STATISTICAL MOLECULAR THERMODYNAMICS

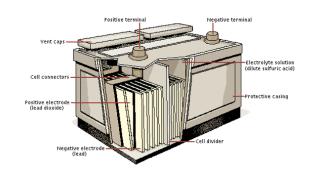
Christopher J. Cramer

Video 13.6

Batteries and Fuel Cells

BATTERIES

A battery is an electrochemical cell that is typically stored open circuit and, when the circuit is closed, does work through discharge of its electromotive force.



Primary: non-rechargeable

Mercury:

Zn(s) | ZnO(s) | KOH(paste) | HgO(s) | Hg(l)

all components are pure phase, so no activity change (constant voltage); mercury content an environmental hazard

Alkaline:

 $Zn(s) \mid ZnO(s) \mid KOH(paste) \mid MnO_2(s) \mid Mn_2O_3(s)$

all components are pure phase, but voltage drops steadily over time

Lithium:

 $Li(s) \mid LiClO_4(glyme) \mid MnO_2(s) \mid Mn_2O_3(s)$

higher potential (voltage) because of alkali metal at anode

Secondary: Rechargeable

Lead:

 $Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid$ $PbO_2(s) \mid PbSO_4(s)$

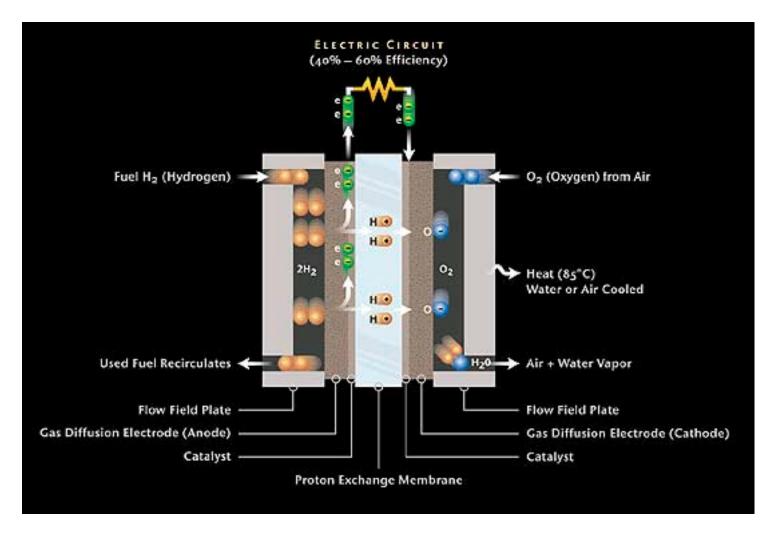
used in car batteries; PbSO₄ is formed at both electrodes during discharge. EMF is about 2 V (6 in series for a 12 V car battery). Acid.

Ni-Cad:

 $Cd(s) \mid Cd(OH)_2(s) \mid KOH(paste) \mid$ $Ni(O)OH(s) \mid Ni(OH)_2(s)$

very steady 1.2 V output. Robust storage characteristics.

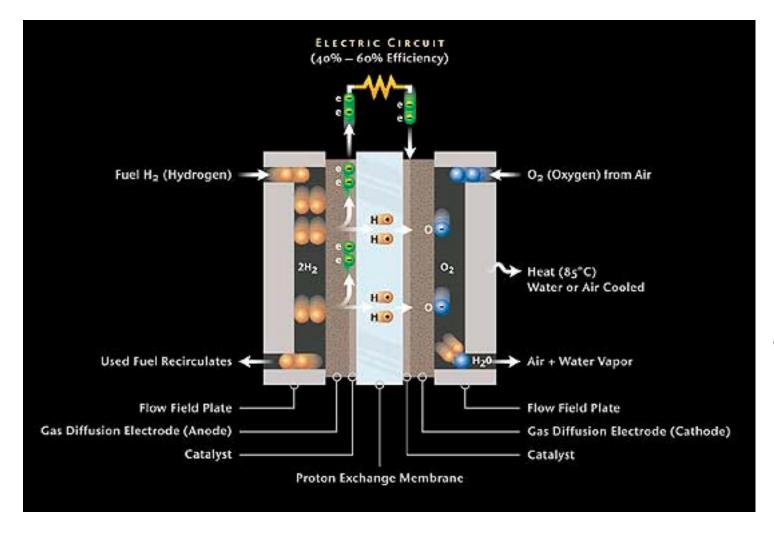
FUEL CELLS



A fuel cell is an electrochemical cell that is continuously charged with fresh sources of oxidant and reductant.

In essence, it "tames" a chemical reaction so that more of its exergonicity can be captured as work.

FUEL CELLS



Fuel cells are far more efficient than heat engines, but the current catalysts are very expensive (e.g., Pt mesh).

