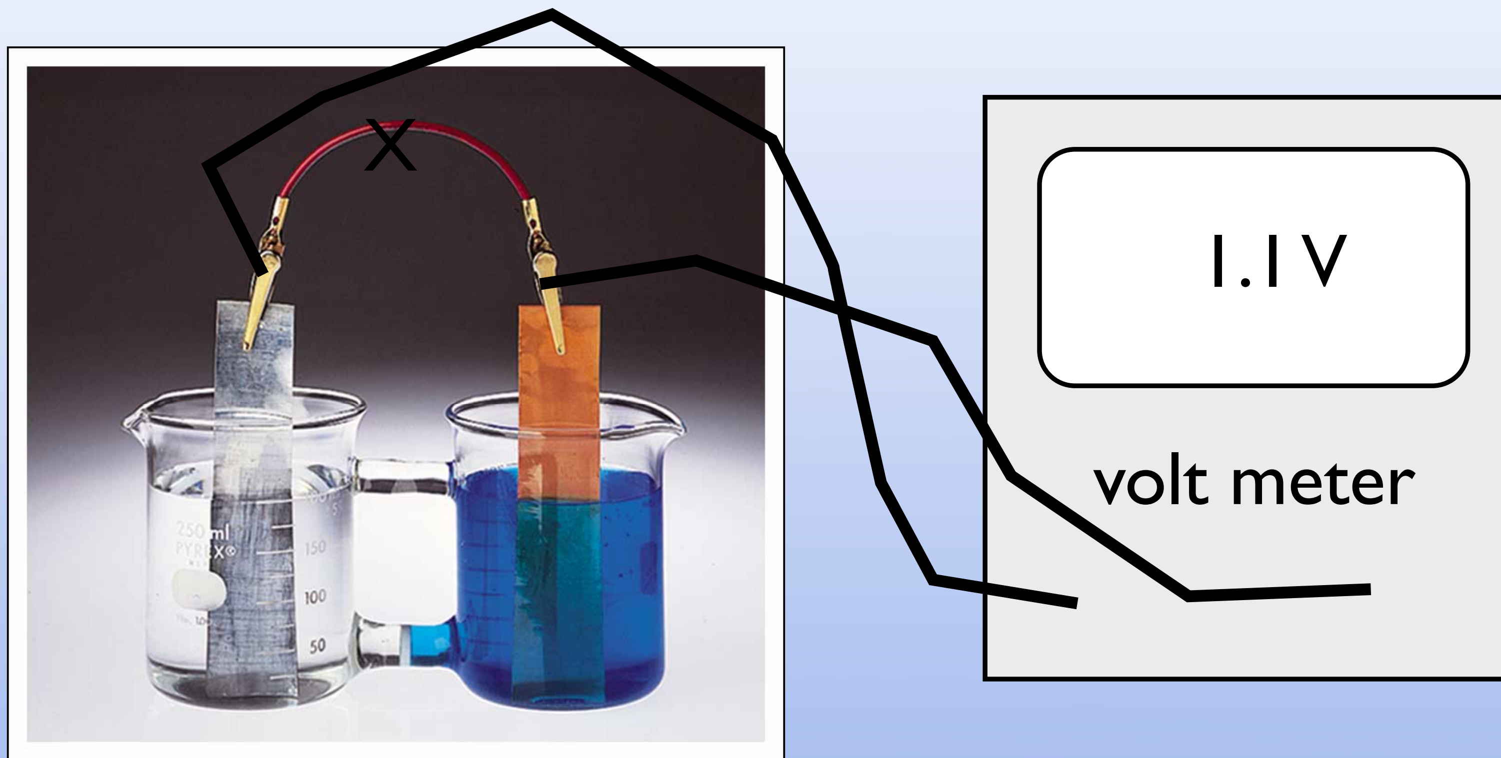
Today

Voltage and Equilibria (again)
Batteries and Fuel Cells

Electrolytic Cells

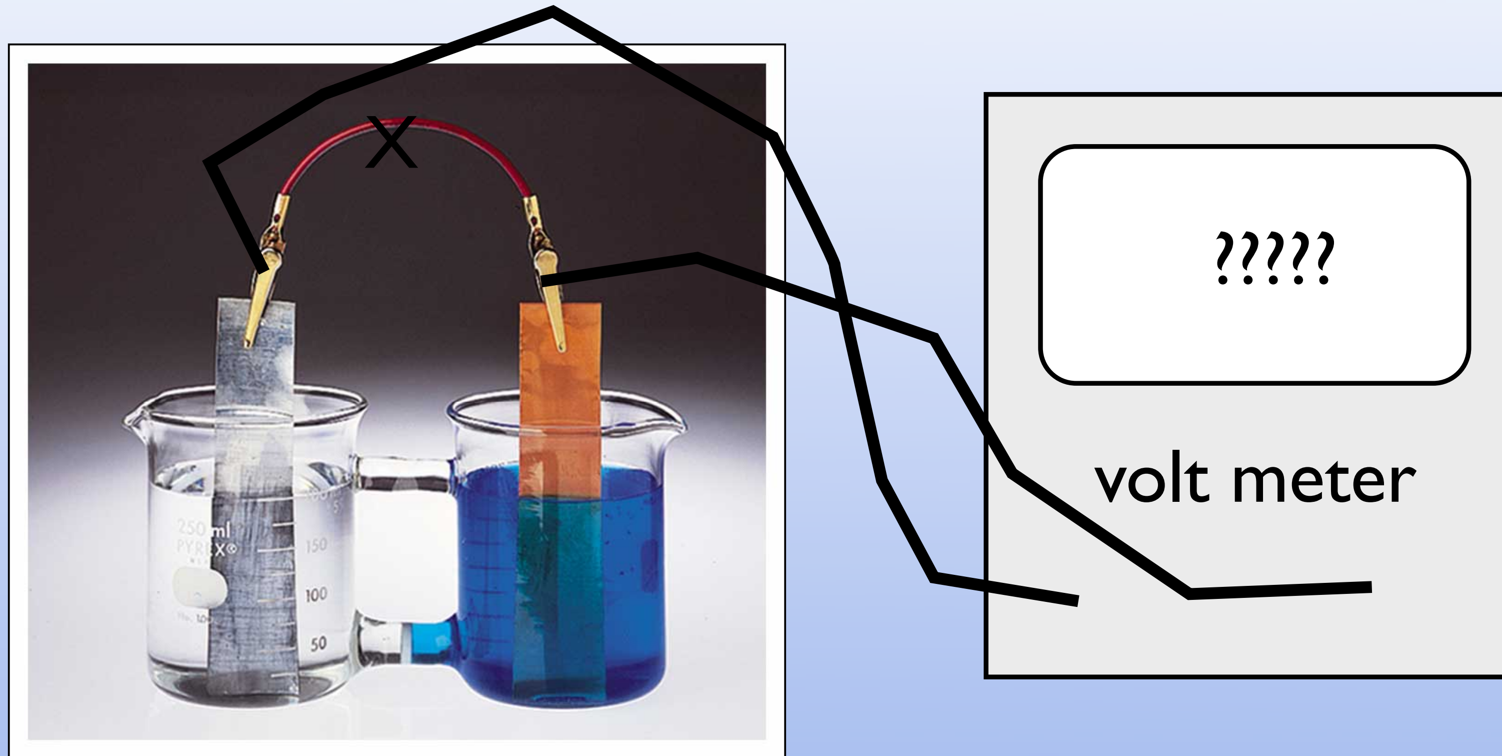
We'll look at standard concentrations

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$



$1\ M\ Zn^{2+}$ (aq) and $1\ M\ Cu^{2+}$ (aq)
(note this is ridiculously concentrated)

What about other concentrations?



$[Zn^{2+}] \neq 1M$ and $[Cu^{2+}] \neq 1M$???

What is voltage for the following reaction at equilibrium?

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A. 1.1 V

B. zero

C. -1.1 V

D. something between 0 and 1.1 V

What is voltage for the following reaction if $[Cu^{2+}] = 10^{-4}$ M and $[Zn^{2+}] = 1.9$ M

