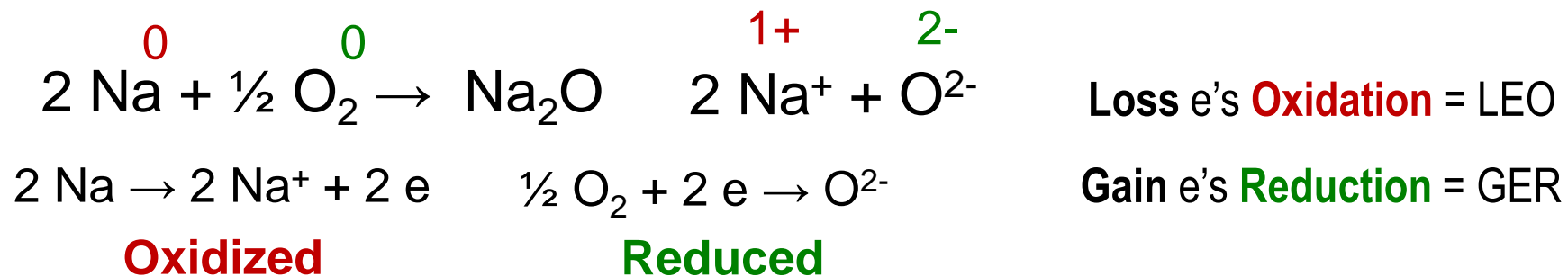


# Reduction-Oxidation (REDOX) Reactions

In chemical reaction **bonds**, both covalent and ionic, are made and broken by **moving electrons**.

So far all in reactions considered the **number of electrons** on each atom has been **preserved**



In **REDOX** reaction electrons are **transferred** between atoms as well as bonds being broken and formed.

The **balance** between ionic/covalency of the bonds in the reactants is **different** from that in the product.

We therefore need to keep **track** of the number of **electrons** of each **atom**.

The **oxidation state** of an atom is used for this purpose, which is related to the idea of the **formal charge**.

# Oxidation State

The **oxidation state** of an element is its **charge** assuming **ionic** bonding

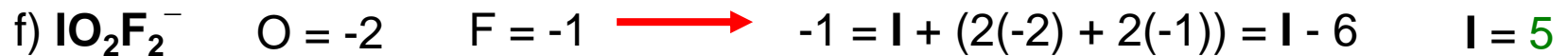
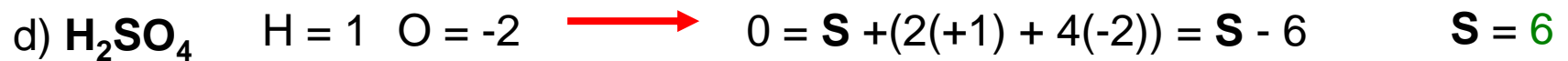
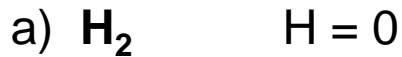
Electrons are not shared they are placed on the **more electronegative** element

## Rules for Assigning Oxidation States

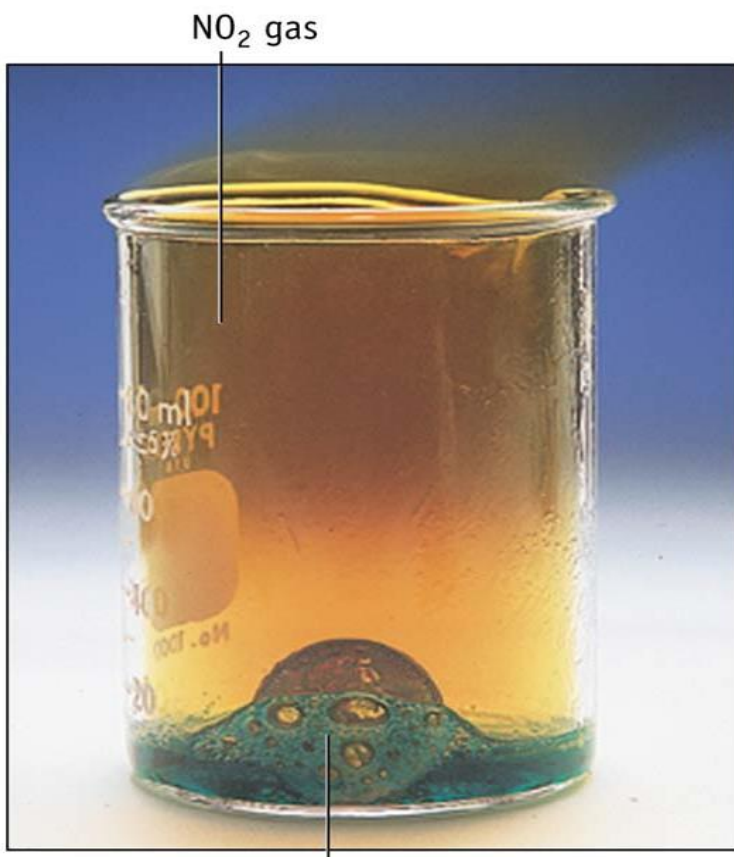
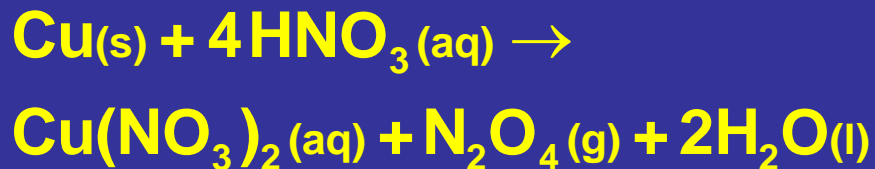
- 1) **Pure elements** have oxidation states of **0**
- 2) **Ions** have oxidation states that add up to the **charge** of the ion
- 3) **Hydrogen** has an oxidation state of **+1** unless bonded to a less electronegative atom. When bound to metals or boron it has an oxidation state of **-1**.
- 4) **Fluorine** has an oxidation state of **-1**
- 5) **Oxygen** has an oxidation state of **-2** unless bonded to fluorine or another oxygen.
- 6) **Halogens** other than fluorine have oxidation states of **-1** unless bonded to oxygen or a more electronegative halogen
- 7) **The rest** are determined by the process of **elimination**, where the oxidation states must add up to the total charge of the molecule or ion.

