

The Effect of pH on the Photocatalytic Ability of Manganese Oxide and Cobalt Oxide

Kevin Tsao, Ellie Parisi, and Gemma Busoni

Abstract: The sun is a promising source of energy to meet rising energy demands, but an effective photocatalyst for the solar powered water splitting reaction is needed in order to make storage of this energy cost efficient. While most SEAL research, a collaborative attempt by many groups throughout the world to find photoelectrochemically active materials, is done on photocatalysts in basic environments, several important light absorbers, such as silicon, are not stable in bases. In addition, photocatalysts often behave differently depending on pH, making it especially important to understand the behavior of promising photocatalysts across in various pHs. Manganese and cobalt oxides have both shown promise as catalysts for the OER reaction. To determine the effect of pH on these catalysts, plates were made by drop casting these solutions on FTO plates and then annealing the plate in a kiln, before testing them in solutions of varying pH made of mixtures of sodium hydroxide, potassium nitrate, and hydrochloric acid. Results for photocatalytic activity were measured with the HARPOON kit, which uses fluorescent oxygen sensing paint and constant current running through the FTO plate to quantify the amount of oxygen that is released in the water splitting reaction. This research into cobalt oxide and manganese oxide demonstrated a significant drop off in the effectiveness of both catalysts as pH decreased with clear oxygen evolution at pH 13 and almost no oxygen evolution beyond pH 11.

1. Introduction

Solar energy, as the leading source of renewable energy, is vital to meeting or increasing energy demands, but there is still no effective and cost-efficient way to store the energy absorbed from the sun (1). The electrochemical splitting of water by solar energy into oxygen and hydrogen is a possible method to store the energy received into chemical fuels. However, the kinetically demanding oxygen evolution half reaction in the process is very inefficient because it must transfer 4 protons and electrons for each oxygen molecule (2). To make this reaction cost efficient, it is necessary to find an earth abundant catalyst that can greatly decrease the energy required for the reaction to proceed.

The photocatalysts discovered so far that have been seen to be effective for the oxidation evolution reaction are too expensive and rare to be used on a global scale (2). In addition, since many of the most promising large-scale solar energy absorbers, such as silicon, are unstable in base, it is important to investigate an oxygen evolution catalyst that is also stable in acid.

Through the use of the HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) kit developed by Professor Shannon Stahl of University of Wisconsin Madison with support from CCI (Centers for Chemical Innovation) Solar, potential catalysts can be tested to see if they assist in producing oxygen when a current is run through it. Compounds are spotted onto FTO (Fluorine doped Tin Oxide) plates using a

micropipette and then annealed in a kiln in order to make metal oxides. A constant current is run through the plate for 10 minutes while the plate is in a mesh covered with oxygen sensing fluorescent paint. While shining violet light on the mesh, pictures can be taken of the mesh to reveal the amount of oxygen produced, thus revealing the catalyst's ability to assist in the oxygen evolution reaction by measuring the final product of the half reaction (3).

In our study, the HARPOON kit was used to investigate the catalytic activity of metal oxides in various pHs. Manganese oxide is one promising photocatalyst to test in the experiments because manganese oxide is an earth abundant material that has seen some success as a photocatalyst (4). In addition, it has been seen that manganese oxide has demonstrated self-healing properties in acid while applying a current (2). Cobalt oxide has also been found to be a promising photocatalyst, as it has been found to release oxygen when current is applied in basic conditions. Due to its effectiveness in high pH solutions, it is important that we also test cobalt oxide in solutions with a lower pH in order to determine how pH effects cobalt oxide's photocatalytic activity. Research has also shown that when adsorbed on silicon nanoparticles, it becomes more stable, which had previously been an issue for cobalt oxide in acidic environments (5).

2. Experimental Section

2.1 Materials

The materials used were cobalt(II) acetate tetrahydrate, iron nitrate, nickel nitrate, potassium nitrate, sodium hydroxide, and hydrochloric acid. Spots were drop-cast on fluorine doped tin oxide (FTO) coated glass

plates. Isopropanol was used for wiping the FTO plates. Distilled water was used to rinse the glassware.

2.2 Solution Preparation

0.05 M cobalt acetate was prepared by pouring 0.31 g of cobalt acetate tetrahydrate into 25 mL of distilled water. The reference solution was created by using 0.05 molar cobalt nitrate, 0.05 molar iron nitrate, and 0.05 molar nickel nitrate, diluting them by adding distilled water and then mixing them together in a 1:2:2 ratio. Solutions of pH greater than 7 were made by adding sodium hydroxide to 0.1M potassium nitrate solution until desired pH was reached, while solutions of pH less than 7 were made by adding hydrochloric acid to 0.1M potassium nitrate.

