactured by Gamry Instruments connected to a Gamry Series G 750 Test System Bipotentiostat. Electrodes included the Gamry RDE710 rotating working electrode prepared as described, Pt foil as the counter electrode, and a Hg/HgO reference electrode (Hach, 0.1 M KOH, potential= 0.171 V vs. NHE). The percent peroxide was calculated from RRDE data using  $100\% \times X(\text{H}_2\text{O}_2)$ ;

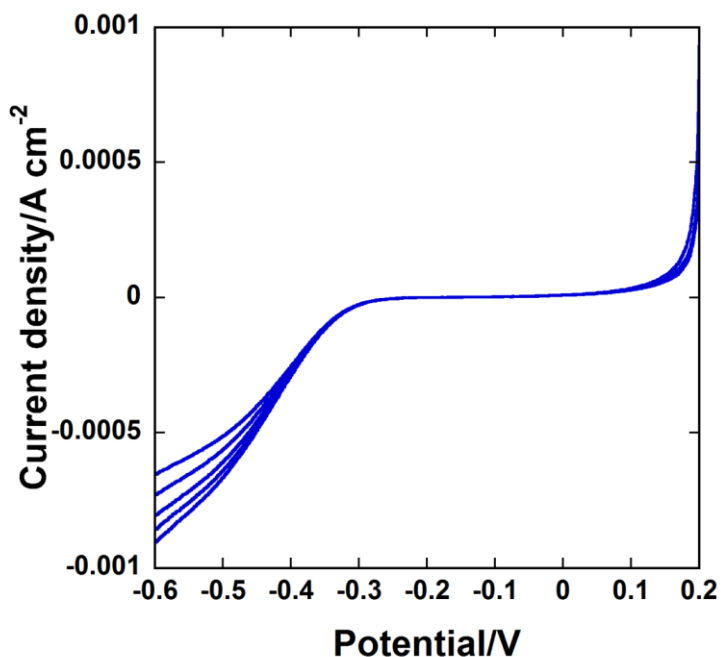
$X(\text{H}_2\text{O}_2) = [2I_r / N] / [I_d + I_r/N]$ .<sup>6</sup>  $I_r$  and  $I_d$  are the respective ring and disk currents, respectively, and  $N$  is the measured collection efficiency of the ring electrode.<sup>6</sup>

Charge transfer resistances were calculated from the slope of the linear portion of the current-potential curve at low overpotential (within  $\pm 10$  mV), recorded at 2500 rpm. Similar values were obtained using the 500 rpm data. Onset potentials were calculated from the intersection of approximated tangent lines from 0 V (base region before activation) and the half-wave potential ( $E_{1/2}$ ), recorded at 2500 rpm.

Chronoamperometric studies were performed in a three-electrode configuration as described. The working electrode was subjected to a linear scan (2500 rpm) for which the terminal potential was -0.350 V vs. Ag/AgCl unless otherwise stated. The electrode was held at this potential for 250 seconds, at which time 2 weight percent methanol was rapidly injected into the electrochemical cell. The experiment continued for 600 seconds following the methanol injection, and the current response was monitored.

### 5.3 Results and Discussion

Rotating disk electrode studies were used to analyze the catalytic behavior of pure GNRs prepared by the unzipping procedure. The linear scanning voltammograms are shown in Figure 5.3.



