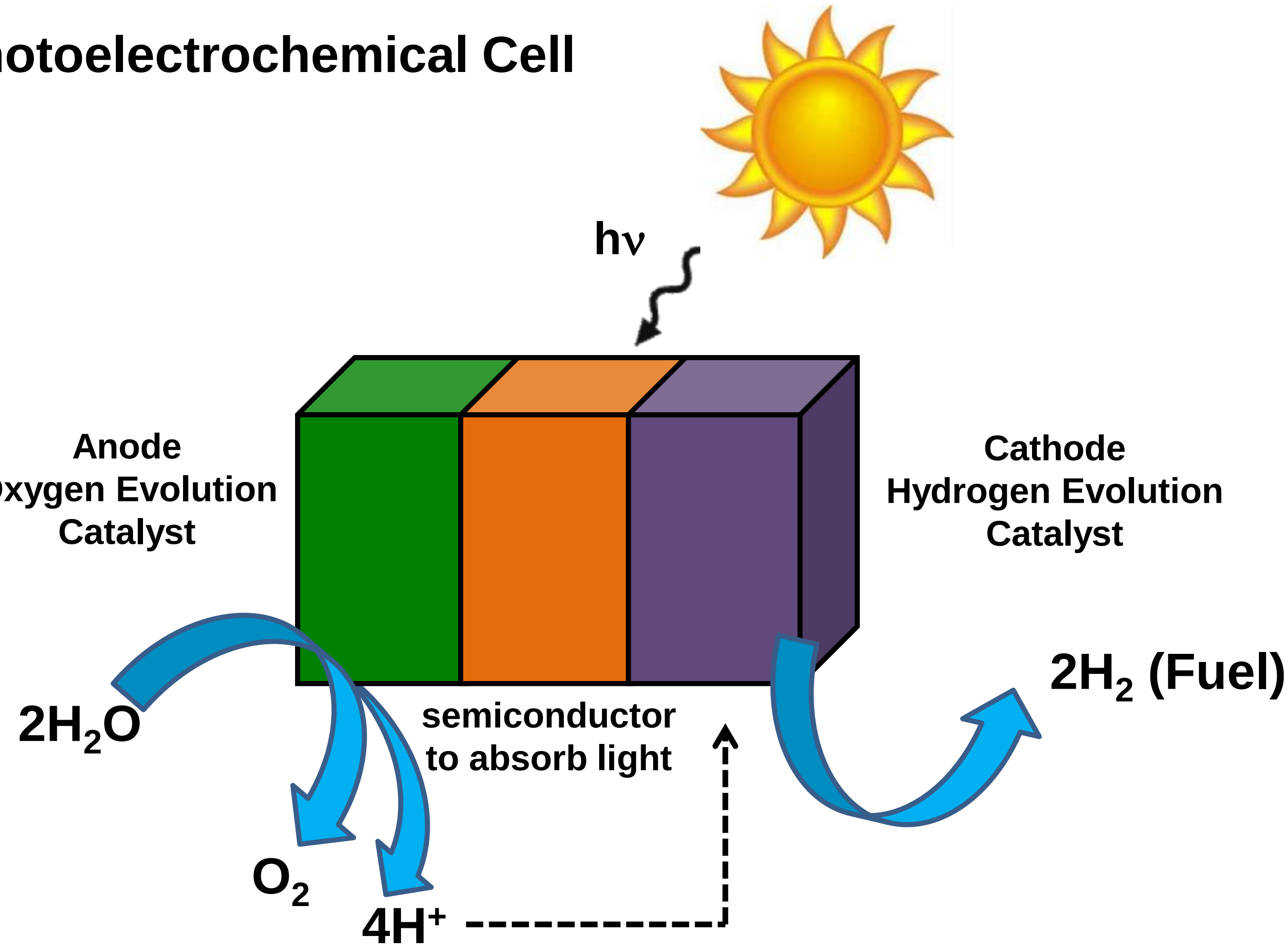
HARPOON

Heterogeneous **A**nodes **R**apidly **P**erused for **O_2** **O**verpotential **N**eutralization

