

Electrochemical Oxygen Production: Catalyst Development to Meet the World's Oxygen Demands

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*Dedicated to my parents,
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have made my education possible.*

ABSTRACT

Gas separation processes have received extensive interest over the past few years due to concerns over global carbon dioxide emissions. Most of these processes have inherently low efficiencies which need to be solved before carbon dioxide can be captured in the volumes necessary from point sources such as coal plants. To accomplish this, new technological advancements will be made.

In this work, an electrochemical gas separation process is used which separates carbon dioxide and oxygen from various feed sources including air and simulated flue gas streams. When capturing carbon dioxide from more concentrated feed gas streams, large amounts of carbon dioxide can be captured for every mole of oxygen, up to 3.56:1 moles of carbon dioxide to oxygen. Cell potentials lower than 1.23 V were used to carry out this separation. An anion exchange membrane is used in this device which lowers cell resistive losses over previous oxygen electrochemical separation cells. An energy analysis was conducted which showed that cell potentials of 0.5 V will need to be reached if this separation process is to be used in conjunction with carbon dioxide capture from a pulverized coal plant.

To lower the cell potentials necessary for this separation further, catalyst development into lowering the reaction barriers is necessary at both the anode and the cathode used in this process. The oxygen evolution reaction taking place at the anode was examined, and an investigation into lowering the potential requirements of this reaction was carried out. Perovskite catalysts of the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{BO}_3$ B = [Ni, Co, Fe, Mn] were synthesized using an evaporation-

induced self-assembly process (EISA) which resulted in surface areas between 4-32 m²/g. Catalysts were then tested for their oxygen evolution capability at overpotentials up to 0.7 V. Perovskite catalysts were found to be active for oxygen evolution but the overpotentials of reaction were in excess of those found previously for NiO.

Transition metal oxides and mixed oxides were examined for the oxygen evolution reaction (OER). NiO, Co₃O₄, and Fe₂O₃ as well as mixed oxides of Ni-Fe and Ni-Co were investigated. Catalysts were synthesized using the EISA synthesis process and catalysts with surface areas between 7-31 m²/g were made. A synergistic effect towards oxygen evolution previously shown by other researchers between Ni and Fe was shown here with these higher surface area EISA catalysts. A peak in activity at 10 mol% Fe in the mixed Ni-Fe oxide system was found. Mixed Ni-Co oxide catalysts showed no synergistic effect towards oxygen evolution. Co₃O₄ had the highest activity of the catalysts in this system.

Surface spectroscopy of the mixed Ni-Fe oxide catalysts using XPS showed a mixed surface of NiO and Fe oxide. No identification of the exact Fe oxide phase could be made due to the low signal readings. No evidence of alloying between Ni and Fe was found to be present meaning separate phases of these oxides are found on the surface of this high surface area powder. XAS analysis showed phases of NiO and Fe₂O₃ present in these mixed catalysts. *in situ* EXAFS showed further oxidation under oxygen evolution conditions occurring on Fe sites while NiO sites remained unchanged.

Table of Contents

1. INTRODUCTION.....	1
References.....	13
2. ELECTROCHEMICAL GAS SEPARATIONS.....	20
2.1 Introduction.....	20
2.2 Experimental.....	24
2.2.1 Catalyst Preparation.....	24
2.2.2 Electrode Preparation.....	25
2.2.3 Membrane Electrode Assembly.....	27
2.2.4 Electrochemical Testing.....	28
2.3 Gas Separation Results.....	29
2.3.1 Energy Analysis of Gas Separation Process.....	45
2.4 Conclusions.....	47
References.....	49
3. PEROVSKITE OXIDES ELECTROCATALYSTS.....	53
3.1 Introduction.....	53
3.2 Experimental Methods.....	55
3.2.1 Catalyst Synthesis.....	55
3.2.2 Catalyst Characterization.....	56
3.2.3 Catalyst Activity.....	56
3.3 Results and Discussion.....	57
3.4 Conclusions.....	67
References.....	68
4. MIXED OXIDE Ni-Fe and Ni-Co ELECTROCATALYSTS.....	71
4.1 Introduction.....	71
4.2 Experimental Methods.....	77
4.2.1 Catalyst Synthesis.....	77
4.2.2 Catalyst Characterization.....	78
4.2.3 Catalyst Activity.....	78
4.3 Mixed Ni-Fe Oxide Catalytic Activity.....	79

4.4 Ni-Co Oxide Catalytic Activity.....	92
4.5 Surface Investigation on Mixed Ni-Fe Oxides.....	98
4.6 Conclusions.....	107
References.....	108
5. CONCLUSIONS.....	113
5.1 Electrochemical Gas Separation Outlook.....	113
5.2 Perovskite Possibilities.....	115
5.3 Ni-Fe Mixed Oxide Activity.....	116
5.4 Catalyst Spectroscopy Work.....	117
References.....	119

List of Tables

Table 3.1. Lattice constants calculated from (0 2 0) peak of each catalyst which closely match reported perovskite values [17-20].....	59
Table 3.2. Perovskite surface areas measured with BET ranged between 4-32 m ² /g.....	60
Table 4.1. BET surface areas for mixed Ni-Fe oxide catalysts.....	80
Table 4.2. Lattice constants for NiO and Co ₃ O ₄ phases for each oxide sample...	94
Table 4.3. BET surface areas of Ni and Co oxide catalysts.....	95

List of Figures

Figure 1.1. The selective electrochemical concentration of gas A can be efficiently accomplished by using 2 electrocatalysts and a selective membrane ...	3
Figure 2.1. SEM image of nickel particles on coated carbon paper. Ni particle sizes were in the range of 1-5 μm .	26
Figure 2.2. SEM image of Pt/C ink on coated carbon paper. The Pt/C catalyst was acquired from ETEK. The relatively porous structure of the catalyst is depicted above.	27
Figure 2.3. The membrane electrode assembly consisting of the cathode, anode, and anion exchange membrane (AEM) between two graphite flow fields.....	28
Figure 2.4. Setup depicting the electrochemical cell in conjunction with the Hidden MS and NUV10 potentiostat along with the gas feeds. In this system, a NUV10 potentiostat is used to apply cell potentials and gas evolution rates are monitored using a Hidden mass spectrometer.	29
Figure 2.5. Cyclic voltammagram between 0.4 V and 1.2 V for CO_2/O_2 transport. Cell potentials in excess of 0.6 V were necessary to produce observable current density. Current density reaches a maximum of $6 \text{ mA}/\text{cm}^2$ in this process at 1.2 V.....	30
Figure 2.6. Current interrupt technique used to determine the contribution of membrane resistance to the cell potential. The membrane resistance was relatively low in this case, measuring only $5.06 \Omega \text{ cm}^2$	31
Figure 2.7. Gas evolution flux at the anode depicts an increase in the CO_2 reading corresponding to the change in the feed gas from oxygen to a mixture of oxygen and carbon dioxide and then to turning the cell potential off.	32
Figure 2.8. Electrolysis of 0-3M bicarbonate solutions. The hydrogen evolution rate (filled symbols) was nearly independent of the carbonate concentration but the gas evolution rate at the anode increased with bicarbonate concentration due to the co-evolution of carbon dioxide.	35
Figure 2.9. Oxygen and carbon dioxide were successfully separated from an air gas feed using cell potentials below 1.23 V. The resulting gas stream was highly concentrated in carbon dioxide.	38

Figure 2.10. Carbon dioxide was highly concentrated from a gas composition of simulated flue gas with 12% by volume carbon dioxide and 3% by volume oxygen.....	40
Figure 2.11. Carbon dioxide flux as a function of cell potential and inlet gas composition. Oxygen concentration in the feed gas does not have a large impact on the carbon dioxide flux through the electrochemical cell.	41
Figure 2.12. Oxygen flux as a function of cell potential and inlet gas composition. Increasing the oxygen concentration in the feed gas does increase the oxygen flux through the cell, although not to a large degree.	43
Figure 2.13. Calibration conducted using a new calibration gas to better capture lower oxygen concentrations. Highly accurate gas flow rates can be predicted using this calibration even at low oxygen concentration levels.....	44
Figure 2.14. This graph shows the percent power loss for different ratios of CO ₂ :O ₂ vs. the cell potential. The DOE's target is 35% or lower cost of electricity (COE) increase to capture carbon dioxide from post-combustion coal-fired power plants. The shaded triangle above shows the rather large region where this capture process becomes more favorable, but capital costs will have to be taken into account in the future to meet the DOE's goal.	46
Figure 3.1. This volcano-type relationship by Bockris shows the oxygen evolution activity of multiple perovskite oxides of the formula La _{1-x} Sr _x MO ₃ M=[Ni, Co, Fe, Mn, Cr, and V] as a function of the metal-to-hydroxide bond strength. A hypothetical relationship is mentioned on the left hand side of the plot showing a possible relationship for the 4d transition metals based on known bond strength values.	54
Figure 3.2. XRD for La _{0.7} Sr _{0.3} MO ₃ M=[Ni, Co, Fe, Mn] perovskites. Present in these diffraction patterns are peaks corresponding to perovskite phases and a few peaks not associated with perovskites including a peak for SrCO ₃ in each pattern as well as characteristic peaks for pure NiO present in the La _{0.7} Sr _{0.3} NiO ₃ pattern.	58
Figure 3.3. Loss of catalyst on the surface of the electrode as 12 hours of oxygen evolution testing. These electrodes did not contain a binder in the ink solution.	61
Figure 3.4. Catalytic activity was tested as a function of ionomer concentration. By increasing the concentration above 44 wt%, no increase in activity on a per mass basis was seen. Catalyst stability on the electrode surface was obtained with the inclusion of this ionomer in the ink solution.....	62

Figure 3.5. Perovskite catalyst activity towards oxygen evolution at overpotentials between 0.2-0.55 V. At higher overpotentials, $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ shows the highest activity while $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ shows the highest activity at lower overpotentials. These activities are normalized by their respective BET surface areas. 63

Figure 3.6. Perovskite catalytic activity as a function of overpotential and normalized by mass of catalyst used. 64

Figure 3.7. Air separation experiment using a $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ anode and Pt/C cathode in conjunction with a Neosepta anion exchange membrane. Cell potentials of 0.8 V and higher were necessary to see gas separation from the air feed gas. 65

Figure 3.8. Perovskite activity versus pure NiO activity. $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and all of the perovskites have much lower activity than pure NiO on a per mass basis. 66

Figure 4.1. Jacobsen et al. plotted turnover frequency versus the adsorption energy of nitrogen for active transition metals towards ammonia synthesis. A rational design approach known as chemical interpolation led to the creation of a bimetallic catalyst of Co and Mo which showed higher activity than any existing ammonia catalyst. 73

Figure 4.2. This plot reproduced from Trasatti's data shows the oxygen evolution activity of multiple transition metal oxides as a function of the enthalpy change from a lower-to-higher oxidation state. A combination of oxide materials may show higher catalytic activity through the modification of this enthalpic energy. 74

Figure 4.3. XRD patterns of NiO, Fe_2O_3 , and 3, 4, 5, and 10 mol% Fe mixed Ni-Fe oxides. Lattice constants for NiO and all mixed Ni-Fe oxides were found to be 4.18 Å, suggesting Fe was not substitutionally incorporated into the NiO lattice. 80

Figure 4.4. 5 μm SEM image of a 5 mol% Fe mixed oxide catalyst along with elemental mapping of the surface for Ni and Fe. Particle sizes ranged from under a micron to a few microns. Ni and Fe sites were located across the catalyst surface with some locally higher concentrations. Circled in red is an area of concentrated Fe. 82

Figure 4.5. 1 μm SEM image of a 5 mol% Fe mixed oxide catalyst along with elemental mapping of the surface for Ni and Fe. Ni and Fe catalyst sites are evenly mixed across the surface. 83

Figure 4.6. Catalytic activity versus overpotential is shown here for seven mixed Ni-Fe oxide catalysts. As Fe is added into the system, and large increase in

catalytic activity is observed. A synergistic effect is apparent as mixed Ni-Fe oxide catalysts have higher activity than either NiO or Fe₂O₃. 84

Figure 4.7. A peak in catalytic activity is observed as a function of Fe content with 10 mol% Fe content having the highest activity. There exists a synergistic effect between Ni and Fe which leads to an increase in the oxygen evolution activity..... 85

Figure 4.8. The activity for each catalyst has been normalized by their respective BET surface areas. A peak in catalytic activity is again observed at 10 mol% Fe. This result points towards an intrinsic catalytic parameter that has increased the activity of the catalyst beyond a surface area effect. 86

Figure 4.9. The double layer charging was examined on a 5 mol% Fe mixed Ni-Fe oxide catalyst surface at scan rates ranging from 100 to 1500 mV/s..... 87

Figure 4.10. Tafel data for mixed Ni-Fe oxides. Decreases in the Tafel slope is evident with increases in the Fe concentration. 88

Figure 4.11. A substantial decrease in the Tafel slope is observed when Fe is added into the catalyst. The Tafel slope decreases by roughly 10 mV/dec when 5 mol% Fe is added, and the slope continues to decrease as more Fe content is added into the catalyst..... 89

Figure 4.12. A durability study was conducted on a 5 mol% Fe mixed Ni-Fe oxide. Activity was found to be constant throughout the 12 hours of testing. 91

Figure 4.13. XRD patterns shown for NiO, Co₃O₄, and mixed Ni-Co oxides. As the concentration of Cobalt is increased beyond 10 mol%, distinctive peaks are formed which are indicative of Co₃O₄ phases form in addition to NiO phase. The lattice constant of the NiO phase does not move from 4.18 Å in all of these cases which would mean no Co is incorporated into the NiO lattice..... 93

Figure 4.14. Catalytic activity of Ni-Co mixed oxides as a function of applied potential. Pure Co₃O₄ showed the highest performance with no distinct trend in activity observed for mixed-oxide samples. No Synergistic effect between Ni-Co was found towards oxygen evolution. 96

Figure 4.15. Catalytic activity of NiO, Co₃O₄, and Ni-Co mixed oxide catalysts. No synergistic effect between Ni and Co is observed with the highest catalytic activity observed for pure Co₃O₄. Both loading normalized and BET normalized data show the same trends..... 97

Figure 4.16. NiO XPS spectra taken from pure NiO and 5, 10, and 20 mol% Fe-mixed Ni-Fe oxides. All of these samples have characteristic NiO peaks for both the 2p 1/2 and 2p 3/2.....	99
Figure 4.17. Iron oxide XPS spectra from pure Fe ₂ O ₃ and 5, 10, and 20 mol% Fe mixed Ni-Fe oxides. The pure iron oxide sample contains two major peaks and one minor peak, indicative of Fe ₂ O ₃ . The mixed Ni-Fe oxide samples contain 2 iron oxide peaks but no determination as to the actual iron phase can be discerned from this data.	100
Figure 4.18. No change in the NiO phases is shown when increasing the Fe concentration in the mixed oxide catalyst indicating no degree of alloying between Ni and Fe.	102
Figure 4.19. Fe oxide phases show similar patterns for 5, 10, and 20 mol% Fe which appear to be in agreement with pure Fe ₂ O ₃ . An oxide peak is present below 2 Å and a Fe-Fe bond peak appears around 3 Å. None of these patterns resemble the pure Fe foil signal.	103
Figure 4.20. XANES analysis shows that the Fe is present as Fe ₂ O ₃ in the mixed oxide sample containing 10 mol% Fe.	104
Figure 4.21. <i>in situ</i> EXAFS data shows that under oxidizing conditions up to 300 mV, no change in the oxidation state of the NiO in the 10 mol% Fe mixed Ni-Fe oxide could be seen. No change in any of the bond distances was seen for the NiO phases in this mixed oxide sample.....	105
Figure 4.22. <i>in situ</i> EXAFS data shows that under oxygen evolution conditions, the oxide phases present in the 10 mol% Fe mixed Ni-Fe oxide catalyst become more oxidized. This oxidation increases as a function of applied potential. Small increases in the Fe-Fe bond intensity around 3 Å was also seen.	106

1 Introduction

The issue of capturing carbon dioxide from point sources such as coal plants is a complex problem. Current technologies cannot perform this separation in an efficient manner, and the world's energy consumption and subsequent carbon dioxide emissions continue to increase [1]. Solvent-based approaches to capturing carbon dioxide involve expensive chemicals such as monoethanolamine or other proprietary materials, and these solutions can degrade over time by forming stable compounds with the carbon dioxide [2-3]. These solutions also involve heating steps where energy is lost by heating large amounts of water present in the solvent. Due to water's high heat capacity, this heating step can be the source of a large efficiency loss [4]. Sorbent-based capture mechanisms involve profuse amounts of solid material which also need to be heated to regenerate. Some sorbents involve the use of functionalized amines which have been immobilized on the surface of a support, and while these amines can capture relatively large amounts of CO₂, this process has yet to be optimized [5]. All of these current approaches to capturing carbon dioxide, however elegant in some of their solutions, have problems which need to be dealt with before they can be used on a large scale.

The problem with capturing a gas at this magnitude is that a large scale, efficient gas separation process is necessary which can be stable over long periods of time. The work shown here postulates the use of an electrochemical gas separation membrane for this process and the ensuing catalyst development aimed at making the process efficient enough for use in capturing carbon dioxide from a

coal plant. An electrochemical separation cell can solve many of the issues involved with separating gases at this magnitude by operating at room temperature and pressure and operating at theoretical energy requirements substantially lower than current gas separation processes can attain.

Electrochemical gas separations function around the use of an equilibrium reaction where the cathode and the anode are reducing and oxidizing a gas, respectively, using the same equilibrium reaction. A gas separation can be selectively performed by reducing a gas at a cathode, transporting this reduced ion through an appropriate electrolyte, and oxidizing this ion at an anode to reform this gas. As an example, to selectively separate gas A from a mixed feed gas, the equilibrium reaction shown in equation 1 could be used.



This gas could be reduced at a cathode to A^{-} , transported through a membrane selective to A^{-} , and then oxidized back to gas A at the anode. Figure 1.1 shows a simple design which could effectively concentrate A from a mixed gaseous feed. In this manner, gas A can be selectively separated from a mixed gas stream.

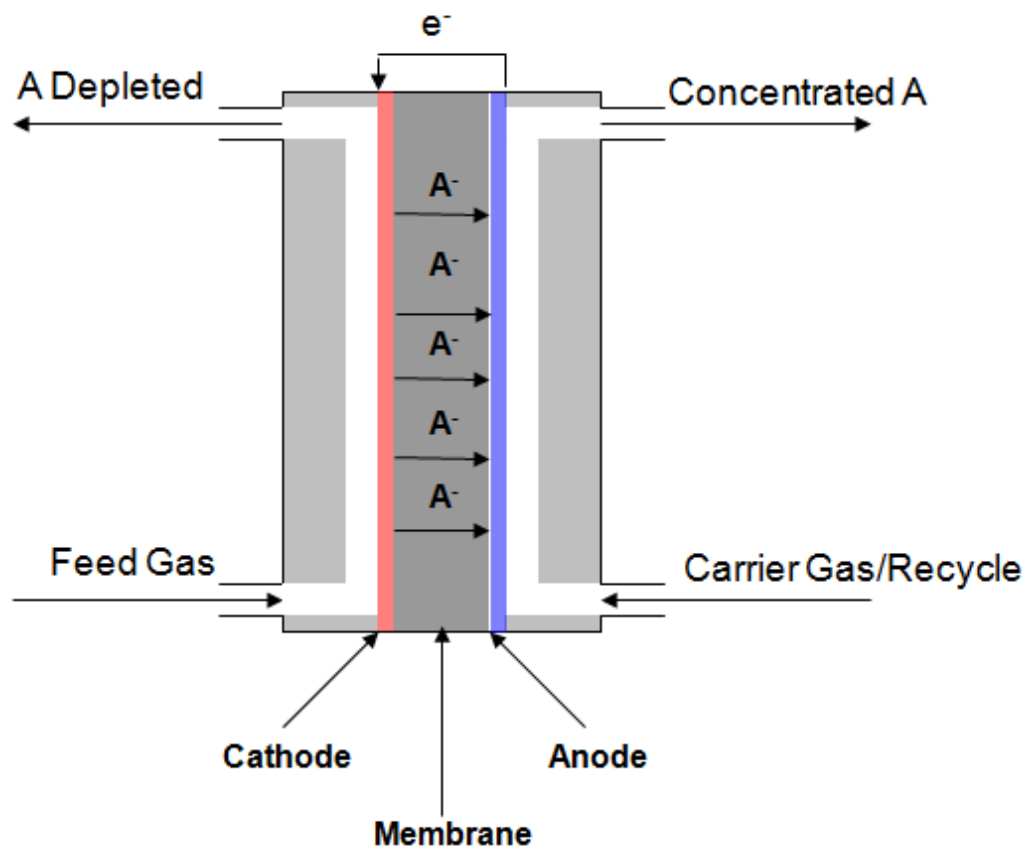


Figure 1.1. The selective electrochemical concentration of gas A can be efficiently accomplished by using 2 electrocatalysts and a selective membrane

The minimum energy requirement for an electrochemical gas separation is simply the reversible compression energy necessary to pressurize a gas from one partial pressure to another. This can be calculated using Gibb's equation shown in equation 2.

$$\Delta G = -nFE \quad (2)$$

The energy necessary to pressurize gas A from a partial pressure of 0.1 atm to 1 atm is only 5.7 kJ/mol. While this energy analysis will be examined in greater detail in the following chapters, it is important to keep in mind that although these electrochemical gas separations have desirable theoretical energy requirements,

extensive catalyst development will be necessary to come close to these low energy values. This work has focused on both the gas separation process and the subsequent catalyst development to make the process more efficient.

Electrochemical gas separation processes have been used in limited cases in the past. In the 1960s, various scientists investigated the use of oxygen concentration cells. Langer and Tomter both investigated the concentration of oxygen from the air using an electrochemical device [6-7]. Langer used rather high loadings of Ni and Pt catalysts, above 10 mg/cm^2 , while Tomter used modified Ni electrodes. Each of these researchers used asbestos matrices as supports for a KOH electrolyte. Anion exchange membranes were not commercially available at the time of this research. These thick electrolytes and the use of lower surface area catalysts contributed to the higher cell potentials which were used. These cell potentials were closer to the water splitting potential of 1.23 V. Advancements in materials could help to alleviate these issues. Carbon dioxide was not investigated in the air feed gas and was removed before entering the electrochemical cell to avoid carbonation issues. These experiments were successful in separating oxygen from the air and producing oxygen purities above 99%. Their research gave promise to this process as a viable means of air separation.

Future research in the 1990's investigated the effect of carbon dioxide present in the feed gas. This research conducted by Xiao and Li looked at carbon dioxide concentrations as high as 4.8% in the feed gas [8-9]. Carbon dioxide and oxygen gas separations were performed, but cell potentials in these cases

approached 3 V. Potentials this high can lead to the possibility of water splitting and are far too high for use with a gas separation process at a coal fired power plant. The effect of hydrogen evolution was not examined extensively even though it was almost certainly present. A porous polyamide support with a potassium carbonate electrolyte was used. Winnick also examined the effect of carbon dioxide in the feed gas [10]. Cell potentials well above 1.23 V were used and evolution of hydrogen was found at the cathode. Anion exchange membranes were again not incorporated here as these materials were still not commercially available.

This research has focused on conducting gas separations with an electrochemical cell similar to previous reports while using modern anion exchange membranes in an effort to decrease resistive electrolyte losses and using more active electrocatalysts. In all of the previously mentioned cases, cell potentials were high, especially when separating carbon dioxide. The use of these modern materials as well as further catalyst development will aid in the adoption of these gas separation cells by increasing their efficiency.

These gas separation cells use both an oxygen reduction and oxygen evolution catalysts to perform the necessary selective separation. The electrochemical oxygen equilibrium equation is shown in equation 3 for a pH 14 solution of interest here.



Proceeding in the forward direction leads to oxygen reduction and occurs at the cathode while the reverse direction leads to oxygen evolution and occurs at the

anode. Both of the electrocatalysts which perform these reactions have known activation barriers leading to high energy costs to conduct the gas separation. The use of a pH 14 solution is desirable here because it enables the use of cheaper transition metal oxides as electrocatalysts such as nickel or cobalt oxide. The use of Pt and Ru in electrocatalysis has limited the scope of applications for these catalysts [11]. An examination into both the oxygen reduction and oxygen evolution electrocatalysts work conducted will be reviewed.

Oxygen reduction catalysts have been examined to a large degree in recent years in the fuel cell community in an effort to reduce the amount of Pt content present in the catalyst [12]. Mentioned previously were Pt catalyst loadings above 10 mg/cm². These loadings are far too high if this process were to be used in a cost effective manner on the large scale necessary here. Research into limiting this Pt content has focused on not only making the Pt catalyst more active through alloying, but also by limiting the Pt content to a surface monolayer of Pt [13]. Pt monolayers over Pd cores have been shown to be more active while decreasing the overall Pt content [13-15]. Mixed monolayers of Pt and Ni have further decreased the Pt content while increasing the activity of the catalyst by modifying the binding energy of reaction intermediates [16-17]. All of this research has led to catalysts which can be incorporated into this gas separation cell in an attempt to provide a more efficient gas separation by reducing the energy requirement of the oxygen reduction catalyst.

Oxygen evolution catalysts have not been as well studied as oxygen reduction catalysts, but in recent years, research into this area has intensified due

to the importance of oxygen evolution catalysts for hydrogen production from water electrolysis [18-22]. Initial oxygen evolution catalysts focused on transition metal oxides. RuO_2 , IrO_2 , and NiO were found to be stable and relatively reactive catalysts [23-30]. While active, RuO_2 and IrO_2 are expensive catalysts and are limited in their use because of this. IrO_2 also needs to be stabilized on a support when used [31]. Pt, while normally a good catalyst, forms a stable oxide layer and is not as active towards oxygen evolution. Perovskite and spinel materials were also found to be possible alternative catalysts [12, 32-34]. This research focuses on investigating some of the perovskite and transition metal catalysts towards oxygen evolution and evaluating their performance as possible catalysts as an anode material in an electrochemical separation cell.

Perovskite catalysts have been examined as oxygen evolution catalysts previously by Bockris and Trasatti [30, 33-36]. These catalysts have the chemical formula ABO_3 where the A site is typically a lanthanum series element and the B site is a transition metal such as Co or Mn. These perovskites which have been found to be active for oxygen evolution are interesting because of the possible modification of their catalytic properties by doping different metals into the A or B site of the structure [12]. Bockris investigated a range of perovskites including B site atoms of Ni, Co, Fe, Mn, Cr, and V. He noted a trend in activity of the 3d transition metals where as the metal-to-hydroxide bond strength increased, there was a decrease in the overall catalytic activity. A lanthanum nickelate was found to be the most active catalyst of those tested and had the weakest metal to hydroxide binding energy. Postulating a similar trend for the 4d transition metals

with known bond strength values, he constructed a volcano plot in oxygen evolution activity. The 4d transition metal perovskites have weaker binding energies to hydroxide than the 3d metals which would lead to a decrease in the activity of these catalysts as this binding energy decreased. This volcano plot as well as the ease with which properties of the catalyst could be modified made this an area of research to explore, and the activity of some of these catalysts is examined in more detail in this document.