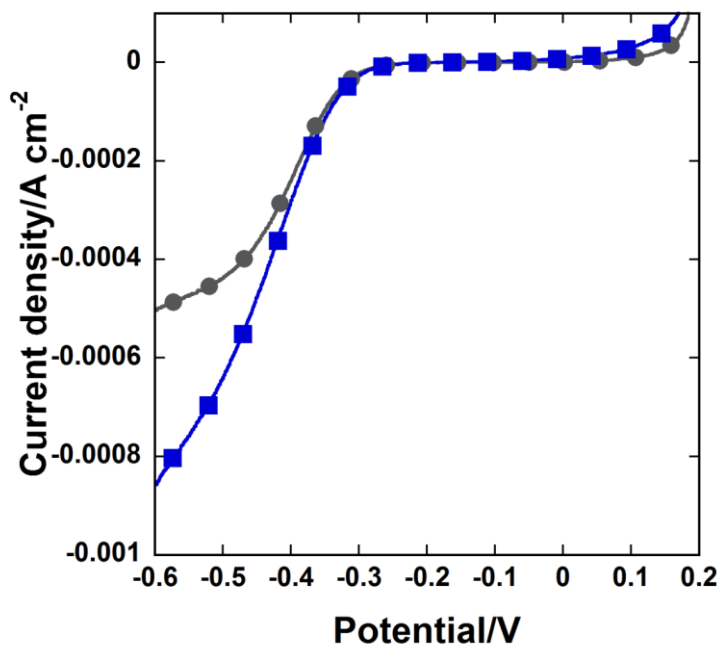
**Figure 5.3:** Linear scanning voltammograms for GNRs at 500, 900, 1600, 2500, and 3600 rpm.

As expected, an increase in electrode rotation rate causes an increase in observed current density. This is due to the resulting increase of  $O_2$  flux to the surface of the catalyst. Applying the Koutecky-Levich equation to the LSV data yields an  $n$ -value of  $1.97 e^-$ , indicating that the ORR is proceeding solely by the peroxide pathway.

High surface area carbons are commonly used in composite catalysts to enhance conductivities of the electrode materials. While the surface area for the GNRs (layers of ~30 to 40 ribbon sheets) was estimated to be 30 to 50  $m^2/g$ , a comparison to a commercially available carbon of higher surface area, Vulcan Carbon, was performed. Because Vulcan Carbon is conductive and possesses a reasonably high surface area, it is commonly used in commercial electrocatalysts, such as the Ag/C and 20% Pt/C catalysts



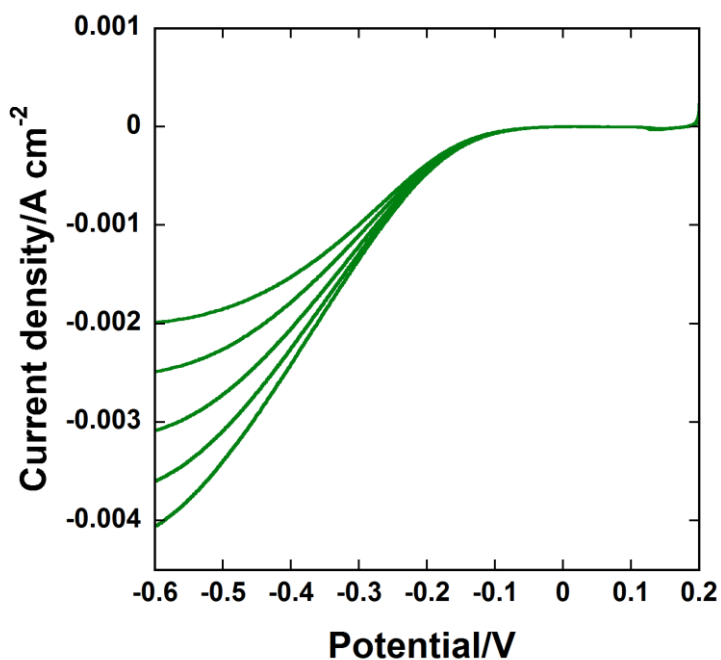
utilized in this study. A comparison of the LSVs obtained at 2500 rpm for GNRs and Vulcan Carbon is provided in Figure 5.4.



