

Assessing the pH Stability of Cobalt and Manganese Oxide as a Oxygen Producing Catalyst in Acid

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ABSTRACT: These experiments sought to find oxygen evolving materials that would split water into oxygen. The subject of this research is based around executing the experiment (HARPOON Kit) using acid and acid stable catalysts. The experiment consists of assessing mixed metal oxides based on their ability to produce O₂ under a constant current. The catalyst array are submerged in an electrolyte solution, constant current is run through it, driving oxygen evolution reaction (OER); the spot will then potentially change color depending on the partial pressure of oxygen. The focus on acids is owing to that many compounds that are stable and work well in bases do not in acids, and vice-versa. Like there are certain successful catalysts within the base category, there will also be those respective to acids; more specifically, catalysts involving manganese (Mn) will be the most successful in promoting oxidization. When testing cobalt (Co) in a solution of NaOH/K(NO₃)₃ at a variety of different pH levels, the highest rate of success will be at a pH of 11-13.

1. INTRODUCTION: Solar water splitting is investigated in order to afford a method to produce a source of renewable fuel. Currently, approximately four-tenths of one percent of the total energy consumed in the United States is solar; this is due to the lack of efficacious sustainable energy resources. The appeal of using abundant resources, such a solar energy and water, is salient: they are easily accessible and ample. The efficient conversion of solar energy into stored chemical benefits technical, economic, environmental, and social fields. Finding oxygen evolving catalysts materials that when illuminated with light will split water into oxygen could further studies and research done in the solar energy and renewable fuel space.

Through CCI Solar, two kits have been made available for experimentation and development: SEAL (Solar Energy Activity Lab) and HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization). The SEAL Kit focuses on the discovery of metal oxide semiconductors that can split water into hydrogen and oxygen using sunlight, while the HARPOON

Kit aims to find oxygen evolving materials that will split water into oxygen. The HARPOON Kit senses oxygen by using a stainless steel mesh coated with an oxygen sensing fluorescent paint to indicate a reaction; the SEAL kit uses a LED pulsar array to illuminate up to 64 different materials in a single run. Research using the aforementioned kits has been conducted in a basic environment. While progress has been made in this area, specifically with compounds like bismuth vanadate, this leaves a vast region of study still uninvestigated: acids. There are many reasons as to why the usage of acids would be valid in experimentation with these kits--the HARPOON Kit, in particular. While some compounds may not be stable in bases, they may be stable in acid; vice-versa. While some compounds may be unsuccessful catalysts in bases, they may be effective in acid; vice-versa.

Therefore, this research is centered around using the HARPOON Kit with acid and acid stable catalysts. This allows for the discovery and usage of catalysts that have not been used with the SEAL or HARPOON Kits. One of the main catalysts being used is manganese oxide (MnO₂), for it has previously been proved to be stable in acid in certain conditions. Cobalt (Co) is tested at varying pH levels in order to quantify the success of catalysts in more acidic environments.

2. EXPERIMENTAL SECTION:

2.1 Preparing Solutions: The Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Co(C₂H₃O₂)₂·4H₂O, and MnO₄S·H₂O 20 mL solutions were prepared at 0.05 M concentration through a combination of their respective metal salts with deionized water. To create the iron standard reference solution, a combined NiFeCo solution at 0.005 M, Ni(NO₃)₂, Fe(NO₃)₃, and Co(C₂H₃O₂) solutions previously prepared were combined with 200 mL of deionized water. An NaOH solution was prepared by mixing, 2 g of pellets of NaOH and deionized water to make a 500 mL solution at 0.1 M concentration. The KOH solution, used for cleaning plates, was prepared by adding 38.6 g of of 30% KOH to deionized water to produce a 100 mL solution. 250 mL of 0.5 M H₂SO₄ or 350 mL of 1 M H₃PO₄ were used as acid electrolytes in some experiments instead of 0.1 M NaOH solution.. 350 mL of H₂SO₄ and 350 mL of H₃PO₄ were prepared by combining 4.7% H₂SO₄ and 85% H₃PO₄, respectively, with deionized water.