# Oxidation State

1) Determine the **oxidation state** of all the element in the following molecules:

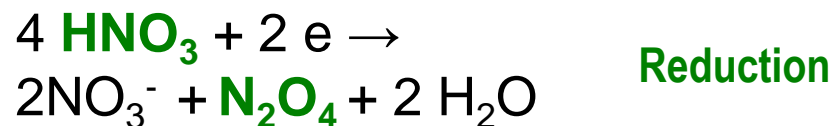


# Recognizing Redox Reactions



Copper metal oxidized to green  $\text{Cu(NO}_3)_2$

Reactants		Products	
Cu	N = 0	$\text{Cu}^{2+}$	N = 2
$\text{HNO}_3$	N = 5	$\text{N}_2\text{O}_4$	N = 4



REDOX equation seem difficult to **balance**

# of e's gained = # of e's lost

The **oxidized** species is the **reducing agent**

**Cu** is the **reducing agent**

The **reduced** species is the **oxidizing agent**

**$\text{HNO}_3$**  is the **oxidizing agent**

# Balancing Redox Reactions in Solution

## *The method of half reactions*

**Step 1.** Recognize the reaction as an **oxidation-reduction**.

**Step 2.** Separate the overall process into **half-reactions**.

**Step 3.** Balance each half-reaction by **mass**.

i) In acid solution,

a) add  $\text{H}_2\text{O}$  to the side requiring **O** atoms.

b) add  $\text{H}^+$  to balance any remaining unbalanced **H** atoms.

ii) In basic solution,

a) add 2  $\text{OH}^-$  to the side requiring **O** atoms, *and*  $\text{H}_2\text{O}$  to the other

b) add  $\text{H}_2\text{O}$  to the side requiring **H** atoms, *and one*  $\text{OH}^-$  to the other side.

**Step 4.** Balance the half-reactions by **charge**.

**Step 5.** Multiply the balanced half-reactions by appropriate **factors** to achieve **common whole number of electrons** being transferred.

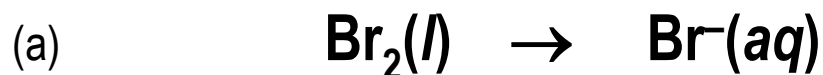
**Step 6.** Add the balanced half-reactions.

**Step 7.** Eliminate common reactants and products.

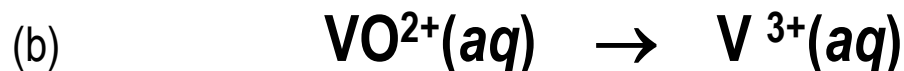
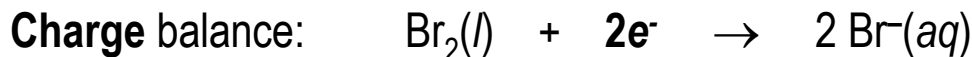
**Step 8.** Check the final result for mass and charge balance.

# Balancing Redox Reactions Sample Problems

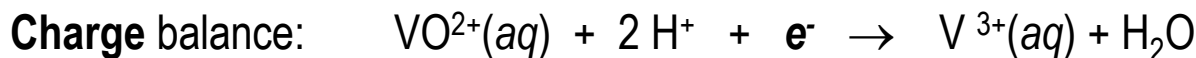
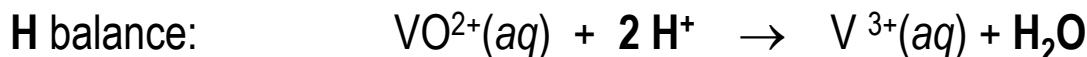
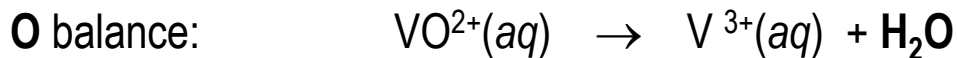
1. **Balance** equations for the half-reactions. Assume these reactions occur in **acidic solution**, meaning that  $\text{H}^+$  or  $\text{H}^+$  and  $\text{H}_2\text{O}$  may be used to balance the equation.