**Figure 5.4:** Comparison of commercial Vulcan Carbon (gray circles) to GNRs (blue squares) at 2500 rpm.

Even though the surface area of Vulcan Carbon (230 - 250 m<sup>2</sup>/g) is significantly greater than that of the GNRs, the GNRs attain a greater terminal current density. As shown in the LSVs, the onset potentials for the Vulcan Carbon and the GNRs are similar (~ -0.322 V vs. Ag/AgCl). However, the kinetic rate constant obtained with GNRs (3.51 x 10<sup>-3</sup> cm/s) is slightly greater than that obtained with Vulcan Carbon (2.69 x 10<sup>-3</sup> cm/s). Also, the charge transfer resistance for the GNR catalyst (7998 Ω) is less than that of Vulcan Carbon (9068 Ω), providing some evidence to support that claim that GNRs lower the energetic activation barriers posed to oxygen adsorption and the initial charge transfer.<sup>78</sup>

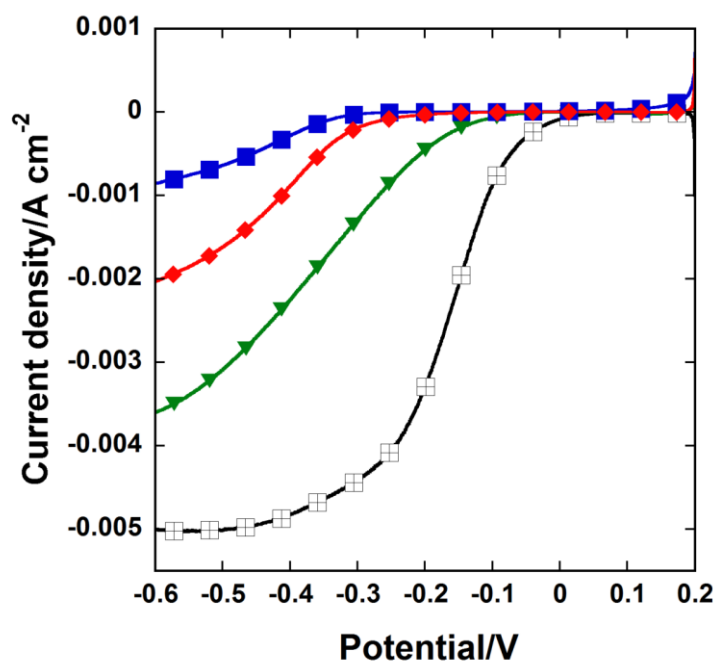
Electrochemical testing of the synthesized Ag-GNR composite catalyst was performed. The LSVs obtained at increasing rotation rates are shown in Figure 5.5.



**Figure 5.5:** Linear scanning voltammograms for Ag-GNR.

It is immediately apparent that the terminal current density for the Ag-GNR composite at 2500 rpm is approximately 4 times greater than that attained by the GNRs alone. The Koutecky-Levich equation yielded an average  $n$ -value of  $3.51 e^-$ . A value of  $3.84 e^-$  was obtained for one trial, which is similar to the reported  $n$ -value of  $3.9 e^-$  for a Ag-RGO composite.<sup>79</sup> The kinetic rate constant of  $1.66 \times 10^{-2} \text{ cm/s}$  was also substantially improved relative to that attained with the GNRs alone. Also, the charge transfer resistance for the Ag-GNR composite ( $4328 \Omega$ ) was much lower than that of the GNRs, indicating that the Ag nanocrystals contribute significantly to the ORR catalysis.

A commercially available Ag/C composite was analyzed along with 20% Pt/C, commonly regarded to be a benchmark catalyst for the ORR. A composite plot of LSVs obtained at 2500 rpm is shown in Figure 5.6 and accompanied by corresponding electrocatalytic data, presented in Table 5.1.