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A. 1.1 V

B. zero

C. -1.1 V

D. something between 0 and 1.1 V

Relationship between E and ΔG

ΔG = - charge x E

$$\Delta G = -nFE$$

Other concentrations and equilibrium
Let's remember equilbrium!

$$\Delta G = \Delta G° + RT\ln Q$$

Other concentrations and equilibrium
Let's remember equilbrium!

$$\Delta G = \Delta G^\circ + RT\ln Q$$

at equilibrium $\Delta G = 0$

so $\Delta G^\circ = -RT\ln K$

$$-nFE = -nFE^\circ + RT\ln Q$$

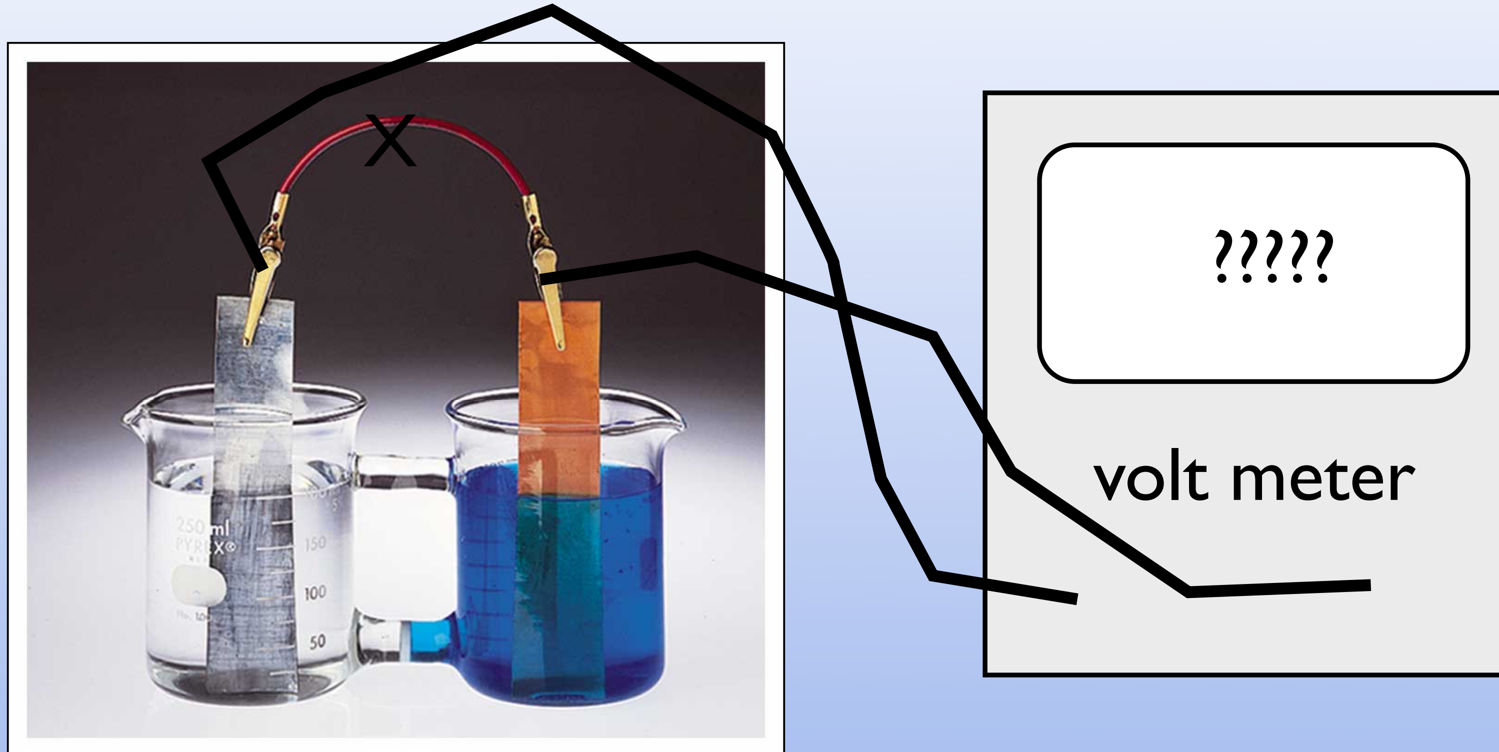
$$E = E^\circ - \frac{RT}{nF}\ln Q$$

assume 25°C

log!

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

What about other concentrations?



10^{-3} M Zn^{2+} (aq) and 10^{-1} M Cu^{2+} (aq) ???