To test cobalt at different pHs, solutions of pH 13, 11, 9, and 1 were made and used as electrolyte solutions. pH 13 solution contained 0.1M NaOH. pH 11 solution contained 0.1M $K(NO_3)$ with 0.1M NaOH to adjust pH. 3.54g of $K(NO_3)$ was combined with deionized water to create a 300 mL solution. 10.5 mL of 0.1M NaOH was added to the $K(NO_3)$ solution to adjust pH to 11. The remaining 39.5 mL of deionized water was added to produce a 350 mL solution. The pH 9 solution was prepared in the same way, using 3.5 mL of 0.1M NaOH instead of 10.5 mL of 0.1M 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 38% HCl to deionized water to create a 400 mL solution at 0.1 M.

2.2 Preparing Samples: 3"×3" fluorine-doped, tin oxide-coated glass (FTO)³ plates were cleaned with isopropyl and the intended metal-oxide solution was drop casted onto the plate at 10 μ L per spot. The second to last row and corners were left blank, for a total of 52 spots of the desired metal-oxide solution. The reference solution of (1:2:2) NiFeCo was drop casted onto all corner spots except for the bottom left corner spot and the second to last row of spots. The plate number was engraved on the second to last row with a diamond-tipped scribe. Plates were annealed for 5 hours at 500°C in atmosphere unless otherwise noted. Plates created for cobalt oxide (CoO_2) tested in varying pHs (plates 19--23) were prepared as described above, but drop casted specifically with 0.05 M cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2$) solution.

2.3 HARPOON Kit: A 350 mL solution of 0.1 M NaOH in a glass bottle was purged for (at least) 30 minutes to be used as an electrolyte. For OER experiments in acid solutions, 350 mL of 0.5 M H_2SO_4 or 350 mL of 1 M H_3PO_4 solution was used as a substitute. The FTO plate was inserted into a plastic holder covered with a fluorescent-paint-coated mesh¹, which was then placed in a polystyrene plastic dish. Copper tape attached to the FTO plate and a graphite rod opposite it was used as an electrode and counter-electrode, respectively. Leads of a constant-current power supply were attached to the electrodes so 5 mA of current ran through the FTO plate. Two LED 400nm (purple) flashlights were attached to ring-stands and placed on either side of the dish. An Android camera phone was placed on top of a yellow filter, capturing images of the mesh (illuminated by the LED flashlights) every 30 seconds for 10 minutes. The 21 pictures taken were downloaded to a computer and analyzed with the ImageJ software using the HARPOON Kit plugin, which enhanced color data in order to recognize catalysts and the oxygen produced.

3.RESULTS:

3.1 Testing pH Stability of Cobalt Results: Using a .1 n solution of NaOH (350mL) at a pH of 13 and a Co spotted FTO plate resulted in an array of colorful spots; a successful combination. The aforementioned plate had no $K(NO_3)$ in it; the environment was already basic solely using sodium hydroxide. A .1m solution of NaOH and .1 $K(NO_3)$ at a pH level of 11 was then run through the HARPOON kit using a FTO plate with the same parameter; no spots appeared, despite the fact that the solution was purged for extra time and the FTO plate allowed to sit in the NaOH/ $K(NO_3)$ solution for an extra ten minutes. Testing cobalt plates with solutions under a pH level of twelve all returned no spots. However, a cobalt plate

submerged in a NaOH/ $K(NO_3)$ solution at pH 12 did result in clear, prominent spots. The pH 12 solution did contain $K(NO_3)$, but a significant amount less compared to any of the solutions that gradually become more acidic.

3.2 Manganese Oxide in the HARPOON Kit: FTO plates were spotted with a .05m solution of manganese sulfate (MnO_4S) and reference solution (1:2:2 NiFeCo) in each corner. Plates were then submerged, in the mesh contraption, in sulfuric acid. Much like previous tests in phosphoric acid, the spots would corrode when submerged in the acid. Further observation revealed that the manganese solution was not adhering strongly to the FTO plate, for it could very easily be washed off by deionized water; the acid, however, would only continue the corrosion of the spotted solution. Many methods were attempted in order to improve the adherence between the solution and FTO plate. Different methods of cleaning the FTO plate, before spotting, were attempted. Instead of using isopropanol (standard cleaning method), a KOH solution was used to clean the plate; this did not noticeably improve the adherence. In aggregate, a UV/Ozone ProCleaner Plus was used to "super clean" the plate; this, too, did not noticeably improve the adherence. The original reference solution, Ni-FeCo, was known to adhere well to the plate; therefore, it was added to the manganese sulfate solution in an attempt to bond the solution to the plate better. This also was not successful. The amount of time each plate was annealed, as well as the temperature, was also changed. They were annealed for 5 hours at 600°C. This created a larger coffee ring, which ultimately adhered better slightly, but still, no spots were achieved while running the manganese oxide and sulfuric acid with the HARPOON Kit.

