SEARCHING FOR AN EFFECTIVE WATER SPLITTING CATALYST

Instructor Notes and Next Generation Science Standard (NGSS) Alignment

Objective

To test the effectiveness of a variety of synthesized mixed metal oxides at catalytically splitting water to produce oxygen gas under the appropriate electrochemical conditions.

Introduction

One of the holy grails of 21st century chemistry is to convert solar energy to chemical potential energy by using solar radiation to generate fuels that can then be stored and used when needed. One approach is to use solar energy to drive the nonspontaneous decomposition of water to produce hydrogen and oxygen gases. Hydrogen gas as a fuel has several advantages over fossil fuels in common use today such as gasoline, in that when it burns, the product of combustion is simply water vapor. The combustion of fossil fuels invariably produces carbon dioxide, a greenhouse gas strongly implicated in global warming and ocean acidification. Apart from the environmental damage caused by fossil fuel usage, transport, and extraction, they are essentially a non-renewable energy source and as stocks dwindle their price will ultimately rise. Finding a less expensive and environmentally safer alternative is a serious challenge, but if successful, promises to transform the world we live in.

The National Science Foundation (NSF) funded Chemical Center for Innovation in Solar Fuels (CCI Solar) is playing a leading role in fundamental research in this area, which has been addressing basic science challenges in solar fuel production since its inception in 2005 as a Phase I "Chemical Bonding Center". The goal of the Center is to develop the fundamental knowledge necessary for large-scale production of solar fuels, which targets critical basic-science challenges facing efficient, solar-driven conversion of water to H_2 and O_2, such as the fundamental processes of light absorption and charge transport. The Center has a significant informal science education (outreach/broader impacts) component called the Solar Army, which encompasses several educational projects related to solar energy conversion, one of which is called HARPOON.

The Solar Army wants to capture the energy in sunlight and use it to split water and yield a chemical fuel, hydrogen. We will need two great catalysts to do this: one to oxidize water to oxygen; the other to reduce protons to hydrogen. The oxidation of water to O_2 is particularly challenging and remains one of the bottlenecks of solar fuel production. This is where mixed metal oxides come in to play.

The HARPOON project goal is to discover inexpensive catalytic materials (which we hypothesize will be mixed-metal oxides, similar to what nature uses) to aid in the decomposition of water. More on the Solar Army and the HARPOON project can be found at the following sites:

http://ccisolar.caltech.edu/

http://thesolararmy.org/

The search for an efficient metal oxide catalyst can be divided into three steps:

Part 1: Mixing different quantities of metal nitrate solutions that are then spotted onto a glass electrode and fired to decompose the metal nitrates into mixed metal oxides.

Part 2: Analysis of the prepared electrode under electrochemical conditions that decompose water and detect any oxygen gas produced.

Part 3: Analysis of the data that quantifies the amount of oxygen produced using ImageJ software, and compares the effectiveness of the metal oxide catalysts..

Information on the materials required to run an entire HARPOON experiment (Part 1-3) is described below and can also be found in the HARPOON Manual.

Reagent and Materials List

The following information provides a quick checklist of materials and reagents required for a class to perform the experiment. Quantities of each solution required will depend on the number of students in the class.

What's included in each kit:

- Acrylic electrode holder (1)
- Two large rubber bands
- Stainless steel mesh coated with fluorescent paint on one side (2)
- Power supply (1)
- 400 nm LED flashlight (1)
- Yellow filter (1)
- Graphite counter electrode (1)
- FTO-coated glass electrodes, 3 × 3” (4)
- Plastic container with lid (1)

Required, but not included in kit:
(Information about purchasing these items can be found at http://thesolararmy.org/harpoon/)

- 0.005 M Metal nitrate, acetate or chloride salt solutions
- 0.1 M NaOH solution
- Methanol, acetone, or ethanol
- Volumetric glassware
- Multimeter
- Syringes or adjustable micropipets 1μL or 10 μL, and 1 mL
- Digital camera or camera phone
- Kiln or furnace that heats to at least 500 °C
- Inert gas (N_2 or Ar)
- Conductive copper tape
- Five AA batteries
- Cardboard box, such as one that holds reams of copier paper
- Computer and Software: Spreadsheet program (such as Excel or Libre Office)
- ImageJ (download available at http://rsbweb.nih.gov/ij/download.html)

Reagents

0.1 M NaOH [CAS: 95077-05-7]

To prepare 1 L of this solution, (enough to run two electrolysis reactions with two separate kits) dissolve 4.00 g of NaOH(s) in 100 mL of DI or distilled water in a 250 mL glass beaker, quantitatively transfer to a 1 L plastic bottle, and bring to a final volume of 1 L. If protected from excessive exposure to air, solutions are stable for months.