1 M Zn^{2+} (aq) and 1 M Cu^{2+} (aq) standard

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

1 M Zn^{2+} (aq) and 1 M Cu^{2+} (aq) standard

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{1} = 1$$

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

$$E = 1.10V - \frac{0.0591}{2}\log(1) = 1.10V$$

10^{-3} M Zn^{2+} (aq) and 10^{-1} M Cu^{2+} (aq) ???

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

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$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{(10^{-3})}{(10^{-1})} = 10^{-2}$$

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

$$E = 1.10V - \frac{0.0591}{2}\log(10^{-2}) = 1.16V$$

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

Current will flow until E = 0

Equilibrium

$$E^\circ = \quad + \frac{0.0591}{n}\log K$$

$$\log K = \frac{nE^\circ}{0.0591}$$

What will happen to the voltage if I lower the Zn^{2+} concentration?

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

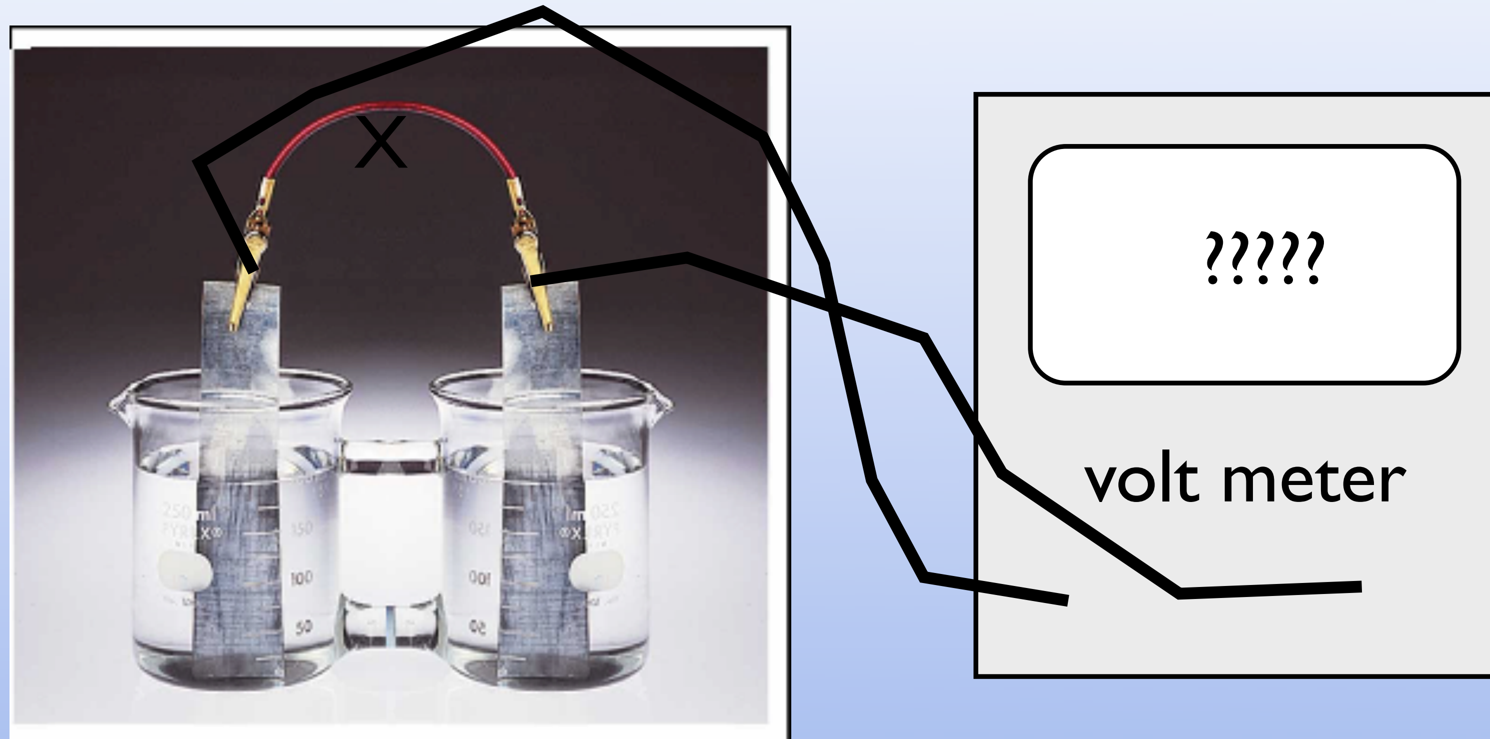
A. the voltage will increase

B. the voltage will decrease

C. the voltage will stay the same

What about this cell?

$Zn \mid Zn^{2+} \parallel Zn^{2+} \mid Zn$



10^{-4} M Zn^{2+} (aq) and 1 M Zn^{2+} (aq) ???

Does this cell have a non-zero voltage?

$$Zn \mid Zn^{2+}\ (10^{-4}\ M)\ \|\ Zn^{2+}\ (1\ M) \mid Zn$$

A. yes

B. no

Which side has the lower free energy?

$$Zn \mid Zn^{2+}\ (10^{-4}\ M) \parallel Zn^{2+}\ (1\ M) \mid Zn$$

A. 1 M solution

B. 10^{-4} M solution

C. they are the same (its at equilibrium)

Will electrons flow spontaneously to the cathode?

$$Zn \mid Zn^{2+}\ (10^{-4}\ M)\ \|\ Zn^{2+}\ (1\ M) \mid Zn$$

A. yes

B. no

Will the potential for this cell be positive?

$Zn \mid Zn^{2+}\ (10^{-4}\ M) \parallel Zn^{2+}\ (1\ M) \mid Zn$

A. yes, $E > 0$

B. no, $E < 0$

C. it is the same reaction so $E = 0$

$$Zn \mid Zn^{2+}\ (10^{-4}\ M) \parallel Zn^{2+}\ (1\ M) \mid Zn$$

$$Zn \mid Zn^{2+}\,(10^{-4}\,M) \parallel Zn^{2+}\,(1\,M) \mid Zn$$

Same reaction! $E° = 0\,V$

$$Q = \frac{[Zn^{2+}]_{anode}}{[Zn^{2+}]_{cathode}} = \frac{10^{-4}}{1} = 10^{-4}$$

$$E = E° - \frac{0.0591}{n}\log Q$$

$$E = 0\,V - \frac{0.0591}{2}\log(10^{-4}) = 0.118\,V$$

each factor of ten will be another 0.0591 V

Take home message!