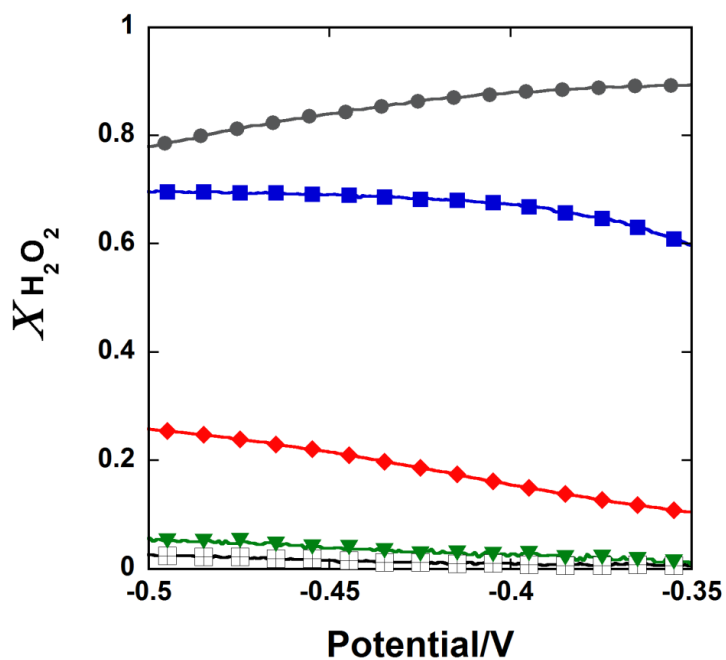
**Figure 5.6:** Composite plot for GNRs (blue squares), Ag/C (red diamonds), Ag-GNR (green triangles), and 20% Pt/C (black crossed squares), 2500 rpm.

**Table 5.1:** Electrocatalytic Data for GNRs, Ag/C, Ag-GNR, and 20% Pt/C

Sample	$n$ -value ( $e^-$ )	$k$ (cm/s)	Onset (V)	$E_{1/2}$ (V)	$R_{CT}$ ( $\Omega$ )
GNR	1.97	$3.51 \times 10^{-3}$	-0.322	-0.445	7998
Ag/C	3.09	$7.51 \times 10^{-3}$	-0.287	-0.428	4590
Ag-GNR	3.51	$1.66 \times 10^{-2}$	-0.133	-0.352	4328
20% Pt/C	3.8	$5.84 \times 10^{-2}$	-0.051	-0.214	2040

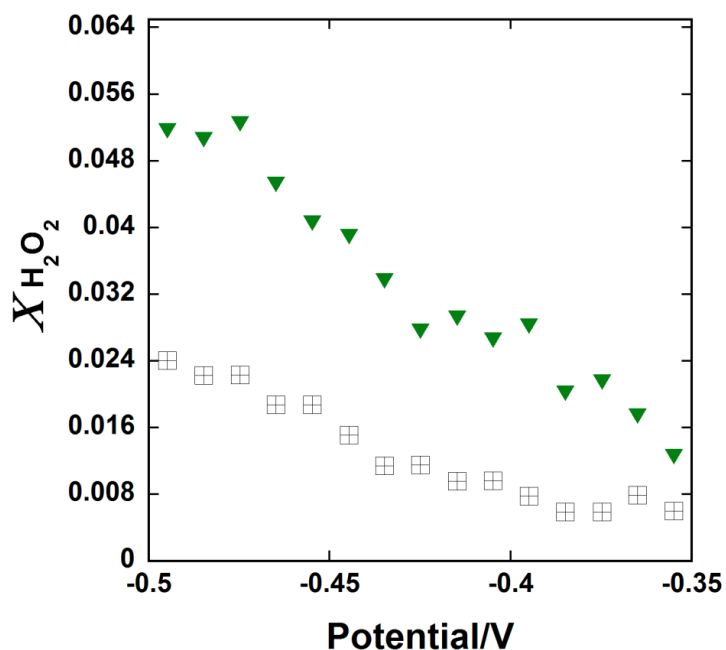
The Ag-GNR composite yields improved onset potentials and half-wave potentials relative to both the GNR and Ag/C catalyst. Compared to the Ag/C composite, the onset potential of the Ag-GNR catalyst is improved by 0.154 V while the half-wave potential improves by 0.076 V. A slight improvement in charge transfer resistance is noted for Ag-GNR as well. However, as expected, the 20% Pt/C benchmark catalyst drastically outperforms the Ag-GNR.

