

# Manganese Oxide Adhesion to FTO and Cobalt Stability in Varying pHs for Oxygen Evolution Reaction

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**ABSTRACT:** A suitable acid and acid-stable catalysts for the oxygen evolution reaction (OER) were the target of investigation to eventually be used to power a solar fuel generator. Earth-abundant metal oxides that are suitable catalysts for OER are sought to catalyze water-splitting in solar fuel generators. An acid-stable catalyst was the focus of experimentation as opposed to a base-stable catalyst, as several acid-stable compounds could potentially be used as catalysts for OER in a solar fuel generator. OER was tested using the HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) kit, which measures the amount of oxygen released by each metal oxide sample when current is applied to the sample, and therefore tests the catalytic abilities of each metal oxide used. Manganese oxide ( $\text{MnO}_2$ ) was especially promising because of its known stability in acid, through the compound did not readily adhere to the FTO. Preparation of manganese oxide ( $\text{MnO}_2$ ) samples was experimented with to successfully adhere the  $\text{MnO}_2$  to the FTO plate. In addition, cobalt oxide ( $\text{CoO}_2$ ) was tested in a wide range of pHs to find the best conditions for cobalt oxide's catalysis of OER.  $\text{MnO}_2$  was found to best adhere when annealed at  $600^\circ\text{C}$  for 5 hours, after being dried on a hot plate.  $\text{CoO}_2$  was found to be an active catalyst at pHs 13 and 12, with a significant decrease in activity at and below pH 11.

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## 1. Introduction

The depletion of fossil fuels has triggered a search for renewable, clean energy sources that can be used to power the planet. Solar energy is especially promising because it can power electrochemical water-splitting to separate hydrogen and oxygen gas. This technology could be used in future solar fuel generators to produce and store energy<sup>1</sup>. A compound could catalyze the reaction by lowering the activation energy needed for the reaction<sup>2</sup>. Earth-abundant metals in particular are desirable as catalysts for their large available quantities and inexpensive cost<sup>2</sup>.

The SEAL (Solar Energy Activity Lab) and HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) kits have been used by high school and college students to assess earth-abundant metal compounds for viability as water-splitting catalysts. Both kits use a parallel screening approach by drop casting metal oxide spots onto an FTO coated glass slide, and submerging the slide in an aqueous solution. However, the HARPOON kit tests the sample under an applied potential, while the SEAL kit illuminates the sample with LED lights and measures the amount of current produced. By directly applying current to the metal compound(s) for testing, the HARPOON kit (using oxygen sensitive fluorescent paint) senses the oxygen gas released from the oxygen evolution reaction (OER) occurring at a specific spot<sup>2</sup>. In contrast, the SEAL kit reads current produced from a sample, which can be from either the OER oc-

curing or from the photocorrosion of the metal oxide spot. The HARPOON kit was chosen to directly analyze the catalysts' water-splitting abilities, and so that we can learn how to successfully implement it in schools across the country.

The HARPOON and SEAL kits have traditionally been used to test the catalytic abilities of metal oxides for OER by submerging the metal oxide in a basic solution of 0.1 M sodium hydroxide (NaOH). Little work has been done with acidic solutions in the kits, though many earth-abundant catalysts are stable in acid but not base. By using an acid solution, acid-stable metal catalysts can be tested for catalytic capabilities. Successful OER catalysts could be implemented in a solar fuel cell, as it is unsure if a future solar fuel cell will operate under acidic or basic conditions (depending on other components of the cell). Because acidic solutions are not normally used in either experiment, another focus is to find an acid solution that will perform best as a medium for OER in conjunction with several potential catalysts. Numerous metal oxide solutions have been previously tested for OER catalysis. Manganese oxide ( $\text{MnO}_2$ ) is known to be stable and an active catalyst for OER in acid, while other oxides such as those of nickel (Ni), iron (Fe), and cobalt (Co) that are successful catalysts in basic solution<sup>3-6</sup> typically corrode in acid solutions<sup>7</sup>.  $\text{MnO}_2$  was experimented with to adhere the  $\text{MnO}_2$  to the FTO plate because of its stability in acid. Cobalt oxide ( $\text{CoO}_2$ ) is also known to be a successful base-stable catalyst. For this reason,  $\text{CoO}_2$  was tested for catalysis

in different pH electrolyte solutions, to test at what pH  $\text{CoO}_2$  is most stable for OER catalysis in acid.