Voltage is a direct measure of the free energy

Therefore it is a direct measure of Q!

If you set up a system where one half of the cell is known, the the other half can be used as a sensor!

Let's look at this reaction

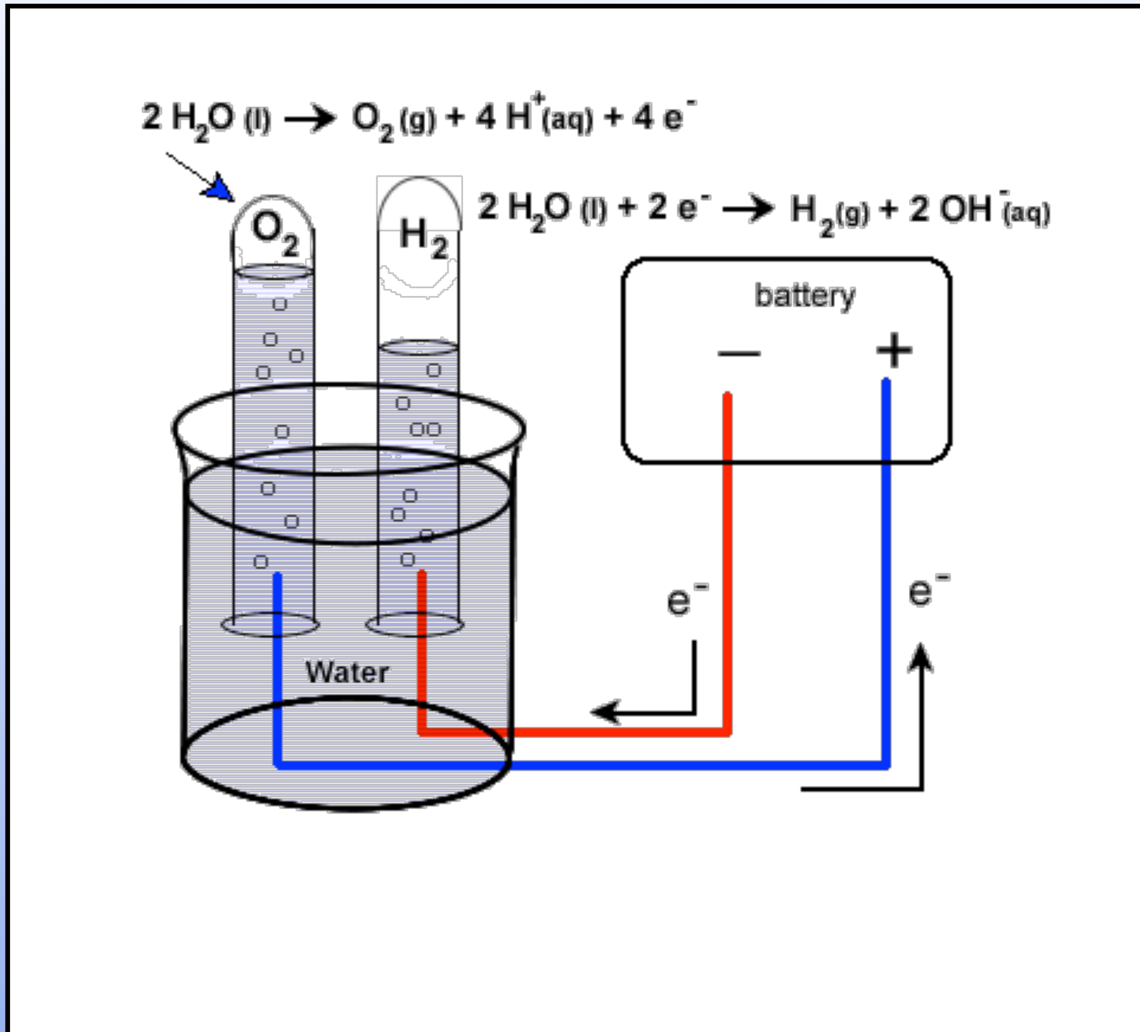
$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

$$\text{Anode (oxidation):} \quad 2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$$

$$\text{Cathode (reduction):} \quad 2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$$

$$E^\circ_{cell} = -2.06\ V$$

Not spontaneous, but if we apply a voltage > 2.06 we can force the reaction to go!



2 H2O (l) → O2 (g) + 4 H+(aq) + 4 e-
2 H2O (l) + 2 e- → H2(g) + 2 OH-(aq)
O2
H2
battery
–
+
e-
e-
Water

You reduce H^+ to H_2 in an electrochemical cell.
Your cell has a current of 1 Amp for 10 minutes
What is the total charge that is passed through the cell?

A. 1 C

B. 10 C

C. 600 C

D. 6000 C

You reduce H^+ to H_2 in an electrochemical cell.
Your cell has a current of 1 Amp for 10 minutes
How many moles of electrons pass through the cell?

A. 600 C / F

B. 600 C x F

C. 1 A x F

You reduce H^+ to H_2 in an electrochemical cell. The number of moles of electrons that pass through the cell is 6.2×10^{-3} . How many moles of H_2 are formed?

$$2H^+ + 2e^- \text{ -----> } H_2(g)$$

A. 6.2×10^{-3}

B. 3.1×10^{-3}

C. 1.2×10^{-2}

You reduce H^+ to H_2 in an electrochemical cell.
Your cell has a current of 1 Amp for 10 minutes.
How many moles of H_2 are formed?