2.3 Spotting on FTO Plates

Spots were made by taking an FTO plate and wiping the FTO side with a kimwipe which had been wetted with isopropanol to clean the surface. Then solutions were spotted on the 3 x 3 plate using a micropipette set to 10 microliters. The pattern used is shown below in figure 1. All plates were then fired in a kiln at 500° C for 5 hours at atmospheric temperature to turn the metal solutions into metal oxides. However, the manganese plates were then fired for an additional 3 hours at 600° C.

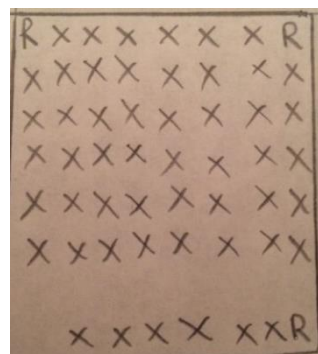


Figure 1. The pattern in which spots are drop casted on the plate, with R as reference and X as the solution being tested.

2.4 Data Collection

Data was collected using the HARPOON kit which uses the process shown below in figure 2. The FTO plate is placed in an electrolyte solution of desired pH that has been purged with nitrogen and stirred over a stir plate for 30 minutes to eliminate the oxygen and then has a current run through it. The current is created by attaching copper tape to the bottom left corner of the plate, placing a graphite rod in the solution, and connecting one wire from the constant current power supply to each. A stainless steel mesh that has been painted with oxygen sensing fluorescent paint that changes color when it senses oxygen is then placed over the plate. A 400 nm violet LED light is shined on the plate and pictures are taken with a camera every thirty seconds for 10 minutes while the current is running.

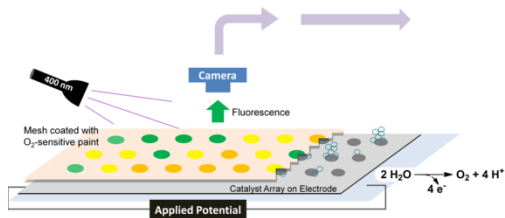


Figure 2(6). Diagram representing the process by which the HARPOON kit runs. 400 nm violet light is shined on the mesh coated with oxygen-sensitive paint. The camera then captures the difference in color of the fluorescent mesh representing oxygen produced.

2.5 Composition Analysis

Plates were broken to isolate a single spot after they were fired in order to determine the elemental composition of the spots. The isolated spots were then placed in the Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) was run, determining mole percentages of the elements in the solution.

2.6 Data Analysis

The pictures taken from the camera are uploaded to the computer and then analyzed using ImageJ. This program detects the differences in color between the pictures so that it can see where the green spots that symbolize oxygen on the mesh are, as opposed to the orange parts where there is no oxygen. By using the pictures, the program can then determine which parts saw the most oxygen production on the plate and combine all of the pictures taken into a single picture that shows the results of the experiment.

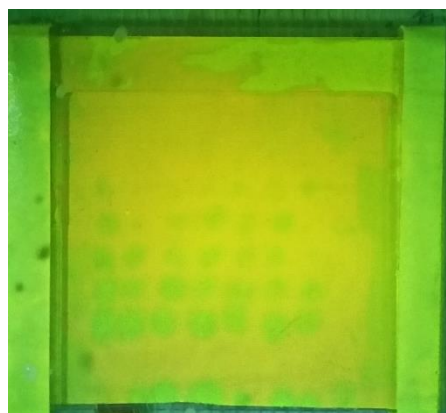


Figure 3. Results from running a 0.05M cobalt oxide plate in 0.1 M NaOH (pH 13).

3. Results

3.1 Effect of pH on Cobalt Oxide

A plate of 0.05M cobalt oxide was tested in a pH 13 solution consisting of 0.1M NaOH. After 10 minutes, it resulted in the picture in figure 3. Another plate of cobalt oxide made with the same method was then tested in a solution with pH 12, made with a NaOH and KNO₃ mixture resulting in the picture in figure 4. A third plate was tested in pH 11 made with 0.003M NaOH and 0.1 M KNO₃ resulting in the picture below in figure 5, with no clear spots appearing.

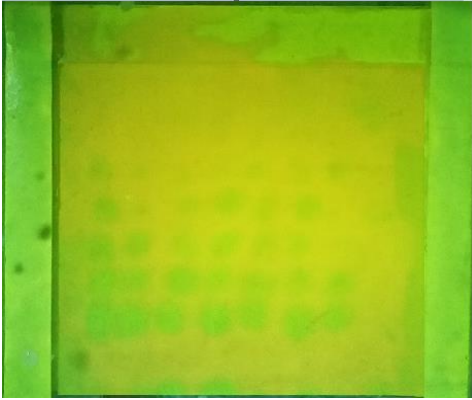


Figure 4. Results from running a 0.05M cobalt oxide plate in a pH 12 mixture of NaOH and KNO₃.



Figure 6. Results from running a 0.05M MnO₂ plate in 0.1M H₂SO₄(pH 2.5).



Figure 5. Results from running a 0.05M cobalt oxide plate in a pH 11 mixture of NaOH and KNO₃.