Ox. St.  $0$   $-1$  **reduction**

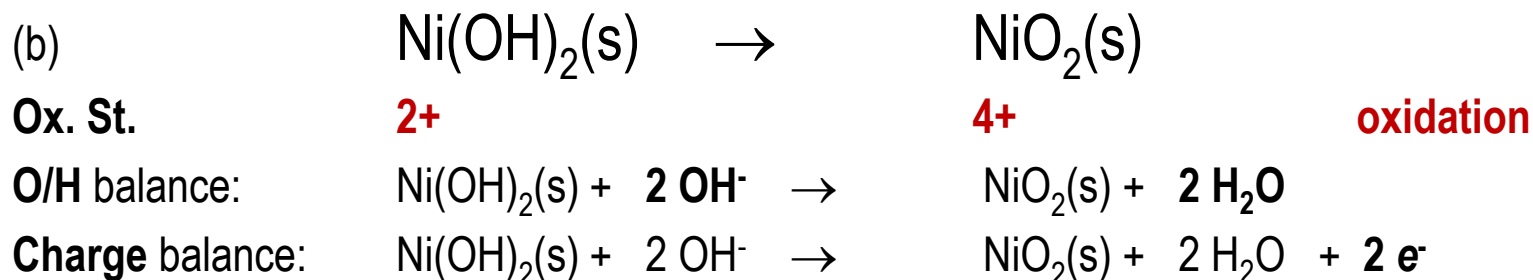
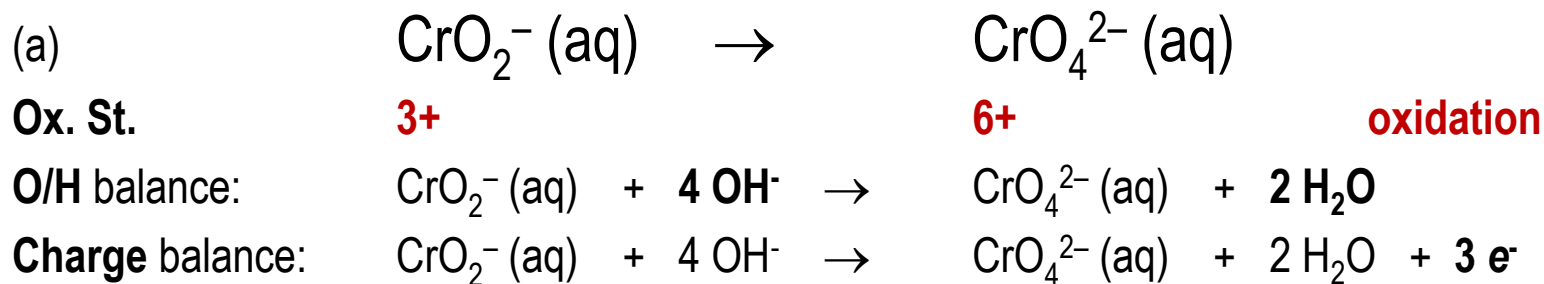


Ox. St.  $+4$   $+3$  **reduction**



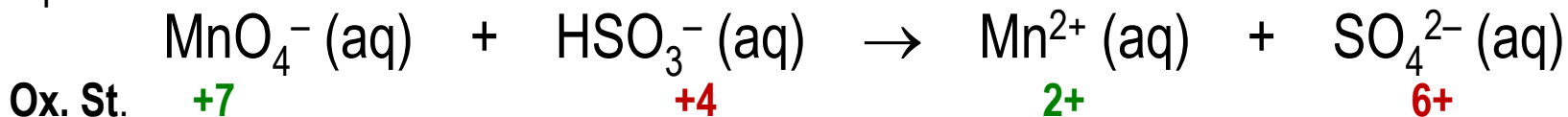
# Balancing Redox Reactions Sample Problems

2. The half-reactions here are in **basic** solution. You may need to use  $\text{OH}^-$  or the  $\text{OH}^- / \text{H}_2\text{O}$  pair to balance the equation.