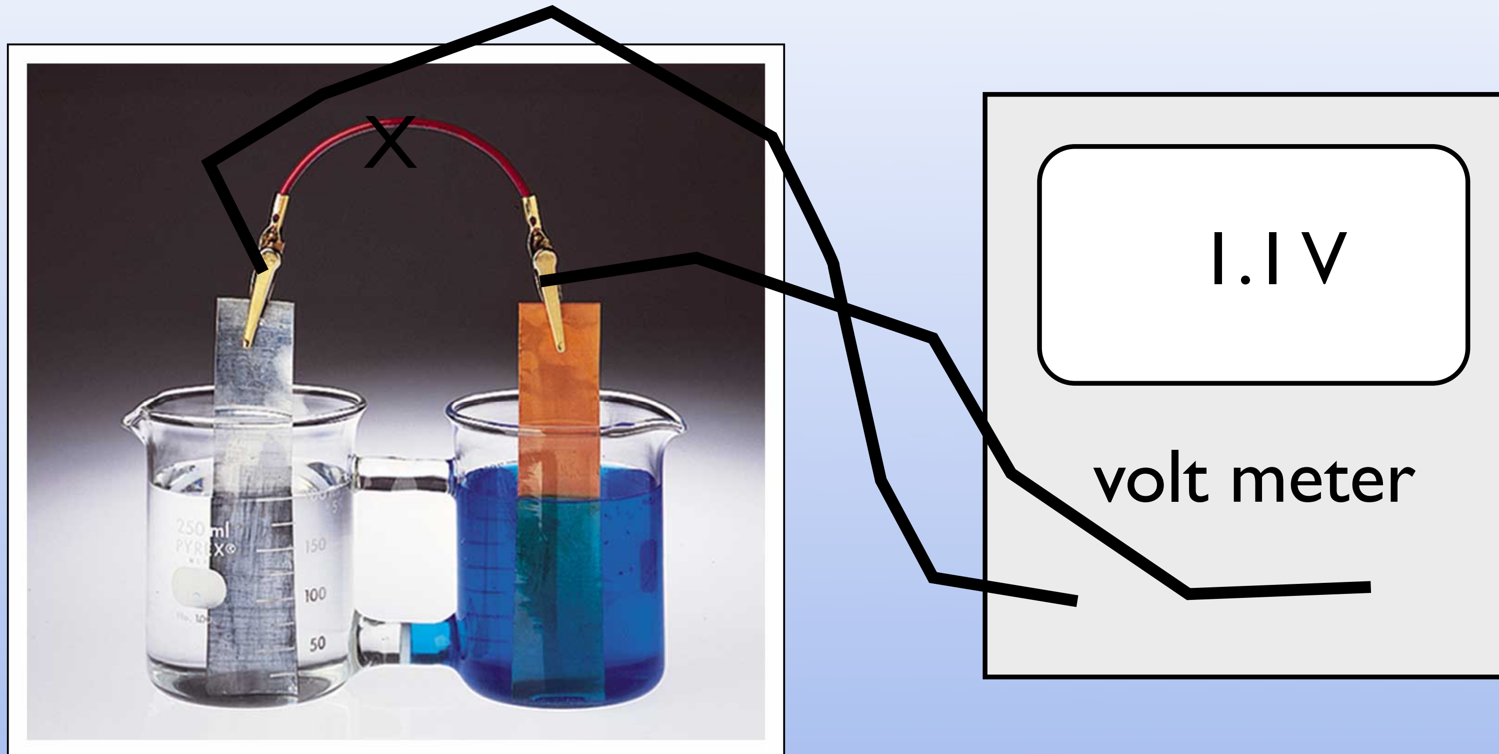
$$2H^+ + 2e^- \text{----->} \quad H_2(g)$$

A. 6.2×10^{-3}

B. 3.1×10^{-3}

C. 1.2×10^{-2}

This is the most impractical 1.1 V battery



How can we get rid of the beaker and salt bridge?

What is the voltage when 90% of the Cu^{2+} has reacted?

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

1.9 M Zn^{2+} (aq) and 0.1 M Cu^{2+} (aq) ???

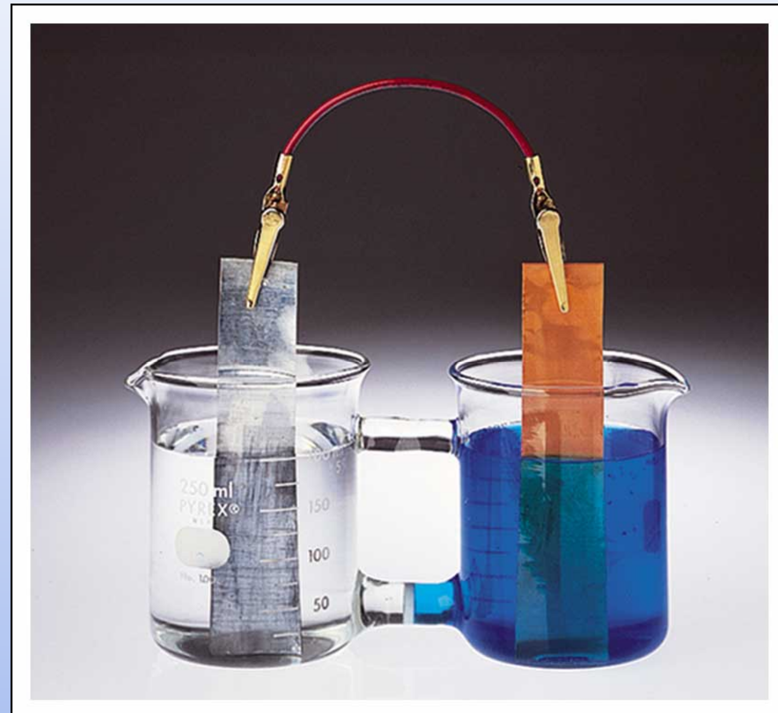
$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{(1.9)}{(.1)} = 19$$