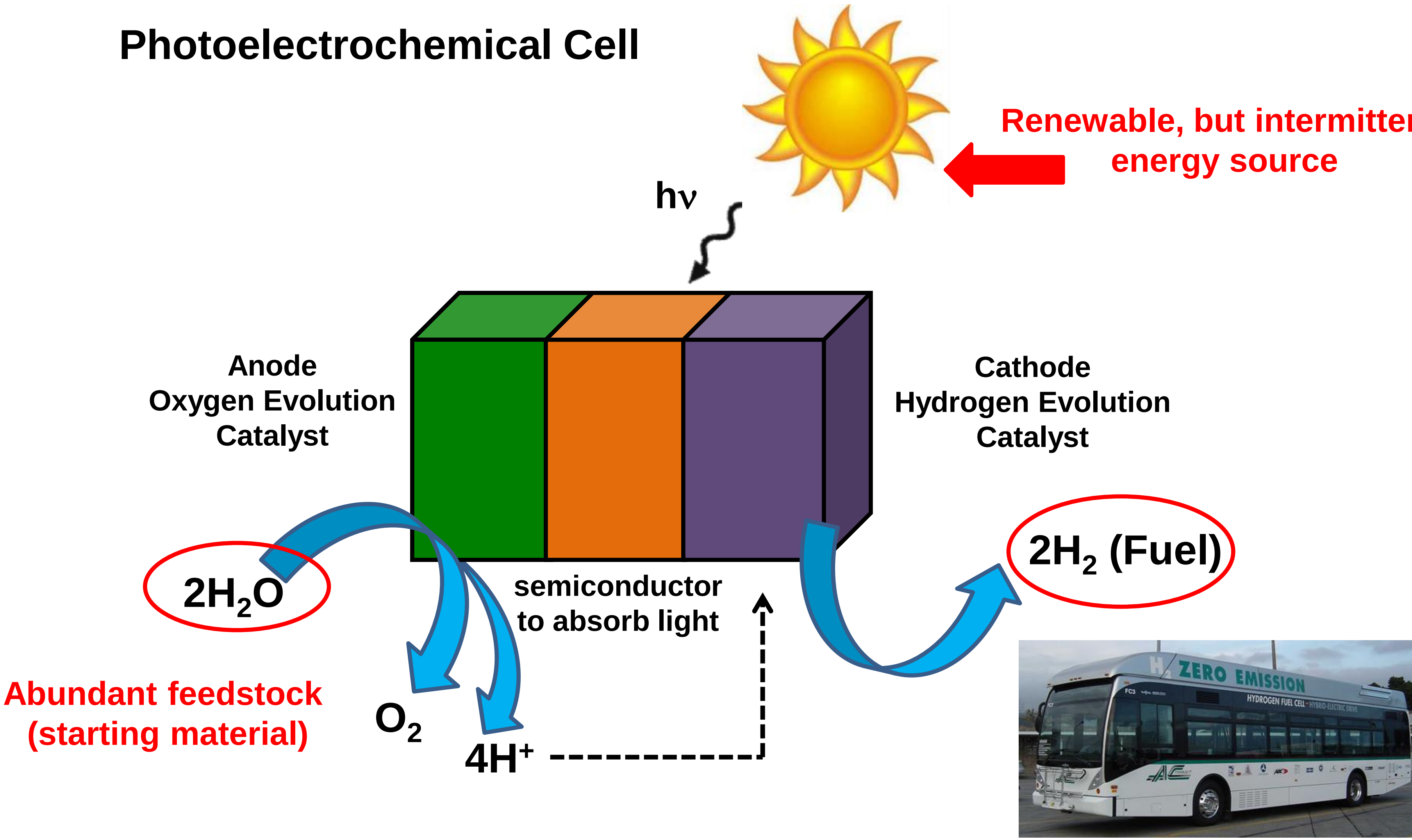
Photoelectrochemical Cell



- 2001 rate of energy consumption of 13.5 TW (86% from fossil fuels)
- 2050 consumption rate is projected to be 27 TW
- Solar energy is abundant and can yield carbon-neutral fuels

Lewis, N.S.; Nocera, D.G. *Proc. Natl. Acad. Sci.* **2006**, 103, 15729.

Photoelectrochemical Cell



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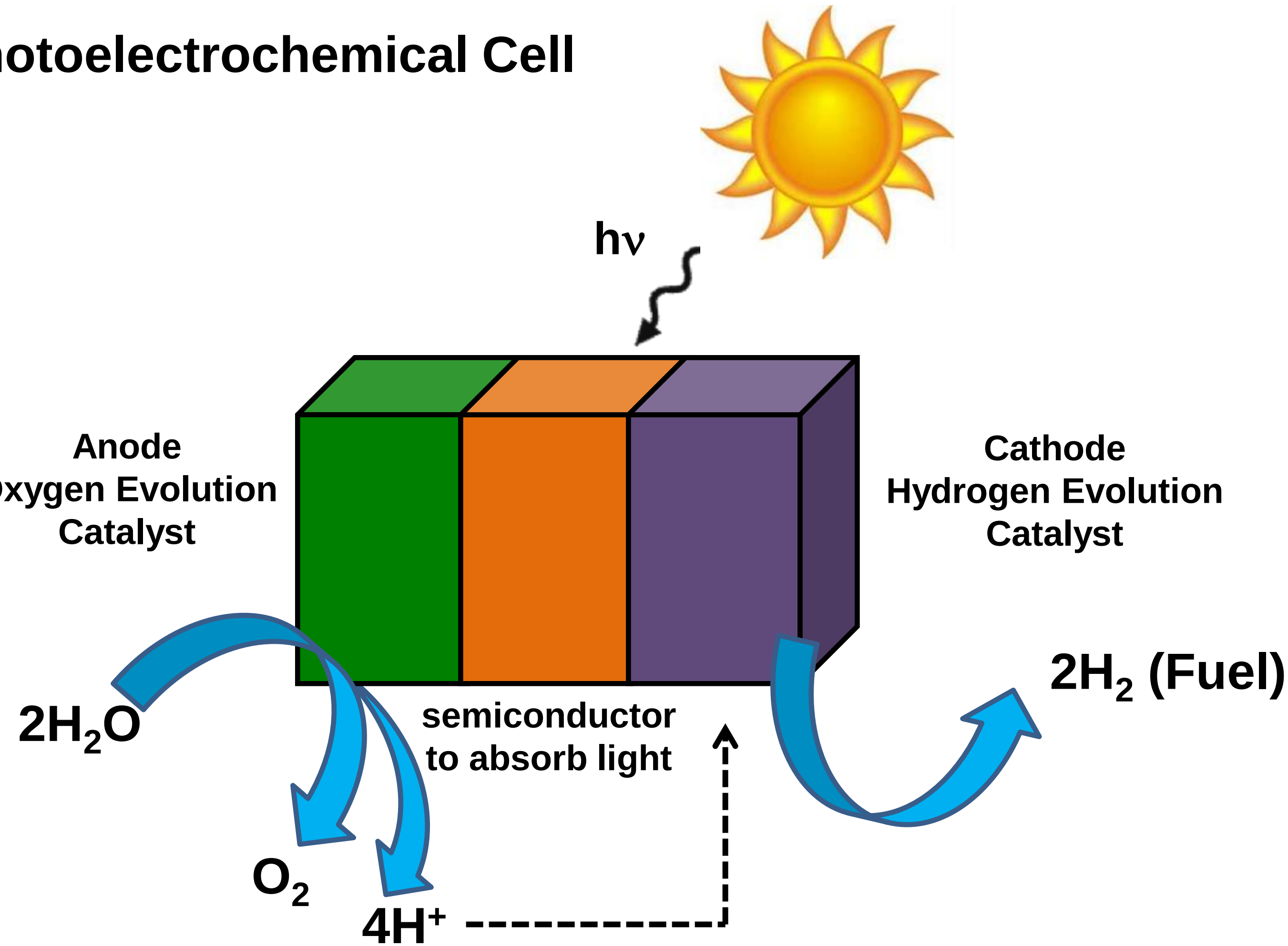