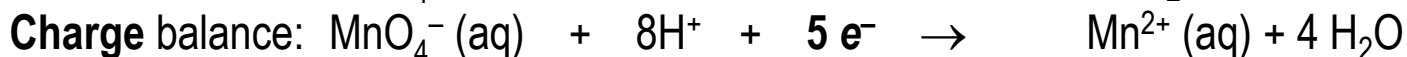
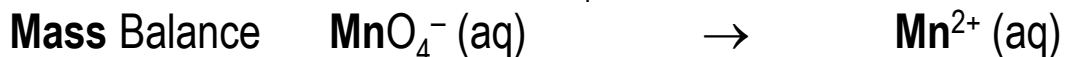


# Balancing Redox Reactions Sample Problems

3. The reactions here are in acid solution, meaning that  $H^+$  or  $H^+$  and  $H_2O$  may be used to balance the equation.

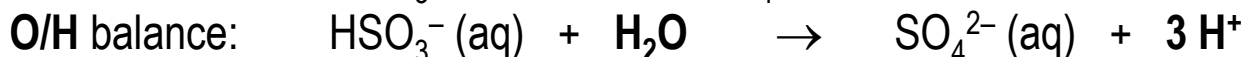
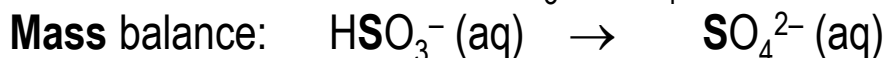


**Reduction half reaction:**  $\text{MnO}_4^- / \text{Mn}^{2+}$

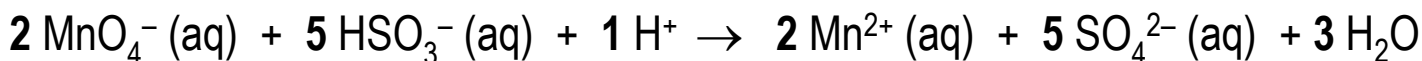
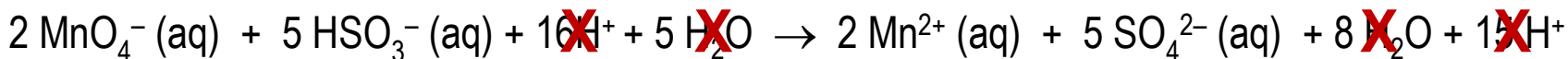


x 2

**Oxidation half reaction:**  $\text{HSO}_3^- / \text{SO}_4^{2-}$



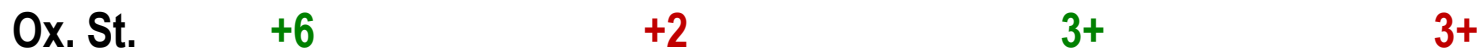
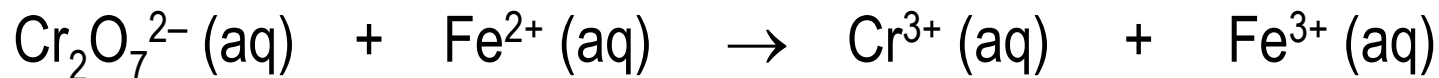
x 5



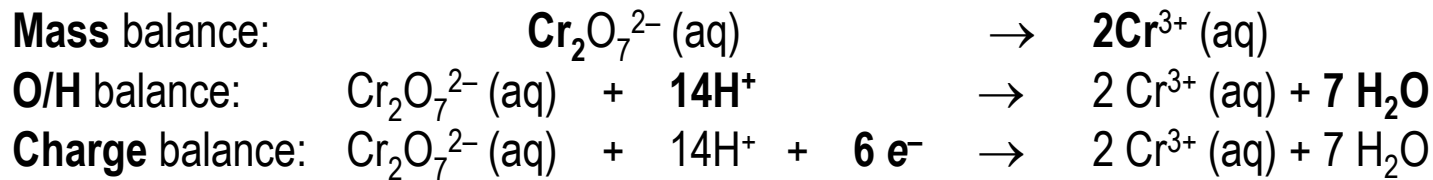


# Balancing Redox Reactions Sample Problems

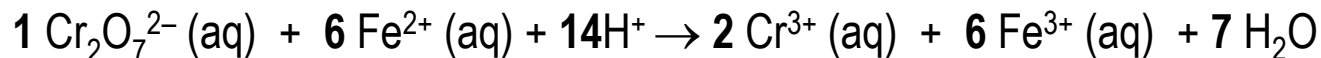
4. The reactions here are in **acid** solution, meaning that  $\text{H}^+$  or  $\text{H}^+$  and  $\text{H}_2\text{O}$  may be used to balance the equation.