Rotating ring disk electrode studies were conducted to provide additional insight into the predominant reaction pathway for each catalyst material. Figure 5.7 shows  $X(\text{H}_2\text{O}_2)$  plotted as a function of potential where  $X(\text{H}_2\text{O}_2) = [2I_r/N]/[I_d + I_r/N]$ .<sup>6</sup> The percent of evolved peroxide can be obtained by  $100\% \times X(\text{H}_2\text{O}_2)$ .



**Figure 5.7:** RRDE data obtained at 500 rpm for Vulcan Carbon (gray circles), GNR (blue squares), Ag/C (red diamonds), Ag-GNR (green triangles), and 20% Pt/C (black crossed squares).

The RRDE data for the Vulcan Carbon and GNRs corroborates the  $n$ -values  $\sim 2 e^-$  obtained by the Koutecky-Levich equation. Over a potential range of -0.350 V to -0.500 V, the Vulcan carbon produces more than 80% peroxide, and the GNRs produce more than 60% peroxide. While the percentage of formed peroxide is decreased further with the Ag/C composite, the percentages are even lower for the Ag-GNR composite and 20% Pt/C, as shown in Figure 5.8.

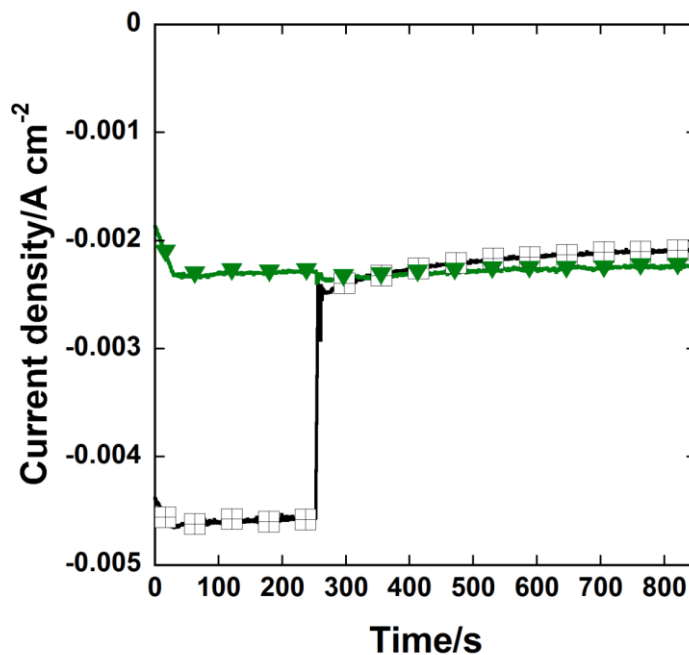


**Figure 5.8:** RRDE data for Ag-GNR (green squares) and 20% Pt/C (crossed squares), 500 rpm.

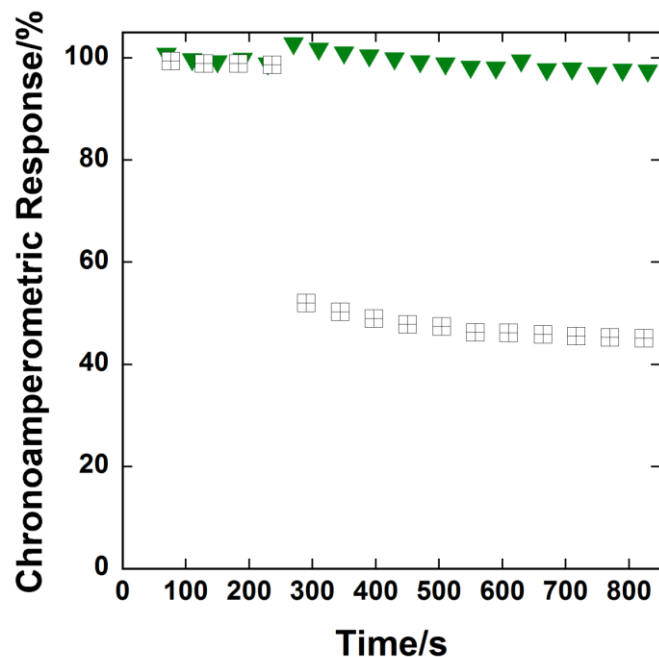
The amount of peroxide evolved for the Ag-GNR catalyst ranges from  $\sim 1.6\%$  to  $5.2\%$ , whereas the 20% Pt/C generates  $\sim 0.8\%$  to  $2.4\%$  peroxide. For both catalysts, more peroxide is produced at more negative potentials. These results indicate that an apparent four-electron pathway is the predominant process for the Ag-GNR composite.