Mixed transition metal oxides have also received a considerable amount of attention recently for oxygen evolution. Specifically, mixed Ru-Ir and Ir-Sn catalysts have been investigated to create stable and more active catalysts [22, 37]. Tunold investigated different concentrations of Ir and Sn and showed that a decrease in the overpotential for oxygen evolution is possible with these bimetallic catalysts. As Sn is added into the system, large gains in the catalytic activity can be found which results in higher activity than either pure oxide. Forgie also investigated bimetallic catalysts, Ru-M M=[Ni, Pd, Cr, Re, Co, Cu, Ir], and found that when Ru is alloyed with a secondary component that higher activities on a per mass Ru basis can be attained [37].

Research into developing more active bimetallic catalysts such as the Ru-M catalysts mentioned previously has also lead to investigations into more active bimetallic catalysts using NiO. Trasatti initially conducted an investigation of multiple pure transition metal oxide catalysts towards oxygen evolution [30]. He examined the activity of RuO₂, IrO₂, Co₃O₄, Fe₃O₄, NiO, PbO₂, MnO₂, and PtO₂ and plotted their activity as a function of the energy change from a lower-to-

higher oxidation state. RuO_2 was found to be the most active of these oxide materials with NiO and Co_3O_4 also showing reasonably high activity. This result confirms other investigations which have shown the best performance with Ru-based catalysts. Of interest here is the activity of NiO catalysts and the possibility of modifying the activity of NiO catalysts in bimetallic systems.

Indeed, prior work has examined the catalytic activity of bimetallic NiO systems [26, 38-42]. In these investigations, the activity of Fe-doped NiO and Ni-Co mixed oxides were examined. In the Fe-doped NiO work, various synthesis techniques including electrodeposition and ion-sputtering were examined for electrode creation. Corrigan examined the co-precipitation of Ni and Fe from a mixed nitrate solution using electrodeposition to create a bimetallic catalyst. Small additions of Fe into the catalyst showed dramatic increases in the oxygen evolution activity. Miller reactively sputtered mixtures of Ni and Fe onto a range of substrates including titanium and conductive glass. Again, the overpotential of reaction was found to be a function of the Fe content in the catalyst. As the Fe concentration was increased, decreases in the overpotential of reaction were found. Miller also conducted stability tests and found the catalysts to be active and stable after 7000 hours. In both of these cases, the optimal concentration of Fe to maximize the activity was not investigated. This was partly due to the lack of a synthesis technique to exactly tailor the catalyst composition. Higher surface area catalysts were also difficult to attain using these techniques. The work in this dissertation will review this catalyst system while utilizing a newer synthesis procedure capable of creating exact molar compositions of catalysts while

attaining high catalyst surface areas. A peak in activity will also be shown as a function of the Fe concentration. These catalysts are promising as future oxygen evolution electrodes.

There have also been many recent and interesting oxygen evolution findings including more complex catalytic systems which should be noted. Some recent work into oxygen evolution catalysts has investigated the *in situ* formation of catalytic sites [43-44]. Kanan and Nocera have shown the formation of Co-P-K catalysts under reaction conditions in a KPi electrolyte. These oxygen evolving catalysts function in neutral solutions and are self-repairing as they are formed under reaction conditions. A similar result was also found by Dincă when examining Ni in a borate solution [45]. These oxygen evolving catalysts would be of interest where caustic solutions are simply too unsafe to be used and for the fact that they are self-repairing. Finally, Esswein and Bell have shown that the activity of an oxygen evolution catalyst is also a function of particle size [46]. They have examined Co_3O_4 nanoparticles and found that by decreasing the size of the particle, there is an intrinsic change in the catalytic activity of the particles which is beyond the effect surface area would have on the activity. All of this current research shows the growing interest in the area of oxygen evolution catalysis.

Increased interest into oxygen evolution catalysis also inherently leads to the question of why certain catalysts are more active than others. This fundamental question is crucial to the understanding of creating more active catalysts. It has been mentioned that volcano plots can be used to predict certain

bimetallic catalysts to be more active for a reaction of interest based on a chemical descriptor, but this method is not infallible. The synthesis of these bimetallic systems necessitates the use of detailed spectroscopy methods in order to ascertain exact compositions of the catalyst surface and structure. In the case of oxygen evolution catalysis, the mechanism with which the reaction pathway proceeds is also still debated [36]. To answer these questions, more sensitive spectroscopy and *in situ* spectroscopy techniques are necessary. Current advancements in surface enhanced Raman spectroscopy (SERS) may lead to conclusive proof as to which pathway oxygen evolution takes on a particular catalyst surface, but current methods cannot fully explain the increased performance seen in some bimetallic systems [47-48]. New advancements in ion scattering spectroscopy (ISS) may also lead to a stronger understanding of the catalyst surface for these bimetallic systems. Some recent spectroscopy into analyzing the Ni-Fe oxygen evolution catalyst system will be examined in this dissertation as well as possible future techniques.

The creation of more active catalysts involves a rational catalytic design approach, robust synthesis method, physical and electrochemical characterization, and proper spectroscopy to analyze the activity of the system. With these points, a more active catalyst can be created and understood. In this work, a range of perovskite and mixed transition metal oxides have been examined for use as oxygen evolution catalysts in an electrochemical gas separation cell. A more detailed investigation of mixed Ni-Fe oxide catalysts will be shown, and increased activity of the mixed oxide towards oxygen evolution than either pure oxide will

be revealed. These catalysts will aid in decreasing the energy requirement of the gas separation process.

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2 Electrochemical Gas Separations

2.1 Introduction

The capture of carbon dioxide from point sources such as coal plants is an area of intense research due to concerns about rising atmospheric CO₂ levels and the potential for climate change [1]. Established technology using liquid solvents such as monoethanolamine is currently being investigated to capture carbon dioxide from power plants [2]. However, due to thermal degradation of the solvents and the high energy costs for regeneration, many other capture possibilities are being investigated [3-5]. Electrochemical gas separation is an alternative method which can be used to capture CO₂ [6-10].

In electrochemical gas separation, a gas is selectively oxidized (reduced) at one electrode to an ion; the resulting ion is transported to and selectively reduced (oxidized) back to the gas at another electrode. Examples of electrochemical gas separations include separating H₂ from CH₄ [11], reformat gas [12], and N₂ [13]. In these separations hydrogen gas is oxidized to protons and electrons at the anode. The protons travel through an electrolyte membrane where they are reduced back to hydrogen gas at the cathode. The separation is effective because hydrogen gas is selectively oxidized at the anode, and it is primarily ionic species that are transported across the membrane. The separation occurs at ambient temperatures and pressures. Electrochemical separations can in principle be accomplished using very low energy requirements. The minimum energy required to conduct an electrochemical separation can be calculated through the Nernst equation shown below in equation 1.

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (1)$$

In this equation, E^0 is the standard cell potential, R is the gas constant, T is the temperature, n is the number of electrons, F is Faraday's constant, and Q is the reaction quotient determined by the partial pressures of the gas to be separated on each side of the membrane. For example, the cell potential required to concentrate oxygen from 0.1 atm to 1.0 atm at room temperature assuming a 4 electron reaction is only 0.015 V. Currently, under operating conditions catalyst activation losses due to slow oxygen kinetics lead to larger cell potentials than 0.015 V, but future, more active catalysts can help to address this issue and yield a cell potential closer to the minimum presented above.

The cell potential can be converted into standard free energy values representing the energetic cost of separation using Gibb's equation (equation 2).

$$\Delta G = -nFE \quad (2)$$

In this equation, n is the number of electrons involved in the reaction, F is Faraday's constant, and E is the applied potential. Using the cell potential reported above of 0.015V, the required energy to concentrate oxygen gas is approximately 5.7 kJ/mol of O₂. This value is quite low and corresponds directly to the reversible compression energy cost. An electrochemical concentration cell could provide a low energy cost means to producing oxygen, and as we will show for separating carbon dioxide as well.

Electrochemical gas separations have been reported for oxygen separation [14-22]. In these experiments oxygen is reduced to water or hydroxide ions at a cathode, and oxygen is evolved from water or hydroxide ions at the anode [15-17,

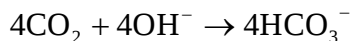
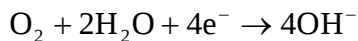
23, 24]. Haldeman as well as Tomter examined electrochemical oxygen separation from the air [17, 24]. Haldeman used Ni and Pt electrodes with catalyst loadings as high as 11.2 mg/cm^2 while Tomter used Ag and Pt/Pd catalyzed Ni electrodes. An asbestos matrix saturated with a KOH electrolyte was used in both cases. Appreciable current densities were reached with cell voltages in excess of 0.4 V and a product gas purity of >97% was achieved. However, the effect of carbon dioxide in the feed gas on the product purity was not examined in that work. CO_2 in these cases was scrubbed from the feed gas before entering the electrochemical cell to avoid carbonation of the electrolyte. CO_2 reacts readily with hydroxide ions to form carbonates and bicarbonates, which should affect the oxygen separation. Buehler and Winnick also investigated electrochemical oxygen concentration [15]. They utilized a NiCo_2O_4 spinel oxide as the anode and a Pt black catalyst as the cathode. A KOH electrolyte was again used, and the results were mainly in agreement with Haldeman and Tomter were found. CO_2 effects on the product purity were also not examined.

Electrochemically separating CO_2 from a feed stream has been examined in the context of removing carbon dioxide from breathing air in confined spaces. Xiao and Li investigated the removal of carbon dioxide from breathing gas mixtures where the feed was 4.8% CO_2 and 17% O_2 with the balance being nitrogen [10]. A porous polyamide support saturated with potassium carbonate was used as the membrane separating nickel screen electrodes. Cell voltages ranged from 1-3 V. CO_2 fluxes as high as $0.05 \text{ ml}/(\text{min} \cdot \text{cm}^2)$ were observed. Cell voltages above 1.23 V could possibly lead to water splitting, and while this is

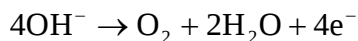
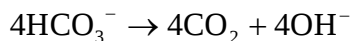
mentioned in the paper, further examination would be necessary before considering using a device with these high energy requirements. Scovazzo et al. examined the electrochemical separation of carbon dioxide using a redox cycle to concentrate CO₂ from gas mixtures as low as 1% in CO₂ [8]. In that work, the redox carrier was reduced using a potential of -1.5 V vs. Ag/AgCl and CO₂ was adsorbed from a gas mixture containing <7% CO₂. CO₂ was then desorbed using positive potentials near 1.6 V vs. Ag/AgCl. The potentials used to concentrate CO₂ were high, and the redox carriers were unstable to oxidation and unselective in the presence of oxygen. Finally, Winnick studied electrochemical CO₂ concentration systems [9]. Potassium carbonate supported in an asbestos matrix was used as the membrane and the cell potentials again exceeded 1.23 V. The product gas was composed of a mixture of H₂ and CO₂ gas due to these high potentials.

The previously reported examples of electrochemical CO₂ separation used high cell potentials which require too much energy to be suitable for CO₂ capture in power generation applications in addition to possibly resulting in water splitting. One reason for the high cell potentials is electrolyte resistance; most of the cells used thick films of supported electrolytes. An alternative approach that has not been reported is the use of a thin anion exchange membrane to minimize the ohmic resistance. In this work, an electrochemical cell utilizing an anion exchange membrane is used to electrochemically separate carbon dioxide and oxygen from a gaseous stream at lower cell potentials than previously reported. This separation was accomplished according to the reactions shown in equation 3.

Cathode :



Anode :



(3)

Oxygen is electrochemically reduced at the cathode to hydroxide ions which homogenously react with carbon dioxide present in the gas feed to form bicarbonate ions, effectively reducing the concentration of both oxygen and carbon dioxide in the feed gas. These bicarbonate ions are transported across the anion exchange membrane due to diffusion and under influence of the applied potential to the anode where oxygen and carbon dioxide gas are evolved. Up to four moles of carbon dioxide for every 1 mole of oxygen can be separated from a feed gas stream by this mechanism if all the hydroxide ions react with CO_2 at the cathode before migrating to the anode.

2.2 Experimental

An electrochemical cell was designed with the use of known active electrocatalysts and an anion exchange membrane for the purpose of oxygen and carbon dioxide concentration from a mixed gaseous feed. A nickel catalyst was employed as the oxygen evolution catalyst, and a platinum catalyst was utilized as the oxygen reduction catalyst. The preparation of these materials is described in the following sections.

2.2.1 Catalyst Preparation

Nickel was used as the electrocatalyst for the anode while platinum supported on carbon black was used as the electrocatalyst for the cathode. The

nickel used for the anode was made through a polyol process using nickel chloride, ethylene glycol, and sodium hydroxide as precursors [25]. This solution was uniformly mixed and then heated at 160 °C for 1 hour. A color change from light green to dark gray was observed as the reaction completed. Afterwards, the mixture was allowed to cool to room temperature. The platinum used for the cathode catalyst was made from a Pt on Vulcan XC-72 powder (E-TEK 20% HP Pt). An ink was made with this platinum using de-ionized water, methanol, isopropanol, Nafion, and Teflon as prescribed by NuVant Technologies [26]. An anion ionomer was unavailable for use in these inks at the time the work was performed.

2.2.2 Electrode Preparation

Each electrode was made with a 2.3 cm × 2.3 cm square piece of Toray TGPH-060 carbon paper (E-TEK) as a conductive support with a total area measuring 5 cm². The carbon paper was sealed on one side by a uniform layer of XC-72R carbon black (fuelcellstore.com) that was sprayed on with an air brush and dried at 120 °C. The carbon loading was 1 mg/cm². The nickel polyol reaction mixture was then painted on to the coated carbon paper anode and dried at 300°C in air repeatedly until a 1 mg/cm² loading was achieved. A SEM image of the nickel catalyst on the coated carbon paper is shown in Figure 2.1.

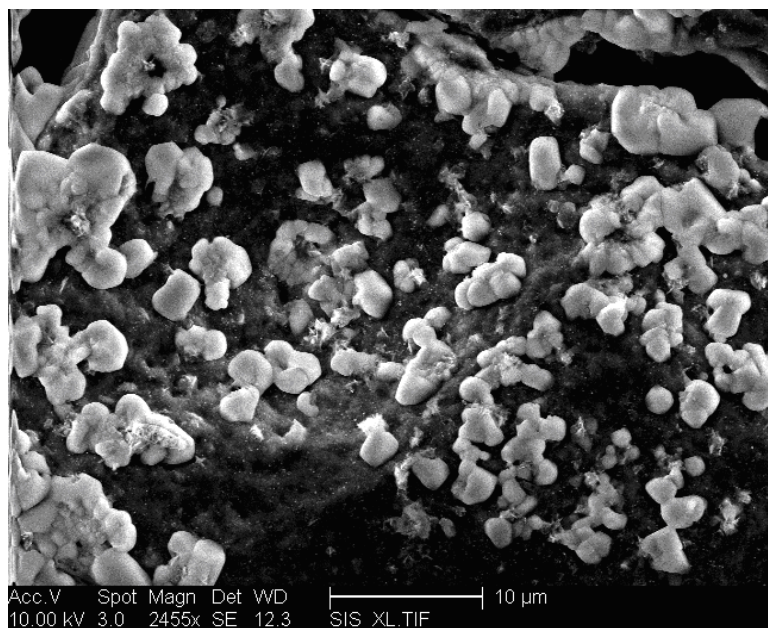


Figure 2.1. SEM image of nickel particles on coated carbon paper. Ni particle sizes were in the range of 1-5 μm .

Nickel particles ranged in size between 1 and 5 μm . The Pt/C ink was painted on to the carbon paper cathode and heated at 120°C in air in repeated cycles until a 1 mg/cm^2 loading was reached. An SEM image of the Pt/C catalyst on the coated carbon paper is shown in Figure 2.2.

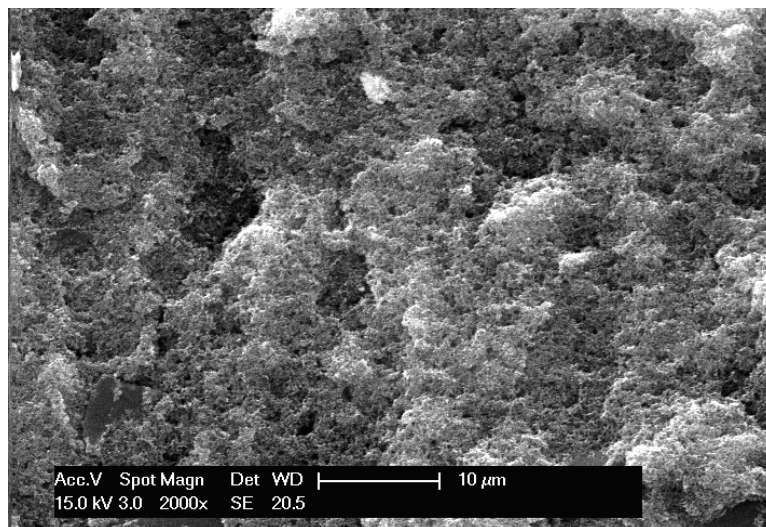


Figure 2.2. SEM image of Pt/C ink on coated carbon paper. The Pt/C catalyst was acquired from ETEK. The relatively porous structure of the catalyst is depicted above.

2.2.3 Membrane Electrode Assembly

Neosepta AHA, an anion exchange membrane, was used as an electrolyte support (Ameridia, Inc.). This membrane was stored in a 0.5M NaCl solution. Prior to use, the membrane was transferred to a 1M KOH solution and allowed to soak for at least 1 hour to exchange chloride ions with hydroxide ions. Afterwards, the membrane and the previously made electrodes were sandwiched between two conductive graphite flow fields. Teflon gaskets were placed between each electrode and the graphite blocks to prevent any cracking of the carbon paper due to compression and to prevent short-circuiting of the electrochemical cell. The cell was then bolted together using 10 lb-in of force on each bolt. Figure 2.3 shows the membrane electrode assembly between two graphite flow fields with C and A signifying the cathode and anode, respectively.

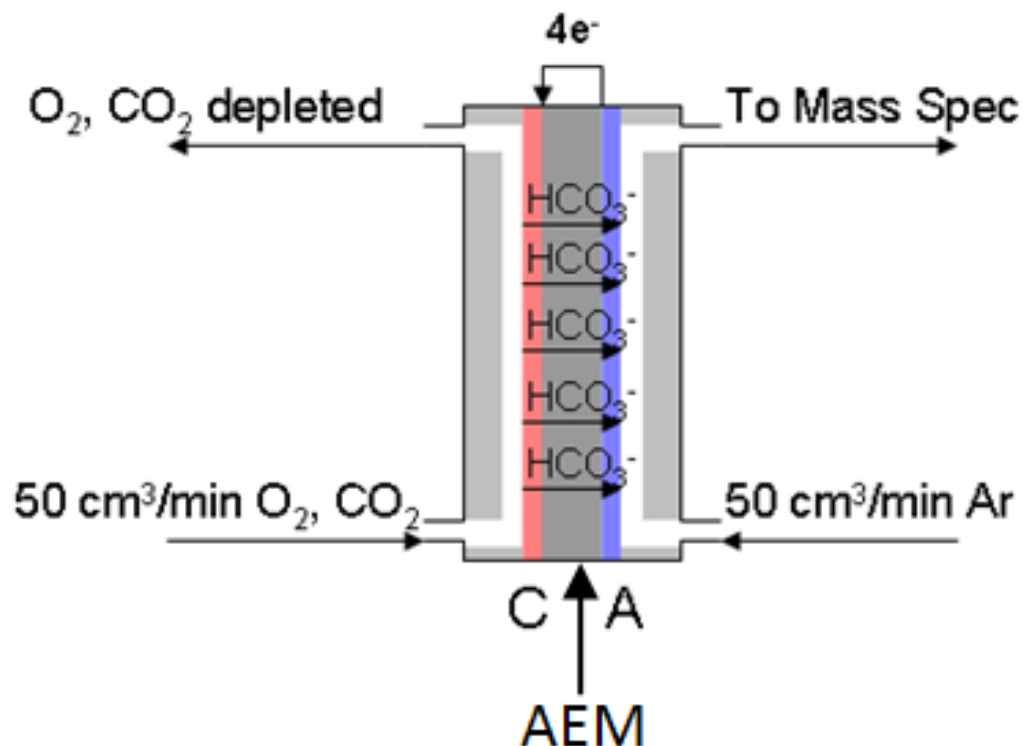


Figure 2.3. The membrane electrode assembly consisting of the cathode, anode, and anion exchange membrane (AEM) between two graphite flow fields

2.2.4 Electrochemical Testing

Electrochemical experiments were carried out using a NUV10 potentiostat supplied by Nuvant Systems, Inc. The working electrode lead was placed on the anodic side while the counter and reference electrode leads were placed on the cathodic side. A potential ramp between 0 V and 1.2 V was applied to the cell and the current monitored. All gases were humidified at room temperature using humidity bottles supplied by Fuel Cell Technologies. A 50 cm³/min gas feed composed of a 50:50 mixture of carbon dioxide and oxygen was fed to the cathode. At the anode, 50 cm³/min of humidified argon gas was used as a carrier gas. Gases evolving at the anode were analyzed using an HPR20 mass spectrometer (Hidden Analytical). The cell setup used in the lab is shown in

Figure 2.4.

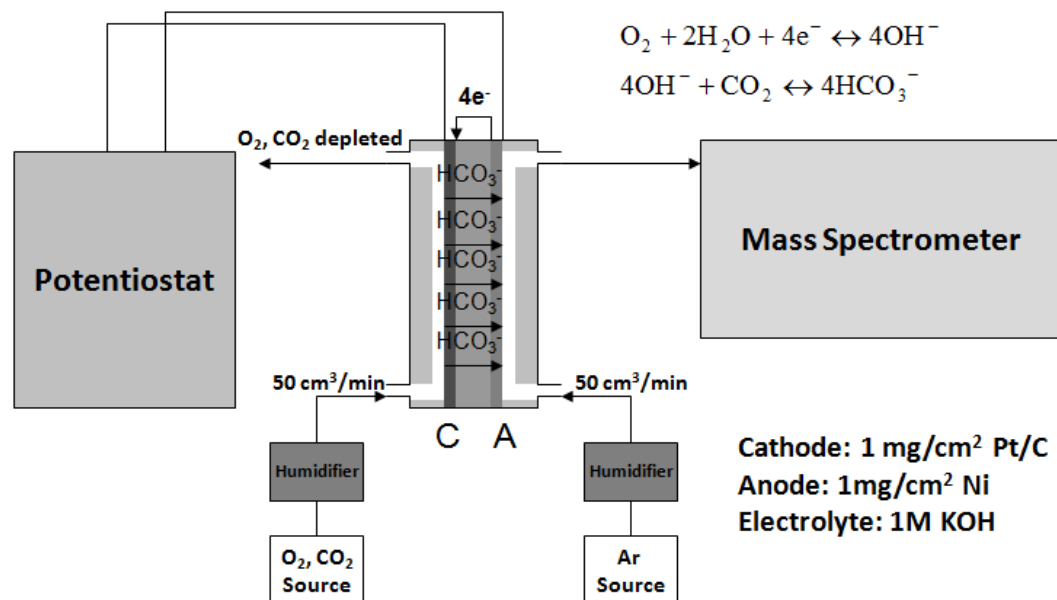


Figure 2.4. Setup depicting the electrochemical cell in conjunction with the Hidden MS and NUV10 potentiostat along with the gas feeds. In this system, a NUV10 potentiostat is used to apply cell potentials and gas evolution rates are monitored using a Hidden mass spectrometer.

2.3 Gas Separation Results

Oxygen and carbon dioxide separation was studied as a function of cell potential. A maximum cell potential of 1.2 V was used in these experiments. This cell potential was chosen because it lies below the water splitting potential of 1.23 V, ensuring we could be certain that water splitting reactions do not occur and are not responsible for any gas formation or current. Normal resistances for these membrane electrode assemblies are 1-6 $\Omega \text{ cm}^2$ [27], meaning cell potentials slightly higher than 1.23 V could even be used without the possibility of water splitting. With a current density of a 20 mA/cm² and a cell resistance of 5 $\Omega \text{ cm}^2$, a cell potential of 1.33 V could be used without the possibility of water splitting occurring. A typical cyclic voltammagram between 0 V and 1.2 V of the cell is

shown in Figure 2.5.

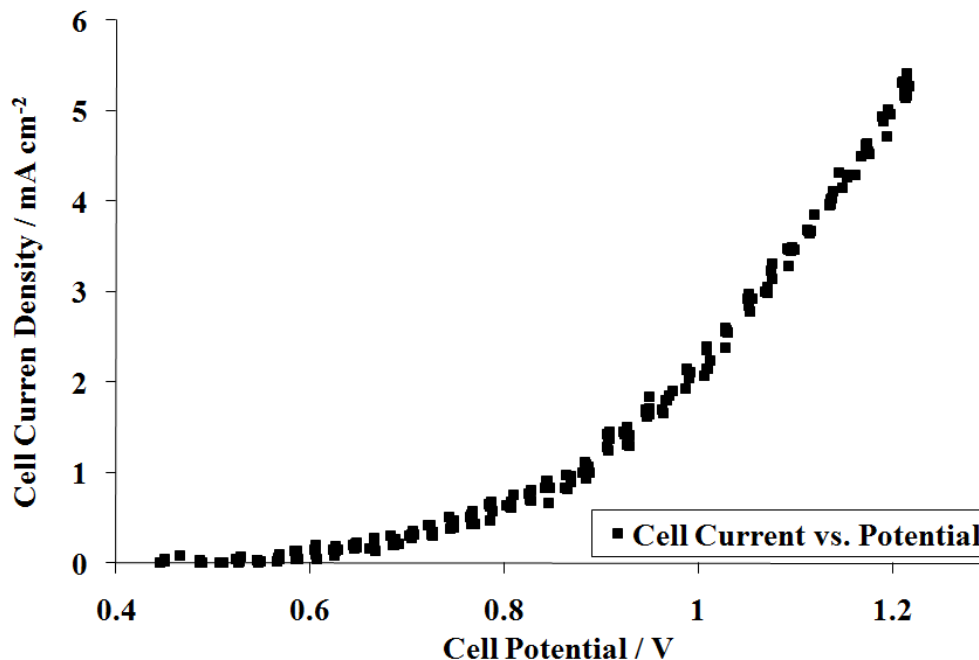


Figure 2.5. Cyclic voltammagram between 0.4 V and 1.2 V for CO₂/O₂ transport. Cell potentials in excess of 0.6 V were necessary to produce observable current density. Current density reaches a maximum of 6 mA/cm² in this process at 1.2 V.

The onset of measurable current density was observed at 0.6 V. Current density then steadily rose until it reached a maximum value of 6 mA/cm² at 1.2 V.

A current interrupt technique was employed using the NUV10 potentiostat to determine the membrane resistance and its contribution to the cell potential under operating conditions. At 1.2 V, the membrane resistance was calculated to be 5.06 Ω cm². While the cell is operating at a steady current density, in this case around 8 mA/cm², the current is interrupted and driven to 0 mA/cm². The change in potential due to this current change is used to then calculate the resistance of the membrane. Figure 2.6 shows the current interrupt response of the electrochemical cell.