**Reduction half-reaction:**  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$

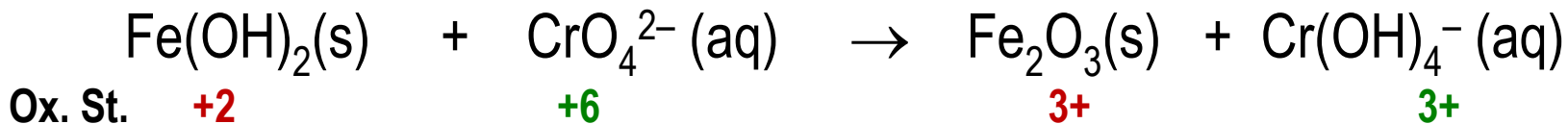


**Oxidation half-reaction:**  $\text{Fe}^{2+}/\text{Fe}^{3+}$

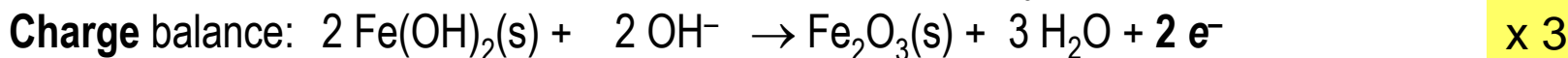
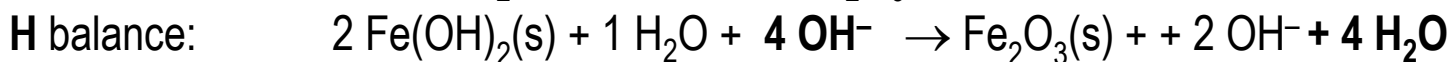
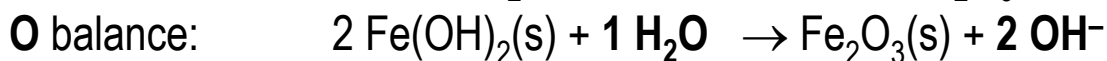
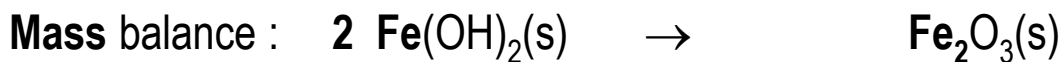


# Balancing Redox Reactions Sample Problems

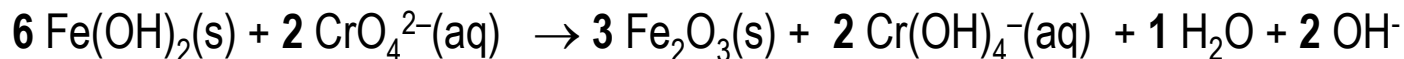
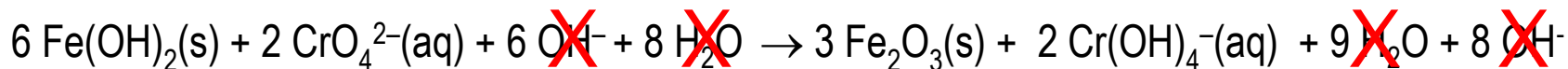
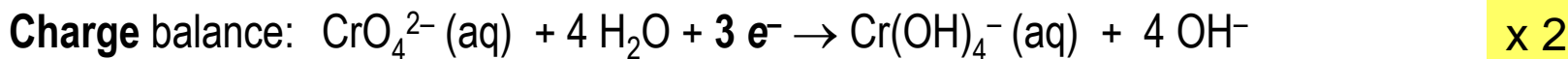
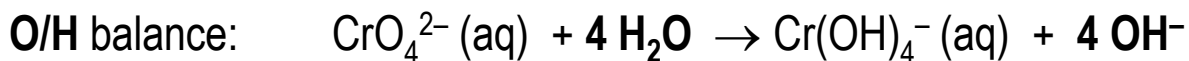
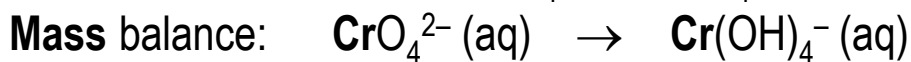
5. The reactions here are in **basic** solution. You may need to add OH<sup>-</sup> or the OH<sup>-</sup> / H<sub>2</sub>O pair to balance the equation.



**Oxidation half-reaction:** Fe(OH)<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>



**Reduction half-reaction:** CrO<sub>4</sub><sup>2-</sup>/Cr(OH)<sub>4</sub><sup>-</sup>



# Gibbs Free Energy and Cell Potential

The **Gibbs Free Energy** of reaction tells us whether a certain reaction is **product** favored or **reactant**-favoured in the forward direction

The **electrochemical** analogue is the **cell potential** given by the symbol  $E^\circ$

$E^\circ$  is expressed in the common electrical unit of **volts**. ( $v = J/C$ )  $C = \text{Coulomb} = 6.24 \times 10^{18}$

The exact **relationship** between **cell potential** and **Gibbs energy** is given by:

$$\Delta G = -n F E \qquad F = 96485 \text{ C/mol} \qquad \Delta G^\circ = -n F E^\circ$$

**Faradays Constant**

The **cell voltage**  $E$  has the **opposite sign convention** to that of  $\Delta G$ :