## 2. Methods

### 2.1 Preparing Solutions.

The  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  20 mL solutions were prepared at 0.05 M concentration by combining the respective metal salts with deionized water. To make a combined NiFeCo reference solution with a 1:2:2 ratio of Ni:Fe:Co at 0.005 M,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ , and  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$  solutions previously prepared were combined with 200 mL of deionized water. To make a combined  $\text{MnSO}_4$  and reference solution (after annealing to be MnNiFeCo) at 0.05 M with a 10:1 ratio of  $\text{MnSO}_4$ :reference, 10  $\mu\text{L}$  of  $\text{MnSO}_4$  were combined with 10  $\mu\text{L}$  of reference solution per each spot in a well plate. To prepare the NaOH solution, 2 g of pellets of NaOH were combined with deionized water to make a 500 mL solution at 0.1 M concentration. The KOH solution was similarly prepared by adding 38.6 g of pellets of 30% KOH to deionized water to produce a 100 mL solution. 250 mL of 0.5 M  $\text{H}_2\text{SO}_4$ , 350 mL of 1 M  $\text{H}_3\text{PO}_4$ , or 350 mL of 0.1 M HCl solution were used as acid electrolytes in some experiments instead of 0.1 M NaOH solution. 350 mL of  $\text{H}_2\text{SO}_4$  and 350 mL of  $\text{H}_3\text{PO}_4$  were prepared by combining 4.7%  $\text{H}_2\text{SO}_4$  and 85%  $\text{H}_3\text{PO}_4$ , respectively, with deionized water. 0.1 M HCl solution was prepared by combining 3.24 mL 36.5-38.0% HCl with deionized water to create a 400 mL solution.

To test cobalt at different pHs, solutions of pH 13, 12, 11, 9, and 1 were made and used as electrolyte solutions. 0.1 M NaOH previously prepared was used as pH 13 solution. To prepare a pH 13 solution with  $\text{K}(\text{NO}_3)$ , 7 g of NaOH was added to a 250 mL volumetric flask, which was then filled with deionized water. The 250 mL was added to a bottle along with 100 mL deionized water. 0.2 g of  $\text{K}(\text{NO}_3)$  were added to adjust pH to 13. To create a pH 12 solution, 1.01 g of  $\text{K}(\text{NO}_3)$  was added to 100 mL deionized water to create a 0.1 M solution. 20 mL  $\text{K}(\text{NO}_3)$  was added to 250 mL NaOH to create a 0.1 M solution with pH 12. The remaining 230 mL of NaOH were added to produce a 500 mL solution. 3.54 g of  $\text{K}(\text{NO}_3)$  was combined with deionized water to create a 300 mL solution of 0.1 M concentration. pH 11 solution comprised of 0.1 M  $\text{K}(\text{NO}_3)$  combined with 10.5 mL prepared 0.1 M NaOH to adjust pH. The remaining 39.5 mL of deionized water was added to produce a 350 mL solution. The pH 9 solution was prepared similarly, using 3.5 mL instead of 10.5 mL 0.1 M NaOH to adjust pH. 46.5 mL of deionized water was added to the pH 9 solution to create a 0.1 M solution. The pH 1 solution was prepared by combining 3.24 mL of 36.5-38.0% HCl to deionized water to create a 400 mL solution at 0.1 M concentration.

### 2.2 Preparing Samples.

$3'' \times 3''$  fluorine-doped, tin oxide-coated glass (FTO)<sup>2</sup> plates were cleaned with isopropyl alcohol and the desired metal-oxide solution was drop casted onto the plate at 10  $\mu\text{L}$  per spot according to an LED spotting array (Figure 1). The second to last row and corners were left blank, for a total of 52 spots of the desired metal-oxide solution.

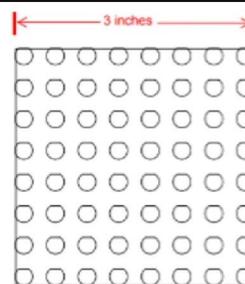


Figure 1: LED Spotting Array<sup>9</sup>.

