HARPOON Experiment Prelab Assignment

Name: _______________

Each student/group will pick three metals to test. Your instructor will tell you which metals are available. You can pick any three of these you would like, but at least one of the metals must be able to have more than one oxidation state (for metal cations, this is the same as charge) when it forms compounds with other elements. As a reminder, alkali metals and alkaline earth metals usually only have one oxidation state in compounds, +1 and +2, respectively, but many transition metals can have different oxidation states in compounds. For instance, chromium can have charges between Cr^{1+} to Cr^{6+}.

Here is a list of the metal precursor salts you can choose from:

Instructor Note: Below is a selection of relatively inexpensive metal nitrate salts that can be used in the experiment. Let your students know which metals are available for them to choose from. It is also possible to use acetate and chloride salts, but these have not been explored as thoroughly. Sensible choices of metal nitrates should be relatively inexpensive and nontoxic. The solutions used are relatively dilute, and, as only ~15 mL of solution is needed per student (each student will need 5 mL of solution for each of the three metals selected), the amount of consumables used in the lab exercise is small. The metal nitrate solutions are all 0.0050 M with respect to the metal cation. If available, the metal solutions can be prepared with water that contains glycerol (9 % by volume). The inclusion of glycerol promotes even evaporation of the aliquots and produces more uniform catalyst spots, but it is not crucial to running the experiment for educational purposes.

Nickel, iron, and cobalt nitrates are required to prepare the reference used in this experiment. A 2:4:4 ratio (by volume) of these nitrate salts produces an active metal oxide catalyst.

copper(II) nitrate	cobalt(II) nitrate	cerium(III) nitrate*
calcium nitrate	barium nitrate	bismuth nitrate*
aluminum nitrate	iron(III) nitrate	magnesium nitrate
nickel(II) nitrate	zinc nitrate	chromium(III) nitrate
strontium nitrate	gallium nitrate*	manganese(II) nitrate

Instructor note: For the metal salts marked with an asterisk, it is recommended that HNO_3 is included in the solution to help prevent precipitation.

1. List your choices below, and put an asterisk (*) beside the metal(s) that can have more than one oxidation state in a compound.

   Metal 1: ___Example: copper* (copper (II) nitrate solution)_________

   Metal 2: ___Example: strontium (strontium nitrate solution)_________

   Metal 3: ___Example: aluminum (aluminum nitrate solution)_________

2. Our goal will be to identify which mixtures of metals can be used to produce mixed-metal oxides that are promising water oxidation catalysts. There are already effective catalysts that are made from iridium and ruthenium oxides. To understand why these catalysts could never be used on a global scale for widespread solar energy conversion, fill in the table below. Also, include the three metals that you chose.

Metal	Abundance of metal in the earth's crust (ppm)	Cost of the metal per gram (dollars/g)	Cost of the metal per mole (calculate this from dollars/g)
Iridium			
Ruthenium			
Metal 1: Cu			
Metal 2: Sr			
Metal 3: Al			

Where did you find this information? (It's ok to cite a website, as long as it seems reasonable)
Sources:

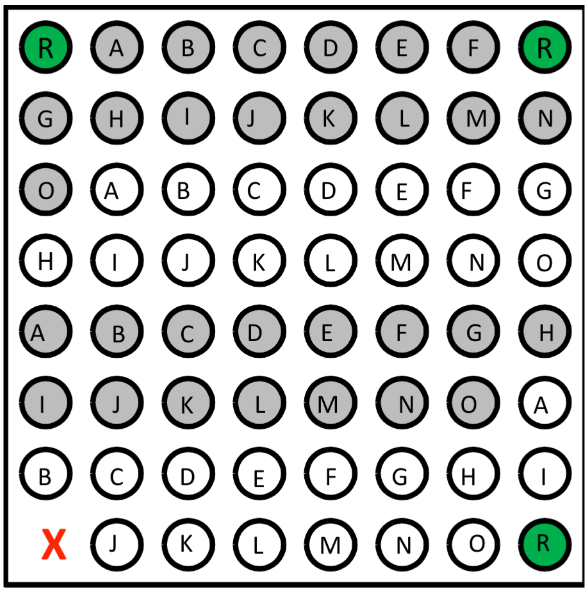
3. Complete this **Experiment Design Table** before coming to Week 1 of the HARPOON Lab.