Water oxidation half reaction (anode):	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
Reduction half reaction (cathode):	$4H^+ + 4e^- \rightarrow 2H_2$
Overall water splitting reaction:	$2H_2O \rightarrow O_2 + 2H_2$

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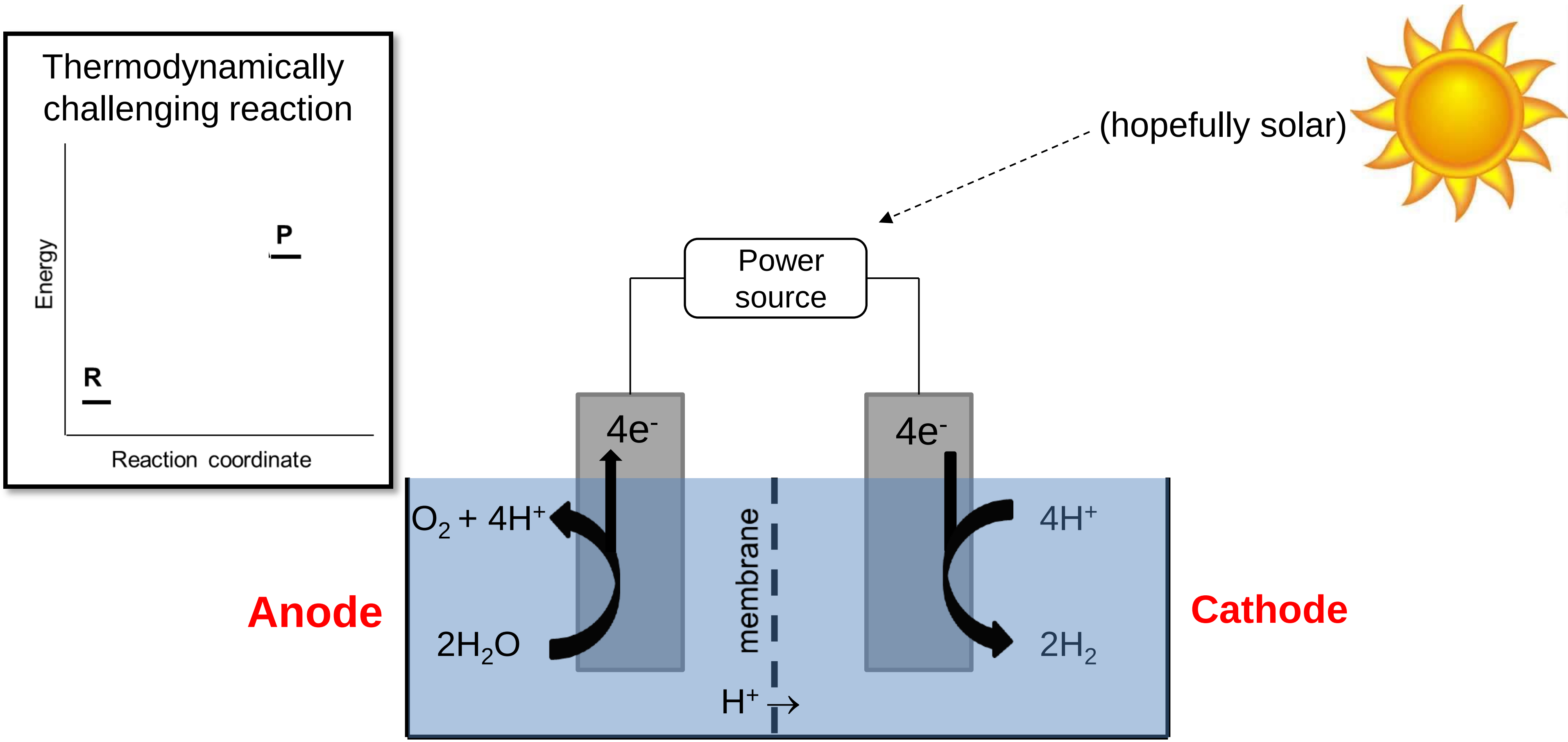


O_2 evolution rxn (OER):

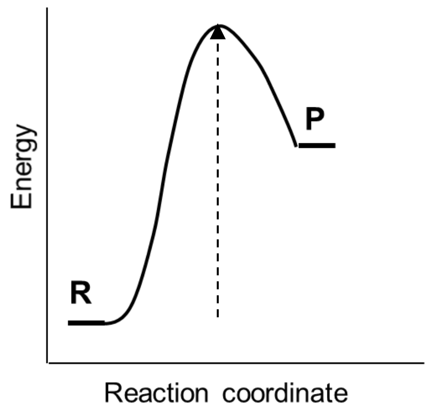
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

H_2 evolution rxn (HER):

$4H^+ + 4e^- \rightarrow 2H_2$

Overall water splitting reaction: $2H_2O \rightarrow O_2 + 2H_2$ $E_{cell} = -1.23\ V$