The reference solution of NiFeCo was drop casted into all corner spots except for the bottom left corner, and the second to last row of spots remained blank as a negative control. The plate number was engraved on the second to last row with a diamond-tipped scribe. Plates were annealed for 5 h at 500°C in atmosphere unless otherwise noted. Cobalt oxide ( $\text{CoO}_2$ ) plates (19-21, 23-26) created for testing in varying pHs were prepared as described above, but drop casted specifically with 0.05 M cobalt acetate tetrahydrate ( $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) solution.

### 2.3 HARPOON Kit.

A 350 mL solution of 0.1 M NaOH (or substituting electrolyte solution) in a glass bottle was purged for 30 minutes<sup>1</sup>. For OER experiments in acid solutions, 350 mL of 0.5 M  $\text{H}_2\text{SO}_4$ , 350 mL of 1 M  $\text{H}_3\text{PO}_4$ , or 350 mL of 0.1 M HCl solution was substituted. The FTO plate was placed under a fluorescent-paint-coated mesh<sup>1,7</sup>, which was then placed in a polystyrene plastic dish. Copper tape connected to the FTO plate acted as an electrode, and a graphite rod in the opposite end of the dish was used as a counter-electrode<sup>1</sup>. Leads of a constant-current power supply were attached to the electrodes so 5 mA

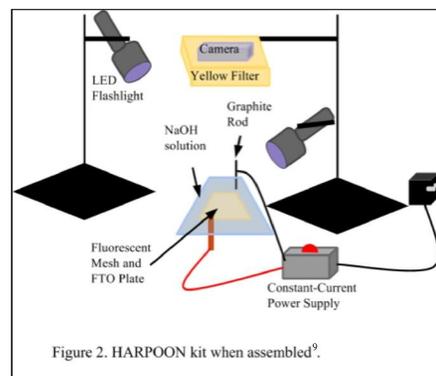
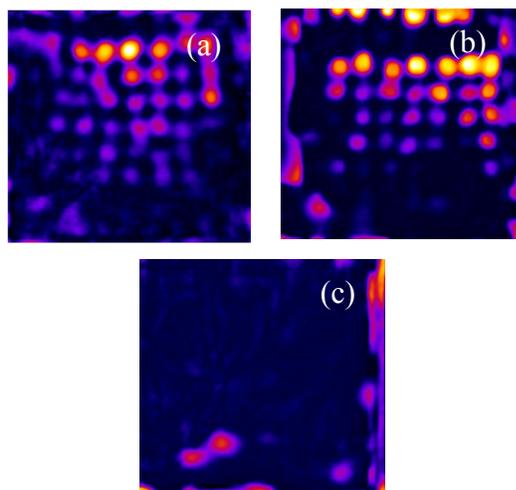


Figure 2. HARPOON kit when assembled<sup>9</sup>.

of current through the FTO plate<sup>1</sup>. Two LED 400nm flashlights were attached to ring-stands and placed on either side of the dish. A camera phone was placed on top of a yellow filter, and took pictures of the mesh (illuminated by the LED flashlights) every 30 seconds for 10 minutes. The 20 pictures taken were downloaded to a computer and analyzed with ImageJ software. Some plates were EDX/SEM tested with FEI Nova NanoSEM 450.

### 3. Results

**3.1 Cobalt oxide in incremented pH solutions with HARPOON kit.** Cobalt oxide ( $\text{CoO}_2$ ) plates (19-21, 23-26) were prepared as described in 2.2. Results in the form of oxygen spots were received when plate 19 was tested in 0.1 M NaOH solution of pH 13. However, when cobalt plates 20-21 were tested in 0.1 M NaOH basic solutions with 0.1 M  $\text{K}(\text{NO}_3)$  solution added to lower the pH (pH 11 and 8.5, respectively) no oxygen was detected. Plate 23 was tested in a pH 1 solution of 0.1 M HCl, and no oxygen spots on the fluorescent-paint-coated mesh were observed. Plate 26 was tested in 0.1 M NaOH basic solution with 0.1 M  $\text{K}(\text{NO}_3)$  solution added to lower the pH to 12. Oxygen spots were detected (Figure X-comparison). Plate 21 was retested in a pH 13