Caution: NaOH(s) is a strong base and the pellets are caustic and hygroscopic. Gloves should be worn when measuring out the solid reagent and any spills immediately dealt with according to the lab protocol.

0.005 M Metal Nitrate Solutions

To prepare 100 mL of these solutions, weigh out the required amount of metal nitrate, dissolve in DI or distilled water. Additionally, solutions can also be created containing 0.9 % by volume of glycerol (glycerin) [CAS: 8043-29-6] to aid in the formation of uniform circular spots upon firing. If the solutions are not forming uniform spots (but instead you might see a ring or multiple colors in one spot), add 9 mL of glycerol (glycerin – available from most grocery stores) with the required amount of metal nitrate and bring the final volume of 100 mL with DI or distilled water. Volumetric flasks can be used, but are not essential.

For example, to prepare 100 mL 0.005 M $Fe(NO_3)_3$ [0.005 M Fe^{3+}(aq)] dissolve 0.0005 moles/0.20 g of $Fe(NO_3)_3 \cdot 9H_2O(s)$ [CAS: 7782-61-8] in DI water, add the 9 mL of glycerol, and make up to a final volume of 100 mL. The stability of each metal nitrate solution depends on the metal ion and will vary from days to months. Before using a metal nitrate solution, it should be checked to ensure that it is clear and free of floating particles indicating decomposition.

Some metal cations are prone to precipitation. To help stabilize solutions of these metals, 5 – 10 mL of nitric acid can be included in place of some of the water when preparing 100 mL of the 0.005 M solution. This step is not required for many metal salts, but should be included if gallium nitrate, cerium nitrate, or bismuth nitrate are used.

The reference solution is more conveniently made up before the experiment is undertaken by the class as each student requires this solution and if from the same source, will give consistent results. The reference solution is a mixture of Ni:Fe:Co nitrates in a 2:4:4 volume ratio. 100 mL can be prepared by combining 20 mL:40: mL:40mL respectively of the 0.005 M metal nitrate solutions.

Disposal of excess metal nitrate solutions should be in accordance with all local, state, and federal ordinances.

Alignment of HARPOON with NGSS Standards

NGSS #	STANDARD DESCRITPION	Alignment with HARPOON
HS-PS1-6	*Refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.*	In the clarification statement, it says “Examples of designs could include different ways to increase product formation including adding reactants or removing products.” Different combinations of metal oxides are attempted by the students to find the best material. Students must balance the cost of the material, relative abundance, and overall activity.

HS-PS3-3	*Design, build, and refine a device that works within given constraints to convert one form of energy into another form of energy.*	In the clarification statement, it says “Examples of devices could include Rube Goldberg devices, wind turbines, solar cells, solar ovens, and generators. Examples of constraints could include use of renewable energy forms and efficiency.” Students being by creating different model systems of mixed metal oxide semiconductors. These systems are constrained by factors such as abundance, activity, cost, light absorbing capability, ease of use, and stability.
HS-ESS3-2	*Evaluate competing design solutions for developing, managing, and utilizing energy and mineral resources based on cost-benefit ratios.*	The students will be able to compare their current materials to ones in the database or the internal standard, while evaluating the usage of different metal precursors based off of their earth abundance. Additionally, the method of water splitting can be compared to other methods such as PV technology.
HS-ESS3-4	*Evaluate or refine a technological solution that reduces impacts of human activities on natural systems.*	The projects goals to produce oxygen and hydrogen from sunlight using an inexpensive, earth abundant material providing another option for renewable energy. The students will be able justify their choices of precursors vs. earth abundance and compare the current results to the results within the projects. Also, students will able to hypothesize ways to make the projects work on a large scale, then compare their idea to the current technologies and how those technologies can impact natural systems.