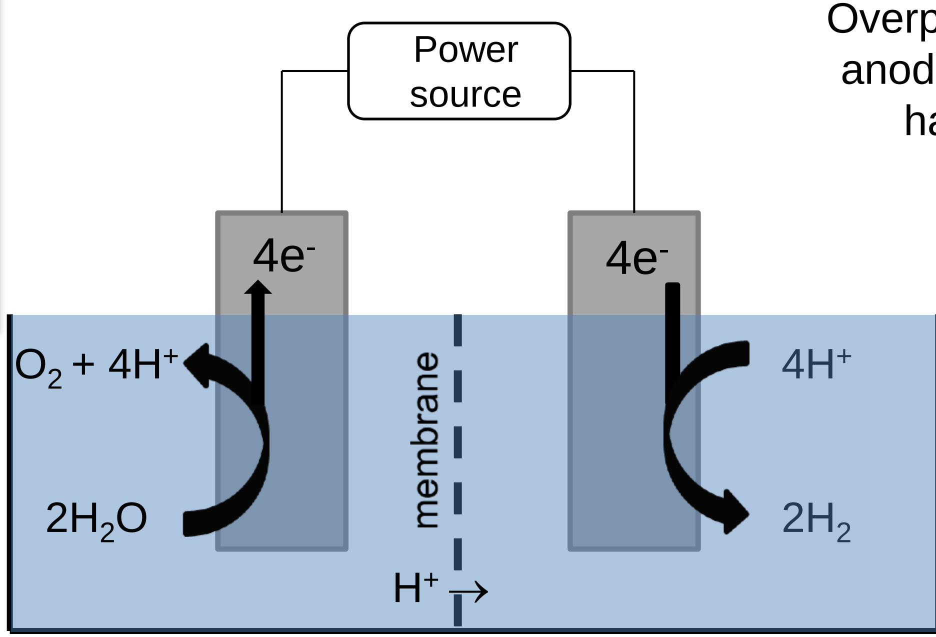
Also kinetically challenging



$$E_{applied} = E_{cell} + \eta_a + \eta_c$$

Overpotentials for the anodic and cathodic half reactions

Anode



Cathode

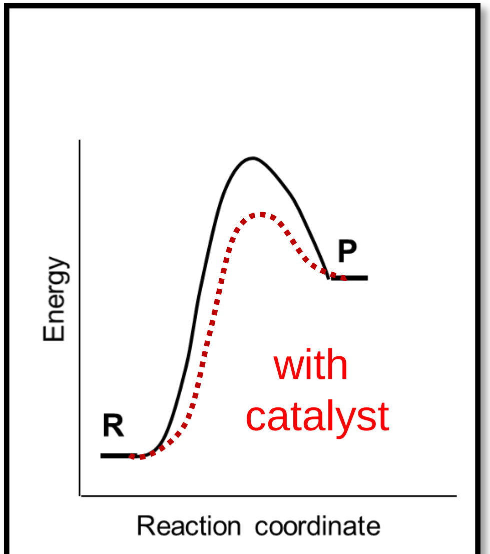
O_2 evolution rxn (OER):

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

H_2 evolution rxn (HER):

$4H^+ + 4e^- \rightarrow 2H_2$

Overall water splitting reaction: $2H_2O \rightarrow O_2 + 2H_2$ $E_{cell} = -1.23$ V



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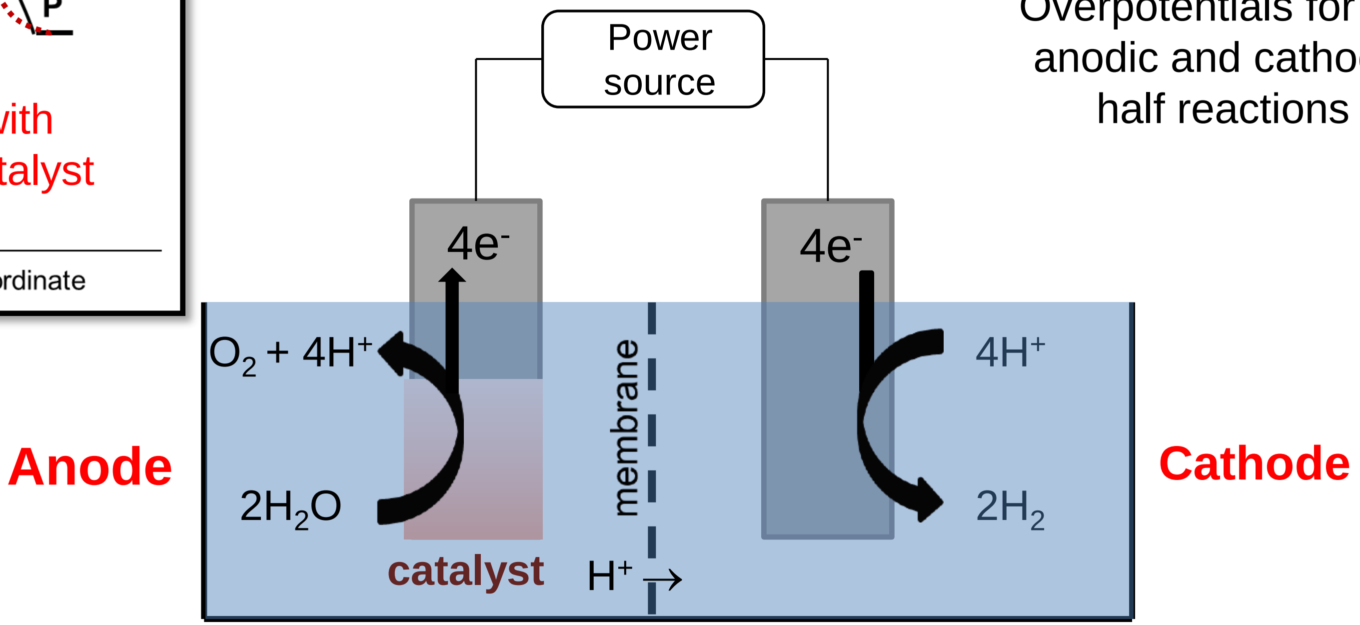