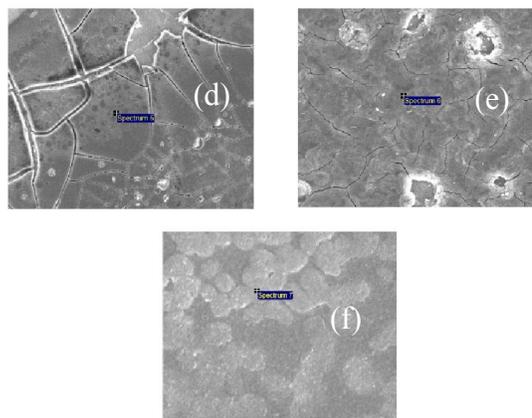


**Figure 3.**  $\text{CoO}_2$  catalysis of oxygen in pH 13 (a), 12 (b), and 11 (c) electrolyte solutions of 0.1 M NaOH and  $\text{K}(\text{NO}_3)$  analyzed with ImageJ software. Brighter spots represent more oxygen present.

solution of 0.5 M NaOH solution combined with 0.1 M  $\text{K}(\text{NO}_3)$  solution added to adjust the pH. Oxygen was detected during this test. A comparison of  $\text{CoO}_2$  catalysis in pHs 13, 12, and 11 is shown in Figure 3.

**3.2 Manganese Adhesion.** Manganese oxide ( $\text{MnO}_2$ ) plates, when prepared as outlined in 2.2 with 0.05 M  $\text{MnSO}_4$  solution (plates 6,8), neither adhered to the FTO plate during testing nor produced oxygen spots in the HARPOON kit. 0.05 M  $\text{MnSO}_4$  solution was combined with the 0.005 M reference solution (NiFeCo 1:2:2  $\mu\text{L}$  ratio) for drop casting and testing (plate 10), but no oxygen was detected when tested and metal oxide spots had almost completely flaked off the plate. Plates 10, 17 (0.05 M  $\text{MnNiFeCo}$  solution with 10:1 ratio of  $\text{MnSO}_4$  solution to reference, untested in HARPOON kit), and 16 (reference solution, untested in HARPOON kit) were EDX/SEM tested with no metal oxide detected other than FTO. Plates 27 (0.05 M reference solution, untested in HARPOON kit), 28 (0.5 M  $\text{MnNiFeCo}$  solution with 10:1 ratio of  $\text{MnSO}_4$  to reference, untested in HARPOON kit), and 29 (0.5 M  $\text{MnNiFeCo}$  solution with 10:1 ratio of  $\text{MnSO}_4$  to reference, tested in HARPOON kit with 0.1 M HCl) were created at 10 times the concentration of the original

solutions to ensure detection by the EDX/SEM. The EDX/SEM did sense the metal oxide spot on each sample except the tested sample of  $\text{MnO}_2$  and reference solution (plate 29). The plate 27 sample had two varying degrees of "coffee ring" (Figure 4).



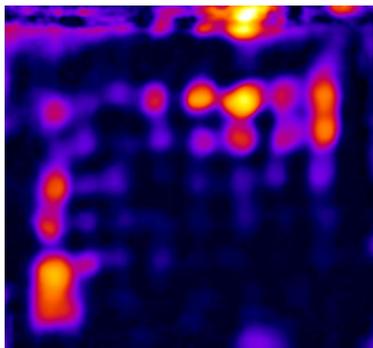
**Figure 4.** "Coffee rings" of NiFeCo spot at 0.05 M (plate 27) with scanning electron microscopy (SEM). A "coffee ring" forms where the compound was unequally deposited along the spot, so a greater concentration of solution occurs around the perimeter of the spot.