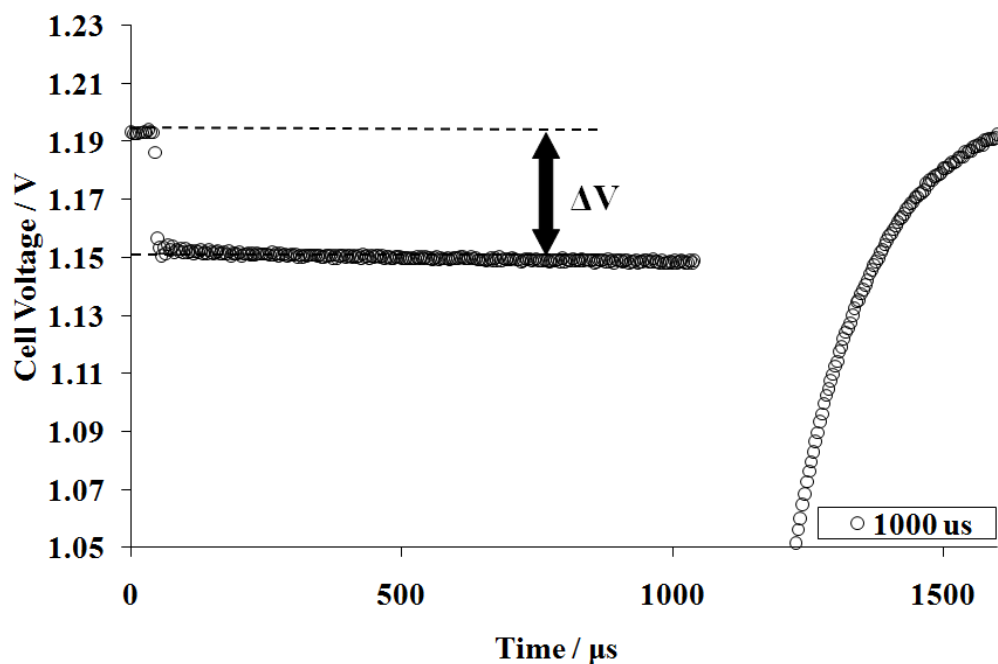


Figure 2.6. Current interrupt technique used to determine the contribution of membrane resistance to the cell potential. The membrane resistance was relatively low in this case, measuring only $5.06 \Omega \text{ cm}^2$.

This membrane contributes only 30-40 mV towards the cell potential under these conditions leading to the conclusion that the majority of the cell potential is due to the overpotentials on each electrode.

To show that oxygen reduction and evolution are the redox reactions responsible for the separation we first show that pure oxygen separation is possible, and that it is not affected by the introduction of CO_2 . A pure oxygen feed of $50 \text{ cm}^3/\text{min}$ was used initially at the cathode in this experiment. The cell potential was then increased to 1.2 V using a ramp rate of 2 mV/s. Oxygen separation was shown for a period of 19 hours, evidenced by the detection of oxygen in the purge stream of the anode. This demonstrated oxygen separation through an anion exchange membrane using cell voltages below the water

splitting potential. The small amount of carbon dioxide present in the signal before 19 hours is due to some initial carbonation of the electrolyte due to exposure to the atmosphere. The CO₂ signal is shown to be decreasing prior to 19 hours but at a slow rate due to the low current density. At approximately 19 hours, the feed gas was changed from a pure oxygen feed gas to a 50:50 mixture of carbon dioxide and oxygen.

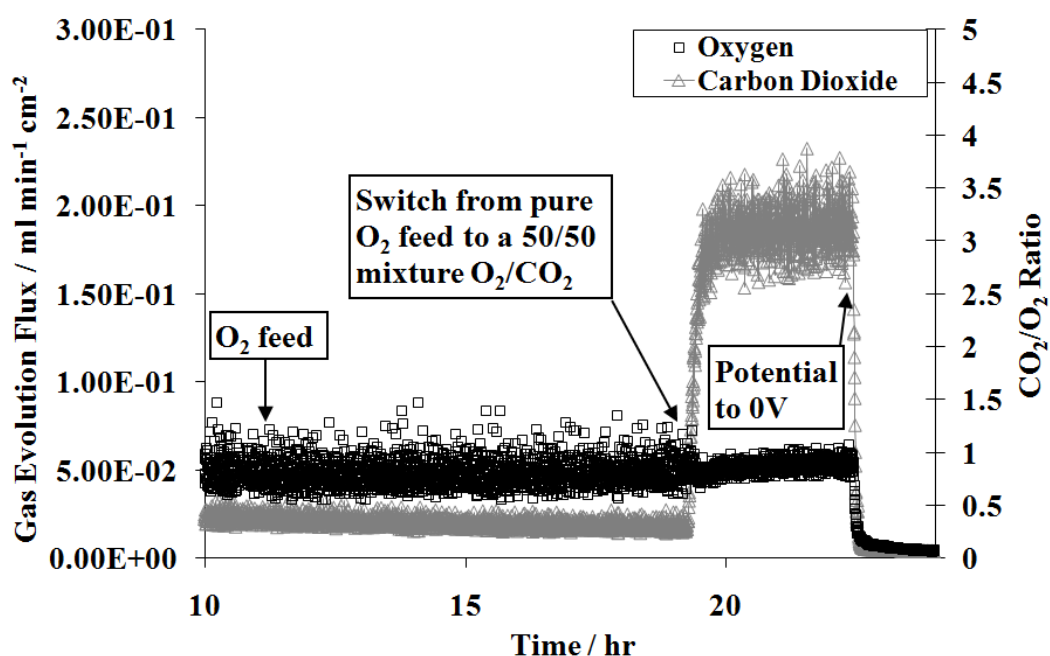


Figure 2.7. Gas evolution flux at the anode depicts an increase in the CO₂ reading corresponding to the change in the feed gas from oxygen to a mixture of oxygen and carbon dioxide and then to turning the cell potential off.

As seen in Figure 2.7, the oxygen evolution flux remains constant while the carbon dioxide evolution flux increases dramatically. This increase was indicative of the homogenous reaction occurring between carbon dioxide in the feed and hydroxide ions which were electrochemically formed from oxygen to produce bicarbonate and carbonate ions as the transport ions present in the anion

exchange membrane. Finally, when the cell potential was set back to 0 V, the flux of both oxygen and carbon dioxide was undetectable, showing that the separation is electrochemically driven.

The carbon dioxide and oxygen evolution fluxes at the anode were analyzed to determine the amount of carbon dioxide separated. This analysis was done using the mass spectrometer signal and a calibration curve, and an average ratio of 3.56:1 carbon dioxide to oxygen was attained using a cell potential of 1.2 V. A maximum of 4 moles of carbon dioxide for every mole of oxygen can be obtained if the electrolyte is fully composed of bicarbonate ions. If a carbonate electrolyte is instead formed, the ratio drops to a maximum of 2 moles of carbon dioxide for every mole of oxygen. By attaining a ratio of 3.56:1 carbon dioxide to oxygen, an electrolyte composed of carbonate and bicarbonate ions is postulated to have been formed, with bicarbonate ions being the primary species.

Other mechanisms were considered as possible routes for CO₂ and O₂ transport across the membrane in addition to the electrochemical mechanism previously discussed. One mechanism could be the direct electrochemical reaction between carbon dioxide and oxygen to form carbonate ions [28]. This is unlikely to be a large contributor due to the high ratios of CO₂:O₂ we observe. The direct electrochemical reaction would lead to an overall ratio closer to 2:1 of CO₂:O₂. Electroosmosis could also result in the transport of CO₂ and O₂ by dragging the dissolved gases due to the transport of water that is solvating ions moving towards the anode. Using standard estimates for the velocity of electroosmotic flow in water [10, 29] as well as saturated concentrations of

carbon dioxide and oxygen, we estimate that the maximum flux that electroosmotic flow could add to the flux at the anode is approximately 4% of the flux we observed. Therefore, electroosmosis is also unlikely to be a major contributor to the overall carbon dioxide and oxygen flux. Diffusion of CO₂ and O₂ through the membrane was also not detected as is evident in the flux readings shown in Figure 2.7 when the applied cell potential is set to 0 V and neither of these gases was detected.

As further confirmation that the evolution of carbon dioxide and oxygen at the anode is from the neutralization of bicarbonate ions, bicarbonate solutions were electrolyzed in a Nafion-based water electrolyzer. Gases were collected from both the anode and the cathode, and flowrates of the resulting gases were monitored. The flowrate of gases from the anode is shown in Figure 2.8 for the four bicarbonate concentrations examined.

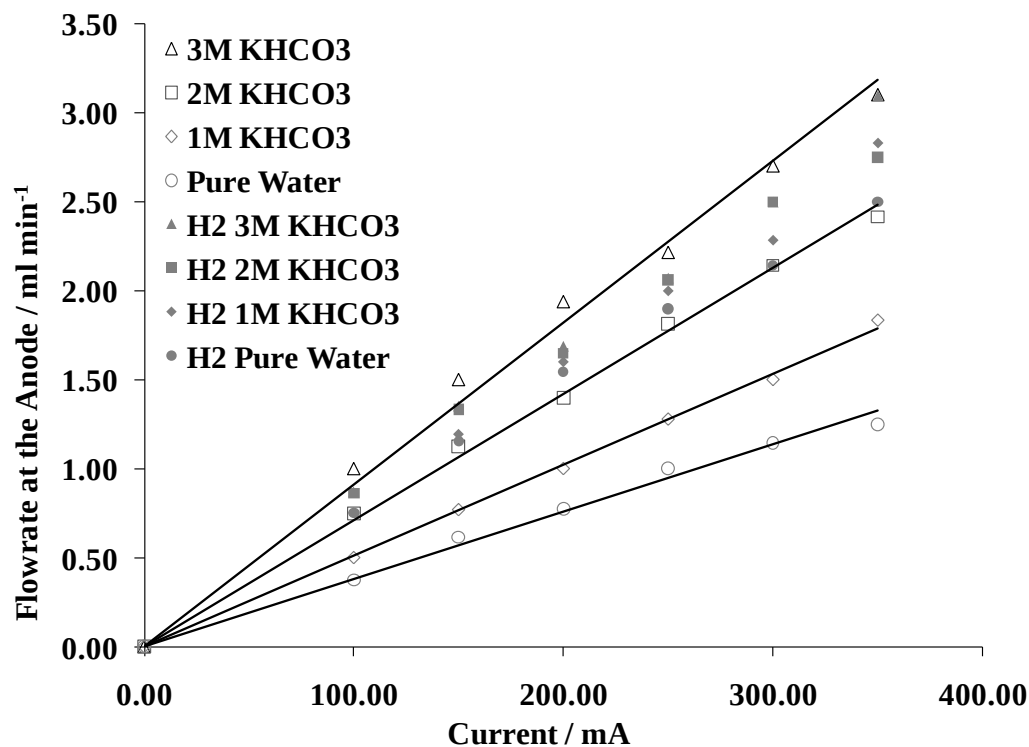


Figure 2.8. Electrolysis of 0-3M bicarbonate solutions. The hydrogen evolution rate (filled symbols) was nearly independent of the carbonate concentration but the gas evolution rate at the anode increased with bicarbonate concentration due to the co-evolution of carbon dioxide.

For pure water, the gas evolution rate was consistent with the evolution of pure oxygen which was in stoichiometric agreement with the rate of hydrogen evolution from the cathode and in good agreement with the evolution rates expected for 100% Faradaic efficiency at each current density. As the concentration of bicarbonate increases, the cathode gas evolution rate remains constant, indicating that bicarbonate electrolytes do not affect the rate of hydrogen evolution or Faradaic efficiencies. However, there is a large increase in the rate of gas evolution from the anode. This is the result of the co-evolution of carbon dioxide with oxygen. A ratio of $\text{CO}_2:\text{O}_2$ as high as 1.48 is reached at 350 mA for the 3M KHCO_3 . That ratio is not as high as we observed in the gas separation

experiment because Nafion is a proton conductor and some of the protons may transfer through the membrane before they have a chance to neutralize bicarbonate ions in solution, thus reducing the observed $\text{CO}_2:\text{O}_2$ ratio. The membrane in the gas separation experiment was an anion exchange membrane and the bicarbonate ions were formed and neutralized in the membrane, as opposed to in solution outside the membrane. Nevertheless, these results further support that once a bicarbonate solution is formed, oxygen and carbon dioxide can be evolved at the anode.

As a means of carbon dioxide capture, this gas separation scheme could separate large amounts of carbon dioxide from a mixed gaseous stream provided there is sufficient oxygen present for the production of hydroxide ions. This separation could be useful for flue gas separation as there is CO_2 as well as residual oxygen left after combustion. Assuming that CO_2 could be effectively separated from flue gas by this method, the resulting gas stream would have a composition that is 60-80% CO_2 with the balance being oxygen. This gas stream would be particularly useful if combined with an auxiliary oxycombustion unit [30]. In oxycombustion pure oxygen is used to burn fossil fuels, and some of the flue gas has to be recycled to dilute the incoming oxygen stream to about 26% to prevent the flame temperature from getting too hot. The gas composition from an electrochemical separator is already close to the desired oxygen composition which would reduce the need for flue gas recycle in the oxycombustion unit. The additional power generated by the auxiliary oxycombustion unit could help offset the power needs of the CO_2 capture from the air-fired power plant.

In addition to looking at a highly concentrated carbon dioxide stream, more relevant coal plant gas compositions were examined for both oxygen and carbon dioxide separation. These gas compositions included air, simulated flue gas, and higher concentration oxygen flue gas streams. Each one of these gas compositions is applicable towards carbon dioxide capture possibilities being investigated for use with coal fired power plants.

An air feed gas was examined as a means of providing an oxygen and carbon dioxide enriched stream to an oxy-fired coal plant. Due to the low theoretical energy requirements of these electrochemical gas separations mentioned previously, this method could be used to separate oxygen and carbon dioxide from the air and used for the burning of coal in the absence of nitrogen. In this manner, the flue gas stream would not require a nitrogen separation step. Similar to the previous CO_2/O_2 concentration experiment, platinum supported on carbon was used as the cathode for the electrochemical reduction of oxygen to hydroxide ions, and nickel was used as the anode for oxygen evolution. A Neosepta anion exchange membrane was used as the electrolyte which had previously been soaked in 1M KOH for a period in excess of 1 hour. Oxygen and carbon dioxide concentrations were examined at a range of potentials from 0.4 V to 1.2 V. These concentrations are shown in Figure 2.9 as a function of both time and cell potential.

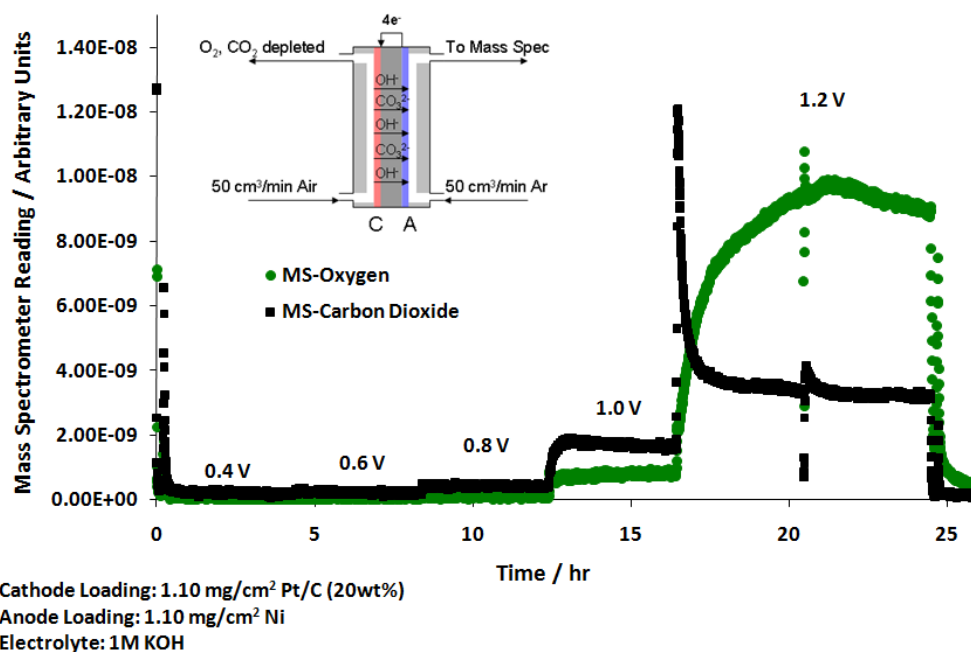


Figure 2.9. Oxygen and carbon dioxide were successfully separated from an air gas feed using cell potentials below 1.23 V. The resulting gas stream was highly concentrated in carbon dioxide.

As the cell potential is increased, an increase in the oxygen and carbon dioxide concentration is shown at the anode indicating an increase in the concentration of these two gases from the air feed gas. This experiment proves that both oxygen and carbon dioxide can be concentrated from the air and makes possible the capture of carbon dioxide from gas concentrations as low as 400 ppm. Even at these low concentrations, the reaction between hydroxide ions and carbon dioxide to form carbonate and bicarbonate ions is favored.

It is important to note that while oxygen and carbon dioxide are being separated from the air, the ratio of carbon dioxide to oxygen is much lower in this case than in the previous highly concentrated carbon dioxide feed. Due to the low concentrations of carbon dioxide in the feed gas and current densities remaining

below 10 mA/cm², the ratio of carbon dioxide to oxygen is lower than 1:1. This ratio is mass transfer limited in this case as most of the carbon dioxide present in the feed gas is being captured. At higher concentrations of carbon dioxide in the feed gas such as in flue gas concentrations, this ratio can increase. A possible application of this gas separation would be to use it in conjunction with an oxy-fired coal plant, supplying a feed of oxygen and carbon dioxide to the boiler. An energy analysis concerning all of these gas separations will be discussed later which will show a percent power loss as a function of both the cell potential and the ratio of carbon dioxide to oxygen.

Carbon dioxide and oxygen concentration from a simulated flue gas stream containing 12% CO₂, 3% O₂, and 85% N₂ by volume was also investigated. This gas composition was chosen to examine the possibility of using an electrochemical gas separation device in conjunction with retrofitting a pulverized coal plant and to confirm that highly concentrated carbon dioxide streams could be realized from flue gas streams. Flue gas streams have low concentrations of oxygen, and therefore, it was important to examine the effects of this low oxygen concentration on the carbon dioxide separation process. A mass spectrometer reading showing the gas concentrations for carbon dioxide and oxygen evolution as a function of cell potential and time is shown in Figure 2.10.

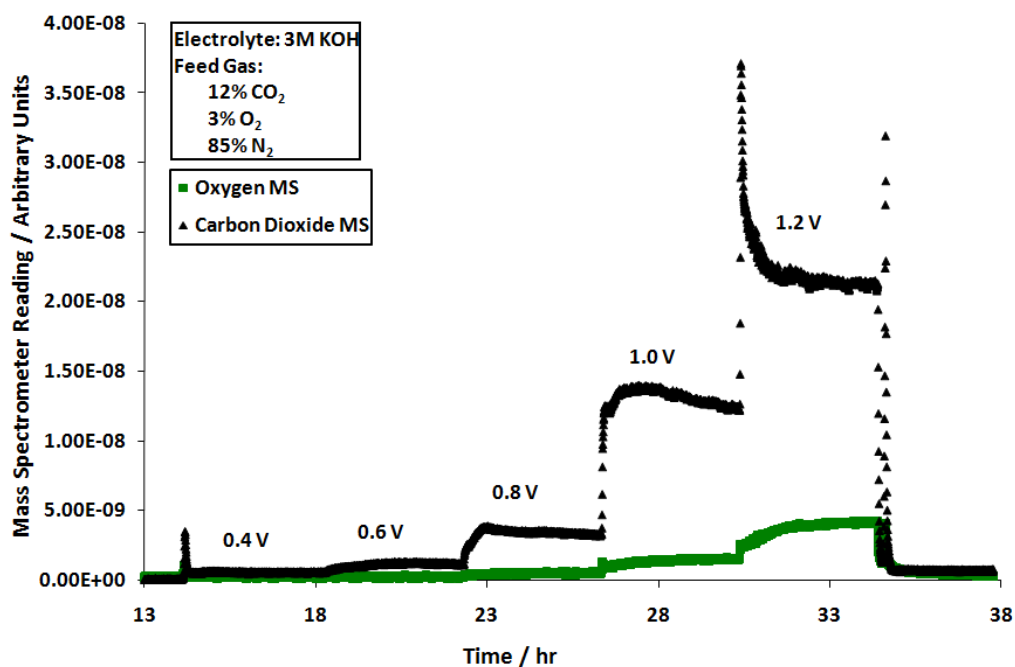


Figure 2.10. Carbon dioxide was highly concentrated from a gas composition of simulated flue gas with 12% by volume carbon dioxide and 3% by volume oxygen.

When using a simulated flue gas feed stream, it was possible to highly concentrate carbon dioxide resulting in a gas mixture composed of mostly carbon dioxide. Similar results to the highly concentrated CO₂/O₂ gas concentration experiment were found where the amount of carbon dioxide separated per mole of oxygen was close to 4:1. This result further proved that this process could be used in the retrofit of a coal plant by showing that even with low levels of oxygen present in the flue gas, both gases could be concentrated using an electrochemical gas separation cell resulting in a highly concentrated carbon dioxide stream.

The effects of oxygen concentration in a flue gas stream was studied with the intent of observing if increasing the oxygen concentration could have a noticeable impact on the gas fluxes through the electrochemical cell. Oxygen concentrations of 0%, 3%, 5%, 10%, and 15% by volume were examined in the

feed gas with the carbon dioxide concentration being held constant at 12% by volume and the balance of the feed gas composed of nitrogen. By increasing the oxygen concentration, the production of hydroxide ions should increase with increasing current which would lead to the possibility of more carbon dioxide being captured. Figure 2.11 shows the carbon dioxide flux at the anode as a function of cell potential and oxygen concentration of the feed gas.

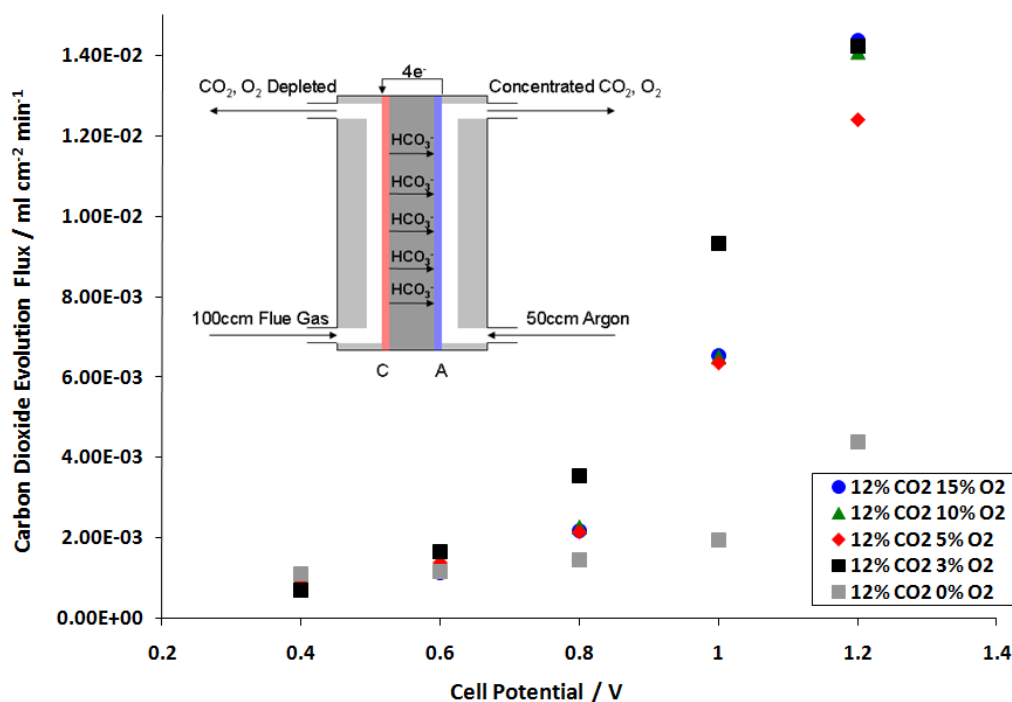


Figure 2.11. Carbon dioxide flux as a function of cell potential and inlet gas composition. Oxygen concentration in the feed gas does not have a large impact on the carbon dioxide flux through the electrochemical cell.

As the oxygen concentration in the feed gas is increased, there is no noticeable increase in the carbon dioxide evolution rate at the anode. A few points show higher CO_2 fluxes for the 3% by volume oxygen feed gas, but there is not enough data to determine if this is statistically significant. The results from these experiments indicate that oxygen concentration in the feed gas does not have a

clear impact on the carbon dioxide separation possible from a flue gas stream provided there is sufficient oxygen already present in the feed gas and low current densities. With low current densities, mass transfer effects are not an issue. Referencing Figure 2.11, there is a carbon dioxide flux present even with 0% oxygen in the feed gas. This flux is due to oxygen and carbon dioxide being present at the cathode while no feed gas was supplied. If given long enough, this flux would eventually go to zero as the oxygen and carbon dioxide present in the separation cell were exhausted, but this time limitation was not reached here. From these flue gas separation experiments, it is shown that a 3% by volume oxygen concentration should be a sufficient oxygen concentration to capture the 12% by volume carbon dioxide in the flue gas stream, especially considering the high CO_2/O_2 ratio achieved in capturing from various inlet streams.

The oxygen evolution rate was also examined as a function of the oxygen concentration in the feed gas. Figure 2.12 shows the oxygen evolution flux as a function of cell potential and oxygen concentration.

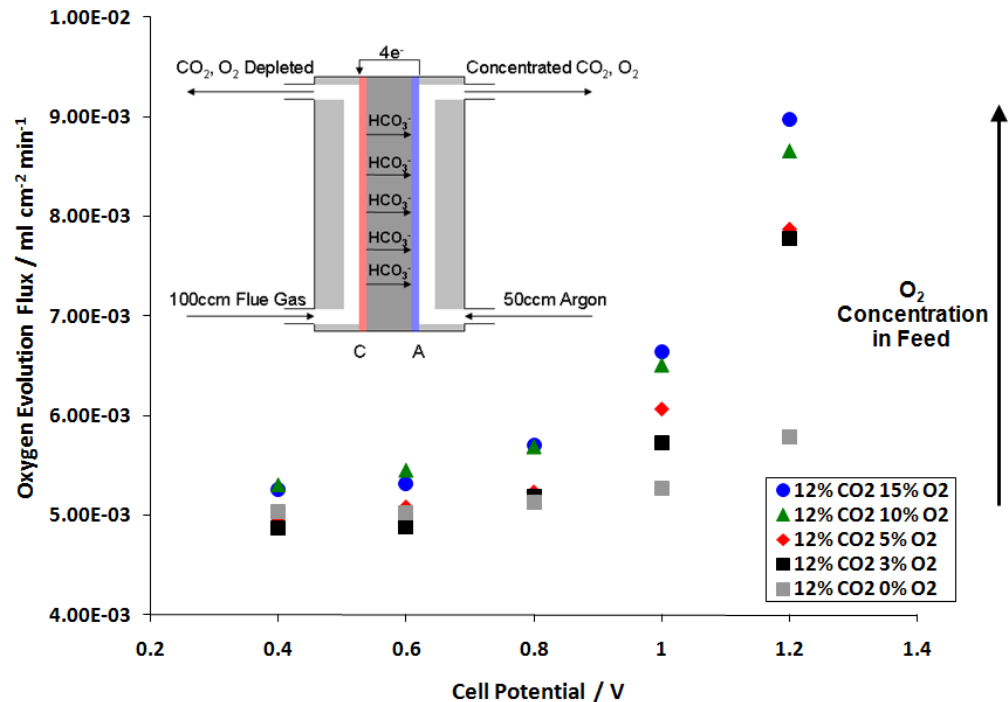


Figure 2.12. Oxygen flux as a function of cell potential and inlet gas composition. Increasing the oxygen concentration in the feed gas does increase the oxygen flux through the cell, although not to a large degree.