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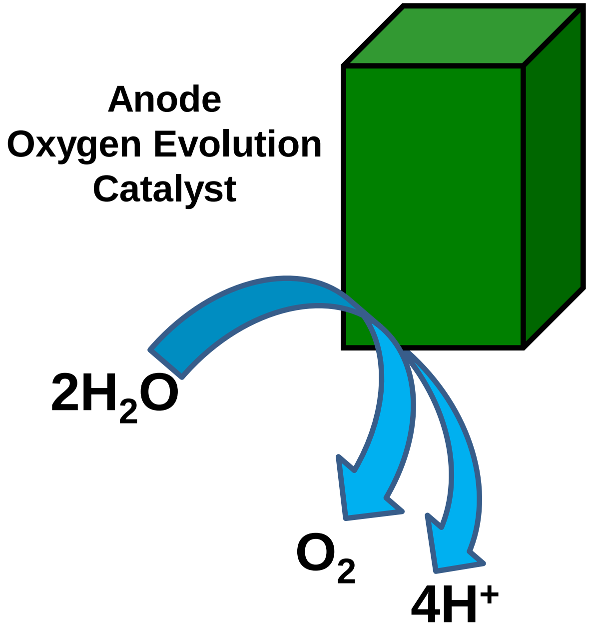
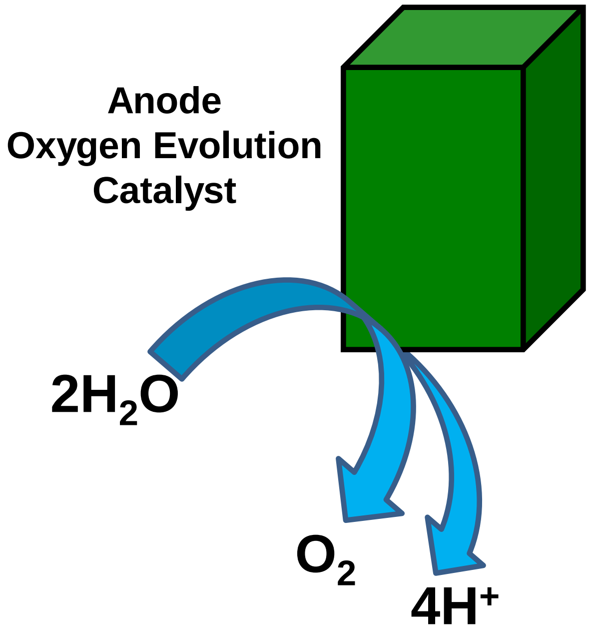


We will ignore the challenges associated with the absorption of light and the reduction half reaction for now and focus on the water oxidation reaction.

Water oxidation half reaction (anode): $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Iridium and ruthenium oxides are able to catalyze water oxidation, but these metals are expensive and rare.

Ideally, catalysts would be stable, relatively inexpensive, and earth abundant!



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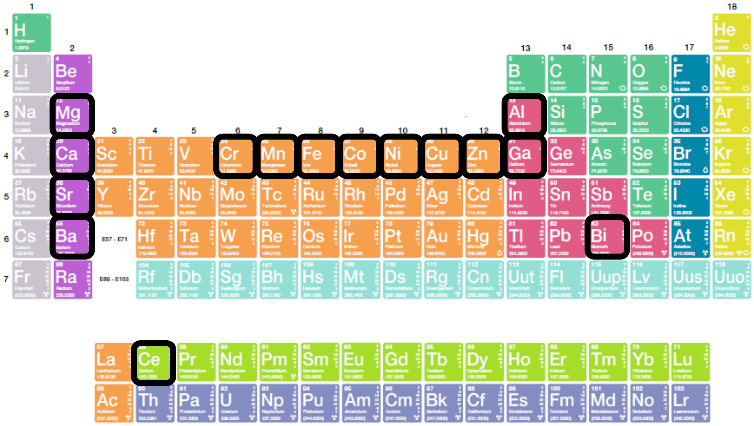
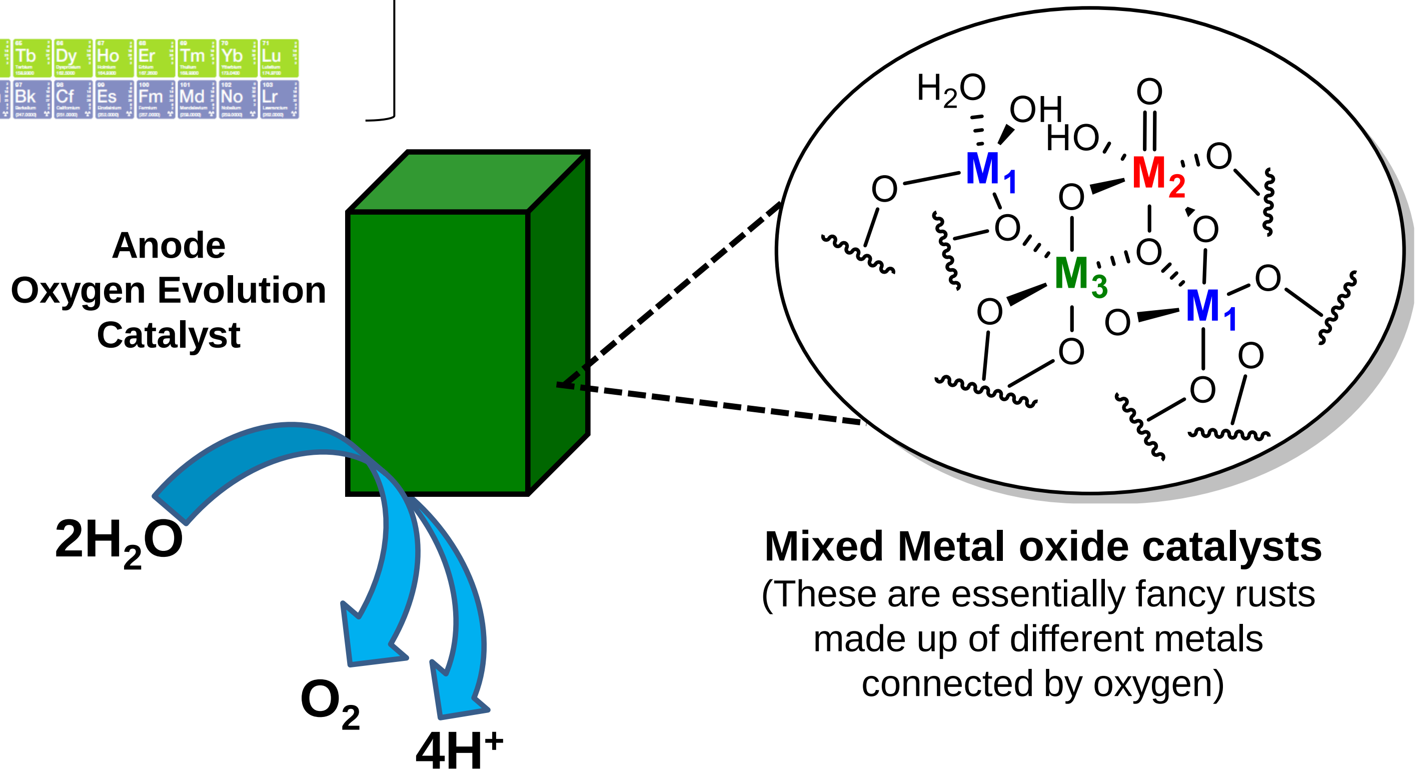