Pt/C catalysts are susceptible to deactivation by methanol crossover effects and carbon monoxide poisoning, thus severely limiting performance. As a preliminary probe

to test potential crossover effects in alkaline fuel cells, the electrocatalytic selectivities of Ag-GNR and 20% Pt/C were studied via chronoamperometry at a constant potential of -0.350 V vs. Ag/AgCl. The results are shown in Figures 5.9 and 5.10.



**Figure 5.9:** *i-t* chronoamperometric data for Ag-GNR (green triangles) and 20% Pt/C (crossed squares), 1000 rpm. Electrodes were held at a constant potential of -0.350 V vs. Ag/AgCl. Injection of 2 weight percent methanol occurred at  $t=250$  seconds.



**Figure 5.10:** Percent chronoamperometric response data for Ag-GNR (green triangles) and 20% Pt/C (crossed squares) at -0.350 V upon injection of 2 weight percent methanol at  $t=250$  seconds.

Upon the addition of 2 weight percent methanol into the electrochemical cell, 20% Pt/C suffers a drastic decrease in current density of  $\sim 50\%$ . In contrast, the Ag-GNR composite shows a stable response with  $< 5\%$  decrease in current density, as exhibited in Figures 5.9 and 5.10. In the presence of methanol, the Ag-GNR composite is generating about the same amount of current as the 20% Pt/C catalyst, indicating that it is not subject to the potential deleterious effects of methanol crossover.

#### 5.4 Summary and Conclusions

Graphene nanoribbons are an interesting type of graphene material with electrocatalytic properties that had not yet been employed in a composite catalyst. Ag is a catalytically active metal that has been successfully utilized in graphene composites and

is significantly more viable economically than Pt. Therefore, the study of a novel Ag-GNR composite was of interest, and our catalytic studies revealed that the Ag-GNR composite outperforms the composite Ag/C catalyst for the ORR. This composite material operates by an apparent four-electron process with < 5% peroxide produced in 0.1 M KOH. When subjected to simulated methanol crossover effects, the Ag-GNR demonstrated electrocatalytic selectivity much better than the commercial benchmark, 20% Pt/C.



## Chapter 6

### Summary and Conclusions

The oxygen reduction reaction (ORR) is a critical electrochemical process that occurs in both fuel cells and metal-air batteries. While Pt and Pt-based alloys are currently considered the benchmark catalysts for this reaction due to their remarkable catalytic behaviors, these materials are costly and relatively rare, accelerating the need for novel, highly active, affordable catalyst materials.

Nanoscale manganese oxides have been extensively investigated as catalysts for the ORR in alkaline electrolyte. Nanowires have been demonstrated to be the most active nanoscale morphology.<sup>19</sup> In addition,  $\alpha$ -MnO<sub>2</sub> has been identified as the most active crystalline phase. Previous studies have demonstrated that doping manganese oxide catalysts with transition metals can improve the catalytic performance relative to the undoped species. Building upon recent work,<sup>24</sup> the current study sought to gain more insight into the roles of Cu and Ni-dopants in  $\alpha$ -MnO<sub>2</sub> nanowire electrocatalysts.