0.005 M metal nitrate salts will be provided for you. Assume you want to make 1 mL of each of the mixed metal salt solution (A – O) and that you have an adjustable automatic pipet that can deliver volumes between 0 and 1000 μL.

		Composition		
Ratio M1:M2:M3	**Solution**	Metal 1 (M1): ___Cu____ Volume (μL) of the M1 nitrate solution	Metal 2 (M2): ____Sr____ Volume (μL) of M2 nitrate solution	Metal 3 (M3): ____Al____ Volume (μL) of M3 nitrate solution
100:0:0	A	1000 μL	0 μL	0 μL
75:25:0	B	750 μL	250 μL	0 μL
75:0:25	C	750 μL	0 μL	250 μL
50:50:0	D	500 μL	500 μL	0 μL
50:25:25	E	500 μL	250 μL	250 μL
50:0:50	F	500 μL	0 μL	500 μL
25:75:0	G	250 μL	750 μL	0 μL
25:50:25	H	250 μL	500 μL	250 μL
25:25:50	I	250 μL	250 μL	500 μL
25:0:75	J	250 μL	0 μL	750 μL
0:100:0	K	0 μL	1000 μL	0 μL
0:75:25	L	0 μL	750 μL	250 μL
0:50:50	M	0 μL	500 μL	500 μL
0:25:75	N	0 μL	250 μL	750 μL
0:0:100	O	0 μL	0 μL	1000 μL
Ref.	Ni:Fe:Co 20:40:40	←This solution will be prepared for you		

Spotting template: Three metal electrode

Print this page and bring it to lab



Preparing the electrode array:

1. Determine which side of the electrode is coated with FTO
2. Rinse the electrode with water, then methanol.
3. Print this page, and place your electrode, FTO-side-up, on top of the square above.
4. Pipet 1 μL aliquots of the indicated solution onto the electrode at of the 63 positions
5. Evaporate the solvent on a hotplate.
6. Heat the electrode at 500 °C for 6 h to convert the metal nitrates into metal oxides.

<u>Instructor Note:</u> Instructors may wish to select specific Pre Laboratory questions from the list below depending on where this laboratory experiment is integrated into the chemistry curriculum. Select a sampling of pre-laboratory assignment questions for your students to answer.

Additional Pre Laboratory Questions

Information that will allow you to answer the questions below can be found in your textbook, experiment handouts, and at the following websites:

http://ccisolar.caltech.edu/webpage/95
http://thesolararmy.org/#

Experimental Overview Questions

1. Explain the importance of sustainable energy sources from water and sunlight.

   Enough sunlight falls on the earth in one hour to meet the energy needs of our planet for a year. If the energy from sunlight can be used to generate a chemical fuel, we will no longer need to burn fossil fuels. Energy from the sun can be used to split water into O_2 and H_2. The H_2 can be used as a chemical fuel, and the O_2 is a benign byproduct.

2. Iridium and ruthenium make good electrocatalysts, but they are expensive and not earth-abundant.
   a. Compare the abundance of these elements with three of the metals that are available to use for making your electrocatalysts. (The United States Geological Services has comparisons of this data.) Include references.
   b. Compare costs of the pure elements you compared in part a by gram. Include references.

3. Explain the importance of finding an effective, inexpensive, and earth-abundant electrocatalyst.

   Water oxidation is a challenging reaction that requires a catalyst. In order for solar water splitting to become economically viable source of H_2, all of the materials that are used must be available in large quantities and be relatively inexpensive.

4. There are two half reactions that comprise the splitting of water into hydrogen and oxygen. Write the two half reactions.

   Water splitting: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
   Oxidation half reaction: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
   Reduction half reaction: $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

5. Write the half reaction that is catalyzed in the HARPOON experiment.
   Oxidation half reaction: $2H_2O(l) \rightarrow O_2(g) + 4H+(aq) + 4e-$

6. Why is it important to find catalysts for the reaction that splits water into hydrogen and oxygen?

The water splitting reaction is a redox reaction that involves two half reactions. Both reactions require a catalyst in order to use sunlight to drive the half reactions at useful rates.

7. The efficient and economical conversion of solar energy into stored chemical fuel is described as one of the "holy grails" of chemistry. Explain.