Examples of the metals you can choose to include in your catalyst are circled



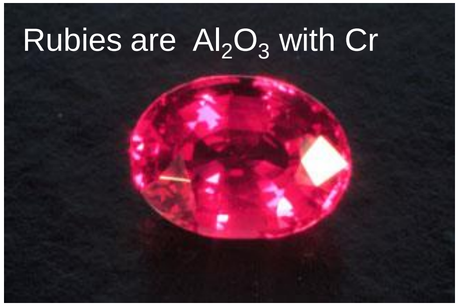
Mixed Metal oxide catalysts
(These are essentially fancy rusts made up of different metals connected by oxygen)

Mixed-metal oxides composed of earth-abundant metals may be able to compete with expensive iridium and ruthenium oxide catalysts!

Water oxidation half reaction (anode): $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

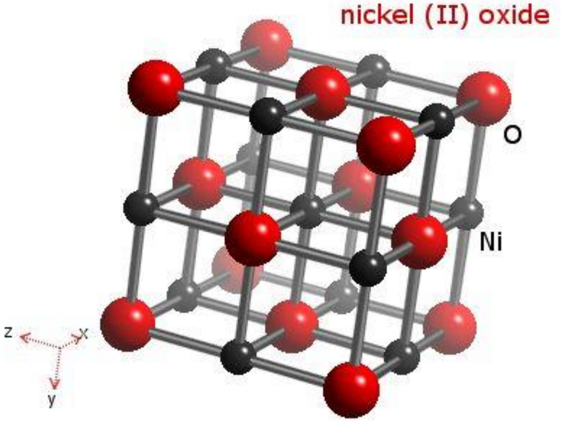
Metal oxides

Pottery glazes



Gemstones

Rust



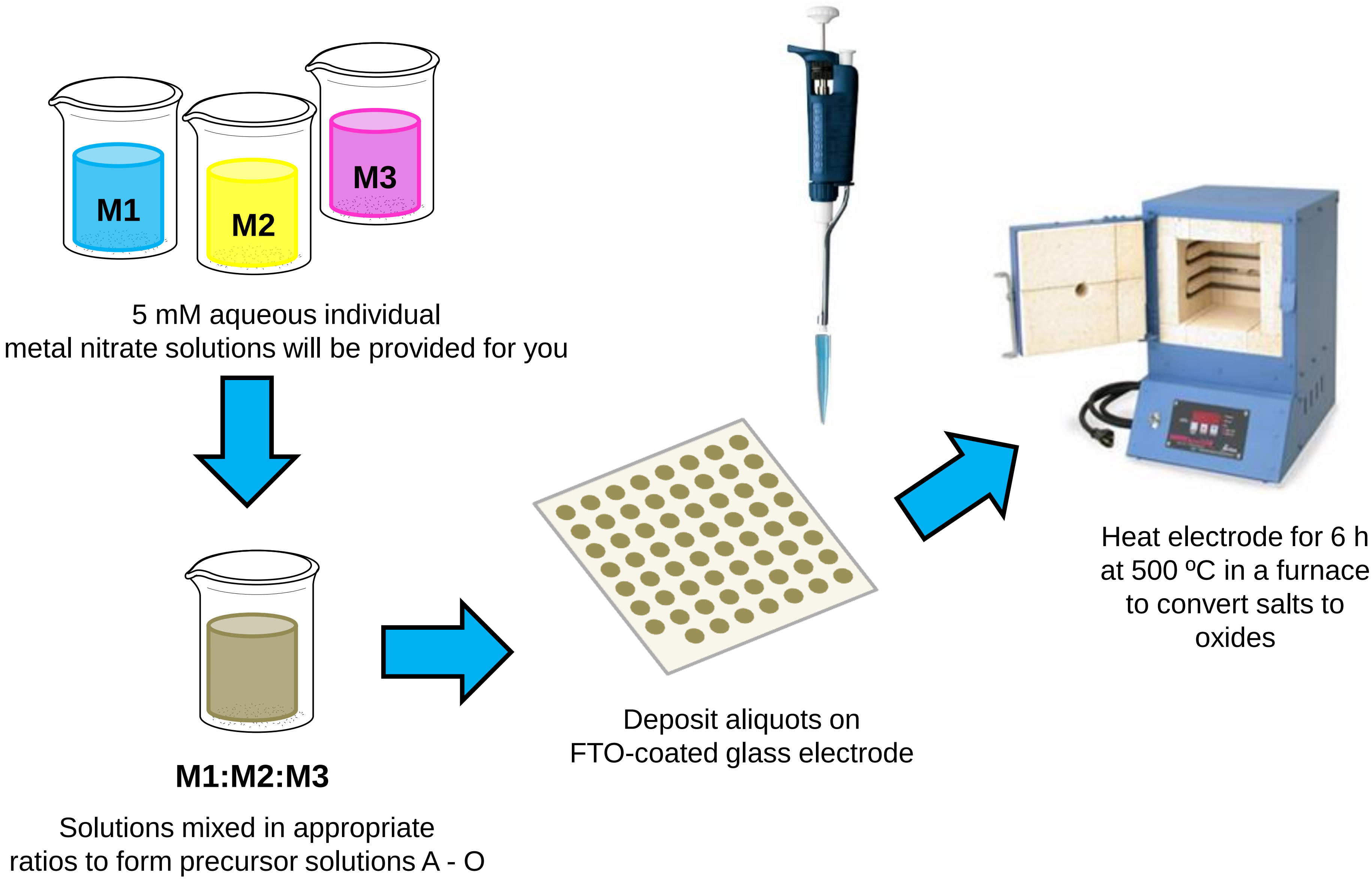
http://www.webelements.com/compounds/nickel/nickel_oxide.html