On the outermost ring (d), there was an approximate 1:4:3 ratio of Ni:Fe:Co (5.5%: 20.9%: 13.6%; all EDX percentages in atomic%), with oxygen (60.0%) also present but no readings of tin from the FTO. On the secondary ring (e), an approximate 1:1:2 ratio of Ni:Fe:Co (6.3%: 7.8%: 17.8%) was detected, as well as readings of tin (2.7%) and oxygen (65.2%). At the center of the spot (f), nickel, iron (7.9%), and cobalt (17.8%) were all found but nickel not listed as having a significant atomic percentage. Oxygen (73.1%), tin (not listed as having a significant atomic percentage), and silicon (2.4%) were also detected. All the oxides of the metals in the original solution from plate 28 were found ( $\text{MnNiFeCo}$ , and  $\text{O}_2$ : 17.9% Mn, 0.6% Fe, 67.0% O), additionally finding approximately 11% sulfur. A small quantity of tin (0.4%) was also detected.

Plate 11 (reference solution) was tested in  $\text{H}_3\text{PO}_4$  acid solution using the HARPOON kit without the fluorescent-paint-coated mesh and timed how long was taken for the reference solution to flake in acidic solution. After 40 minutes the spots had faded but still remained. Plates 12 (0.05 M  $\text{MnNiFeCo}$ ) and 13 (0.05 M  $\text{MnO}_2$ ) were dried on a hot plate instead of air drying prior to annealing. The  $\text{MnNiFeCo}$  on Plate 12 flaked off in the 0.5 M  $\text{H}_2\text{SO}_4$  acid solution when touched or initially placed in solution. The spots remained when current was applied to the plate, while the metal oxide spots on Plate 13 disappeared immediately after potential was applied. Plates 14 and 15 (both 0.05 M  $\text{MnO}_2$ ) were cleaned with KOH and 15

minutes in a UV/Ozone Procleaner, respectively, prior to drop casting. Spots on plate 14 were not visible after testing in 1 M  $\text{H}_3\text{PO}_4$  acid for 90 minutes using the SEAL kit. A single spot on plate 15 was wiped with a Kimwipe and deionized water, and was completely removed.

Spots on plate 22 ( $\text{MnO}_2$ ), when annealed for 3 h at  $600^\circ\text{C}$ , did not flake off the FTO plate when tested in 0.1 M HCl acid, and only top layer of spot flaked off when wiped with a Kimwipe and deionized water.  $\text{MnO}_2$  when annealed for 5 h at  $600^\circ\text{C}$  (plate 18) ex



**Figure 5.** Plate 32 ( $\text{MnO}_2$ ) tested in 0.1 M NaOH solution and analyzed with ImageJ. Brighter spots represent more oxygen present.

perienced similar results--the majority of the spot flaked off except for the coffee ring. No oxygen results were obtained through testing in 0.1 M HCl, and only coffee ring remained after cleaning the plate with deionized water. A final  $\text{MnO}_2$  plate (plate 32) was annealed for 5 h at  $600^\circ\text{C}$  after being dried on a hot plate. When wiped with deionized water and a Kimwipe, only the coffee ring slightly flaked off. When tested in 0.1 M NaOH solution, oxygen was detected on most spots.

**Table 1. Adhesion of manganese oxide ( $\text{MnO}_2$ ) solution based on preparation of plate and testing conditions.**

Plate Number	Plate Description*	Test Conditions	$\text{MnO}_2$ Adhesion
6	0.05 M manganese sulfate ( $\text{MnSO}_4$ ) solution.	Tested in 1 M $\text{H}_3\text{PO}_4$ acid solution with HARPOON kit.	All $\text{MnO}_2$ spots had flaked off the plate after testing, but the reference spots remained intact.
8	0.05 M $\text{MnSO}_4$ solution.	Adhesion tested <sup>†</sup> .	Spots came off of the plate when adhesion tested.
10	0.05 M $\text{MnNiFeCo}$ solution.	Tested in 0.5 M $\text{H}_2\text{SO}_4$ acid solution with HARPOON kit; EDX/SEM tested	Spots had almost completely flaked off the plate after testing.
11	0.005 M reference solution.	Tested in 1 M $\text{H}_3\text{PO}_4$ acid solution with SEAL kit.	Spots had almost completely faded.
12	0.05 M $\text{MnNiFeCo}$ solution; dried on a hot plate.	Current applied in 0.5 M $\text{H}_2\text{SO}_4$ acid solution in HARPOON kit without mesh, and timed how long was taken for the spots to flake.	Spots flaked off the FTO plate into the solution when initially placed in the solution or touched when submerged, though spots remained stable when current was applied.
13	0.05 M $\text{MnSO}_4$ solution dried on a hot plate.	Current applied in 0.5 M $\text{H}_2\text{SO}_4$ acid solution in HARPOON kit without mesh, and timed how long was taken for the spots to flake.	Spots adhered when the plate was initially placed in the solution, and disappeared immediately after current was applied.
14	0.05 M $\text{MnSO}_4$ solution; plate cleaned with KOH prior to drop casting.	Tested in 1 M $\text{H}_3\text{PO}_4$ acid solution in SEAL kit; adhesion tested.	Spots faded when adhesion tested. After testing with SEAL kit, all spots had flaked off except one reference spot.