$$E = E^\circ - \frac{0.0591}{n}\log Q$$

$$E = 1.10\,V - \frac{0.0591}{2}\log(19) = 1.06\,V$$

Issue to deal with

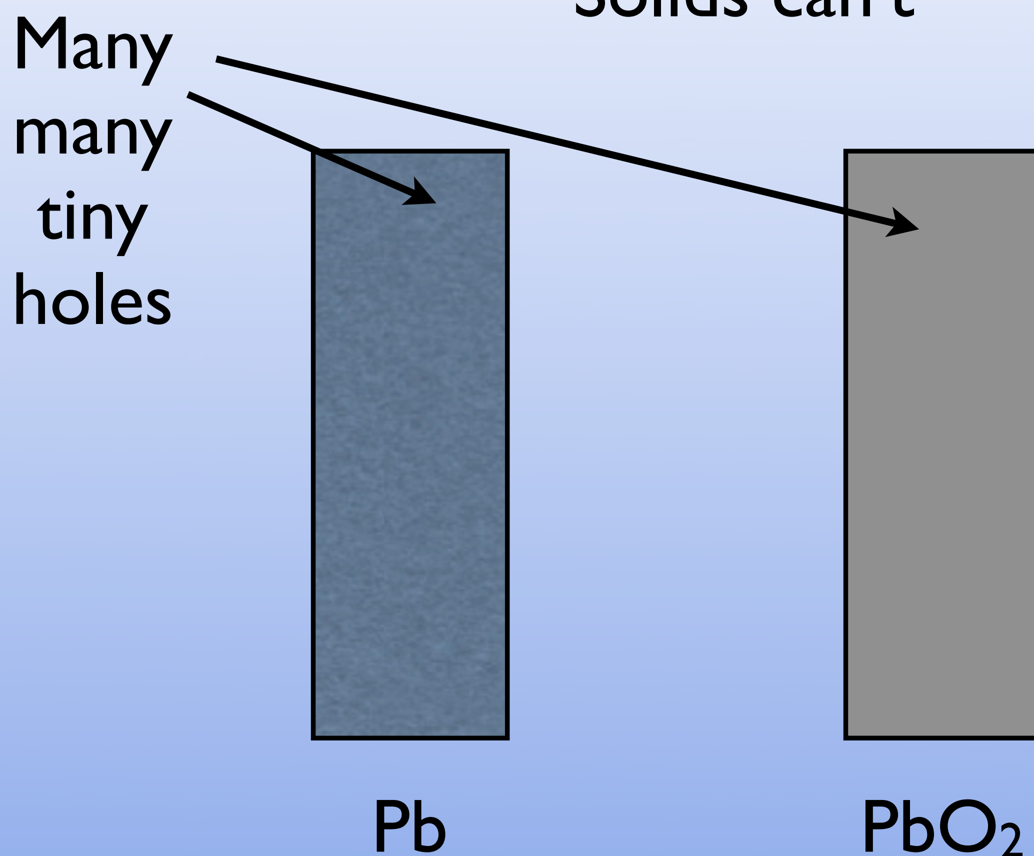
Beakers keep the oxidation and reduction reactions physically separated from one another



Salt bridge connect the circuits by allowing ions to flow between the two regions

No Beakers is easy. Put chemical into a porous medium

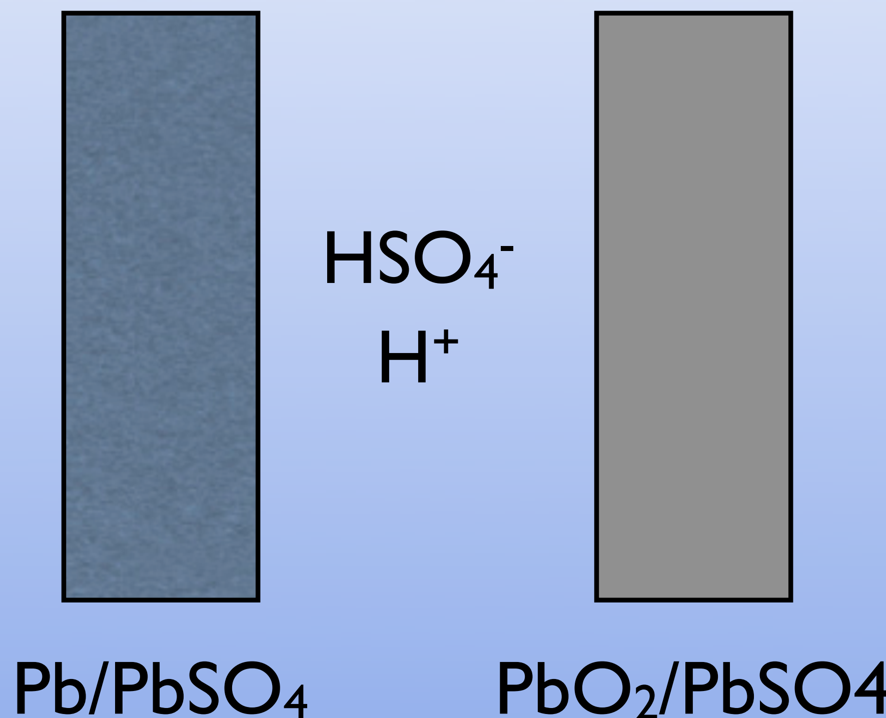
Water and ions can flow in and out
Solids can't



How to connect them?

Use a common electrolyte

Same chemical is common to both the oxidation and reduction



Lead Acid Battery

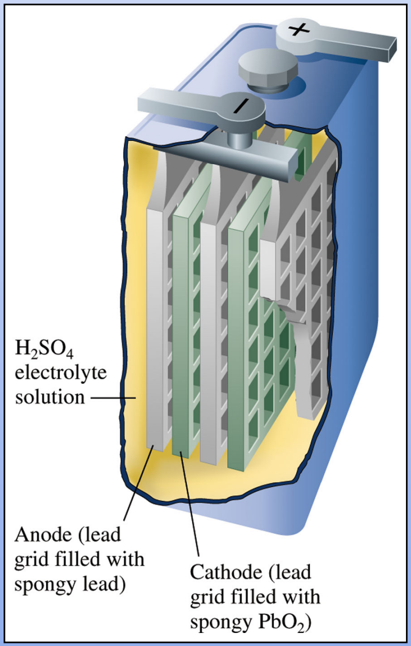
Anode

reduction potential

$$Pb(s) + HSO_4^-(aq) + H_2O(l) \leftrightarrow PbSO_4(s) + H_3O^+(aq) + 2e^-$$ E° = -0.356V

$$PbO_2(s)+3H_3O^+(aq)+HSO_4^-(aq)+2e^- \leftrightarrow PbSO_4(s)+5H_2O(l) \quad \epsilon^o = 1.685\ \text{V}$$