Noble metals tend not form oxides

Metal oxides are compounds composed of oxygen atoms and at least one other element

digitalfire.com/4sight/glossary/r.html www.pbs.org/wgbh/nova/earth/gemstone-primer.html www.cepolina.com/chain-rust-old.html http://itsno.name/

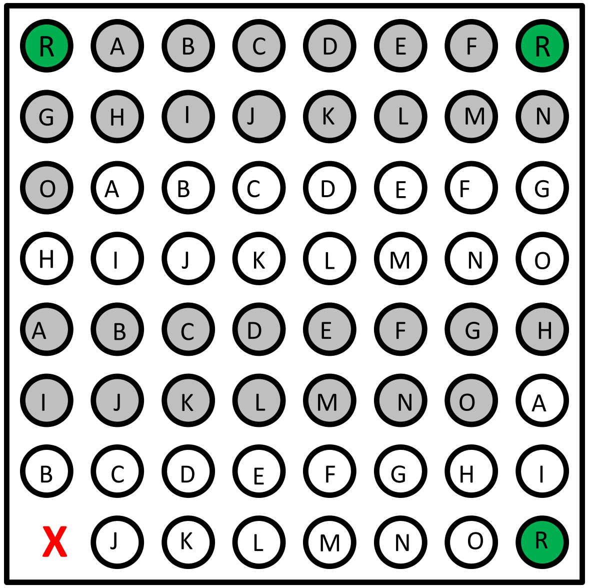
Preparation of mixed-metal catalyst arrays on an FTO-coated glass electrode



Complete this table before preparing your array. Assume you have 0.005 M solutions of each of the three individual metal nitrates. Plan to make 1 mL of each mixed metal nitrate solution, and assume that you have an adjustable pipet or syringe that can deliver volumes between 0 and 1000 μL.

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

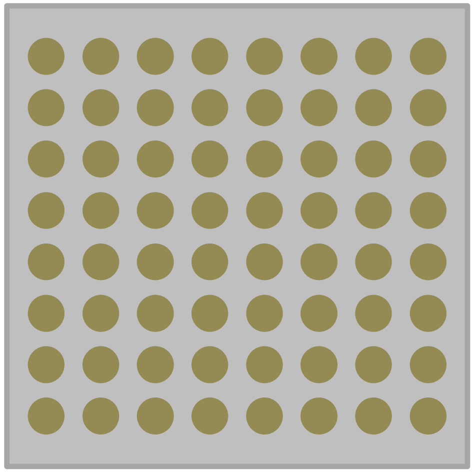
Spotting template: Three metal electrode



Preparing the electrode array:

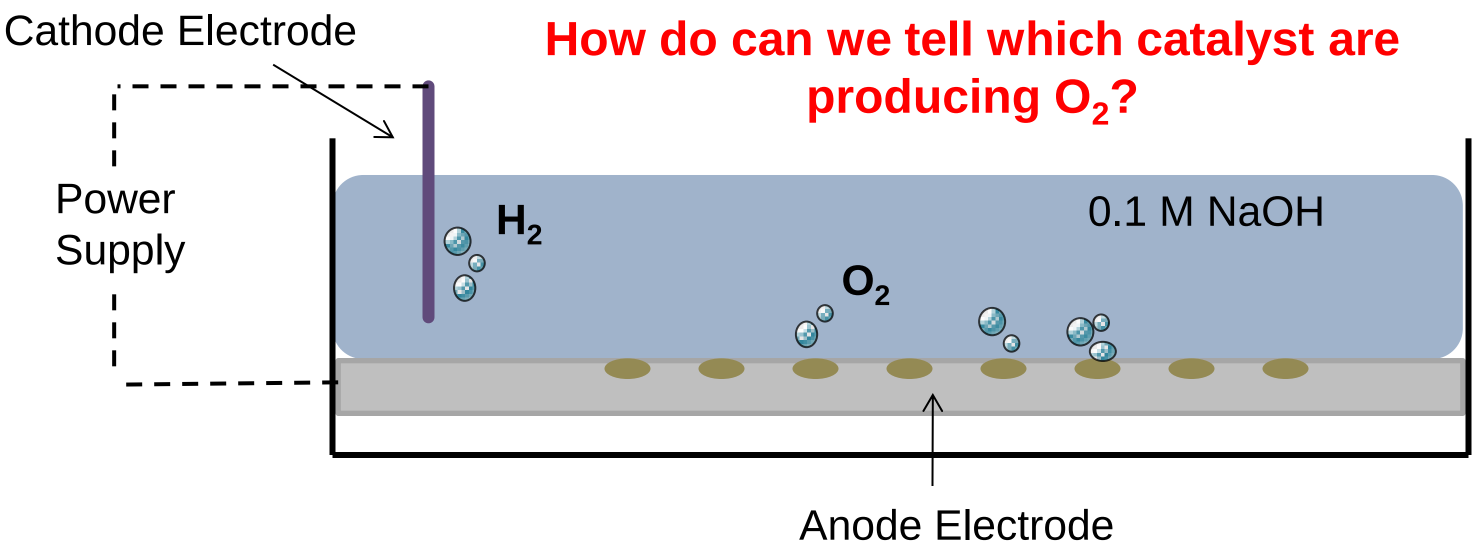
1. Determine which side of your electrode is coated with FTO (your instructor will show you how).
2. Place your electrode, FTO-side-up, on top of the square above.
3. Pipet 1 μL of the indicated solution onto the electrode at each position of the 8 × 8 array.
4. If the electrode will not be heated in a kiln that day, evaporate the solvent on a hotplate.
5. Heat the electrode at 500 °C for 6 h to convert the metal nitrates into the corresponding metal oxides.