15	0.05 M MnSO <sub>4</sub> solution; plate UV/ozone cleaned prior to drop casting; spots spread when drop casted.	Adhesion tested.	The spots flaked off the plate completely when wiped.
16	0.005 M reference solution.	EDX/SEM tested.	N/A
17	0.05 M MnNiFeCo solution.	EDX/SEM tested.	Spots visible before and after EDX/SEM; not tested for adhesion.
18	0.05 M MnSO <sub>4</sub> annealed for 5 h at 600°C.	Tested in 0.1 M HCl solution in HARPOON kit; adhesion tested.	When adhesion tested, most spot flaked off except for coffee ring; after testing and washing with DI water, spots significantly faded but coffee ring remained.
22	0.05 M MnSO <sub>4</sub> annealed for 3 h at 600°C.	Adhesion tested.	Only top layer of spot wiped off, but not entire spot.
27	0.5 M reference solution.	EDX/SEM tested.	N/A
28	0.5 M MnNiFeCo solution.	EDX/SEM tested.	Spot did not flake off but was not tested for adhesion.
29	0.5 M MnNiFeCo solution.	Placed in 0.1 M HCl solution with current applied; EDX/SEM tested.	Spots partially flaked off when tested, but when plate was washed with DI water, spots flaked off more; no spot visible at EDX/SEM.
32	0.05 M MnSO <sub>4</sub> annealed for 5 h at 600°C, dried on a hot plate prior to annealing.	Tested in 0.1 M NaOH solution with HARPOON kit.	Only coffee ring of spot flaked off slightly when adhesion tested.

\*plates cleaned with isopropyl alcohol prior to drop casting, air dried, and annealed for 5 h at 500°C unless otherwise specified. All corners of plates except for the bottom left corner were drop casted with reference solution.

†Adhesion Tested: Single spot wiped with a Kimwipe and deionized water.

## 4. Discussion

### 4.1 Cobalt oxide in incremented pH solutions with HARPOON kit.

When plates with cobalt oxide (CoO<sub>2</sub>) spots were tested in different pHs, only the plates tested in electrolytes with pHs above pH 11 (plates 19, 21, 28) produced oxygen from catalysis of the OER reaction. When CoO<sub>2</sub> was tested in 0.1 M pH 13 NaOH solution (plate 19), the CoO<sub>2</sub> was an active catalyst as strong O<sub>2</sub> spots were produced. In pH 12 solution, oxygen still resulted, but was not as strong as the O<sub>2</sub> spots produced in pH 13. CoO<sub>2</sub> was tested in a pH 13 solution of both NaOH and K(NO<sub>3</sub>) as a control to ensure K(NO<sub>3</sub>) added to the solutions was not inhibiting the catalytic abilities of CoO<sub>2</sub>. The same OER catalysts occurred as in the pH 13 solution of 0.1 M NaOH. The plates in electrolyte solutions with pHs of 11, 9, and 1 did not produce any oxygen results. There was a sharp change in the catalytic abilities of cobalt between the pHs of 13 and 11, which is attributed to the K(NO<sub>3</sub>) added to lower the pH of the NaOH solution. CoO<sub>2</sub> is not known to be stable in acid and significant oxygen was not expected to be produced in pH 1 HCl.