It is estimated that the amount of convertible solar energy during a solar day reaching the Earth is 10^{18} kJ. The amount of energy utilized by humans is also about 10^{18} kJ/day, with most of this generated by the burning of fossil fuels. Being able to harness and store the convertible solar energy would end our reliance on dwindling fossil fuel reserves, with much benefit for the environment.

8. Briefly explain the scientific goals of the HARPOON project.

The HARPOON project (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) seeks to find inexpensive mixed metal oxide systems that are effective catalysts that will speed up the decomposition of water to oxygen gas in an alkaline (basic) environment.

9. The approach to finding a mixed metal oxide catalyst in this project is described as a "combinatorial" approach where many mixed metal oxides are synthesized and tested. As almost every element in the Periodic Table forms an oxide, there are literally millions of possible combinations. Why don't chemists simply design an oxide system that would be effective?

The mechanism of water oxidation is not sufficiently well understood to allow for the intentional chemical design of an effective catalyst.

10. What are some practical properties of the mixed metal oxide systems that would make them potential candidates as an effective catalyst?

The metal oxide mixtures need to be chemically stable under the reaction conditions, e.g., they should not dissolve in the basic solution where the electrolysis takes place. The metal oxides should also be relatively inexpensive as to be practical they would be needed in large quantities, and preferably nontoxic. They would also have to be effective catalysts!

11. Write an equation that describes the breakdown of water to its constituent elements and determine the ΔG^o and K and for the reaction at 25 °C. State the spontaneity of this reaction and indicate if it is reactant or product favored.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

$$\Delta G^o_{298} = \Sigma\nu\Delta G^o_f(\text{products})\text{-}\Sigma\nu\Delta G^o_f(\text{reactants})$$

$$\Delta G^o_{298} = \left[1\text{ mole}\left(0\,\frac{\text{kJ}}{\text{mol}}\right) + 1\text{ mole}\left(0\,\frac{\text{kJ}}{\text{mol}}\right)\right] - \left[1\text{ mole}\left(-285.8\,\frac{\text{kJ}}{\text{mol}}\right)\right]$$

= 285.8 kJ

$$\Delta G^o_{298} = -RTlnK, \quad 285.8\times10^3 = -8.314\times298.15lnK, \quad K = 8.5\times10^{-51}$$

This is a non-spontaneous reaction and very reactant favored.

12. Why don't scientists simply employ fossil fuels to convert water to its elements?

The goal is to replace fossil fuels. Using them to covert water to hydrogen and oxygen gas would be less efficient than simply burning them to produce energy in the first place.

13. The electrochemical oxidation process employed to test the metal oxide catalysts will be the production of oxygen from water taking place in an electrochemical cell. Write down the half equation for this reaction indicating the standard potential for the reaction you have written, and whether it would take place at the anode or cathode.

Oxidation: $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^o = -1.23\ V$

As this is an oxidation half reaction it will take place at the anode.

14. The solution actually used in this experiment will be 0.10 M NaOH(aq). Qualitatively explain how this solution will enhance the oxidation process.
(Hint: Le Chatelier's Principle)

The OH^- present in the basic NaOH solution will react with the H^+ produced further driving the reaction towards the products and resulting in the more favorable thermodynamic production of oxygen.

Experimental Details Questions

1. Draw a schematic of the HARPOON experimental set up for collecting data. Include in your drawing the following: camera, flashlight, mesh, array, graphite electrode, NaOH solution, copper tape, and power supply.

   See Question 6 below.

2. Explain the purpose of each of the following for the experiment: camera, flashlight, mesh, array, graphite electrode, NaOH solution, copper tape electrode, and power supply.

- *Camera – Used to take photos that record the fluorescence from the paint. These images can be used to determine the best catalyst on the array*
- *Flashlight – Provides the 400 nm light that excites the fluorescent molecules in the O_2 sensitive paint*
- *Mesh – The mesh is coated with an O_2-sensitive paint that can be used to detect O_2 formed by the different catalysts*
- *Array – The array on the FTO-coated glass electrode contains the mixed metal oxide materials that are tested as water oxidation catalysts*
- *Graphite electrode – This is the counter electrode. Since every electrochemical cell must contain both an anode and a cathode, and the FTO electrode is the anode, the graphite rod is the cathode*
- *NaOH solution – This solution is called the electrolyte solution, and it contains ions (Na^+ and OH^-) needed to transport charge through the solution in the electrochemical cell. Also, the 0.1 M NaOH is used to keep the pH constant (pH = 13).*
- *Copper tape – This tape is conductive and used to make an electrical connection between the glass electrode and the power supply*
- *Power supply – The water splitting reaction (in which water oxidation is the oxidation half reaction) is not a spontaneous reaction. A potential must be applied to facilitate the reaction.*