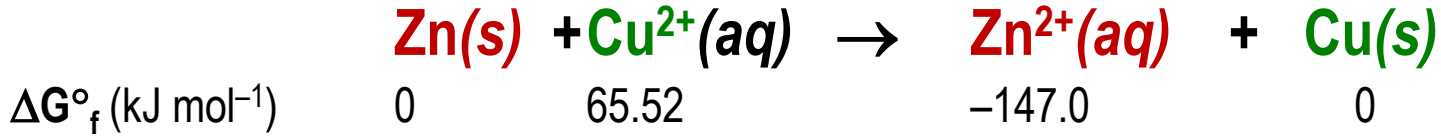
- |  |                                  |           |                           |
|--|----------------------------------|-----------|---------------------------|
| i) <b>Product</b> Favoured Reaction:   | <b>-ve <math>\Delta G</math></b> | <i>or</i> | <b>+ve <math>E</math></b> |
| ii) <b>Reactant</b> Favoured Reaction: | <b>+ve <math>\Delta G</math></b> | <i>or</i> | <b>-ve <math>E</math></b> |

**A product favoured** reaction **produces** a voltage, a.k.a. a **Voltaic cell** ( in honor of Alessandro Volta).

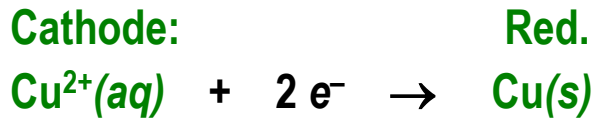
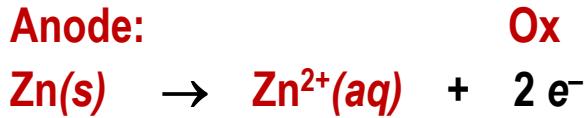
**A reactant favoured** reaction is **driven** by an **opposing** voltage, a.k.a. an **electrolytic cell**, where the process is referred to as **electrolysis**.

# Voltaic Cells

Consider the reaction:



$$\Delta G^\circ_{\text{rxn}} = -212.5 \text{ kJ mol}^{-1} < 0 \quad \& \quad n = 2$$



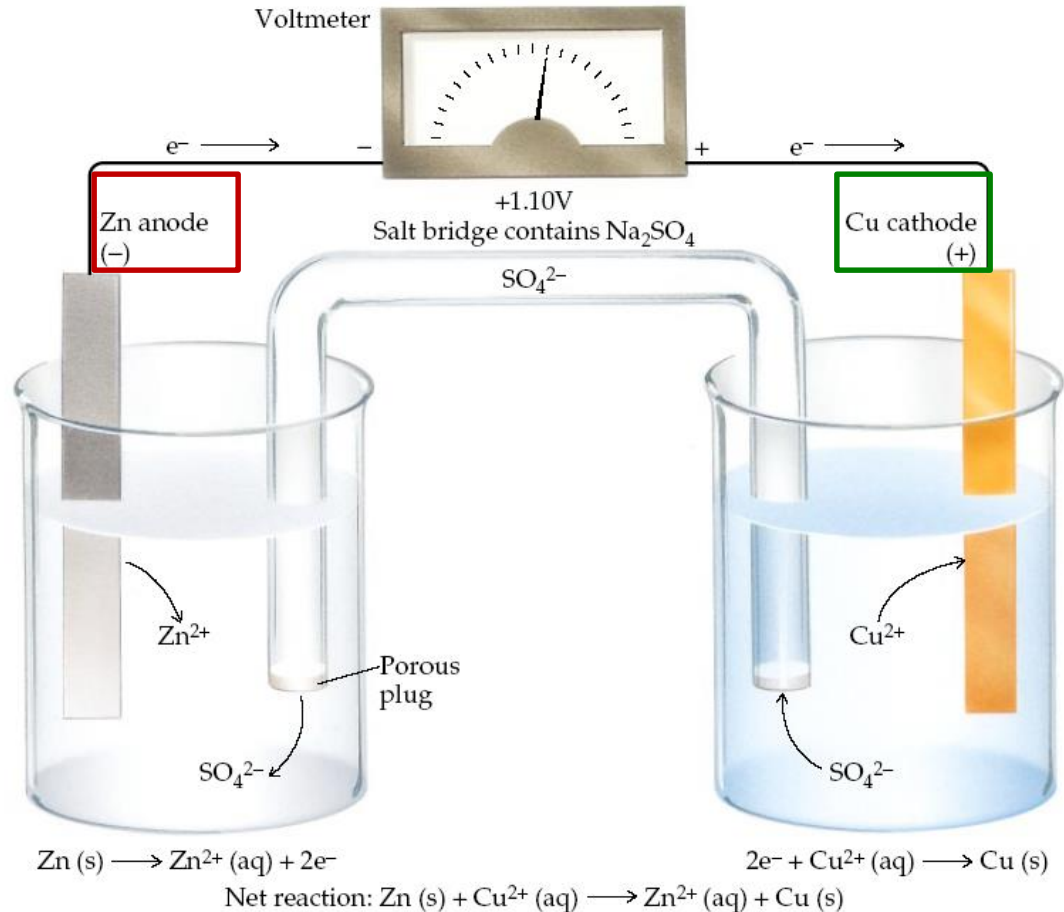
$$\Delta G^\circ = -n F E^\circ$$

$$E^\circ = -\Delta G^\circ / nF$$

$$= -(-212,500 \text{ J/mol} / 2 * 96,485 \text{ C/mol})$$

$$= 1.10 \text{ V}$$

**> 0** under zero load conditions



# Reversible cell reactions and cell notation

Although the reaction only requires a **copper(II) salt** and **metallic zinc**, the cell is constructed such that **both metallic zinc** and **copper** are present, along with copper and zinc sulfate.