Cathode



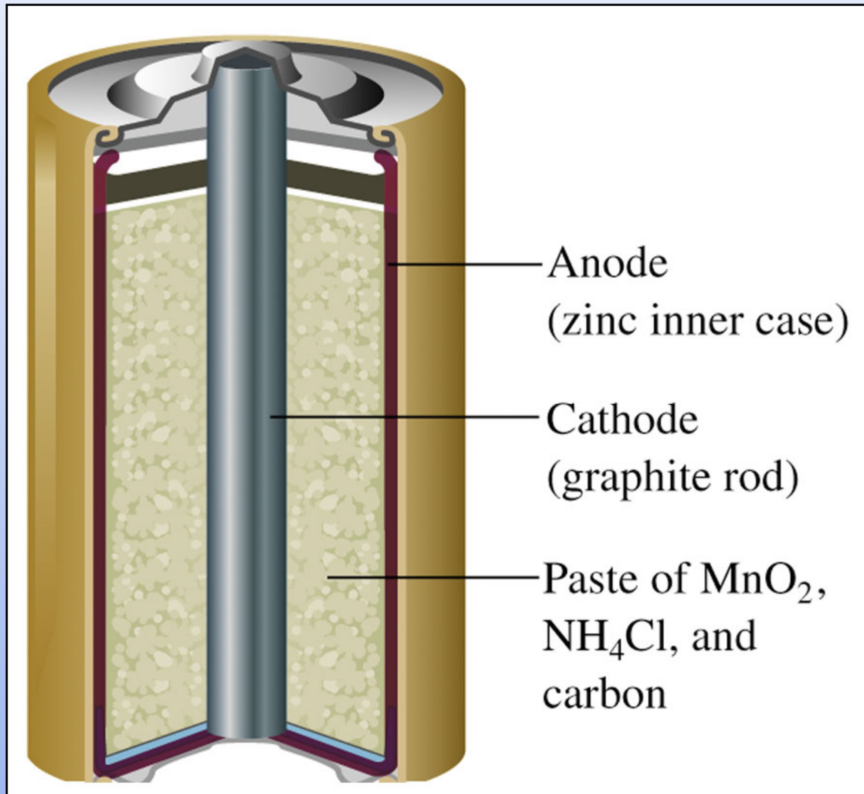
$E°_{cell}$ = 1.685 - (-.356) = 2.041 V

Everything in liquid
Therefore the reaction can be fast!

Fast = High current

Batteries without liquids

Dry Cell



$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

$2MnO_2(s) + 2\ H^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + H_2O(l)$