A new energy economy would benefit from renewable sources of fuel (e.g., H₂ from solar water splitting) and cheaper fuel cells — green power.

Self-assessment

We previously worked out that splitting water into hydrogen and oxygen is a 4-electron process requiring 1.23 V per electron (reaction in *reverse* (i.e., exergonic) shown below)

$$2H_{2(g)} + O_{2(g)} \qquad \qquad = 2H_2O_{(l)} \qquad \qquad E^{\circ} = 1.23 \text{ V}$$

$$2H_{2(g)} \qquad \qquad = 4H_{(aq)}^{+} + 4e^{-} \qquad E^{\circ} = 0.00 \text{ V}$$

$$O_{2(g)} + 4H_{(aq)}^{+} + 4e^{-} \qquad = 2H_2O_{(l)} \qquad \qquad E^{\circ} = 1.23 \text{ V}$$

What is the longest wavelength a photon can have in order to provide 1.23 eV or more of energy?

Self-assessment Explained

$$2H_{2(g)} + O_{2(g)}$$
 \leftrightarrows $2H_2O_{(l)}$ $E^{\circ} = 1.23 \text{ V}$

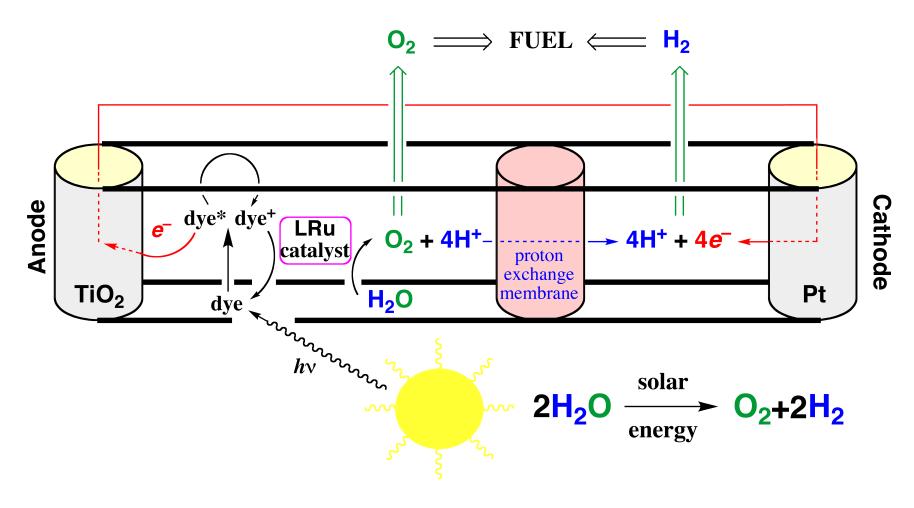
$$2H_{2(g)} + 4H_{(aq)}^{+} + 4e^{-} \qquad \leftrightarrows$$
 $2H_2O_{(l)}$ $E^{\circ} = 0.00 \text{ V}$

$$O_{2(g)} + 4H_{(aq)}^{+} + 4e^{-} \qquad \leftrightarrows$$
 $2H_2O_{(l)}$ $E^{\circ} = 1.23 \text{ V}$

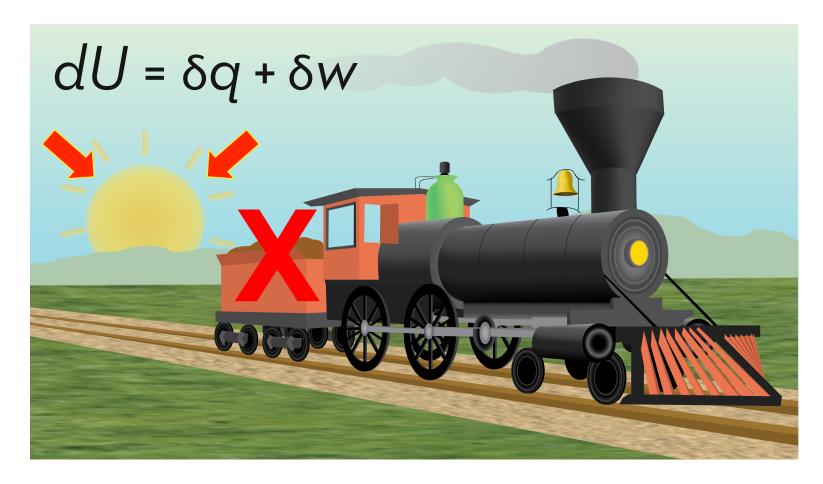
What is the longest wavelength a photon can have in order to provide 1.23 eV or more of energy?

A: 1008 nm, which is in the near infrared region of the spectrum. Thus, the sun offers a ready supply of photons that might be usefully harvested to split water!

DYE-SENSITIZED SOLAR FUEL CELL



Sequential photons must be used to drive a *chemical* process to split water, one electron at a time.



Next: Review of Module 13