4.DISCUSSION:

4.1 Manganese Adhesion: FTO plates spotted with MnO_2 were exceedingly difficult to derive results from, for the annealed manganese sulfate solution, now manganese oxide, would not sufficiently adhere to the plate. Flaking of the spots was observed in sulfuric acid, phosphoric acid, and hydrochloric acid. Upon further investigation, it was observed that the MnO_2 spots could be easily removed with a simple pass of deionized water and kimwipes. Therefore, it was not the acidic solution at fault for the removal of the spots, but of the adhesion between the manganese oxide spot and the FTO plate. Different methods were attempted in order to remedy this: KNO_3 cleaning, ozone cleaning (using UV/Ozone ProCleaner Plus), combinations with a successful iron standard solution, and annealing at different temperatures and time limits. Impurities on the plate were also present. After running samples through an SEM, sulfate was still present on the FTO plate, implying that the annealing process had not successfully created manganese oxide. With further testing, a successful adhering method could be developed in order to derive more accurate results involving the use of manganese oxide as an acid stable catalyst in the HARPOON Kit.

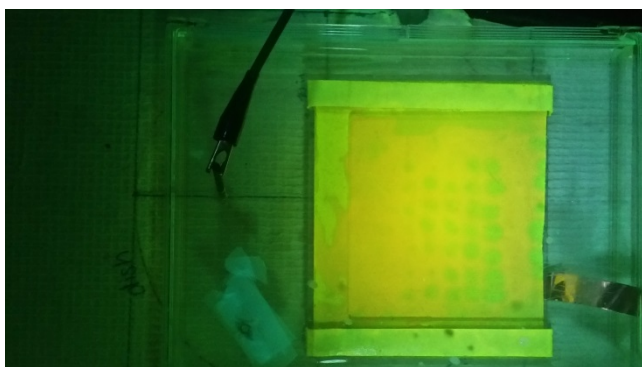
4.2 pH Levels and OER Drop-Off using Cobalt:

When experimenting with FTO plates spotted with cobalt in NaOH with a KNO_3 buffer, oxygen was produced only in pH levels of 12 and 13; as pH levels grew less basic, and gradually acidic, spots indicating OER were no longer present. It was originally thought that the KNO_3 buffer might be responsible for the lack of indicators, for the pH 13 solution contained

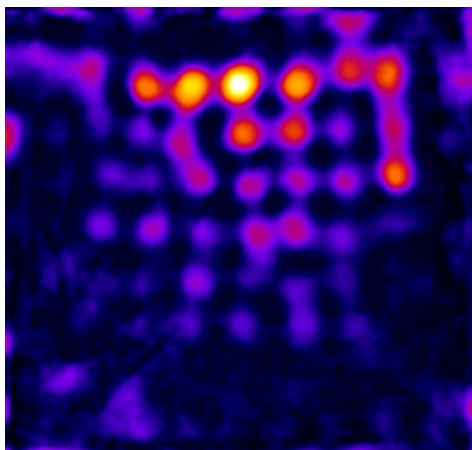
only NaOH. However, a cobalt plate in a pH 12 solution not containing KNO_3 was tested and produced indicators, proving that notion wrong. Aggregately, cobalt is not known to be acid stable, and no salient amount of oxygen was expected to be produced from these experiments.

5. Conclusion: The results we have gotten from both the manganese oxide tests, as well as the cobalt pH stability tests, do not support the idea of acid stable catalysts being effective in the HARPOON kit. The manganese oxide tests were successful in displaying the corrosive powers of sulfuric acid, with it disintegrating the manganese solution spots and gradually leaving one of our oxygen sensing meshes inefficacious. The cobalt pH stability tests supported the use of bases with the HARPOON Kit, for the best results were achieved at a pH level of 12 and above. In future work, a more acid stable mesh should be used in order to more properly identify potentially successful catalysts. Additionally, it would be beneficial to conduct most experiments with the HARPOON kit in a more basic environment.

FIGURES:



[1] Cobalt pH 12 plate halfway through testing; some indicator spots have appeared .



[2] A plate with spots indicating OER after being processed through ImageJ.

ACKNOWLEDGMENT

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SEAL LED Array Spotting Template:

http://solararmy.harpoonproject.org/wp-content/uploads/2014/11/LED_spotting_array.pdf

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