The Key
Solid Electrolyte
Paste
NH_4^+, NH_3, H_2O

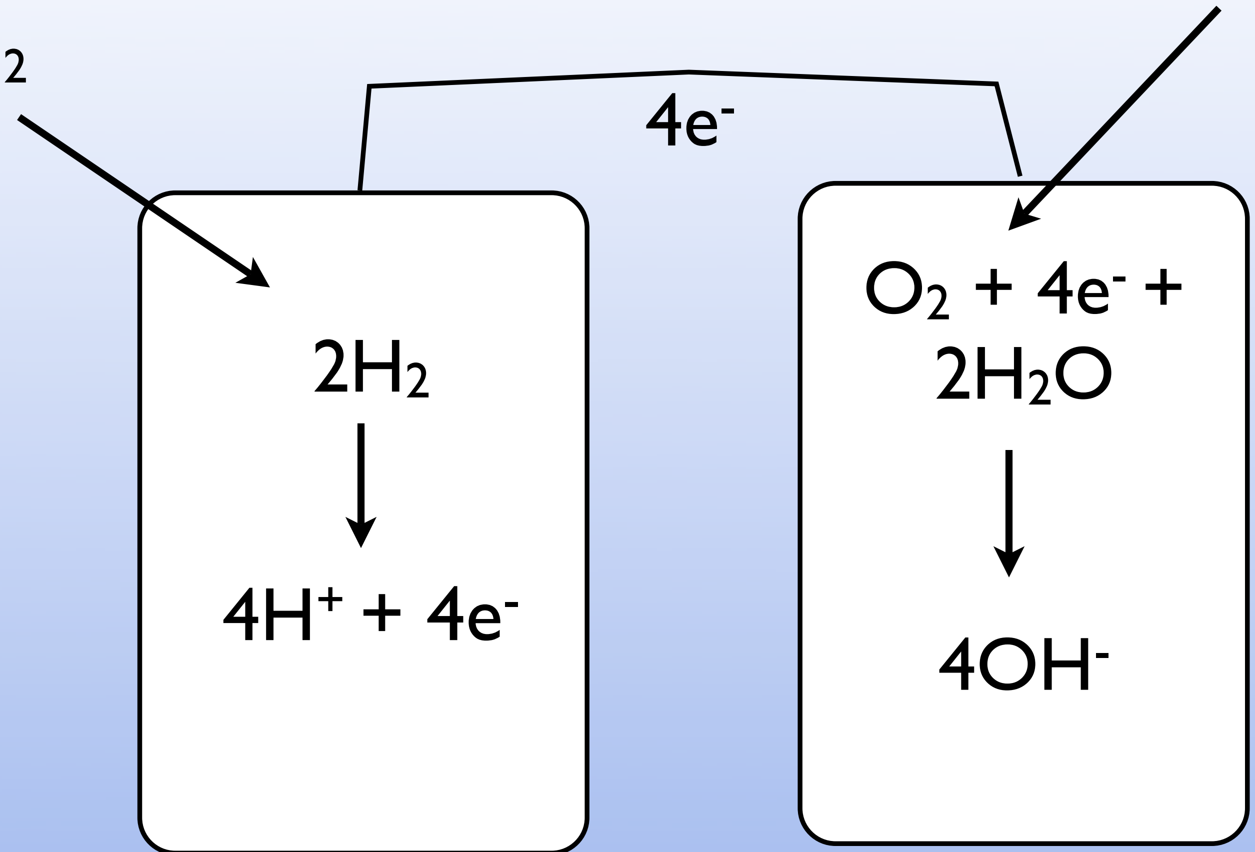
Carbon makes electrical connection

Very slow reaction. Constant V. Very low current

Fuel Cells

"fill up" with H_2

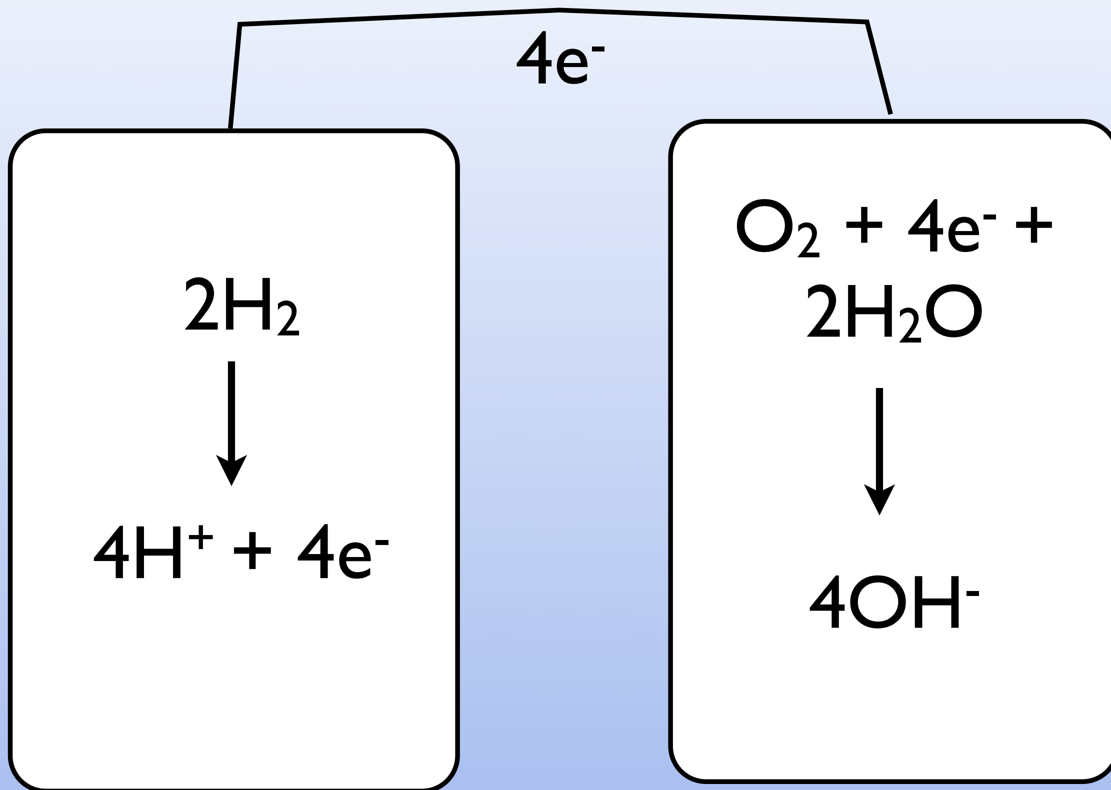
O_2 from air



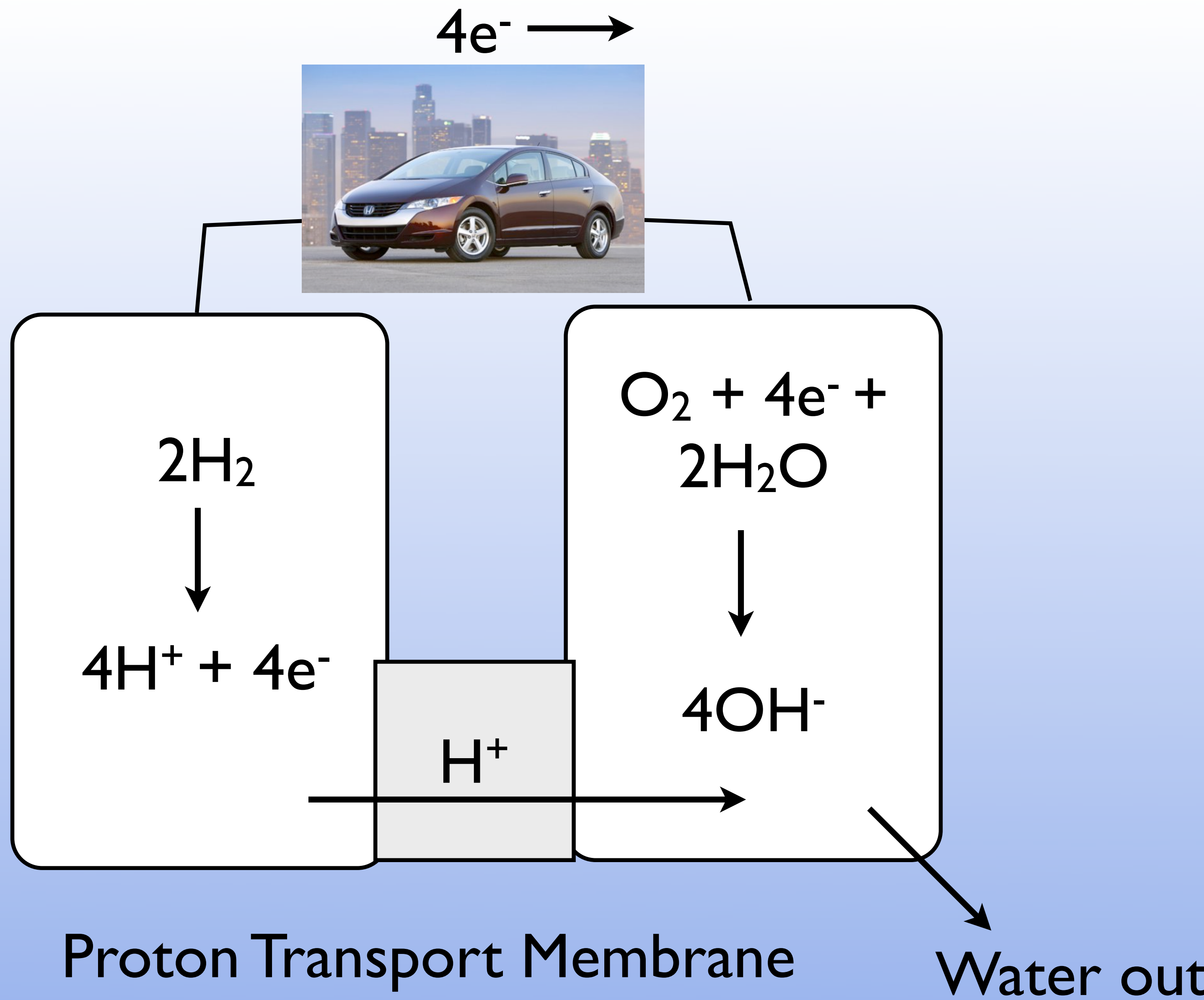
Anode
oxidation

Cathode
reduction

Fuel Cells



We need a salt Bridge!



$4e^-$
$2H_2$
$4H^+ + 4e^-$
H^+
$O_2 + 4e^- +$
$2H_2O$
$4OH^-$
Proton Transport Membrane
Water out