As the oxygen concentration is increased in the feed gas, there are increases in the oxygen evolution rate at the anode. These increases are rather small but do show the impact that feed gas composition can have on the gas evolution rate. As with the carbon dioxide flux values, even with 0% oxygen in the feed gas, there is a small flux value for oxygen. Again, this reading is due to oxygen already present in the cell which would be exhausted if given long enough to react. The oxygen evolution rate does not go to zero at the lower cell potentials which was a function of the gas calibration process. More detailed gas calibrations were examined in future experiments which more accurately capture the low oxygen concentration levels that were not available during these gas separations. While these trends would not change with a more detailed calibration, the flux values at 0.4 V were

found to be zero in later gas separation experiments, and this is noted here to avoid any confusion.

In an effort to better capture lower oxygen concentration readings, a new calibration gas was used to perform gas calibrations. This gas calibration gas contained only 10% oxygen by volume in comparison to the pure gases used previously. By using similar gas flow rates to prior calibrations and this lower oxygen concentration, and more accurate gas flux values could be calculated from the low oxygen evolution rates present at lower cell potentials. Figure 2.13 shows the gas calibration results which could more accurately predict the gas evolution rates which were shown in Figure 2.9 and Figure 2.10. This calibration process should be used in future gas separation experiments.

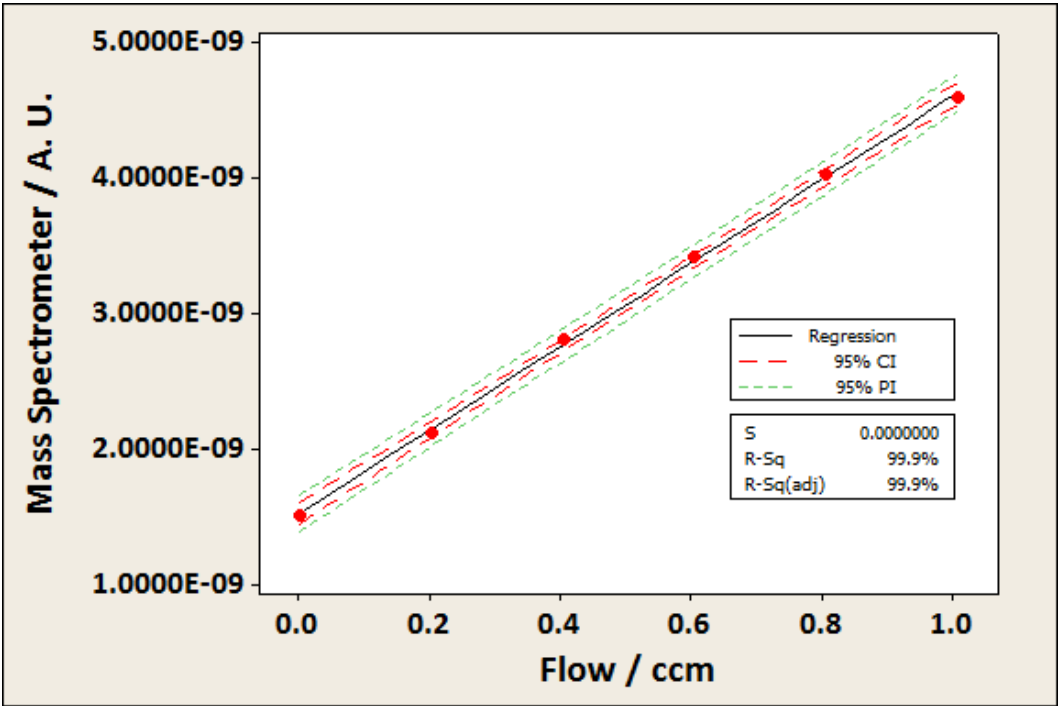


Figure 2.13. Calibration conducted using a new calibration gas to better capture lower oxygen concentrations. Highly accurate gas flow rates can be predicted using this calibration even at low oxygen concentration levels.

This gas calibration process can be used to better predict gas flow rates at lower oxygen concentration readings.

2.3.1 Energy Analysis of Gas Separation Process

An energy analysis was carried out to determine the feasibility of using this carbon dioxide capture method to capture CO₂ from the flue gas of a 500 MW coal plant operating at 40% efficiency. We assumed the coal used to power the plant had an energy density of 24 MJ/kg [31] and 75% carbon content. With 100% conversion of the coal, this plant generates approximately 3250 mol/s of CO₂. The energy cost of the CO₂ capture depends on the ratio of carbon dioxide to oxygen evolving at the anode and the cell potential used to conduct the separation. The power consumption was determined from the flow of carbon dioxide in the flue gas, and the ratio of carbon dioxide to oxygen being captured. The equation for this calculation is shown in equation 4.

$$\text{Power Consumption} = \Delta G \times \frac{\text{Moles O}_2}{\text{Moles CO}_2} \times \text{Flow CO}_2 \quad (4)$$

Finally, the percent power loss is calculated from

$$\% \text{Loss} = \frac{\text{Power Consumption (MW)}}{500 \text{ MW}} \times 100 \quad (5)$$

A graph showing the percent power loss as a function of the CO₂/O₂ ratio and the cell potential is shown in Figure 2.14.

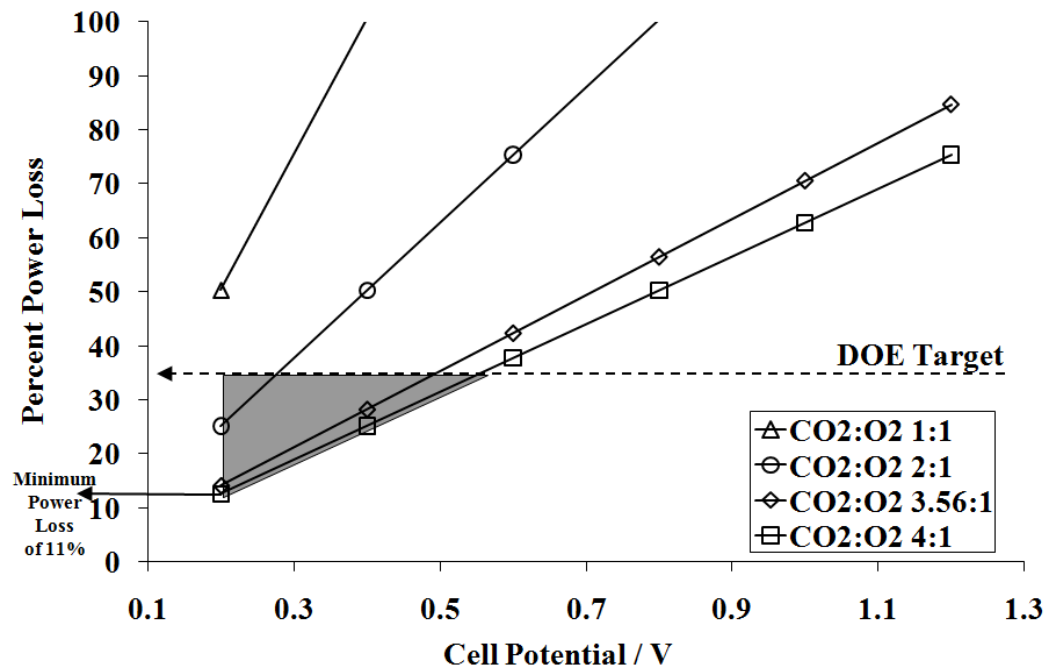


Figure 2.14. This graph shows the percent power loss for different ratios of $\text{CO}_2:\text{O}_2$ vs. the cell potential. The DOE's target is 35% or lower cost of electricity (COE) increase to capture carbon dioxide from post-combustion coal-fired power plants. The shaded triangle above shows the rather large region where this capture process becomes more favorable, but capital costs will have to be taken into account in the future to meet the DOE's goal.

As the ratio of carbon dioxide to oxygen increases, the percent power loss from the coal plant is minimized because more CO_2 is captured at a constant energy cost. Lower cell potentials also lead to reduced power losses by directly reducing the amount of energy needed to drive the separation. We do not include any power recovery from the auxiliary oxy-combustion unit in this analysis.

The Department of Energy target for post-combustion capture is to achieve 90% capture rates at less than 35% cost of electricity increase. To determine whether electrochemical separation could meet these criteria, we assume that it is at a minimum necessary to have less than a 35% loss of power

output from a power plant with capture. Based on that assumption we can identify a window of technical feasibility carbon dioxide could be captured with a parasitic power loss of less than 35%. This region is highlighted on the lower left portion of Figure 2.14. To achieve this goal one needs practical separation rates at 0.5V with a $\text{CO}_2\text{:O}_2$ ratio of at least 3.5. We have achieved the needed $\text{CO}_2\text{:O}_2$ ratio, but the cell voltage required to achieve the separation results reported in this work are still too high by a factor of two to be practical. We also note here that with the low current densities observed in this electrochemical cell, the device necessary to separate CO_2 from a pulverized coal plant would be much too large to be practical. With the electrocatalysts and membrane used in this work, this device would not be suitable for CO_2 separation from a coal plant. Therefore, to achieve this goal of CO_2 capture, significantly more active electrocatalysts for oxygen evolution and reduction as well as lower resistance membranes that are stable for long periods of time need to be identified. Although we conclude that this approach is not suitable for CO_2 capture from coal plants at this time, it may be suitable for removing CO_2 from the breathing air in confined spaces more efficiently than previous reports that required cell voltages as high as 3V [6, 10].

2.4 Conclusions

Using an anion exchange membrane and cell potentials lower than 1.23 V, carbon dioxide was concentrated from an air feed, simulated flue gas feed, and an equimolar gas mixture of carbon dioxide and oxygen feed. With the equimolar feed gas, 3.56 moles of carbon dioxide evolved, for every mole of oxygen, corresponding to the predominate formation of bicarbonate ions as the electrolyte.

The electrocatalysts used in this work are neither efficient enough nor active enough for use in CO₂ capture/oxy-combustion applications at this time, but they may be suitable for other applications. Higher activity electrocatalysts and thinner, lower resistance membranes are needed to make this electrochemical separation more practical and will be examined in the following chapters.

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3 Perovskite Oxide Electrocatalysts

3.1 Introduction

In order to improve upon the gas separation process mentioned in the previous chapter, sizeable decreases in the energy requirements of this separation are necessary. After examining the performance of the gas separation cell, it is readily apparent that both the oxygen reduction and oxygen evolution catalysts have large activation barriers of reaction. In assessing how to proceed in reducing these energy requirements, fundamental catalyst development is necessary to lower these energy barriers. This work could either focus on developing more active oxygen reduction or oxygen evolution catalysts. Members of the fuel cell community are researching ways of developing more active oxygen reduction catalysts [1-9]. Therefore, this research has focused on developing more active oxygen evolution catalysts which would help to enable a gas separation process of this magnitude.

Bockris, Trasatti, and Jörissen examined the use of perovskites as oxygen evolution catalysts previously [6, 10-14]. Each of them has found perovskites to be active oxygen evolution catalysts with lanthanum nickelate perovskites being shown to have the highest activity amongst the tested perovskite catalysts. Jörissen's review of perovskite materials encompassed a range of conditions with both oxygen evolution and oxygen reduction being of interest. With concerns to lanthanum nickelate, he found surface nickel hydroxide phases would form with repeated cycling between oxygen evolution and oxygen reduction. Towards

oxygen evolution, A-site substitution of strontium into the catalyst yielded much more active oxygen evolution catalysts. Bockris specifically tested a range of 3d transition metal perovskites also with strontium substitution into the perovskite structure. A correlation was found between the metal-to-hydroxide bond strength and the activity of the perovskite towards oxygen evolution. This relationship is shown in Figure 3.1

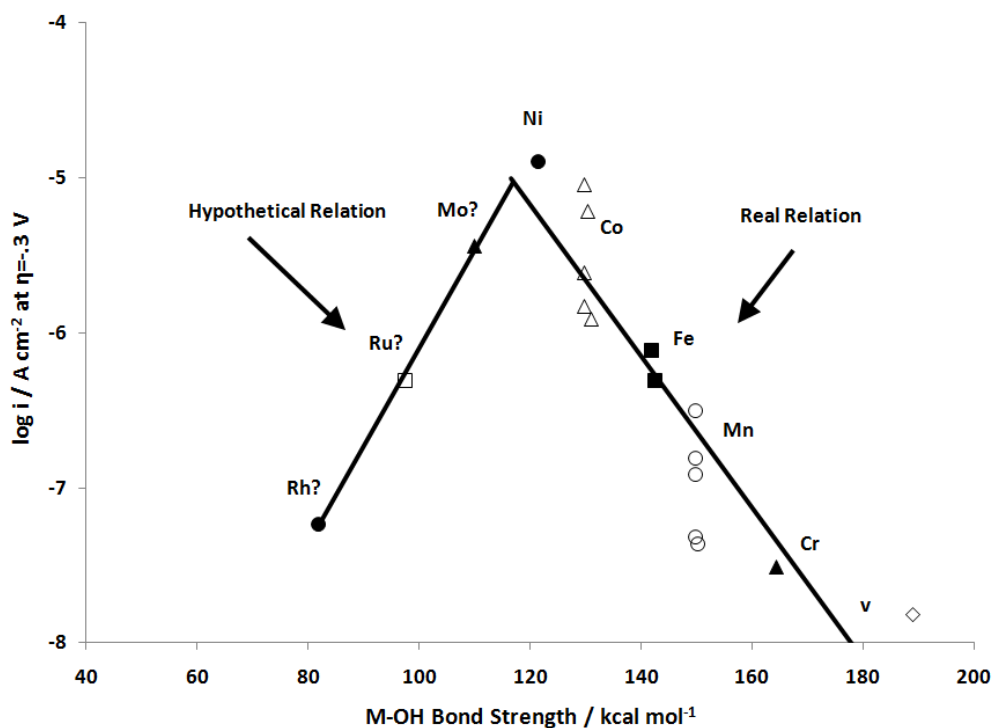


Figure 3.1. This volcano-type relationship by Bockris shows the oxygen evolution activity of multiple perovskite oxides of the formula $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ $\text{M}=[\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}, \text{Cr}, \text{and V}]$ as a function of the metal-to-hydroxide bond strength. A hypothetical relationship is mentioned on the left hand side of the plot showing a possible relationship for the 4d transition metals based on known bond strength values.

Bockris tested the catalytic activity of 3d transition metal perovskite catalysts.

Perovskite catalysts containing nickel were found to be the most active with a

volcano plot in activity found to be present when activity was plotted versus the metal-to-hydroxide bond strength. A hypothetical relationship is shown on the left-hand side of this plot for 4d transition metals which would predict a similar but opposite trend to the 3d transition metals in catalytic activity related to the bond strength values. This relationship is predicted based on the metal to hydroxide bond energies for the 4d transition metals. This research has subsequently focused on examining the activity of these perovskite oxides for oxygen evolution in an alkaline environment. Perovskite catalysts located on the right side of this plot have been examined for their oxygen evolution capability in an effort to reproduce the activity seen by Bockris while using a new synthesis process and electrode substrate.

The synthesis process that Bockris used to create his perovskite catalysts was a high temperature solid-state reaction process and temperatures exceeding 1000 °C. These temperatures were held for a period of 30-70 hours and involved multiple steps of grinding and refiring. While he was able to attain surface areas as high as 25 m²/g, this process was cumbersome and would not make high surface areas samples straightforward. In this work, a new synthesis process, evaporation-induced self-assembly (EISA), was used to create perovskite catalysts which could be carried out at lower temperatures and decreasing the steps required to make high surface area, crystalline samples [15]. The steps of this synthesis process will be described.

3.2 Experimental Methods

3.2.1 Catalyst Synthesis

Catalysts were synthesized using an evaporation-induced self-assembly process (EISA) using the procedure described here [15]. Briefly, 1 gram of P123 surfactant was dissolved into a mixture composed of 5 grams of de-ionized water and 5 grams of ACS grade ethanol. Subsequently, metal nitrate precursor salts were dissolved into this mixture in the desired molar compositions for the final catalyst powder with each powder composed of a 7:3 lanthanum to strontium molar ratio. This solution was then transferred to a ceramic container and heated using a controlled procedure. First, the solution was heated to 120 °C and held there for 12.5 hours. This temperature was used to remove any water and residual ethanol. Next, the solution was slowly ramped to 350 °C at 1 °C/min and held at 350 °C for 4 hours. This step was intended to remove the P123 surfactant while maintaining a high surface area framework. Finally, the remaining material was heated to 650 °C, again at 1 °C/min, and held for 4 hours. The resulting material was then ground using a mortar and pestle and stored for characterization.

3.2.2 Catalyst Characterization

Catalyst crystallinity and composition was examined using a Rigaku Theta-Theta Diffractometer equipped with a Cu detector and an incident beam wavelength of 1.542 Å. The beam energy was set to 30 eV and beam current to 30 mA. Catalyst surface area was examined using the BET method with a Nova 2200 Surface Area Analyzer. Catalyst morphology and surface composition were investigated using a Philips XL30 Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM/EDS).

3.2.3 Catalytic Activity

Catalyst inks were formed by combining 20 mg of catalyst powder, 645 mg of 5 wt% AS4 ionomer solution from Tokuyama Corp., 200 μL of de-ionized water, and 800 μL of isopropanol. This solution was sonicated for 60 minutes. Next, the catalyst ink was painted on to a piece of Toray TGPH-060 carbon paper with 1 cm $\times$ 2 cm dimensions and heated at 120 $^{\circ}\text{C}$ for 10 min to remove any water or alcohol from the surface. This process was repeated until a loading of approximately 1 mg/cm^2 was achieved in all cases, and the results were normalized by this catalyst loading. Electrodes were then tested using a Gamry Reference 600 potentiostat. A Pt counter electrode and Hg/HgO reference electrode were used throughout these experiments. 1M KOH was used as the electrolyte which was deaerated with pure argon for 30 min prior to each experiment. Initialization of the catalyst was carried out at a potential of 0.742 V vs. Hg/HgO for a period of 3 hours. Steady-state catalytic activity was subsequently examined at potentials between 0.542 V to 1.042 V vs. Hg/HgO in 50 mV increments for 20 min at a time. All results have been normalized by reference electrode potential and pH.

3.3 Results and Discussion

Perovskite catalysts were examined for their oxygen evolution activity. Specifically, catalysts with the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_3$ $\text{M}=[\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}]$ were synthesized according to the EISA process mentioned previously. These catalysts were chosen based on a volcano plot in oxygen evolution activity postulated by John Bockris. The first step in examining these catalysts was to synthesize the

perovskite catalysts tested by Bockris and to confirm the trend in activity which was observed.

The EISA synthesized perovskite catalysts of composition $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_3$ $\text{M}=[\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}]$ were first characterized using x-ray diffraction (XRD). The XRD for all of these perovskite structures is shown below in Figure 3.2.

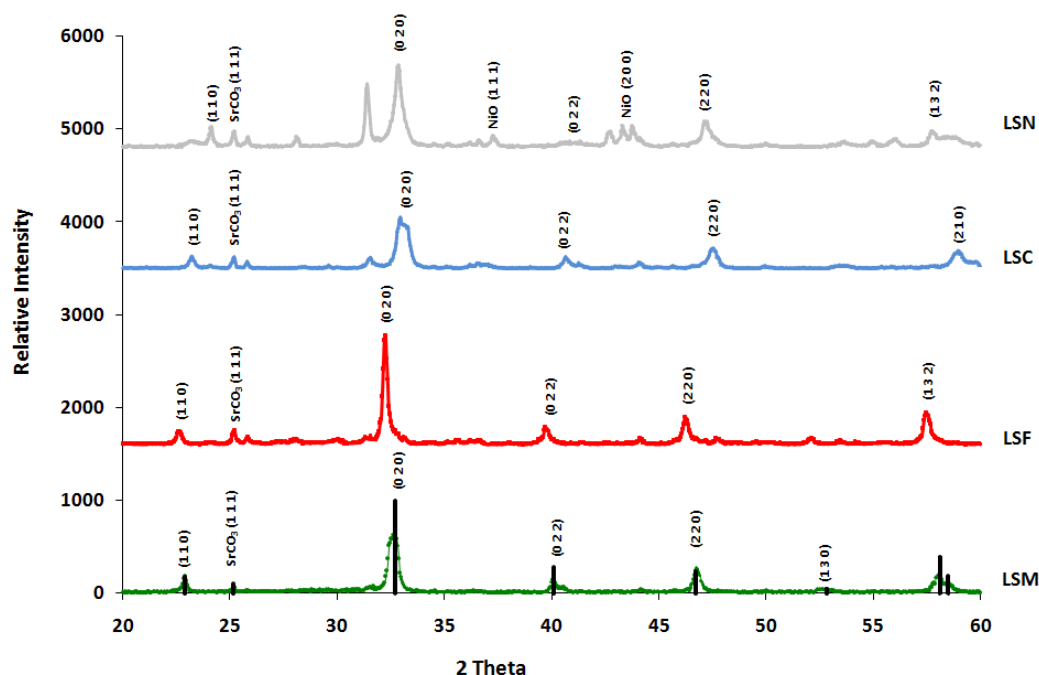


Figure 3.2. XRD for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_3$ $\text{M}=[\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}]$ perovskites. Present in these diffraction patterns are peaks corresponding to perovskite phases and a few peaks not associated with perovskites including a peak for SrCO_3 in each pattern as well as characteristic peaks for pure NiO present in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ pattern.

XRD patterns for each powder show characteristic perovskite peaks, but some impurities are present in these samples. $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ shows characteristic peaks for the perovskite structure in addition to peaks associated with both SrCO_3 and NiO [16]. The SrCO_3 peaks which are present in all of these diffraction patterns are a result of carrying out the synthesis and subsequent calcination of the powders in the air. By carrying out these experiments in an inert atmosphere,

these carbonate phases could be avoided if desired in future experiments but are not a concern for these samples due to the low concentrations and the fact that this is a screening study. The main phases in these XRD patterns remain perovskite structures. NiO peaks are also present in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ pattern due to the probable lack of full incorporation of Ni into the perovskite structure. Primarily, this EISA synthesis process has yielded crystalline phase perovskite powders with some impurities being present. In addition to identifying the phases in each pattern, the lattice constant for each perovskite powder was calculated. These values are shown in Table 3.1.

Table 3.1. Lattice constants calculated from (0 2 0) peak of each catalyst which closely match reported perovskite values [17-20]

Catalyst	Lattice Constant a / Å	
$\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$	5.45	(5.45 Å [17])
$\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$	5.43	(5.45 Å [20])
$\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$	5.54	(5.50 Å [19])
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	5.47	(5.47 Å [18])

Physical surface areas were also examined using the Brunauer-Emmett-Teller (BET) method for each one of these perovskite powders. Reasonably high surface areas were attained with the range being 4-32 m^2/g . These surface area values are shown below in Table 3.2.

Table 3.2. Perovskite surface areas measured with BET ranged between 4-32 m²/g

Catalyst	BET Surface Area / m² g⁻¹
La_{0.7}Sr_{0.3}NiO₃	9.5
La_{0.7}Sr_{0.3}CoO₃	4.4
La_{0.7}Sr_{0.3}FeO₃	32.3
La_{0.7}Sr_{0.3}MnO₃	29.3

Finally, the electrochemical activity for each powder was examined. Each catalyst was fabricated into an electrode, as described previously. The importance of catalyst inks containing a binder was immediately evident. Without the use of an anion binder in the ink, most of the catalyst would be lost from the surface over prolonged periods of testing, approximately 12 hours in this case. Figure 3.3 shows the electrode surface before and after oxygen evolution testing.

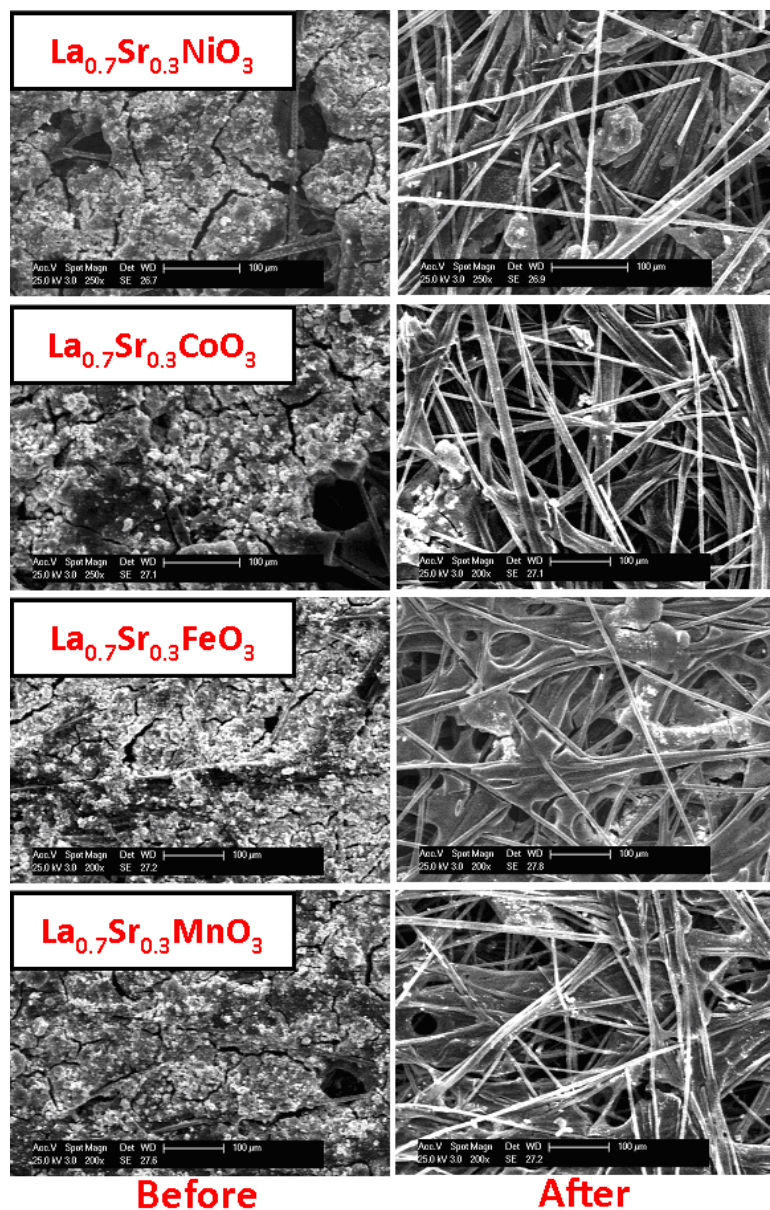


Figure 3.3. Loss of catalyst on the surface of the electrode as 12 hours of oxygen evolution testing. These electrodes did not contain a binder in the ink solution.