How do we test several catalysts at the same time?



Electrode with an array of different metal oxide catalysts

How do can we tell which catalyst are producing O_2?



Gerken, J.B.; Chen, J.Y.C.; Massé, R.: Powell, A.B.; Stahl, S.S. *Angew. Chem. Int. Ed.* **2012**, 51,6676

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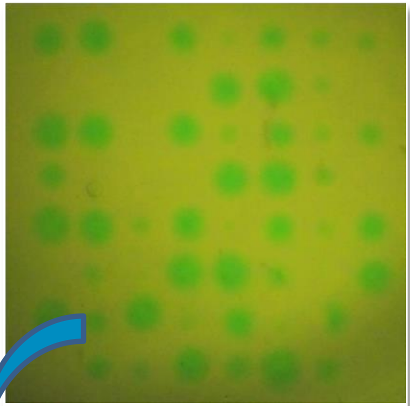
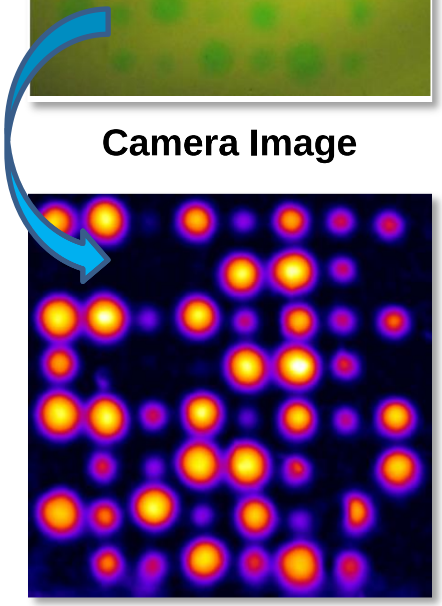
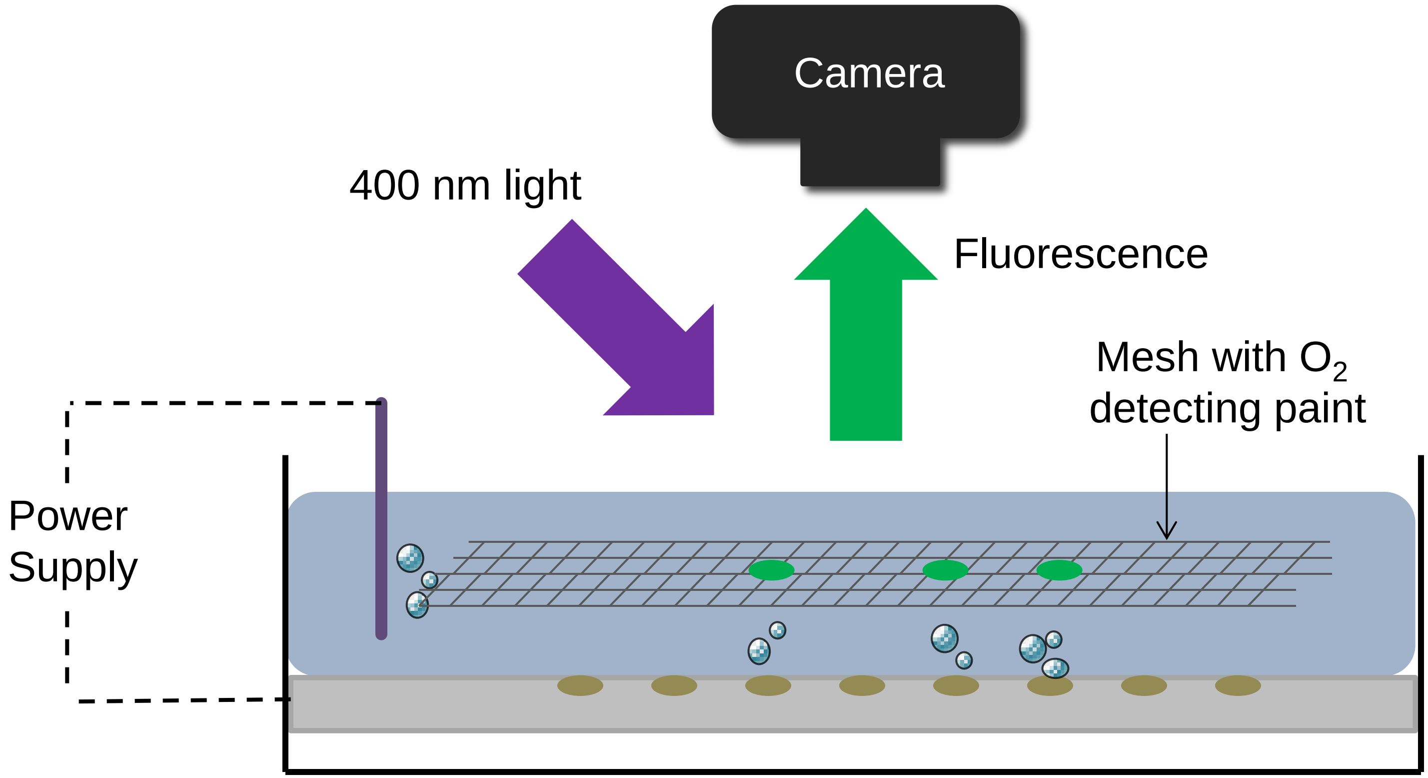


Camera Image



Processed image
Brightness ∝ O_2



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