Cu- $\alpha$ -MnO<sub>2</sub> and Ni- $\alpha$ -MnO<sub>2</sub> nanowires containing varied amounts of dopant were synthesized via a modified hydrothermal technique. The physical properties of the catalysts were characterized. Rotating disk electrode (RDE) studies were performed to assess the catalytic performance of the doped nanowires.

Composite catalyst materials containing graphene are also of interest, as graphene has been demonstrated to enhance the conductivity of the composite while promoting the more favorable four-electron reduction process. The catalytic behaviors of graphene nanoribbons (GNRs) obtained by the chemical unzipping of multi-walled carbon nanotubes (MWCNTs) have not been extensively studied. A novel composite material

consisting of Ag-nanoparticles formed on GNRs (Ag-GNR) was analyzed for its ability to catalyze the ORR.<sup>82</sup>

### **Elucidating the Role of Cu-dopants in $\alpha$ -MnO<sub>2</sub> Nanowire Electrocatalysts for the Oxygen Reduction Reaction in Alkaline Media**

- Doping  $\alpha$ -MnO<sub>2</sub> nanowires with Cu improves their performance as catalysts for the ORR in alkaline electrolyte.
- The inclusion of this dopant species provides for not only higher terminal current densities, but also enhanced kinetic rate constants that exceed rates attained by  $\alpha$ -MnO<sub>2</sub> alone. Also, the charge transfer resistances decrease as the amount of Cu-dopant in the nanowires increases.
- X-ray photoelectron spectroscopy (XPS) revealed an increase in Mn<sup>3+</sup> character in the catalyst that corresponds to an increased amount of Cu-dopant at the surface. Mn<sup>3+</sup>, which is a  $d^4$  species, likely demonstrates enhanced catalytic performance due to asymmetric filling of the  $e_g$  orbital set; the resulting geometric distortion is hypothesized to promote oxygen reduction on the catalyst surface.<sup>63</sup>

### **Efforts to Understand the Role of Ni-dopants in $\alpha$ -MnO<sub>2</sub> Nanowire Catalysts for the Oxygen Reduction Reaction in Alkaline Media**

- There is some data that suggest doping  $\alpha$ -MnO<sub>2</sub> nanowires with Ni improves their performance as ORR catalysts; the catalysts containing 4.4% Ni and 6.1% Ni demonstrated higher terminal current densities than the undoped species. The sample containing 4.4% Ni demonstrated the most improvement in kinetic rate constant relative to the undoped species. The sample containing 6.1% Ni yields an  $n$ -value of 3.45  $e^-$ , greater than  $n=3.1 e^-$  for undoped  $\alpha$ -MnO<sub>2</sub>.

- As observed for the Cu- $\alpha$ -MnO<sub>2</sub> catalysts, the correlation between Mn<sup>3+</sup> character and dopant concentration as studied by XPS can provide some basis for rationalizing the demonstrated catalytic performance of Ni- $\alpha$ -MnO<sub>2</sub> catalysts as well.

### **Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte**

- Catalytic studies revealed that the Ag-GNR composite outperforms a commercial Ag-Carbon (Ag/C) catalyst; the *n*-value (3.51 e<sup>-</sup>) and kinetic rate constant (1.66 x 10<sup>-2</sup> cm/s) were improved, as were the onset potential (-0.133 V) and half-wave potential (-0.352 V).
- Rotating ring disk electrode (RRDE) studies revealed that the Ag-GNR composite generates ~1.6% to 5.2% peroxide, which is significantly lower than the amount generated by commercial Ag/C (10% to 25%) and only slightly higher than the amount generated by 20% Pt/C (~0.8% to 2.4%).
- When subjected to simulated methanol crossover effects, the Ag-GNR demonstrated a slight decrease in current density (< 5%), whereas the benchmark 20% Pt/C suffered a drastic decrease of ~50%; therefore, the electrocatalytic selectivity of the Ag-GNR catalyst is improved significantly relative to the benchmark.

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