To alleviate this issue, a new anion ionomer binder was obtained from Tokuyama Co. Various concentrations of ionomer were tested in an effort to examine a more optimal concentration of ionomer in the catalyst ink. Figure 3.4 shows the catalyst activity as a function of ionomer concentration.

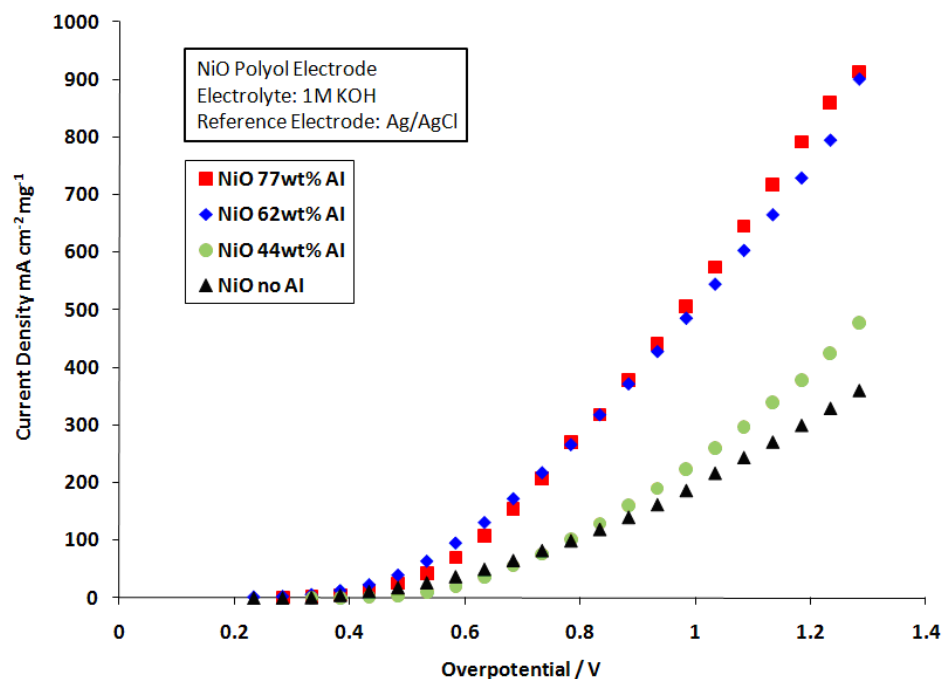


Figure 3.4. Catalytic activity was tested as a function of ionomer concentration. By increasing the concentration above 44 wt%, no increase in activity on a per mass basis was seen. Catalyst stability on the electrode surface was obtained with the inclusion of this ionomer in the ink solution.

The inclusion of the ionomer in the catalyst ink improved the stability of the catalyst on the electrode surface with concentrations above 44 wt% showing the highest activity of the catalyst on a per mass basis.

With the catalyst ink composition determined, the activity towards oxygen evolution was tested at a range of overpotentials. The electrocatalytic activity for all perovskite catalysts is shown in Figure 3.5.

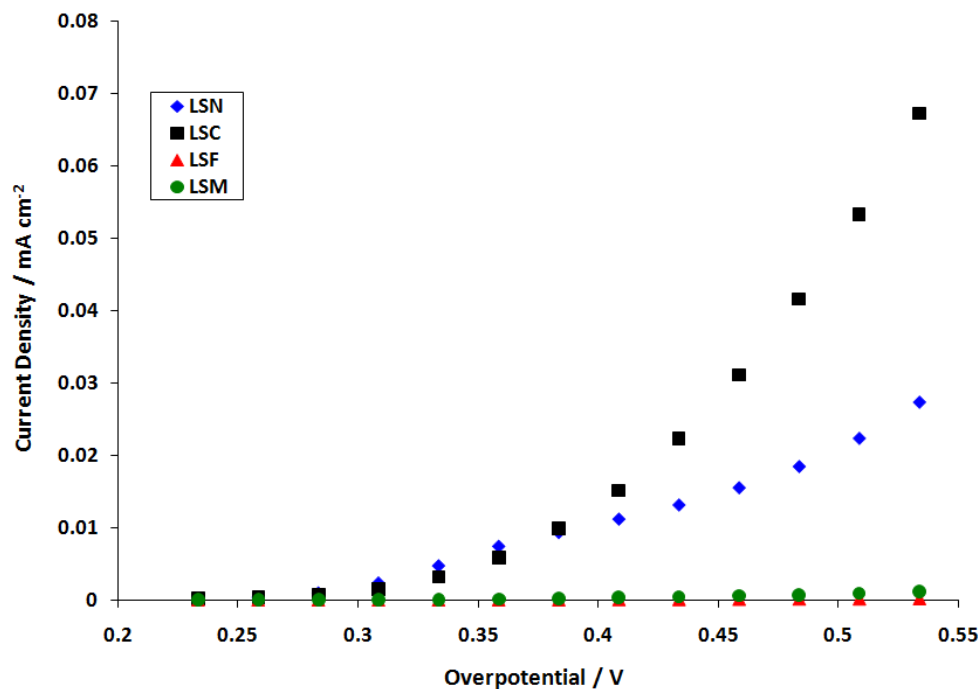


Figure 3.5. Perovskite catalyst activity towards oxygen evolution at overpotentials between 0.2-0.55 V. At higher overpotentials, $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ shows the highest activity while $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ shows the highest activity at lower overpotentials. These activities are normalized by their respective BET surface areas.

The activity for all perovskite oxides was compared after being normalized by their respective surface areas. At overpotentials below 0.4 V, $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ shows the highest activity, but as the overpotential increases, the most active perovskite becomes $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$. The trend observed here, with $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$ showing the highest activity at 0.3 V, is consistent with the trend observed by Bockris. Both $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ show very little activity in the overpotential ranges of interest here. This result is partly a function of normalizing by physical surface area where both the Fe and Mn samples have higher surface area than either the Ni or Co samples. To investigate how much

the surface area affected the catalytic activity, the current was also normalized by catalyst mass and plotted versus the overpotential in Figure 3.6.

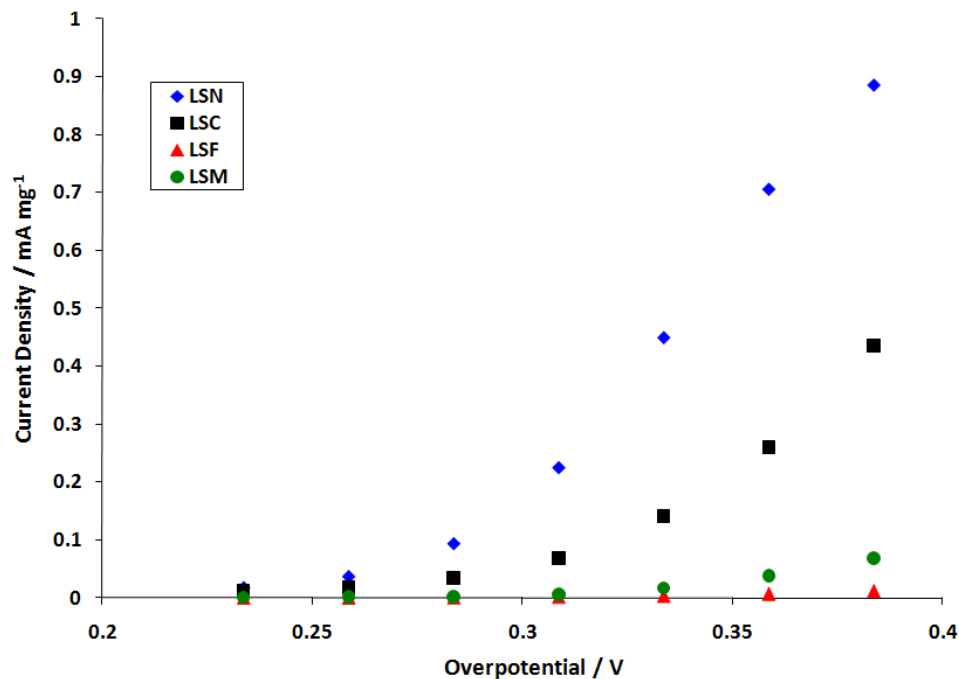


Figure 3.6. Perovskite catalytic activity as a function of overpotential and normalized by mass of catalyst used.

After normalizing the current by the respective electrocatalyst masses and plotting this as a function of overpotential, the Ni-based perovskite still shows the highest activity at overpotentials below 0.4 V. A small increase in the current density can be seen for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ now that the surface area has not been taken into account, but this catalyst remains far less active than either the Ni or Co based perovskites. At potentials around 0.3 V, where Bockris had made comparisons among perovskites, the catalytic activity of both the Mn and Fe based perovskites show almost no activity.

In the assessment of these catalysts for use in the gas separation process described in the previous chapter, it became important to verify that the current density seen in these half-cell experiments corresponded to an actual gas evolution process. Incorporation of the perovskite catalyst into the anode of the gas separation cell would enable us to determine the relationship between O_2 production and current. In this case, the $La_{0.7}Sr_{0.3}CoO_3$ was used as the oxygen evolution anode, while the Pt/C cathode and Neosepta membrane were kept constant from previous experiments. An air feed gas was used as the reactant feed and cell potentials again between 0.4 V and 1.2 V were applied to motivate the gas separation. The results of this gas separation are shown in Figure 3.7.

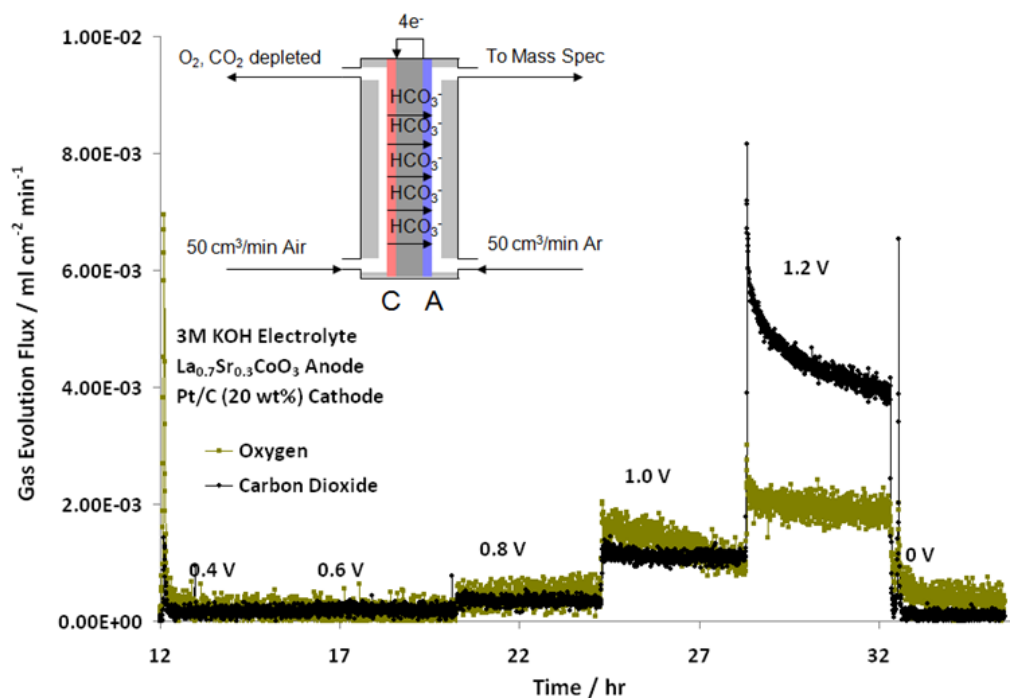


Figure 3.7. Air separation experiment using a $La_{0.7}Sr_{0.3}CoO_3$ anode and Pt/C cathode in conjunction with a Neosepta anion exchange membrane. Cell potentials of 0.8 V and higher were necessary to see gas separation from the air feed gas.

Both oxygen and carbon dioxide were successfully separated from an air gas feed while using a $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ anode. This result confirmed the possibility of using a perovskite catalyst as an oxygen evolving electrode in an electrochemical gas separation cell. However, the cell potentials necessary to accomplish gas separation were even higher than previous cell potentials. In prior experiments, the cell potential necessary to accomplish any separation was 0.6 V, while the cell potential had risen to 0.8 V when a perovskite catalyst was utilized. A comparison between this $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ catalyst and the pure NiO catalysts was conducted. The activity of both catalysts at overpotentials of interest between 0.3 V to 0.5 V is shown in Figure 3.8.

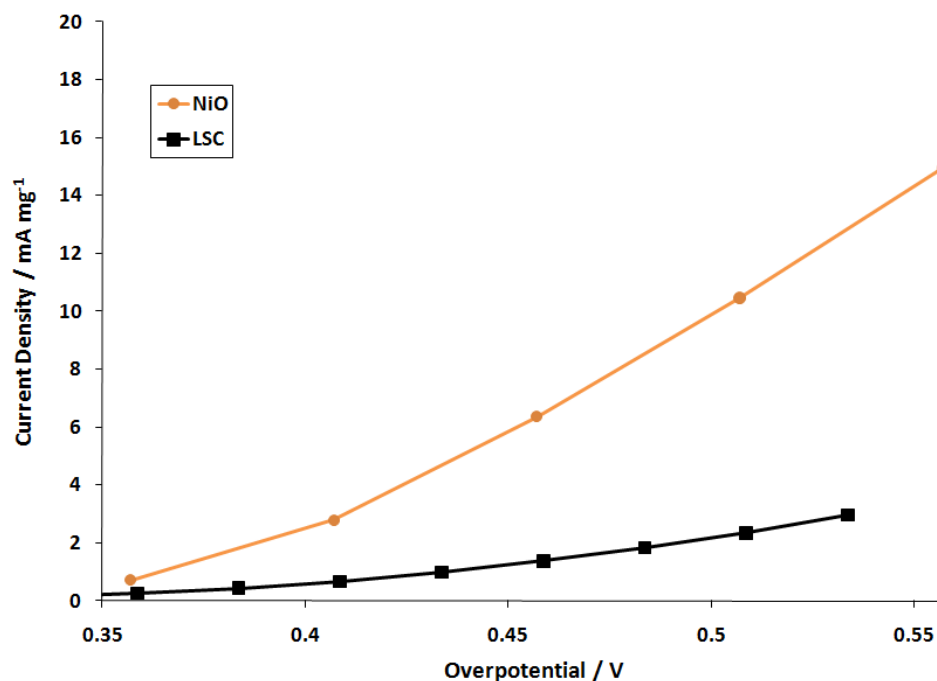


Figure 3.8. Perovskite activity versus pure NiO activity. $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ and all of the perovskites have much lower activity than pure NiO on a per mass basis.

The activity of the perovskite catalyst is far below that of the pure NiO catalyst. This discrepancy contributes to the larger cell potential necessary to conduct the gas separation process.

With the perovskite catalysts showing lower activity than pure transition metal oxides, the process of identifying more active catalysts for this gas separation cell was reevaluated. In the next chapter, the activity of pure and mixed transition metal catalysts will be examined. Higher activity using pure transition metal oxides will be shown.

3.4 Conclusions

Perovskite catalysts of the formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{MO}_3$ $\text{M}=[\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}]$ were synthesized using an EISA process with reasonably high surface areas being obtained between 4-32 m^2/g . The activity of these catalysts was examined towards oxygen evolution and a trend similar to that of John Bockris was found. A $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ based electrode was successfully utilized in a gas separation cell to selectively separate both oxygen and carbon dioxide from an air feed gas. It was found that the activity of this electrode was lower than a previous pure NiO electrode. While these catalysts may have some promise in understanding trends in the oxygen evolution mechanism, future work will concentrate on modifying transition metal oxides for use as more active oxygen evolution electrodes.

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4. Mixed Ni-Fe and Ni-Co Oxide Electrocatalysts

4.1 Introduction

With perovskite catalysts yielding lower oxygen evolution activity than previous transition metal oxide catalysts, catalyst development towards creating a more active transition metal oxide electrocatalyst was undertaken. Before continuing, it is important to describe in some detail what metric is being used to determine electrocatalytic activity. All of these investigations towards determining more active electrocatalysts have focused on getting higher activity at lower overpotentials. The overpotential is defined in equation 1.

$$\eta = E - E^0 \quad (1)$$

The overpotential is a function of the applied potential, E , and the equilibrium potential of reaction, E^0 . The equilibrium potential is also a function of the pH of the solution and the potential of the reference electrode, E_{ref} , used during testing. The general method in assessing the activity of a catalyst is by either comparing the overpotential at which a current density can be reached or by defining a current density and stating the overpotential required to reach that value. Each of these methods compares the activity of different catalysts at a range of overpotentials and makes a determination from this data as to the more active catalyst. In attempting to enhance the activity of these catalysts, the overpotential required for oxygen evolution will need to be decreased.

One method used to modify catalytic activity is catalyst design by chemical interpolation with the use of a volcano plot. Volcano plots are useful

because they can aid in the determination of a range of adsorbate energies where a reaction would be likely to be well catalyzed. This idea uses Sabatier's principle where for a given reaction there will be a volcano in activity as one proceeds through the periodic table with the highest catalytic activity being present on the catalyst surface with an intermediate binding energy [1-2]. The idea of constructing a volcano plot in catalytic activity has previously been experimentally validated to produce more active catalysts with one example shown by Jacobsen et al. [3]. In this case, more active ammonia catalysts were desired due to the cost of using Ru as a catalyst or having to use copious amounts of Fe. A volcano in activity was subsequently created by plotting the turnover frequency as a function of the adsorption energy of nitrogen and is reproduced in Figure 4.1.

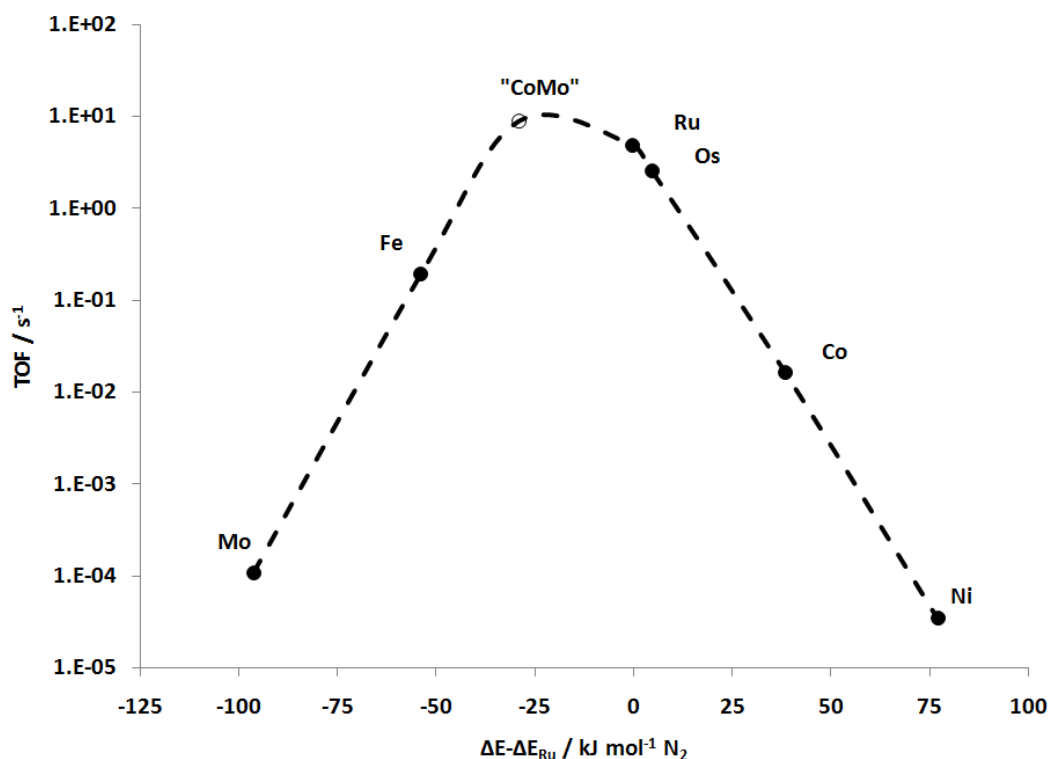


Figure 4.1. Jacobsen et al. plotted turnover frequency versus the adsorption energy of nitrogen for active transition metals towards ammonia synthesis. A rational design approach known as chemical interpolation led to the creation of a bimetallic catalyst of Co and Mo which showed higher activity than any existing ammonia catalyst.

When plotting the turnover frequency as a function of nitrogen's adsorption energy, a peak in activity is found. Ruthenium shows the highest activity with regard to adsorption energy. Subsequently, Jacobsen et al. combined catalysts from either side of this plot to modify the adsorption energy of the catalyst thereby creating a more active catalyst. By taking Mo, a strong nitrogen adsorption site, and combining it with Co, a weak nitrogen adsorption site, a much more active catalyst was created which was even more active than Ru and Fe, the industrial standard catalyst. This "CoMo" catalyst has become the catalyst of choice for ammonia synthesis and was created using this volcano plot and the theory of chemical interpolation.

A similar plan would be useful in the construction of more active oxygen evolution catalysts. Previously work in this area has involved the synthesis of both pure oxide and mixed-oxide catalysts but a rational design approach towards catalyst development was often not used [4-16]. Trasatti conducted a review of oxygen evolution catalysts and plotted their activity as a function of the enthalpy change from a lower-to-higher oxide transition [17-18]. What he found was a volcano in activity with RuO_2 being the most active oxygen evolution catalyst. This data is plotted in Figure 4.2.

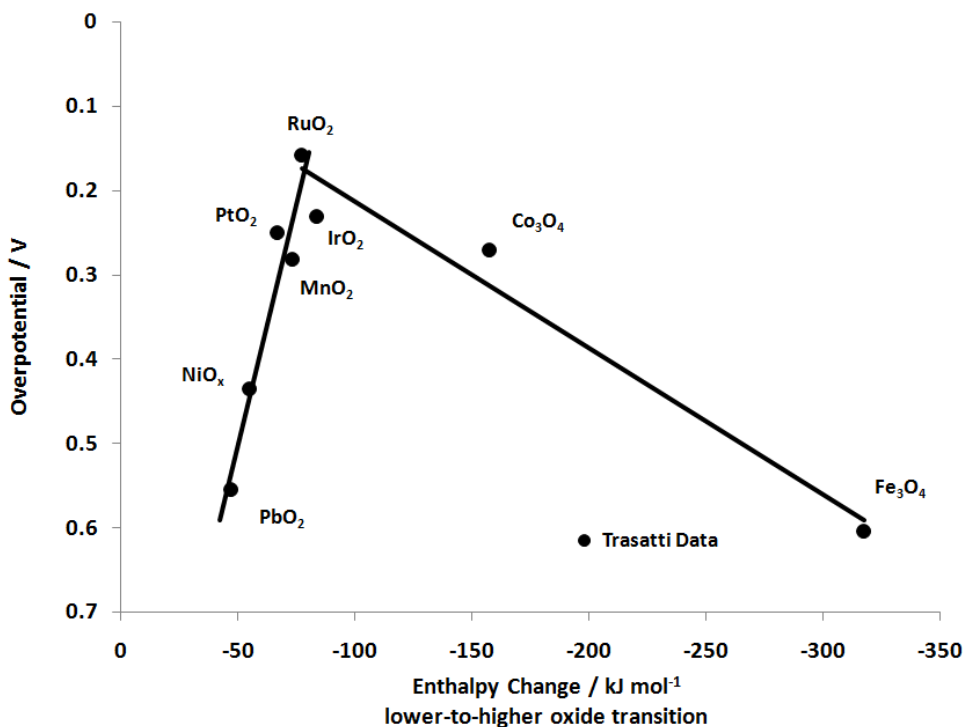


Figure 4.2. This plot reproduced from Trasatti's data shows the oxygen evolution activity of multiple transition metal oxides as a function of the enthalpy change from a lower-to-higher oxidation state. A combination of oxide materials may show higher catalytic activity through the modification of this enthalpic energy.

In Figure 4.2, the plot reproduced from Trasatti's data shows the overpotential necessary for oxygen to evolve versus the enthalpy change for a lower-to-high

oxide transition for each transition metal oxide. Clearly evident in this plot is a volcano relationship between these two values with respect to transition metal oxides. As a singular metal oxide, RuO_2 shows the highest activity towards oxygen evolution which corresponds to an enthalpy change slightly below -100 kJ/mol. However, this enthalpy value may not be the most optimal for this reaction. By combining oxides from both sides of this volcano, a shifting of this energy value could yield a more active overall catalyst and decrease the need to use an expensive material such as ruthenium oxide.

Research into oxygen evolution catalysts has been somewhat substantial, and is an active research area currently [6-7, 11-16, 19-22]. Much of this research has examined Ni catalysts and mixed transition metal catalysts [9-10, 16, 23-25], similar to those catalysts shown in Figure 4.2, along with investigations into more complex structures such as perovskites [26] and spinels [4]. Early research focused on examining which catalysts were active and stable under different reaction conditions with both Trasatti and Jörissen reviewing the oxygen evolution activity for a range of transition metal oxides in both perovskite and spinel structures as well as the standard oxides [4, 17]. This early work was successful at identifying a range of active catalysts.

Building on this early electrocatalyst work, Corrigan examined a mixed oxide system for its oxygen evolution capability, specifically electrodeposited Ni-Fe catalysts [7]. These electrodeposited films did show decreases in the overpotential of reaction over pure Ni or Fe oxide. Miller also investigated a mixed Ni-Fe oxide system by reactively sputtering films of Ni-Fe onto a support

and noted a similar lowering of the reaction barrier as Corrigan [20]. Finally, Guerrini examined these mixed Ni-Fe catalysts and saw the synergistic effect of the mixed oxide over pure nickel or iron oxide [27]. While these papers did examine the benefits of mixed oxide surfaces towards oxygen evolution, the composition of the materials made in these papers was hard to exactly control. Also, no conclusive identification of the mechanism for the improvement was identified. These mixed systems indicate a synergistic effect between Ni and Fe in lowering the reaction barrier for oxygen evolution, but no targeted approach towards developing these catalysts was noted or an optimal composition of the catalyst mentioned.

More recently the size-dependent activity of cobalt catalysts has been examined towards oxygen evolution [28]. Esswein et al. show that by decreasing the particle size of a cobalt catalyst, gains in the electrocatalytic activity can be achieved. This result gives one more design parameter which can be used to modify the activity of a catalyst. The most recent research has even examined the *in situ* formation of cobalt and nickel catalysts which show relatively high activity even under mild conditions [29-31]. The work by Nocera, et al. has been highly cited and highlights the overpotential limitations currently of water splitting and the oxygen evolution reactions. These *in situ* forming Co and Ni catalysts show some improvements in activity in pH neutral solutions and form rather interesting and stable catalytic structures.