3.2 Manganese Oxide in Acid

A plate of 0.05M manganese oxide made from annealing manganese sulfate was placed in 0.1M sulfuric acid with a pH around 2.5. The results from the plate are shown below in figure 5, with no spots appearing after 10 minutes of testing. In addition, when the plate was pulled off, the spots could no longer be observed on the plates.

3.3 Manganese Oxide in EDX

Mixtures of 0.5M manganese sulfate, 0.05M cobalt nitrate, 0.05Miron nitrate, and 0.05M nickel nitrate were drop casted and fired in a kiln first for 5 hours at 500° C and then for 3 more hours at 600° C. Then they were tested using Energy-dispersive X-ray spectroscopy (EDX) in the scanning electron microscope (SEM) to find the percentage of the solution that each element makes up. The first test was taken from the coffee ring, while the second scan was further inside about halfway between the center and the coffee ring as shown in figure 7.

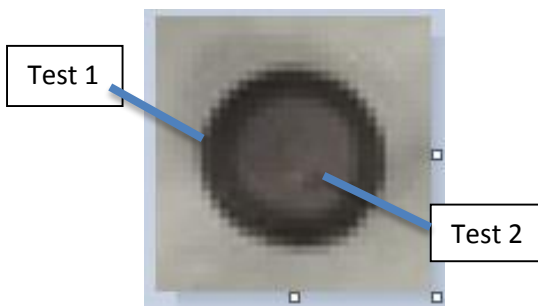


Figure 7: Locations on the spot where the EDX tests were taken

Element	Test 1 %	Test 2 %
O	74.84	66.97
S	10.50	11.13
Mn	13.16	17.94

Figure 8. Table with the atomic percentages of the main elements in the spots. Trace amounts of cobalt, tin, and iron are not shown in the table.

4. Discussion

4.1 Effect of pH on Cobalt Oxide

The results from the cobalt oxide experiments demonstrate that cobalt oxide's effectiveness as a photocatalyst rapidly decreases after pH 13, because the results demonstrate significant oxygen evolution at that pH, and in pH 12 solution, some oxygen was still produced, but when tests were done at pH 11, no oxygen appeared at all. This could either be a result of the pH change, or it could also be caused by the fact that potassium nitrate may have lowered the effectiveness of the electrolyte solution, even though the original purpose of the potassium nitrate in the solution had been to ensure that there was a similar level of electrolytes in the solution between experiments.

4.2 Manganese Oxide in Acid

The manganese oxide similarly saw poor results after testing in acid in the HARPOON kit. This is likely a result of most of the manganese oxide flaking of the plate during the experiment due to poor adhesion. It is also possible that manganese oxide has poor photocatalytic activity in acidic environments, or the HARPOON kit is ineffective with acids, since the fluorescent paint appeared to flake off of the mesh when tests were done using acid electrolytes.

4.3 Manganese Oxide in EDX

From the EDX results, it appears that only about 40% of the manganese sulfate was converted to manganese oxide, because the atomic percentage of sulfate is about 60% of the atomic percentage of manganese, implying that not all of the sulfur has left the spot, unlike our prediction that sulfur would leave the plate as gas. This probably occurred because the plates were not fired at a high enough temperature or for long enough for all of the manganese sulfate to react and convert to manganese oxide. Since manganese sulfate is soluble in water, likely the parts of the solution that remained as manganese sulfate immediately dissolved, which may have resulted in the poor results for the manganese oxide solutions in acidic environments.

5. Conclusion

Testing on the photocatalytic activity of cobalt across varying pHs demonstrate poor effectiveness at lower pH levels. Our results show that below pH 13, the effectiveness rapidly drops, with almost no oxygen being produced by pH 11. Our experiments also demonstrate a method by which manganese sulfate can be used to make manganese oxide effectively through drop casting and annealing in a kiln. This result shows that only by heating at 600°C or higher for about five hours will the solution adhere to the plate. This change in the annealing process may also have resulted in more manganese sulfate reacting and producing manganese oxide, thus assisting adherence.

References

(1) Lewis, N. S.; Nocera, D. G. Proc. Natl. Acad. Sci. U.S.A. 2007, 104, 20142–20142.

(2) Huynh, M.; Bediako, D. K.; Nocera, D. G. *J. Am. Chem. Soc.* 2014, 136, 6002–6010.

(3) HARPOON | The Solar Army.
<http://thesolararmy.org/harpoon/> (accessed July 30, 2015).

(4) H. Y. Su, Y. Gorlin, I. C. Man, F. Calle-Vallejo, J. K. Norskov, T. F. Jaramillo and J. Rossmeisl, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14010–14022

(5) Zidki, T.; Zhang, L.; Shafirovich, V.; Lyman, S. V. *J. Am. Chem. Soc.* 2012, 134, 14275.

(6) Experiment | The Solar Army.
<http://thesolararmy.org/harpoon/experiment/>
(accessed July 25, 2015).