This ensures a **reversible reaction**, as **accurate** potentials can only be measured for reversible electrochemical cells.

## Electrochemical Notation:

A **short-hand** notation indicates the **complete composition** of a given electrochemical cell.

The notation utilizes the **balanced** redox reaction, including both the **reactants** and the **products**.

The notation for the previous example would be:



Left Hand Side

Right Hand Side

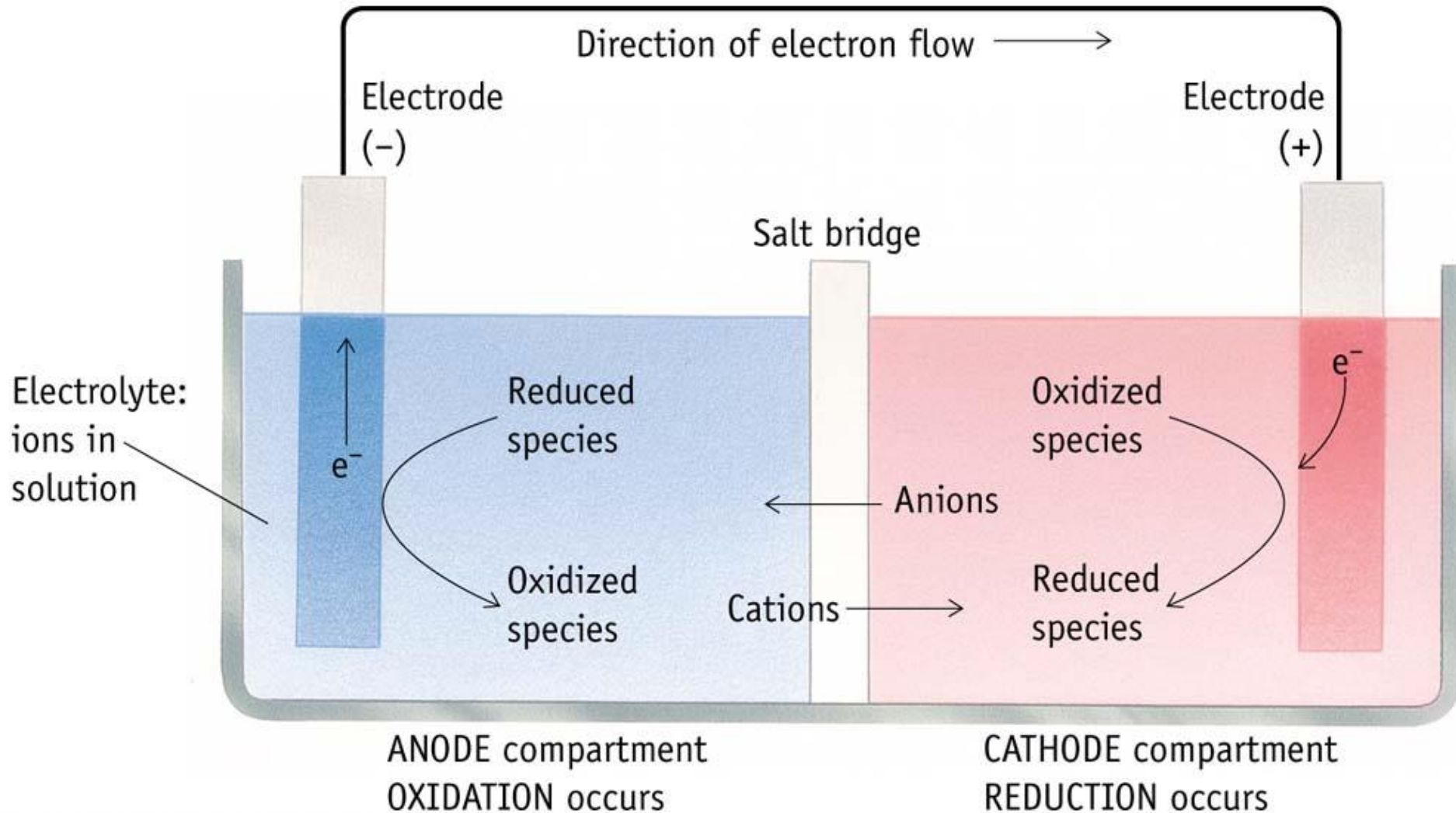
**Anode** reaction  
**Oxidation** reaction.