Most of this research has not used a broad-based systematic and targeted approach towards developing more active oxygen evolution catalysts such as the

volcano plot put forth by Trasatti or incorporated a compositionally-exact and high surface area synthesis method. Earlier work by Miller and Corrigan would agree with results of chemical interpolation from Trasatti's volcano plot, but this approach to catalyst design was not used in these cases. This research has focused on investigating this mixed Ni-Fe catalyst system further with the use of a high surface area synthesis process and investigating what composition of Fe would be more optimal in this mixed oxide system. An evaporation-induced self-assembly (EISA) process was used to exactly tailor catalyst compositions. Chemical interpolation is then applied to mixed Ni-Co oxide catalysts to examine if the activity of oxygen evolution catalysts can be further enhanced with a different mixed oxide system by chemically interpolating catalysts from Trasatti's plot.

4.2 Experimental Methods

4.2.1 Catalyst Synthesis

Catalysts were synthesized using an evaporation-induced self-assembly process (EISA) [32]. Briefly, 1 gram of P123 surfactant was dissolved into a mixture composed of 5 grams of de-ionized water and 5 grams of ACS grade ethanol. Subsequently, metal nitrate precursor salts were dissolved into this mixture in the desired molar compositions for the final catalyst powder. This solution was then transferred to a ceramic boat and heated using a controlled procedure. First, the solution was heated to 120 °C and held for 12.5 hours. This temperature was used to remove any water and residual ethanol. Next, the solution was slowly ramped to 350 °C at 1 °C/min and held at 350 °C for 4 hours.

This step was intended to remove the P123 surfactant while maintaining a high surface area framework. Finally, the remaining material was heated to 550 °C, again at 1 °C/min, and held for 4 hours. The resulting material was then ground using a mortar and pestle and stored for characterization.

4.2.2 Catalyst Characterization

Catalyst crystallinity and composition was examined using a Rigaku Theta-Theta Diffractometer equipped with a Cu detector and an incident beam wavelength of 1.542 Å. The beam energy was set to 30 eV and beam current to 30 mA. Catalyst surface area was examined using the BET method with a Nova 2200 Surface Area Analyzer. Catalyst morphology and surface composition were investigated using a Philips XL30 Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM/EDS).

4.2.3 Catalytic Activity

Catalyst inks were formed by combining 20 mg of catalyst powder, 645 mg of 5 wt% AS4 ionomer solution from Tokuyama Corp., 200 µL of de-ionized water, and 800 µL of isopropanol. This solution was sonicated for 60 minutes. Next, the catalyst ink was painted on to a piece of Toray TGPH-060 carbon paper with 1 cm × 2 cm dimensions and heated at 120 °C for 10 min to remove any water or alcohol from the surface. This process was repeated until a loading of approximately 1 mg/cm² was achieved in all cases, and the results were normalized by this catalyst loading. Electrodes were then tested using a Gamry Reference 600 potentiostat. A Pt counter electrode and Hg/HgO reference electrode were used throughout these experiments. 1M KOH was used as the

electrolyte which was deaerated with pure Argon for 30 min prior to each experiment. Initialization of the catalyst was carried out at a potential of 0.742 V vs. Hg/HgO for a period of 3 hours. Steady-state catalytic activity was subsequently examined at potentials between 0.542 V to 1.042 V vs. Hg/HgO in 50 mV increments for 20 min at a time. All results have been normalized by reference electrode potential and pH and are reported as current vs. overpotential.

4.3 Mixed Ni-Fe Oxide Catalytic Activity

Mixed Ni-Fe oxide catalysts were examined for their oxygen evolution electrocatalytic activity. These catalysts were chosen based on previous work conducted by Miller and Corrigan. As mentioned previously, mixed Ni-Fe oxide catalysts were synthesized using an evaporation-induced self-assembly process (EISA). This synthesis procedure was chosen due to the formation of high surface area catalysts as well as the relative ease with which specific concentrations of mixed Ni-Fe oxide catalysts could be produced. Other procedures such as electrodeposition or reactive sputtering can yield mixed Ni-Fe catalysts but not with the same control that this method would provide [7, 33]. Using this EISA procedure, mixed Ni-Fe oxide catalysts with 0, 3, 4, 5, 10, 15, 20, and 100 mol% Fe were synthesized. Catalyst surface areas for each catalyst are shown in Table 4.1. The surface areas for these catalysts ranged from approximately 13-32 m²/g.

Table 4.1. BET surface areas for mixed Ni-Fe oxide catalysts

Catalyst	Surface Area / m ² g ⁻¹
NiO	13.7
3 mol% Fe	17.5
4 mol% Fe	18.9
5 mol% Fe	18.9
10 mol% Fe	18.2
15 mol% Fe	26.4
20 mol% Fe	31.3
Fe ₂ O ₃	12.7

In addition to BET surface areas, the resulting powders from this synthesis were examined using XRD. The patterns obtained from these experiments are shown in Figure 4.3.

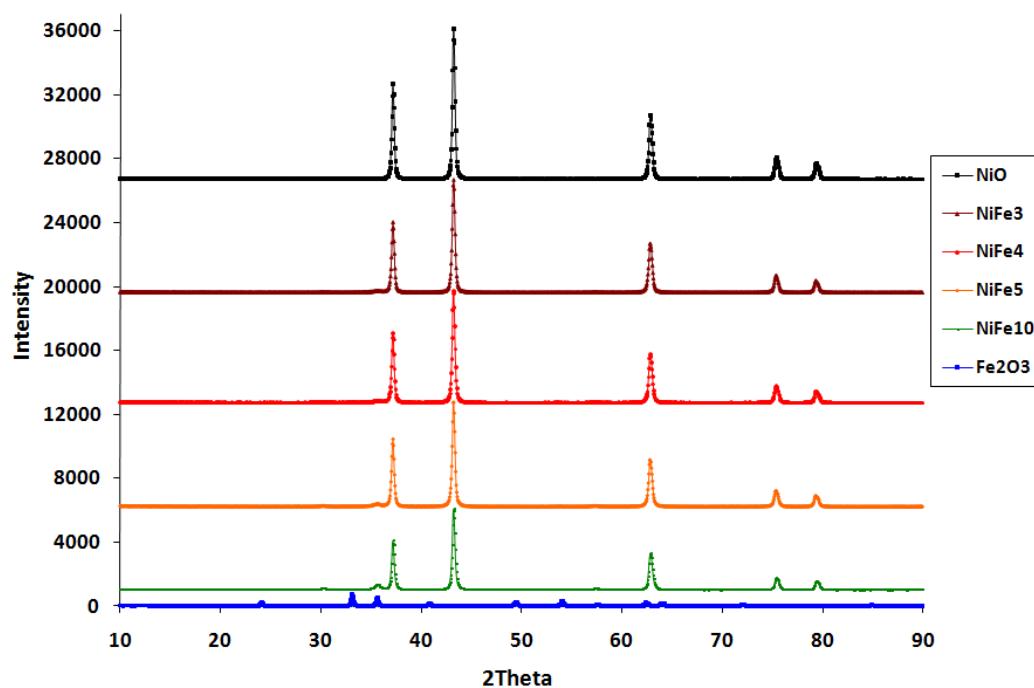


Figure 4.3. XRD patterns of NiO, Fe₂O₃, and 3, 4, 5, and 10 mol% Fe mixed Ni-Fe oxides. Lattice constants for NiO and all mixed Ni-Fe oxides were found to be 4.18 Å, suggesting Fe was not substitutionally incorporated into the NiO lattice.

Shown in Figure 4.3 are the XRD results for six mixed Ni-Fe oxide catalysts including 0, 3, 4, 5, 10, and 100 mol% iron oxide. As Fe-doping is increased up to 10 mol%, the crystallinity of the NiO lattice is maintained. The lattice constants from each of these XRD patterns, excluding pure iron oxide, yielded a value of 4.18 Å. By maintaining this lattice constant even at 10 mol% Fe, it can be assumed that Fe was not being substitutionally incorporated into the NiO lattice as the lattice constant would have been strained as more Fe was doped into the NiO structure. In addition, there is the appearance of a small peak at 35 degrees that would indicate some Fe phase forming as the concentration of Fe in the system is increased. It is thought that Fe may lie outside of the NiO lattice and may be forming some amorphous phase that is not appearing in the XRD patterns. Fe could also be segregating to the surface and forming a monolayer.

To investigate further where the relative locations of Fe and Ni were in these powders, SEM/EDS experiments were carried out. Mixed Ni-Fe oxide powders were applied to a carbon paper support as described previously. SEM images were taken at 1 and 5 µm resolutions and elemental mapping using EDS was conducted. Shown in Figure 4.4 is an SEM image of a 5 mol% Fe catalyst surface on a carbon paper support with a 5 µm scale and elemental mappings of the Ni and Fe locations on the surface.

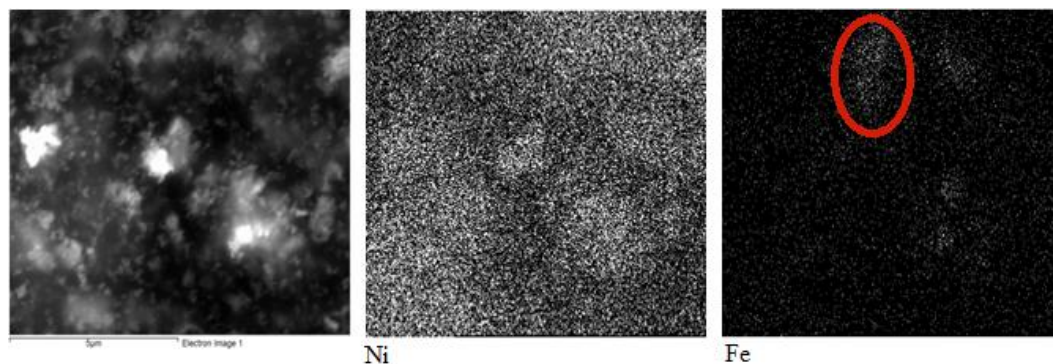


Figure 4.4. 5 μm SEM image of a 5 mol% Fe mixed oxide catalyst along with elemental mapping of the surface for Ni and Fe. Particle sizes ranged from under a micron to a few microns. Ni and Fe sites were located across the catalyst surface with some locally higher concentrations. Circled in red is an area of concentrated Fe.

From the SEM/EDS images, it was shown that Ni and Fe are located across the catalyst surface with relatively even mixing between them. Even if Fe is not incorporated in the NiO lattice, there exists a close proximity between both Ni and Fe catalytic sites. One point to note from Figure 4.4 is that there exist places on the catalyst surface where Fe has locally higher concentrations, one of which is circled in red. These areas probably did not appear in the XRD patterns due to forming amorphous phases. Figure 4.5 shows a magnified view of the catalyst surface.

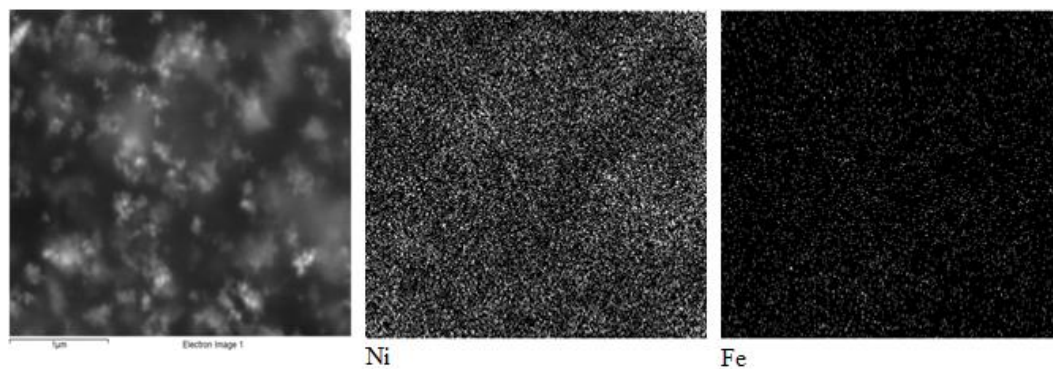


Figure 4.5. 1 μm SEM image of a 5 mol% Fe mixed oxide catalyst along with elemental mapping of the surface for Ni and Fe. Ni and Fe catalyst sites are evenly mixed across the surface.

Again, the surface looks well mixed with an even distribution of Ni and Fe catalytic sites. From this characterization, it has been shown that the EISA process can be used to create high surface area, mixed composition catalytic particles with a highly crystalline NiO phase and possible amorphous Fe phases. It should be mentioned here, that these results do not conclusively indicate what our catalyst surface looks like. There is no strong evidence of alloying between Ni and Fe, but also no evidence of highly segregated, crystalline phases of Fe forming. Further analysis using synchrotron studies and other spectroscopy techniques could help to determine the exact structure of this catalyst, but for the purpose of this work, it has been found that a mixed oxide catalyst has been synthesized.

Mixed Ni-Fe oxide electrodes were tested for their oxygen evolution activity. After initialization of the catalyst surface, activity of each electrode was tested at potentials ranging from 0.542 V to 1.042 V vs. Hg/HgO in 50 mV intervals. Results have been normalized by the catalyst mass unless otherwise noted. Figure 4.6 shows the catalytic activity for 7 of these catalysts versus

overpotential.

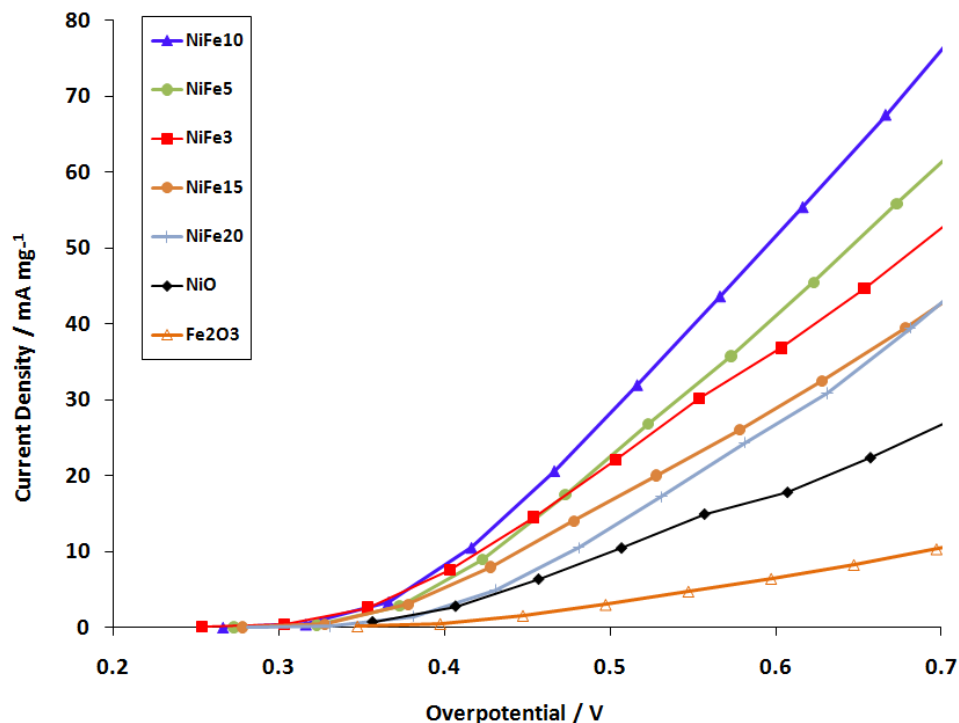


Figure 4.6. Catalytic activity versus overpotential is shown here for seven mixed Ni-Fe oxide catalysts. As Fe is added into the system, and large increase in catalytic activity is observed. A synergistic effect is apparent as mixed Ni-Fe oxide catalysts have higher activity than either NiO or Fe₂O₃.

As the overpotential is increased beyond 0.3 V, catalytic activity subsequently increases. In addition to the overpotential, activity appears to be a strong function of Fe content which could be expected based on synthesizing catalysts using Trasatti's volcano plot. To examine the activity as a function of Fe content, activity was plotted versus Fe content at 3 relevant overpotentials, 0.542, 0.592, and 0.692 V. These results are shown in Figure 4.7.

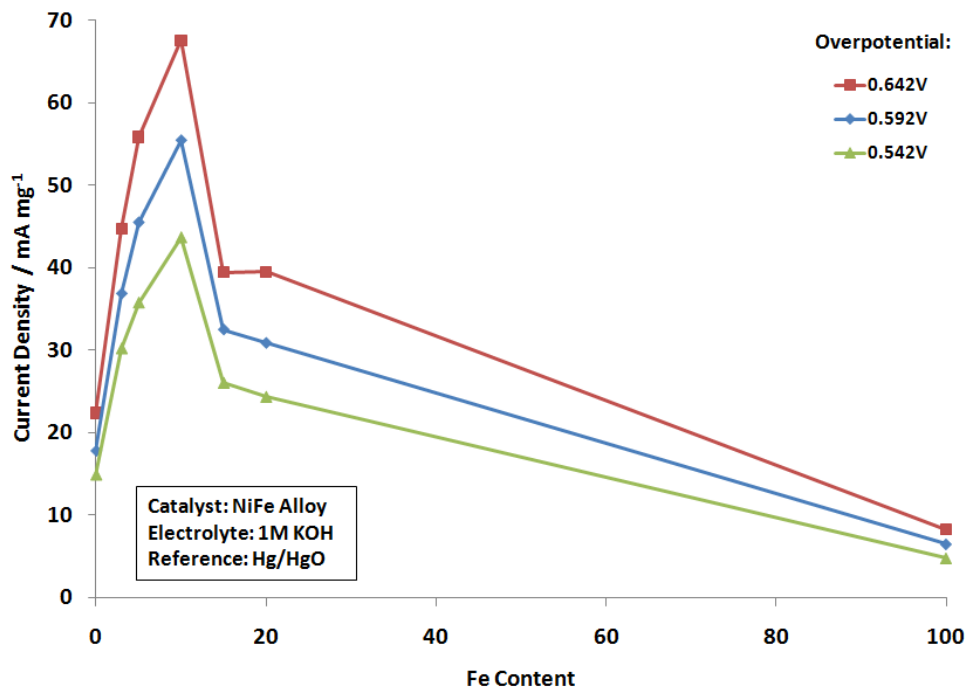


Figure 4.7. A peak in catalytic activity is observed as a function of Fe content with 10 mol% Fe content having the highest activity. There exists a synergistic effect between Ni and Fe which leads to an increase in the oxygen evolution activity.

There exists a synergistic effect between Ni and Fe where there is higher activity for the mixed oxide material than either of the pure components. A clear peak in catalytic activity is observed at 10 mol% Fe. As Fe content is increased beyond 10 mol%, catalytic activity starts to decrease but remains higher than NiO or Fe₂O₃. While increases in activity such as these are sometimes explained by increases in the surface area of the catalyst, the reason for this increase is due to intrinsic catalytic factors. BET surface area was measured for all of these catalysts, and when the catalytic activity is plotted after being normalized by these values, the same trend is observed. A graph showing these normalized values is shown in Figure 4.8.

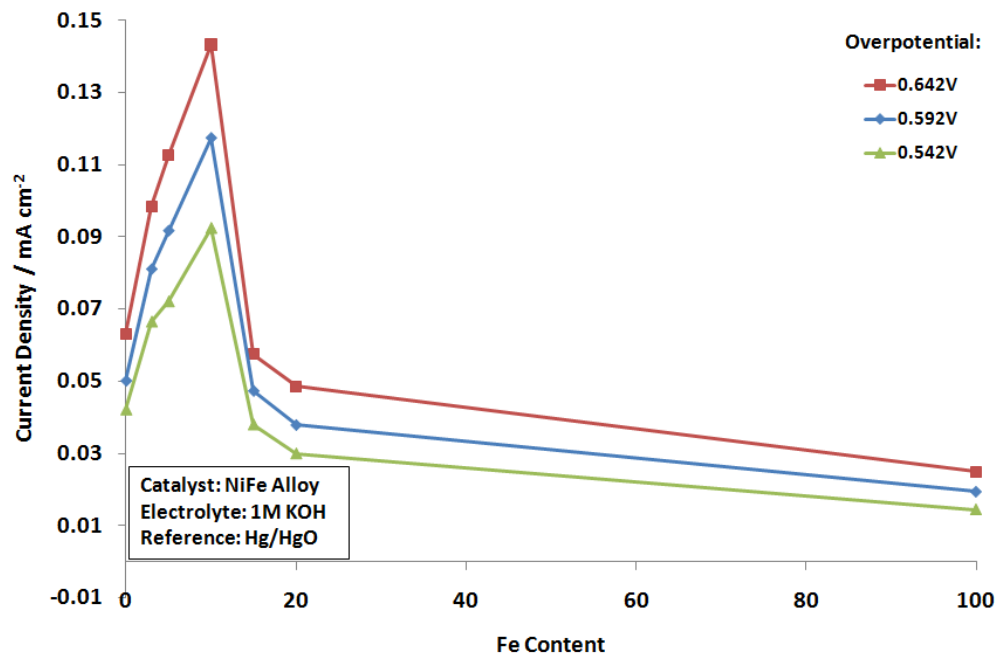


Figure 4.8. The activity for each catalyst has been normalized by their respective BET surface areas. A peak in catalytic activity is again observed at 10 mol% Fe. This result points towards an intrinsic catalytic parameter that has increased the activity of the catalyst beyond a surface area effect.

In other cases, electrochemical surface area can also help to clarify reasons for the increased activity. To elucidate this point, double layer charging area was examined for all of these catalysts. These experiments were carried out between 0.0 and -0.1 V vs. Hg/HgO at scan rates ranging from 100 to 1500 mV/sec. The electrochemical surface area was calculated from these scans and a representative double layer charging plot is shown below in Figure 4.9. Catalyst surface areas calculated from these double layer experiments were far below those shown from the BET measurements, and on the order of a 1-4 cm². This difference could be partially due to the electrolyte not having contact inside of small catalyst pores and also due to the ionomer binder blocking catalytic sites.

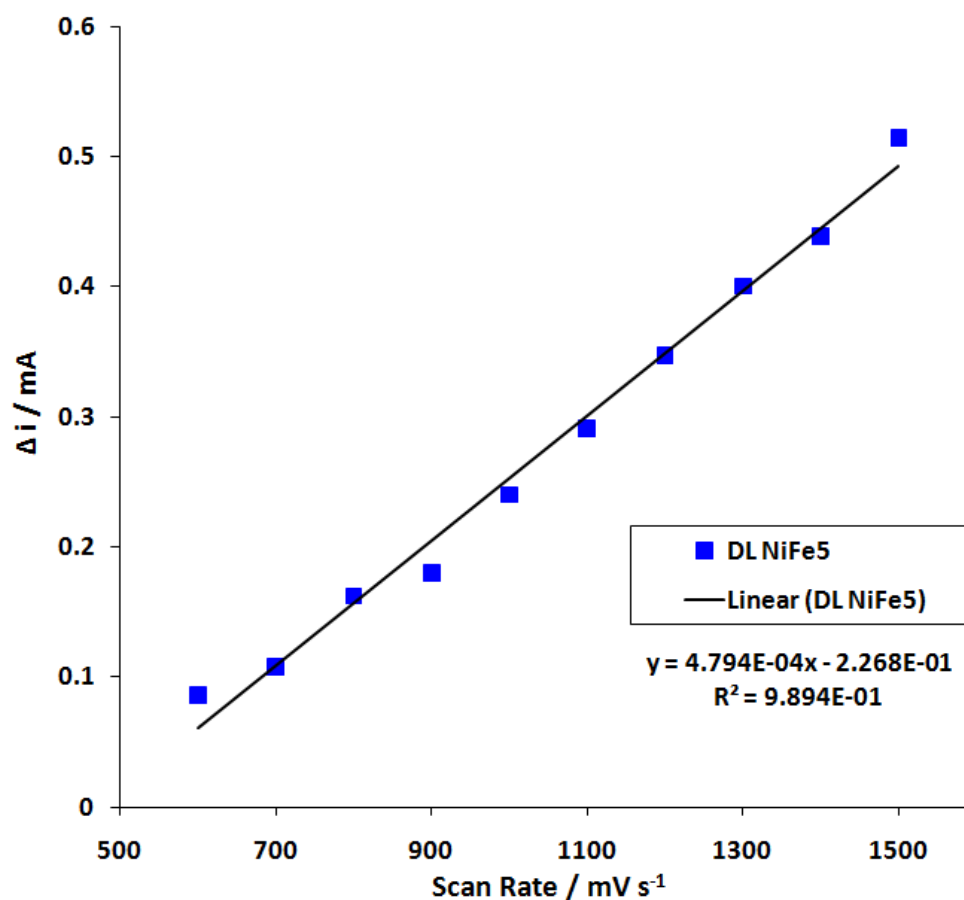


Figure 4.9. The double layer charging was examined on a 5 mol% Fe mixed Ni-Fe oxide catalyst surface at scan rates ranging from 100 to 1500 mV/s.

Again, the same trend in activity is observed when taking into account these electrochemical surface areas. Therefore, there is an intrinsic factor of the catalyst that is increasing the overall activity, and not simply a surface area increase that is causing this effect.

To examine the intrinsic activity factors, Tafel analysis was conducted on these catalysts. Catalytic activity was observed between 0.542 and 0.842 V using a scan rate of 1 mV/s. The Tafel slope was taken from the onset of oxygen

evolution in a region under 1 mA/cm^2 . Figure 4.10 shows the Tafel data taken for these oxygen evolution electrodes.

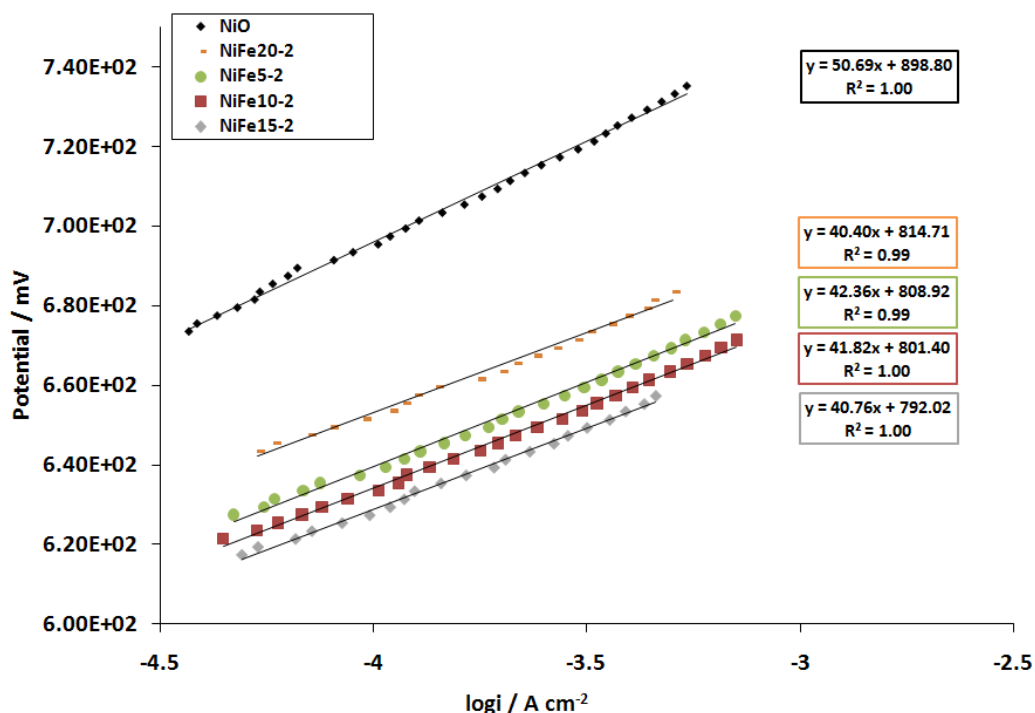


Figure 4.10. Tafel data for mixed Ni-Fe oxides. Decreases in the Tafel slope is evident with increases in the Fe concentration.