3. What type of chemical reaction is catalyzed?
   The oxidation of water is the reaction that is catalyzed in the HARPOON experiment. The chemical equation for this half reaction is:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

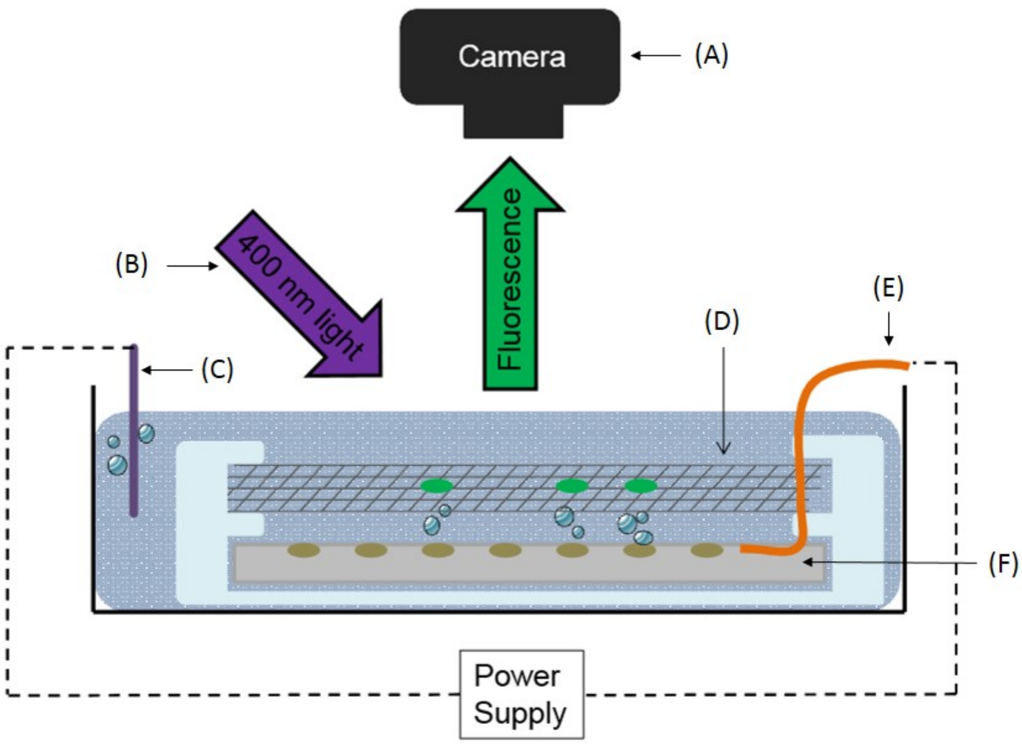
4. Where should the flashlight shine during the experiment?

   The flashlight should illuminate the paint side of the mesh. The 400 nm light from the flashlight causes the paint to fluoresce red (only in the absence of O_2) and green (in the absence and presence of O_2).

5. On the mesh, what do the green and orange colors indicate?

The green fluorescence is observed whenever the paint is illuminated with 400 nm light. The red fluorescence is only observed in the absence of O_2. When O_2 is present, the red fluorescence is quenched. This O_2 could come from the air or be produced at the catalyst

6. Label each item in the schematic drawing of the experimental set-up and describe its purpose.



Label	Purpose
(A) Digital camera or camera phone	Take photos that record the fluorescence from the paint
(B) 400 nm light from the LED flashlight	The light excites the fluorescent molecules in the O_2 sensitive paint
(C) Graphite rod (counter electrode)	Serves as the cathode in the electrochemical cell
(D) Steel mesh with O_2 sensitive paint	Used to detect O_2 produced by the catalysts
(E) Conductive copper tape	Used to make an electrical connection between the glass electrode and the power supply
(F) *FTO-coated glass electrode with catalyst array*	*Anode of the electrochemical cell. Water oxidation occurs at the good catalysts and O_2 is produced*