**4.2 Manganese Adhesion.** Many variations on the preparation of MnO<sub>2</sub> plates were tested to attempt to more successfully adhere manganese oxide (MnO<sub>2</sub>) to the FTO plate. MnO<sub>2</sub> was combined with reference solution originally because the reference spots had not dissolved as readily as the MnO<sub>2</sub> spots in the acidic electrolyte solution. Combining the MnO<sub>2</sub> with the reference solution only slightly prevented the MnO<sub>2</sub> spots from flaking as the plate was being tested. Plates 11 and 14 were tested in the SEAL kit to ob-

serve the corrosion of the metal oxide spots while the sample was being tested for catalysis. However, the dark current did not lower to under 0.5 mA, most likely because of the corrosion of the spots caused by the acidic solution, and so accurate results could not be drawn from the samples. The dark current did not lower to a testable range because the plates were tested in an acidic solution instead of a base, which could have caused corrosion of the spots. MnNiFeCo spots on plate 12 did not adhere because the reference solution, while adhering to the FTO plate, was not completely stable in acid. Plates cleaned with KOH or ozone (14 and 15) were unsuccessful in adhering the MnO<sub>2</sub> to the plate, showing that impurities present on the FTO plate prior to drop casting were not preventing MnO<sub>2</sub> adhesion.

Plates 27, 28, and 29 were tested with the EDX to see whether manganese sulfate solution combined with the reference solution aided the MnO<sub>2</sub> to adhere to the plate. There was possibility that MnO<sub>2</sub> alone flaked off the spots after being tested, so the EDX would reveal whether MnO<sub>2</sub> remained in the spot after testing from being combined with the reference solution. No compound was detected by the EDX on the sample with the tested spot of combined MnO<sub>2</sub> and reference oxides (plate 29). This suggests that both the MnO<sub>2</sub> and reference oxides flaked off the plate during testing. The sample from plate 28 (MnNiFeCo) when EDX/SEM tested was peculiar because there was additional sulfur detected on the plate that had most likely remained from the MnSO<sub>4</sub> solution used in drop casting, and did not evaporate off the plate to the degree expected when the plate was annealed.

Meanwhile, MnO<sub>2</sub> plates (plates 18, 22, 32) which were annealed at 600°C instead of at 500°C were more successful in adhering to the FTO plate. The majority of the spot did not flake off when wiped with a wet Kimwipe, and the spots had only slightly faded after being tested in HCl acid solution. Normally, when MnSO<sub>4</sub> solution is annealed, the SO<sub>x</sub> compound evaporates off the plate to create MnO<sub>2</sub>. Annealing the MnSO<sub>4</sub> solution at a higher temperature allowed the sulfur to evaporate more than when annealed at 500°C, causing more MnO<sub>2</sub> to be present as opposed to MnSO<sub>x</sub>. The less concentration of SO<sub>x</sub> present allowed the MnO<sub>2</sub> to better adhere to the FTO. This would explain why the other variations of preparing the MnO<sub>2</sub> plate were not successful—SO<sub>x</sub> concentrations in the MnO<sub>2</sub> were too high after annealing normally, even if the FTO plate was dried on a hot plate prior to annealing (plates 12-13).

## 5. Conclusion

The adhesion of MnO<sub>2</sub> to an FTO glass slide can be achieved by annealing the plate at 600°C for 5 h instead of 500°C for 5 h. Cobalt oxide (CoO<sub>2</sub>), on the other hand, is an active conductor for OER in basic solutions above pH 11, but its catalytic abilities significantly decrease after pH is lowered to ≤ 11. In the future, MnO<sub>2</sub> should be tested for catalytic abilities for OER on a wider scale of pHs when annealed at higher temperatures. CoO<sub>2</sub> should be tested for catalysis in pHs below 11 when combined with other acid stable metal oxides to stabilize it.

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## ABBREVIATIONS

FTO, fluorine-doped, tin oxide-coated glass; EDX/SEM, energy-dispersive x-ray spectroscopy/scanning electron microscopy; MnO<sub>2</sub>, manganese dioxide; CoO<sub>2</sub>, cobalt dioxide; OER, oxygen evolution reaction.

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