Tafel slopes are shown to be a strong function of the Fe content in the oxygen evolution catalyst with slopes ranging from above 50 mV/dec for pure NiO to 40 mV/dec for the mixed Ni-Fe oxide catalysts. To better illustrate this point, the Tafel slope was also plotted versus the Fe concentration. Figure 4.11 shows the Tafel slope values obtained for five of the catalysts examined in this work.

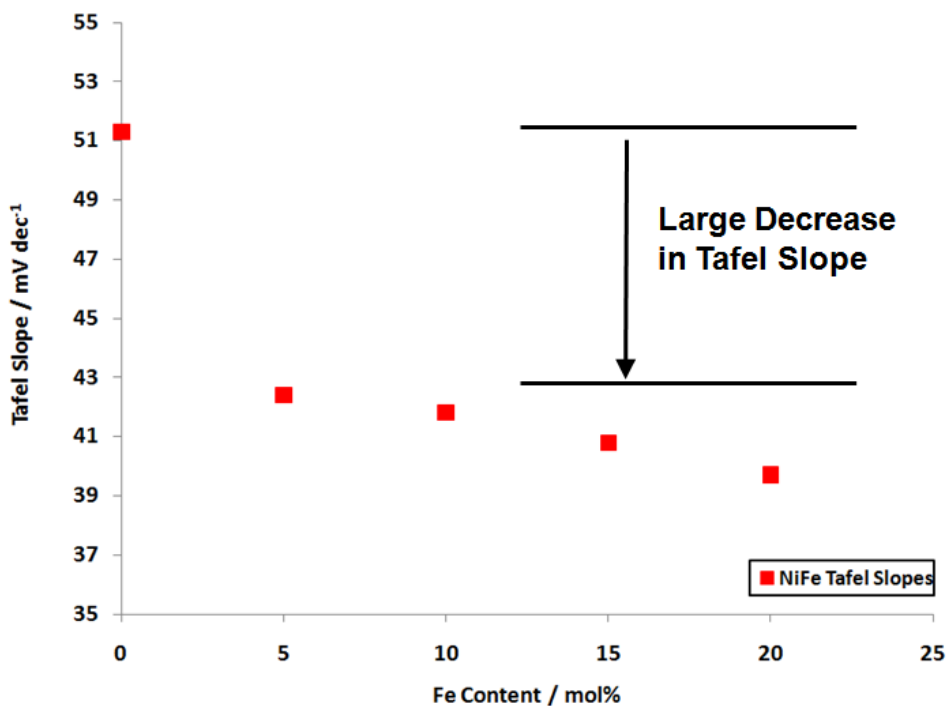


Figure 4.11. A substantial decrease in the Tafel slope is observed when Fe is added into the catalyst. The Tafel slope decreases by roughly 10 mV/dec when 5 mol% Fe is added, and the slope continues to decrease as more Fe content is added into the catalyst.

Evident in Figure 4.11 is the large decrease in the Tafel slope as Fe is added to the NiO catalyst. The Tafel slope changes from over 50 mV/dec to close to 40 mV/dec when 5 mol% Fe is added. This slope continues to decrease as more Fe is added, but the most dramatic effect is immediately following Fe addition into the system. This large decrease in the Tafel slope is indicative of a change in the rate determining step of the reaction process. The oxygen evolution mechanism is rather complex, and an abundant amount of research has tried to examine what the actual mechanism may be. One of the more accepted mechanisms for oxygen evolution in an alkaline solution is the Krasil'shcikov path[17] which was reproduced by Miller [33] and is shown below.



A Tafel slope change from above 50 mV/dec to 40 mV/dec could be indicative of a rate determining step change from equation 4 to 5 where a water discharge step may be the limiting step on an NiO surface but an electron transfer step may be rate limiting on an Ni-Fe oxide surface. More investigation in this area would be necessary to make a more accurate conclusion here as this investigation only provides a plausible explanation for the reactions occurring on the catalyst surface.

One way to convincingly determine what state the surface is in under reaction conditions may be the use of *in situ* spectroscopy techniques such as polarization modulated infrared absorption spectroscopy (PMIRAS). This analysis method would be able to resolve what adsorbates are present on the surface under reaction conditions and if there is a distinct difference between these adsorbates when transitioning from an NiO surface to an Ni-Fe oxide surface. This spectroscopy is certainly an area of work to be conducted in the future along with *in situ* Raman spectroscopy.

A limited durability study was also performed to examine if the catalytic activity degraded with time. A 5 mol% Fe mixed Ni-Fe oxide catalyst was chosen and set to an overpotential of 0.534 V for a period of 12 hours. The current was monitored during this time and is shown in Figure 4.12.

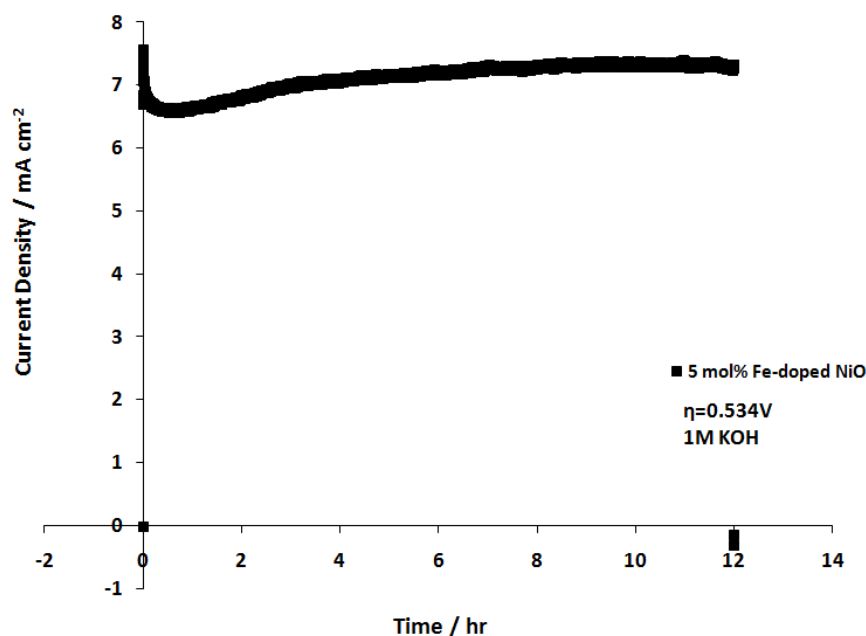


Figure 4.12. A durability study was conducted on a 5 mol% Fe mixed Ni-Fe oxide. Activity was found to be constant throughout the 12 hours of testing.

Evident in Figure 4.12 is that the current is constant over the course of this experiment leading to the conclusion that the catalyst surface is relatively active and stable. This durability study was done for a short period of time, more involved durability studies should be carried out in the future.

Finally, it should be noted that while current densities have been reported as measures of oxygen evolution activity, this value alone does not constitute proof of oxygen evolution. Gas evolution is observed during the course of these experiments, but some of this current density could be due to side reactions such as corrosion that have not been taken into account. To prove that this current density is solely due to oxygen evolution in these half-cell experiments, rotating-ring disk electrode (RRDE) experiments will need to be carried out. In these

experiments, a central disk electrode with the Ni-Fe catalyst on the surface will be set to potentials used here to produce oxygen and a ring electrode surrounding this disk will be set to reduce oxygen. Therefore, oxygen being formed on the disk electrode will be reduced on the ring electrode. The Faradaic efficiency of this reaction process, and subsequently the amount of current density resulting from oxygen evolution will be calculated. It is believed that these catalysts will have a very high Faradaic efficiency due to the limited durability studies which have shown constant current density over the course of many hours. If corrosion were a side reaction occurring, this value would decrease over time. However, to overwhelmingly conclude how much oxygen evolution is occurring on these catalysts, RRDE experiments should be conducted.

4.4 Ni-Co Oxide Catalytic Activity (credit Holden Ranz)

Due to the catalytic improvements evidenced in the mixed Ni-Fe oxide system, a similar plan for testing the catalytic activity of Ni-Co mixed oxide catalysts was followed. Referencing again the volcano plot shown reproduced from Trasatti and shown in Figure 4.2, NiO lies on the left side of this volcano while Co_3O_4 lies on the right side. Large improvements were shown when combining catalysts from either side of this plot in the Ni-Fe oxide system, so examining a mixed Ni-Co system became of interest as well to modify the catalytic activity.

Synthesizing these catalysts was done in the same manner as the Ni-Fe catalysts using the EISA process. Catalyst compositions included 0, 5, 10, 20, 50, 80, 90, and 100 mol% Co with the balance being Ni. All catalysts formed oxides

due to the synthesis technique with calcination occurring in an air atmosphere. Characterization using BET, XRD, and SEM was also carried out.

XRD patterns for each of these synthesized Ni-Co oxides are shown in Figure 4.13.

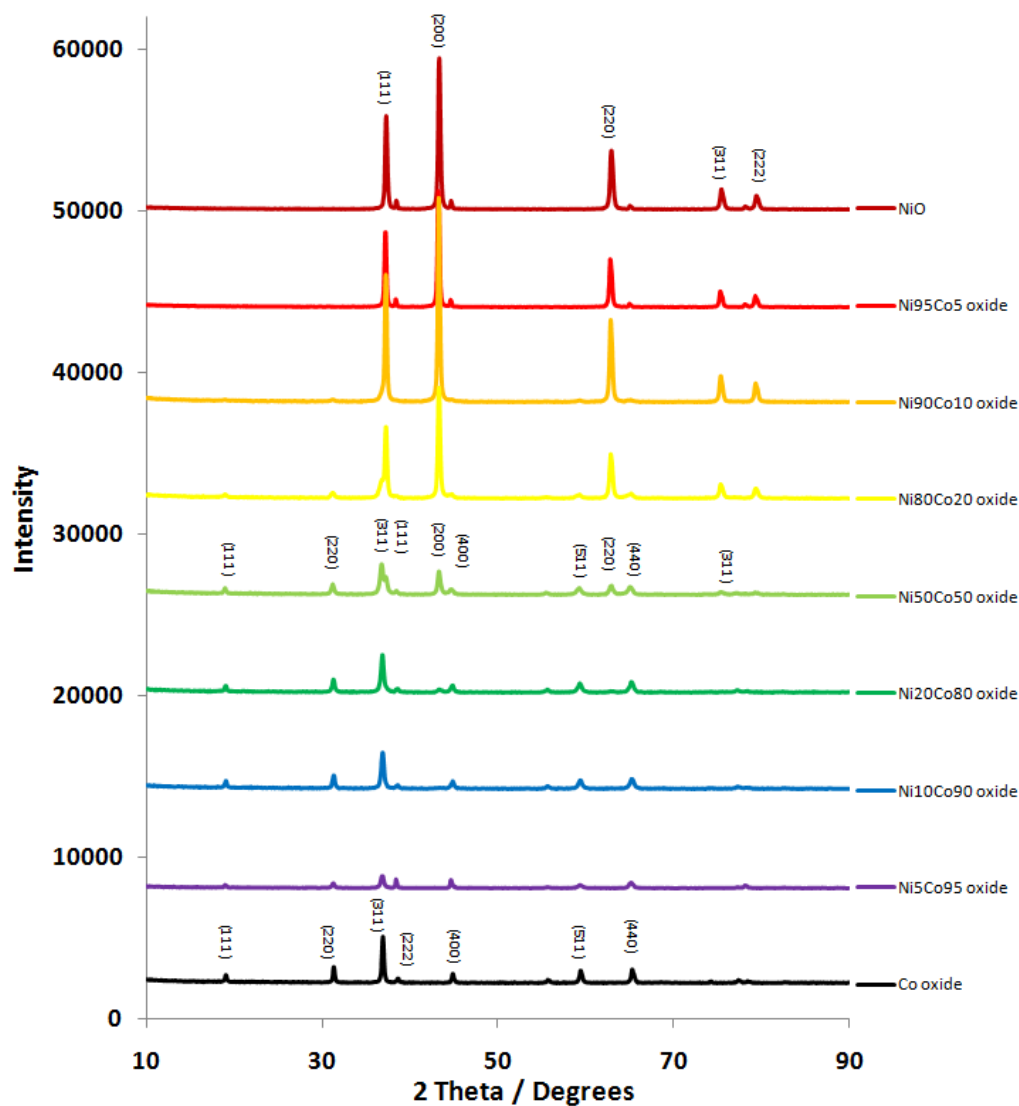


Figure 4.13. XRD patterns shown for NiO, Co₃O₄, and mixed Ni-Co oxides. As the concentration of Cobalt is increased beyond 10 mol%, distinctive peaks are formed which are indicative of Co₃O₄ phases form in addition to NiO phase. The lattice constant of the NiO phase does not move from 4.18 Å in all of these cases which would mean no Co is incorporated into the NiO lattice.

As the concentration of Co is increased beyond 10 mol%, peaks corresponding to a Co_3O_4 phase in addition to NiO phase begin to appear. The lattice constant of the NiO phase stays constant at 4.18 Å, indicating no incorporation of Co into the NiO lattice. The lattice constants for each sample are shown in Table 4.2.

Table 4.2. Lattice constants for NiO and Co_3O_4 phases for each oxide sample

Sample	Lattice Constant / Å	
	NiO phase	Co_3O_4 phase
NiO	4.17	x
5 mol% Co	4.18	x
10 mol% Co	4.18	8.11
20 mol% Co	4.18	8.11
50 mol% Co	4.18	8.11
80 mol% Co	x	8.06
90 mol% Co	x	8.06
95 mol% Co	x	8.11
Co_3O_4	x	8.06

There are distinct phases forming of both pure NiO and Co_3O_4 . No Co_3O_4 phase is evident at the 5 mol% composition, but this finding may be due to either amorphous phases forming or the lack of strong intensity from the Co_3O_4 phase. After reviewing these XRD results, it is concluded that the EISA synthesis process has yielded NiO and Co_3O_4 mixed oxide phases.

In addition to looking at the XRD patterns of these oxides, BET surface area analysis was run on each sample. The surface areas for all of the samples were between 7-14 m^2/g . These areas are listed in Table 4.3.

Table 4.3. BET surface areas of Ni and Co oxide catalysts

Catalyst	Surface Area (m ² /g)
NiO	8.4
5 mol% Co	7.6
10 mol% Co	10.4
20 mol% Co	10.8
50 mol% Co	10.6
80 mol% Co	13.3
90 mol% Co	9.4
95 mol% Co	12.2
Co ₃ O ₄	10.6

The oxide composition did not have a strong impact on the surface area of the samples. All of the surface areas were found to be close to 10 m²/g.

Finally, catalytic testing was carried out to examine if the mixed oxide catalysts had higher activity than their pure components. In a similar manner to the Ni-Fe electrochemical analysis, catalytic performance was observed after initializing each electrode following the procedure mentioned previously and at overpotentials in excess of 0.2 V. The activity was monitored at each potential for a period of 20 min. The results of these catalytic tests are shown below in Figure 4.14.

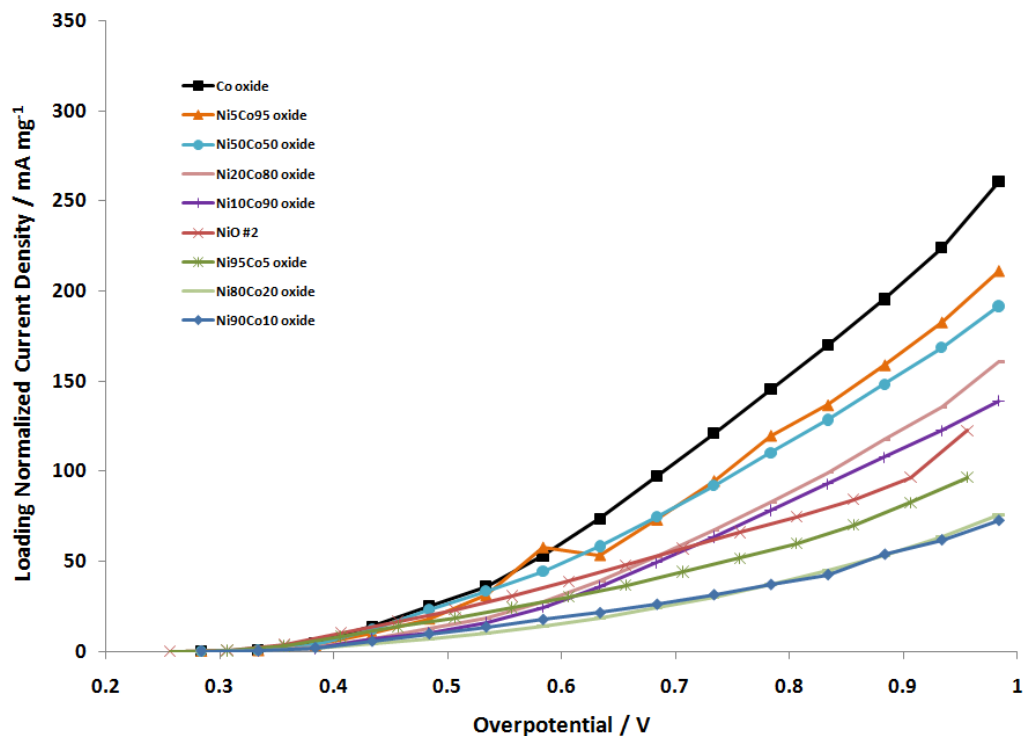


Figure 4.14. Catalytic activity of Ni-Co mixed oxides as a function of applied potential. Pure Co_3O_4 showed the highest performance with no distinct trend in activity observed for mixed-oxide samples. No Synergistic effect between Ni-Co was found towards oxygen evolution.

Oxygen evolution activity is a strong function of catalyst concentration similar to the Ni-Fe system, but the highest activity is observed for pure Co_3O_4 while mixed Ni-Co oxides exhibit diminished activity. Therefore, it can be concluded that in this catalyst system utilizing the EISA synthesis method, no synergistic effect is observed for mixed Ni-Co oxides. The catalytic activity has also been plotted as a function of catalyst composition at overpotentials of 0.534, 0.634, and 0.734 V and is shown in Figure 4.15. These results also show the BET normalized activity as a function of catalyst composition.

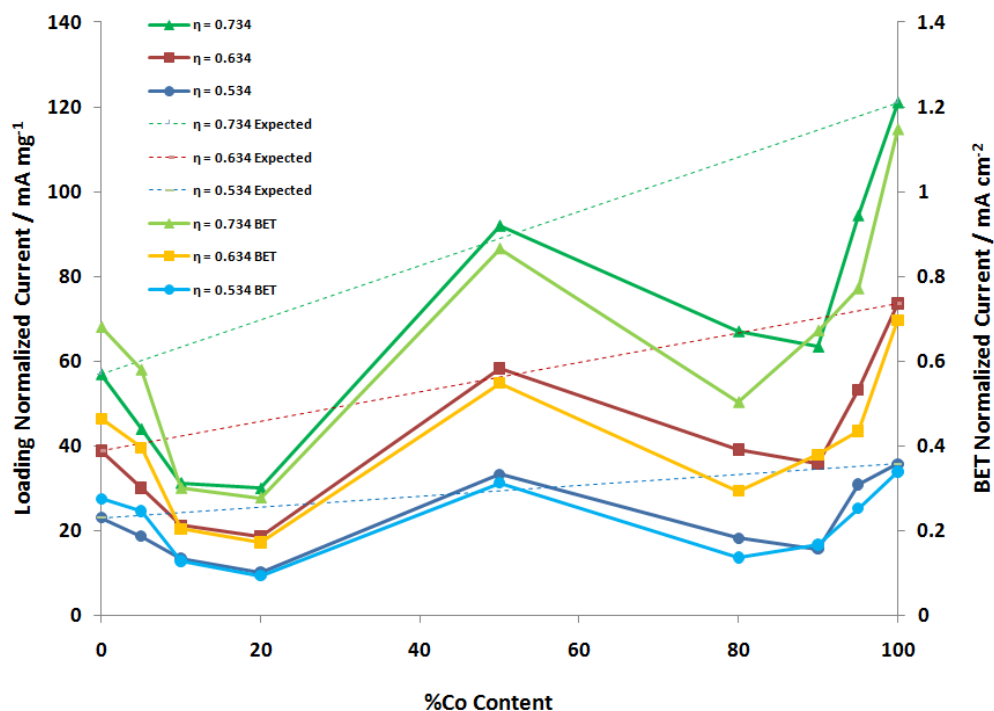


Figure 4.15. Catalytic activity of NiO, Co₃O₄, and Ni-Co mixed oxide catalysts. No synergistic effect between Ni and Co is observed with the highest catalytic activity observed for pure Co₃O₄. Both loading normalized and BET normalized data show the same trends.

While the catalytic activity of the Ni-Fe mixed oxide system was a strong function of the Fe concentration with increases in activity corresponding to increases in Fe, in the case of the Ni-Co mixed oxide system, this synergistic effect was not observed. A more fundamental understanding of the catalyst surface would help in explaining the conclusion behind this observation, but this analysis is suggested future work. Based on the XRD results and activity tests, it can be postulated that the Ni-Co oxide catalysts have formed separate crystalline phases which simply do not interact to form more active catalysts. It is also possible that the desired catalyst composition which would give rise to more active electrocatalysts was not found here. A more exhaustive approach would need to be used to examine further catalyst compositions. More detailed surface

spectroscopy would also help in determining the exact catalyst surface to explain the difference between the Ni-Fe system and the Ni-Co system. Future work investigated the Ni-Fe oxide catalysts and will be reviewed in the following section.

4.5 Surface Investigation on Mixed Ni-Fe Oxides

Reactions occur at the catalyst surface. In order to explain differences between catalyst activities, spectroscopic techniques are necessary. Previous research in this dissertation has focused on determining crystalline phases of the powders through XRD patterns and determining catalyst morphology through SEM images. While these techniques provide valuable insight into the catalyst structure, these tools do not offer information as to the surface composition of the catalyst or explain differences in reaction mechanisms. Other spectroscopy methods are necessary to gain access to this information.

Methods which can be used to determine surface compositions include techniques such as x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS). XPS has been used in here to investigate the surface phases for five of Ni-Fe oxide powders which were previously examined, including NiO, 5, 10, and 20 mol% Fe mixed Ni-Fe oxides, and Fe₂O₃. Ni and Fe phases were examined on the catalyst surface. The Ni phases present for the four samples containing Ni are shown in Figure 4.16.

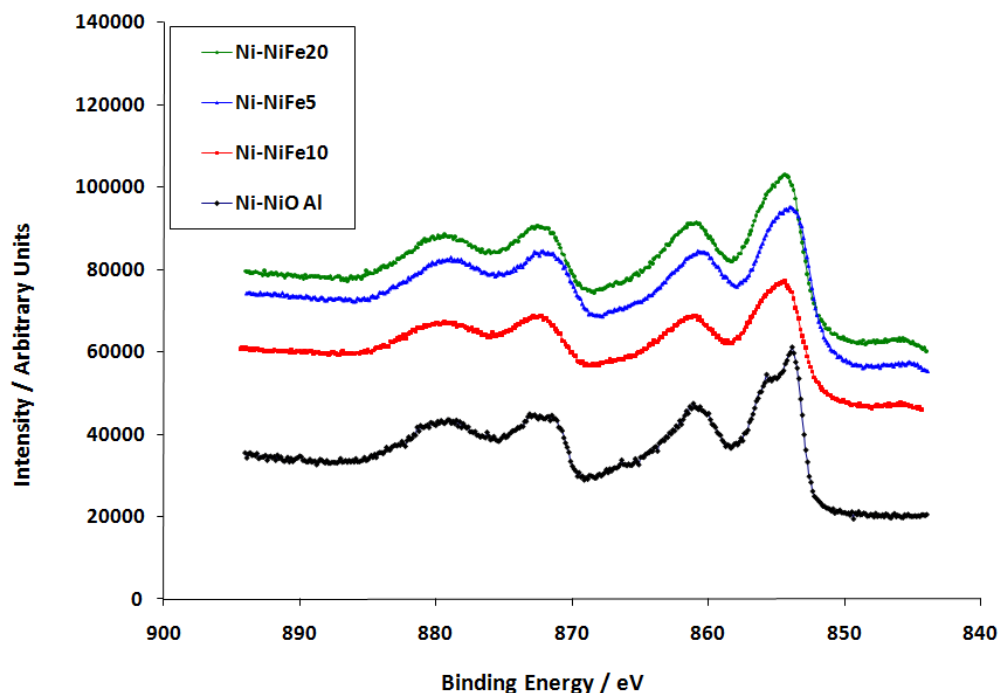


Figure 4.16. NiO XPS spectra taken from pure NiO and 5, 10, and 20 mol% Fe-mixed Ni-Fe oxides. All of these samples have characteristic NiO peaks for both the 2p_{1/2} and 2p_{3/2}

Evident in all four of the Ni containing oxides are characteristic peaks for NiO including the 2p_{1/2} and 2p_{3/2} peaks, at 854 and 873 eV, respectively. All of these oxides appear to have similar phases of NiO present. There is no quantifiable chemical shift in the binding energy for any of these oxides which logically leads to the conclusion that no evidence of surface alloying is present in these oxides. This result means that no alloying would be present between the Ni and Fe atoms. This information matches closely with the results obtained from the XRD experiments which also showed no evidence of alloying between these two atoms.

The surface oxide phases of Fe were also examined on the four samples containing Fe. The results from these studies are shown in Figure 4.17.

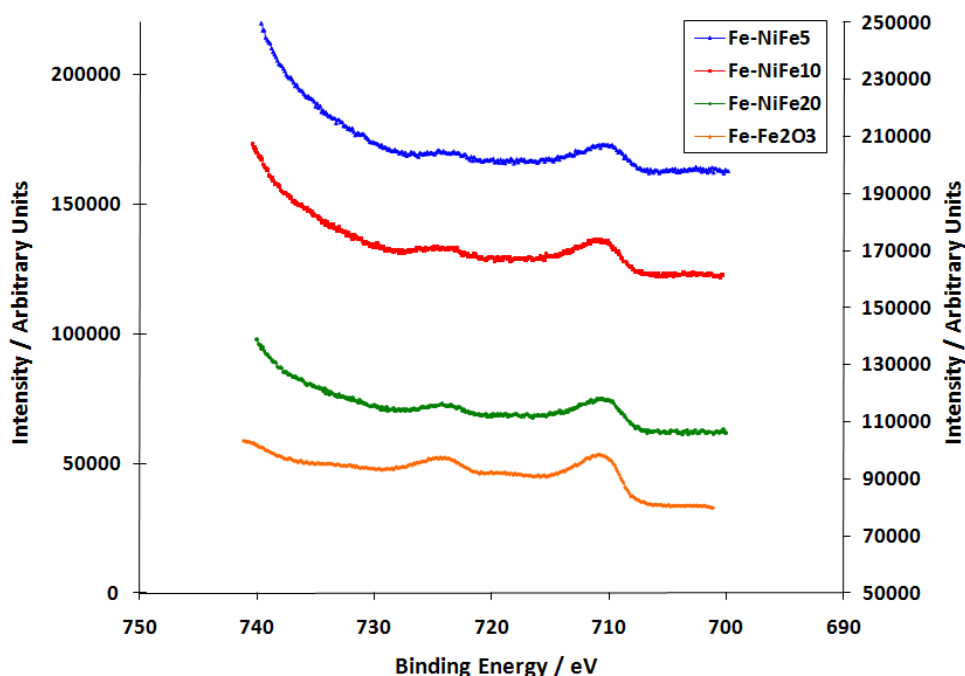


Figure 4.17. Iron oxide XPS spectra from pure Fe_2O_3 and 5, 10, and 20 mol% Fe mixed Ni-Fe oxides. The pure iron oxide sample contains two major peaks and one minor peak, indicative of Fe_2O_3 . The mixed Ni-Fe oxide samples contain 2 iron oxide peaks but no determination as to the actual iron phase can be discerned from this data.

Apparent in all of these samples are surface oxide Fe phases corresponding to either Fe_2O_3 , in the case of pure Fe_2O_3 , or $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ oxide phases in the cases of mixed Ni-Fe oxides. The Fe oxide signals obtained in these experiments are quite low, especially in the case of the mixed oxide samples. Fe_2O_3 phases have three characteristic peaks corresponding to binding energies of 710, 720, and 725 eV. These three peaks can be differentiated in the pure phase Fe_2O_3 , but it is not possible to conclusively identify a peak at 720 eV in any of the mixed oxide

samples. Further analysis would need to be conducted to identify the exact Fe phases present in these samples.

XPS has shown that both NiO and Fe oxides are present on the surface of these catalysts. XPS has also given information as to the lack of alloying present in the mixed oxides phases. These results agree well with prior characterizations in this work. However, the surface structure of these oxides is still unknown. Future experiments were necessary in order to identify which phases are present and what the exact catalyst surface composition is. X-ray adsorption spectroscopy (XAS) experiments were conducted in an effort to determine the extent of alloying present in this mixed oxide system and degree of oxidation. *in situ* XAS was also conducted to gather information as to how the catalyst changes under potential reaction conditions.

XAS analysis was conducted on pure oxide powders with compositions of pure NiO, 5, 10, and 20 mol% Fe, and pure Fe₂O₃. Figure 4.18 shows the extended x-ray adsorption fine structure (EXAFS) signal for pure NiO as well as the Ni signal in the 5 and 10 mol% Fe mixed oxides and pure Ni foil.

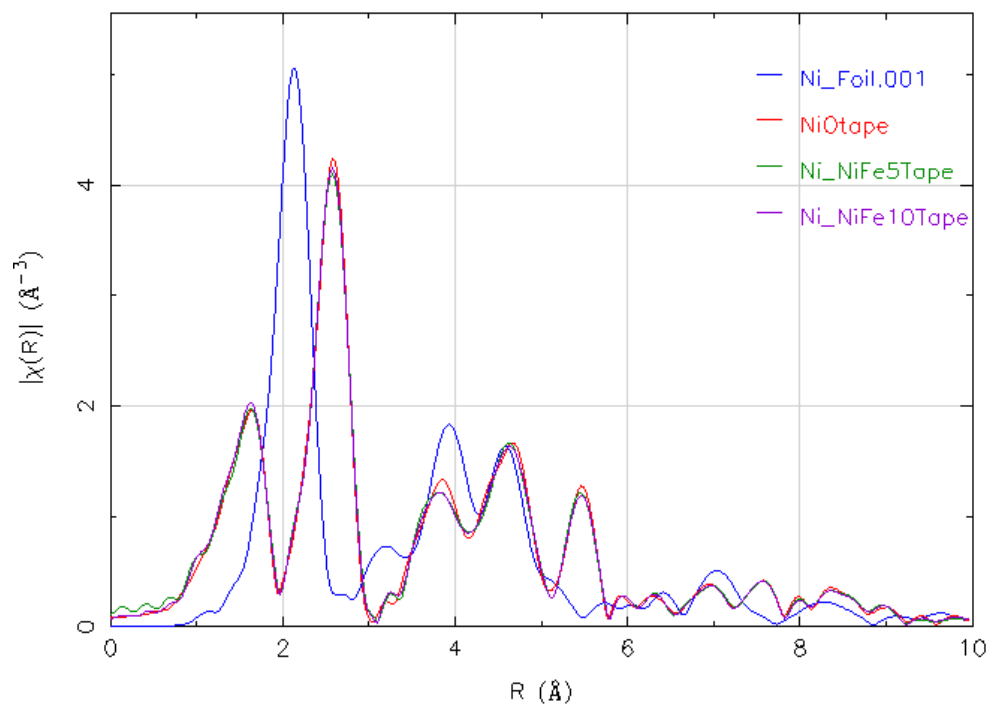


Figure 4.18. No change in the NiO phases is shown when increasing the Fe concentration in the mixed oxide catalyst indicating no degree of alloying between Ni and Fe.

Pure NiO and mixed Ni-Fe oxides have similar Ni EXAFS patterns indicating no change in the oxide state as Fe is added into the system. Ni exists at NiO in all of these mixed oxide samples. Ni foil is shown as a reference, but there is no indication that these oxides have any pure Ni phases present which is in agreement with both the XRD and XPS data shown previously.

Fe oxide phases were also examined in these powders. Figure 4.19 shows the Fe oxide phases present in these mixed oxide samples.

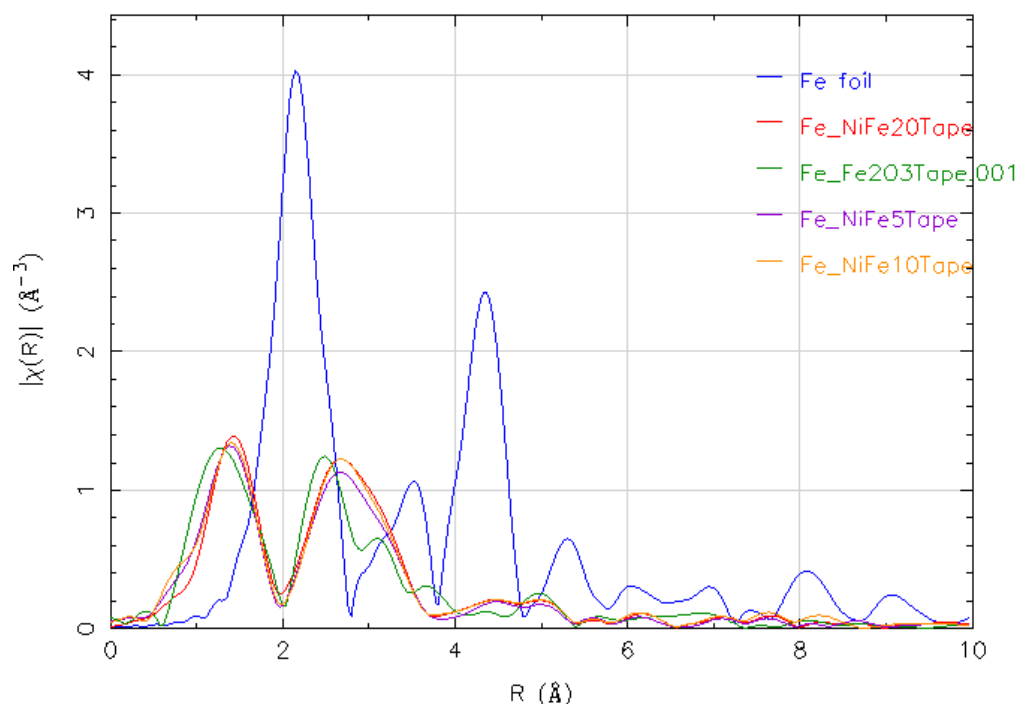


Figure 4.19. Fe oxide phases show similar patterns for 5, 10, and 20 mol% Fe which appear to be in agreement with pure Fe_2O_3 . An oxide peak is present below 2 Å and a Fe-Fe bond peak appears around 3 Å. None of these patterns resemble the pure Fe foil signal.

Fe oxide powders were examined using EXAFS and showed that Fe_2O_3 and 5, 10, and 20 mol% Fe mixed oxides contain similar peak patterns, indicating little change in these oxide phases even at these low concentrations of Fe. An exact determination of the oxide phase of Fe was desired. XPS data previously taken was unable to indicate if the phase present was FeO, Fe_3O_4 , or Fe_2O_3 . This data shows the probability of these powders containing Fe_2O_3 at all levels of Fe concentration. To examine these oxides more, x-ray adsorption near edge structure (XANES) analysis was carried out and is shown in Figure 4.20.

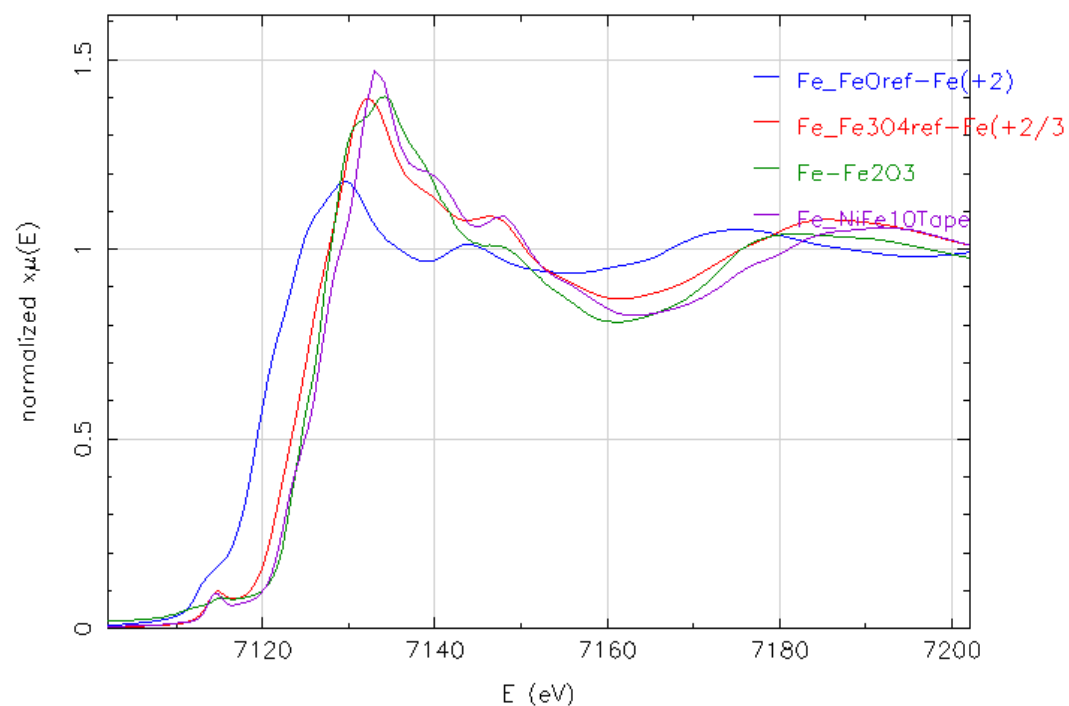


Figure 4.20. XANES analysis shows that the Fe is present as Fe_2O_3 in the mixed oxide sample containing 10 mol% Fe.

By examining reference sample patterns of Fe oxides using the XANES shown above, identification of Fe oxide phase in the 10 mol% sample was possible. It was found that the oxide phase present in all powder samples was Fe^{3+} as the white line is present at higher energy values in agreement with Fe_2O_3 . This result agrees well with the EXAFS as well as XPS data, and points towards the fact that these Fe is not alloyed with Ni.

Finally, *in situ* EXAFS analysis was conducted to show if any change in the 10 mol% Fe mixed oxide powder was apparent under oxygen evolution reaction conditions. Ni EXAFS under reaction conditions is shown in Figure 4.21 with signals for the 10 mol% Fe oxide powder on tape (blue), on carbon paper

(red), and with an overpotential 300 mV being applied for oxygen evolution (green).

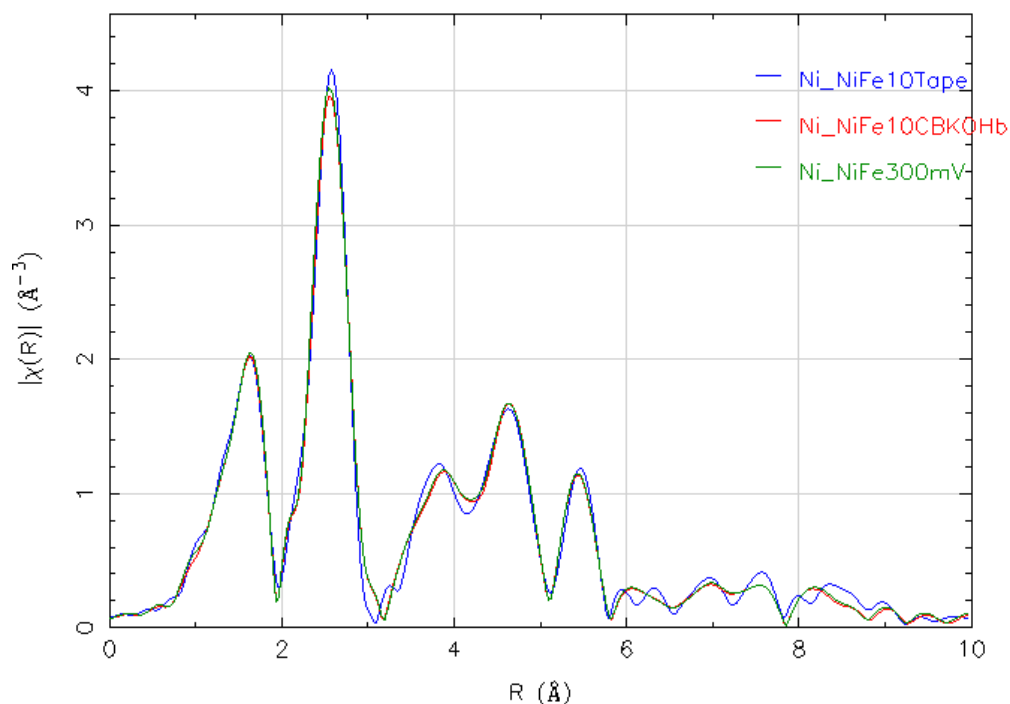


Figure 4.21. *in situ* EXAFS data shows that under oxidizing conditions up to 300 mV, no change in the oxidation state of the NiO in the 10 mol% Fe mixed Ni-Fe oxide could be seen. No change in any of the bond distances was seen for the NiO phases in this mixed oxide sample.

The NiO phase in this mixed oxide sample does not change under reaction conditions. There is no change in the oxidation peak below 2 $\text{\AA}$ or in the Ni-Ni peak close to 3 $\text{\AA}$. Peaks for the pure powder (blue), on carbon paper in 1M KOH (red), and with 300 mV of overpotential (green) all appear similar.

Fe phases were examined under reaction conditions in addition to the Ni phases. Fe signals from the EXAFS data for the 10 mol% Fe powder on tape

(blue), deposited on carbon paper in 1M KOH (red), and with 300 mV of overpotential applied (green) is shown in Figure 4.22.

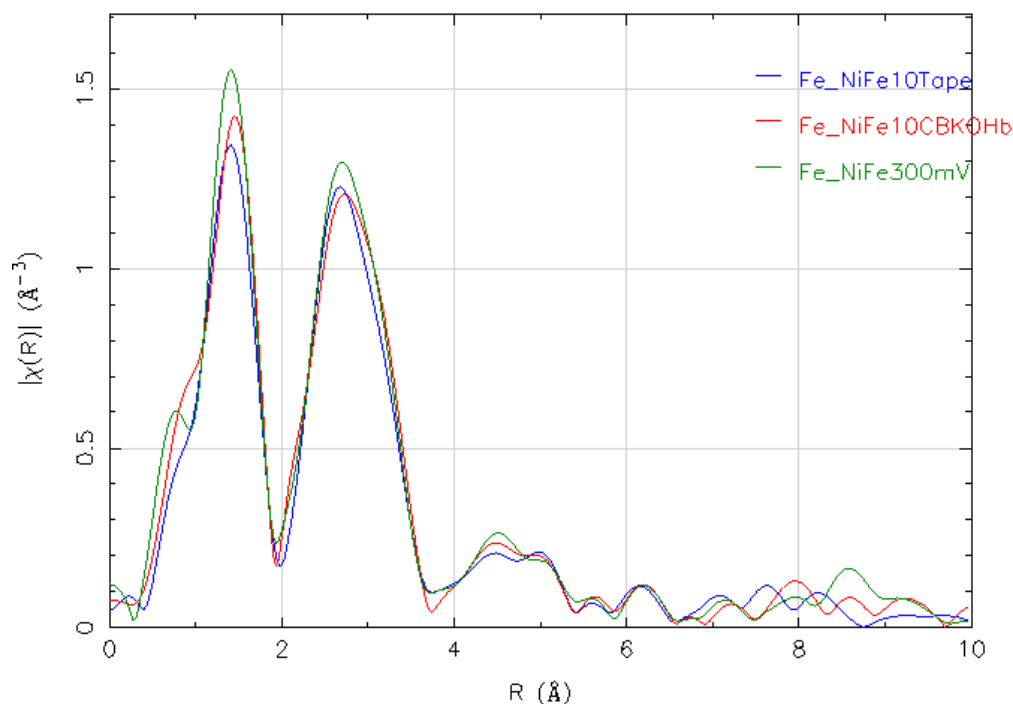


Figure 4.22. *in situ* EXAFS data shows that under oxygen evolution conditions, the oxide phases present in the 10 mol% Fe mixed Ni-Fe oxide catalyst become more oxidized. This oxidation increases as a function of applied potential. Small increases in the Fe-Fe bond intensity around 3 Å was also seen.

Unlike the Ni phases, the Fe phases show some changes under reaction conditions. The Fe oxide peak shown below 2 Å increases with this increase in overpotential. This change is indicative of further oxidation of Fe under oxygen evolution conditions and shows that Fe is involved during this reaction process. This data points towards Fe oxide phases being present on the catalyst surface.

To gain further understanding of this catalyst surface, future work should be conducted on these powders, specifically ion scattering spectroscopy (ISS)

experiments. ISS will be able to determine the exact compositions of the catalyst surface and show if the catalyst surface in this 10 mol% mixed sample is composed of Fe oxide. This work would complete the necessary surface characterization of this catalyst system.

4.6 Conclusions

Mixed Ni-Fe and Ni-Co oxide catalysts have been synthesized using an evaporation-induced self-assembly process and characterized using XRD, BET, SEM/EDS and electrochemical methods. The mixed Ni-Fe oxide catalysts have shown much higher activity towards oxygen evolution than either of the pure oxides. This increase in catalytic activity is due to a change in the rate determining step of the reaction process. No such synergistic effect was found in the mixed Ni-Co oxide catalyst system.

XPS was used to identify surface oxide phases in the mixed Ni-Fe oxides. NiO and Fe oxide phases were both found to be present. No chemical shift in binding energy was identified which would have been evidence of alloying. Exact Fe oxide phases were not possible to identify from the data collected here.

XAS analysis was conducted and showed that both NiO and Fe₂O₃ phases were present in these mixed oxides. No evidence of alloying was shown between Ni and Fe. *in situ* EXAFS shows that while the NiO phases show no change under oxygen evolution conditions, further oxidation of the Fe phase is apparent. These results in conjunction with the XPS results imply that Fe is present at the catalyst surface and is participating in this reaction process which may have led to the higher activity of this mixed oxide over either pure NiO or Fe₂O₃.

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5 Conclusions

The work contained in this dissertation shows a targeted approach towards developing a more active gas separation process. An energy analysis of the electrochemical gas separation process was examined, and an approach towards catalyst development was used to make this process more efficient. While there are still many issues to address concerning electrochemical gas separations, the work contained herein shows improvements towards making this process viable. Some of the issues and possible future work concerning the gas separation process and catalyst development will now be described.

5.1 Electrochemical Gas Separation Outlook

The electrochemical gas separation work presented in this dissertation shows that high concentrations of carbon dioxide and oxygen can be captured from various feed sources including air, simulated flue gas, and highly concentrated carbon dioxide streams. Applications for these separations processes include air separation units for oxy-fired power plants or flue gas separations as a means of retrofitting pulverized coal plants for carbon dioxide capture. In addition to these applications, this gas separation process could find considerable use as an on-demand oxygen generator. The ability to tailor the flowrate of oxygen gas with a small change in the applied cell potential could lead to uses such as an oxygen supply for hospitals or those in need of personal oxygen tanks.

The development of better materials including new membranes and more active electrocatalysts are crucial to the use of this gas separation process on a larger scale. Catalyst development aimed at making this process more efficient has been discussed, but it should also be mentioned that the fabrication methods and device operations are also evolving which will lead to more active and stable gas separation cells. Membrane materials for electrochemical alkaline cells are just recently being made available for applications such as these, and these new membranes can help limit cell resistances by facilitating better contact with electrocatalysts and minimizing cell thicknesses. The use of a binding ionomer in anion catalyst inks is also advancing. These ionomers are currently available and have been instrumental in providing stability during the half-cell testing of new active oxygen evolution catalysts. These ionomers have also made it possible to create electrodes using electrocatalyst powders made from high surface area synthesis methods.

Gas separation cells provide a promising alternative to current separation approaches, but many hurdles still need to be overcome for these cells to be used in commercial applications. These hurdles include a better understanding of optimal catalyst ink compositions, water management in the separation cell, and degradation mechanisms for both the electrocatalysts and the overall cell. These hurdles are in addition to the larger issue of finding more active catalysts for oxygen reduction and oxygen evolution. Further advancements in catalyst materials and processes will assist in the adoption of gas separation processes such as these.

5.2 Perovskite Possibilities

Perovskite catalysts were examined as oxygen evolution electrocatalysts. These perovskite catalysts were found to be less active than previously synthesized oxides, and this result redirected research back to examining transition metal oxide catalysts. While research conducted herein ended up pursuing other catalytic systems, perovskite catalysts still have some promising attributes which warrant examination by future researchers.

These catalysts have a robust chemical structure, and various properties can be examined using this structure. Other researchers are investigating strain effects on these structures and how this affects catalytic properties [1]. Also, doping of the A-site of the material can tailor chemical properties such as conductivity, activity, and the oxidation state [2]. This work is critical in the understanding of how materials can be modified to obtain desired attributes. Future research into these materials will undoubtedly lead to a more fundamental understanding of how these structures function and how more stable catalytic activity for a variety of reactions can be accomplished.

In addition, the synthesis process used to create these perovskite catalysts proved to be useful in future transition metal oxide syntheses. This process was an evaporation-induced self-assembly synthesis process, and catalysts with relatively high surface area and reasonable crystallinity could be made. Some of the synthesized perovskites contained noticeable impurities, but as a whole, this synthesis process was quite robust in its effectiveness. While the catalytic activity

of these materials was not high enough to warrant more investigation, the knowledge gained from this chemical synthesis was helpful for future work.

5.3 Ni-Fe Mixed Oxide Activity

Mixed Ni-Fe oxides were found to have considerably higher catalytic activity than either NiO or Fe oxide. This synergistic effect between Ni and Fe has made the mixed oxide system an interesting candidate for oxygen evolution studies. Previous studies in the research area of oxygen evolution had noted the increased activity in this catalytic system [3-5]. However, these previous researchers did not determine what the optimal concentration of Fe in the catalyst would be or use a high surface area synthesis process for catalyst creation. These properties were examined in the course of this study and an Fe concentration of 10 mol% was found to have the highest activity among the catalysts tested.

Predicting increased activity of a catalyst remains difficult. The idea of using a volcano plot as a predictive tool for catalyst design was presented here, but it was not explicitly followed in the creation of the mixed Ni-Fe oxide system. This synergistic effect was already known, and while it follows logically from Trassatti's volcano plot using chemical interpolation, this catalyst was not created simply due to Trassatti's work. Chemical interpolation was attempted in the case of the Ni-Co mixed oxide system, but no synergistic effects were found. The synthesis of structurally exact mixed oxide systems is quite difficult. In assessing why no synergistic effect was found between Ni and Co, the mere fact that it was difficult to create a well mixed oxide could be the reason. Every catalyst

composition was not examined, and therefore, a region where higher activity was present could have been missed. Chemical interpolation remains a possible route of rational catalyst design, but extensive characterizations and spectroscopy need to be used to verify the synthesized catalyst structure.

Computational studies are another route for predicting catalyst activity based upon intrinsic parameters [6-7]. These studies can aid in the determination of a specific catalyst structure or composition which would increase overall activity [8-9]. While these studies are useful, the matter of synthesizing and characterizing the desired material will remain. Verification of these studies will be crucial in evaluating computational predictive capabilities. As characterization techniques continue to get more precise, catalyst parameters will be easier to identify and tailoring of catalyst properties towards specific reactions will become easier.

5.4 Catalyst Spectroscopy Work

Spectroscopy techniques were used in assessing the catalyst structure and properties of Ni-Fe. The surface spectroscopy methods used here were XPS and XAS. These techniques gave valuable insight into the catalyst surface layer of this mixed Ni-Fe oxide catalyst. XPS conducted on the mixed Ni-Fe oxides showed that the first few catalyst layers were composed of a both NiO and Fe oxide. No determination as to the actual surface Fe oxide could be made, but this information meant that both Ni and Fe were close to the catalyst surface. Also, no noticeable alloying effects between Ni and Fe could be seen in these patterns.

This evidence substantiated the bulk phase analysis supplied by XRD experiments meaning that no interaction between the Ni and Fe oxide phases could be seen.

XAS analysis showed again that these mixed oxides were composed of NiO and Fe oxide, but the Fe oxide phase was able to be identified through XANES as Fe₂O₃ in all of the mixed oxide powders. *in situ* EXAFS was also used to show that further Fe oxidation occurs under oxygen evolution conditions while no change in the Ni oxidation was found. These results point towards the location of Fe oxides at the surface of the catalyst that aid in the increased activity seen in the electrochemical oxygen evolution experiments. If a catalyst monolayer of Fe is forming in these oxide cases, then further spectroscopy such as ion scattering spectroscopy, would be necessary to detect this monolayer. Finally, to determine reaction mechanisms or surface reaction intermediates, spectroscopies such as *in situ* Raman spectroscopy would be useful. This technique would provide surface adsorbate information under oxidizing conditions to indicate what changes are present on the surface between these Ni-Fe catalysts, but this procedure remains difficult as advancements in collecting this type of data are just now being realized.

The area of electrocatalysis remains a vibrant field to study. As surface spectroscopies become more precise and procedures to conduct electrochemical analyses are figured out, this research area will continue to advance. The research shown here presents advancements in the area of oxygen evolution electrocatalysis by combining high surface area synthesis methods with detailed spectroscopy methods to make more active electrocatalysts.

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