**Cathode** reaction  
**Reduction** reaction

The vertical lines, |, indicate a **phase boundary**, such as between a solid and a liquid.

Double lines, ||, indicate double boundaries, such as commonly occur when a **salt bridge** is placed between the two half cells.

# Electrochemical Cell Conventions



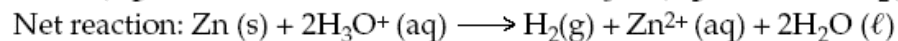
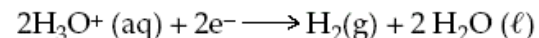
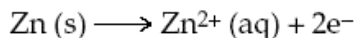
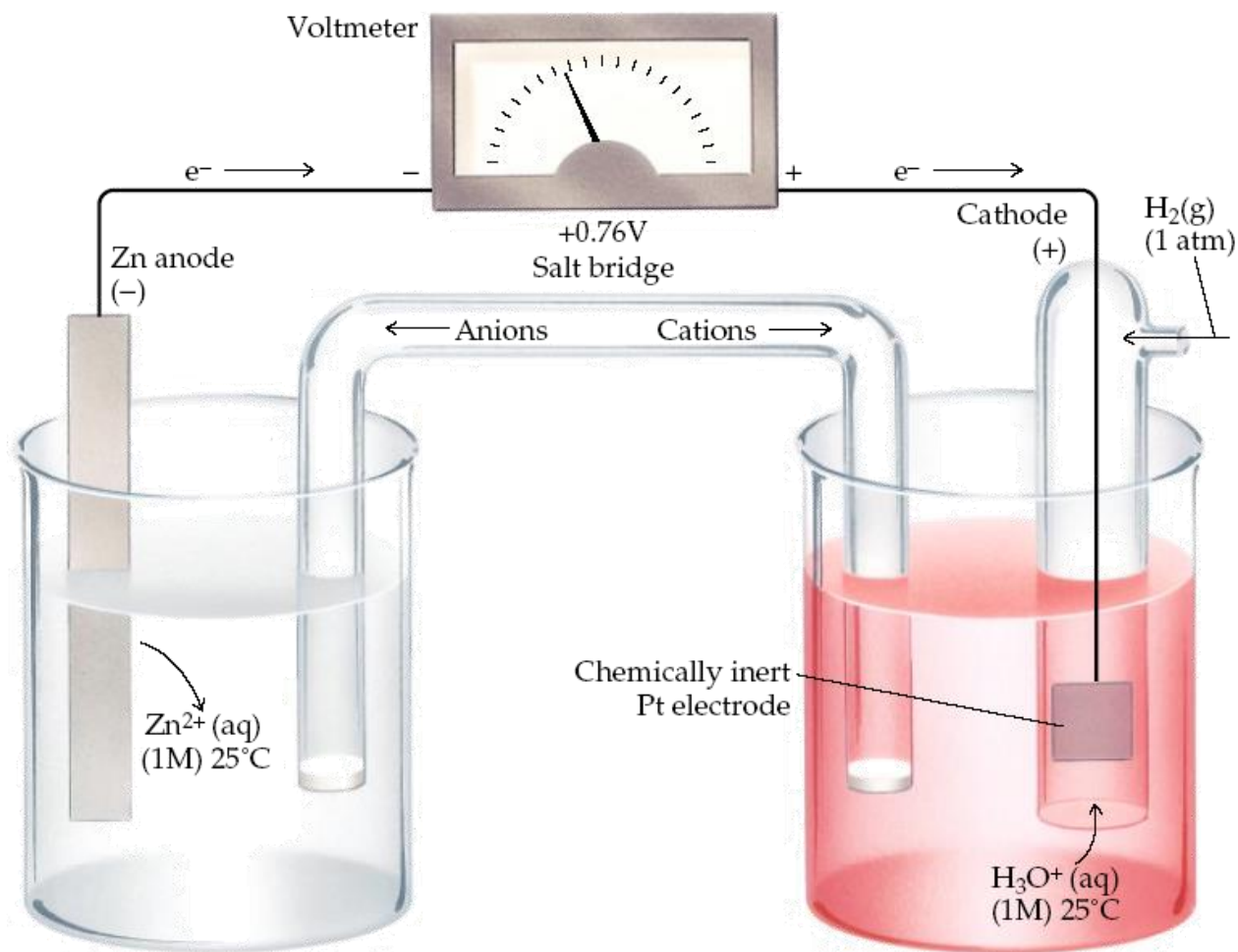
# Standard Half-Cell Reduction Potentials

The Cu/Zn cell has a **standard potential** of +1.10 V

Can we relate this to the voltage of the two “half-cells”?

Choose an arbitrary **reference point**:  
**Standard Hydrogen Electrode**, or SHE

Thus Zn/Zn<sup>2+</sup> has a **voltage** of +0.76 V against a SHE



# Standard Half-Cell Reduction Potentials

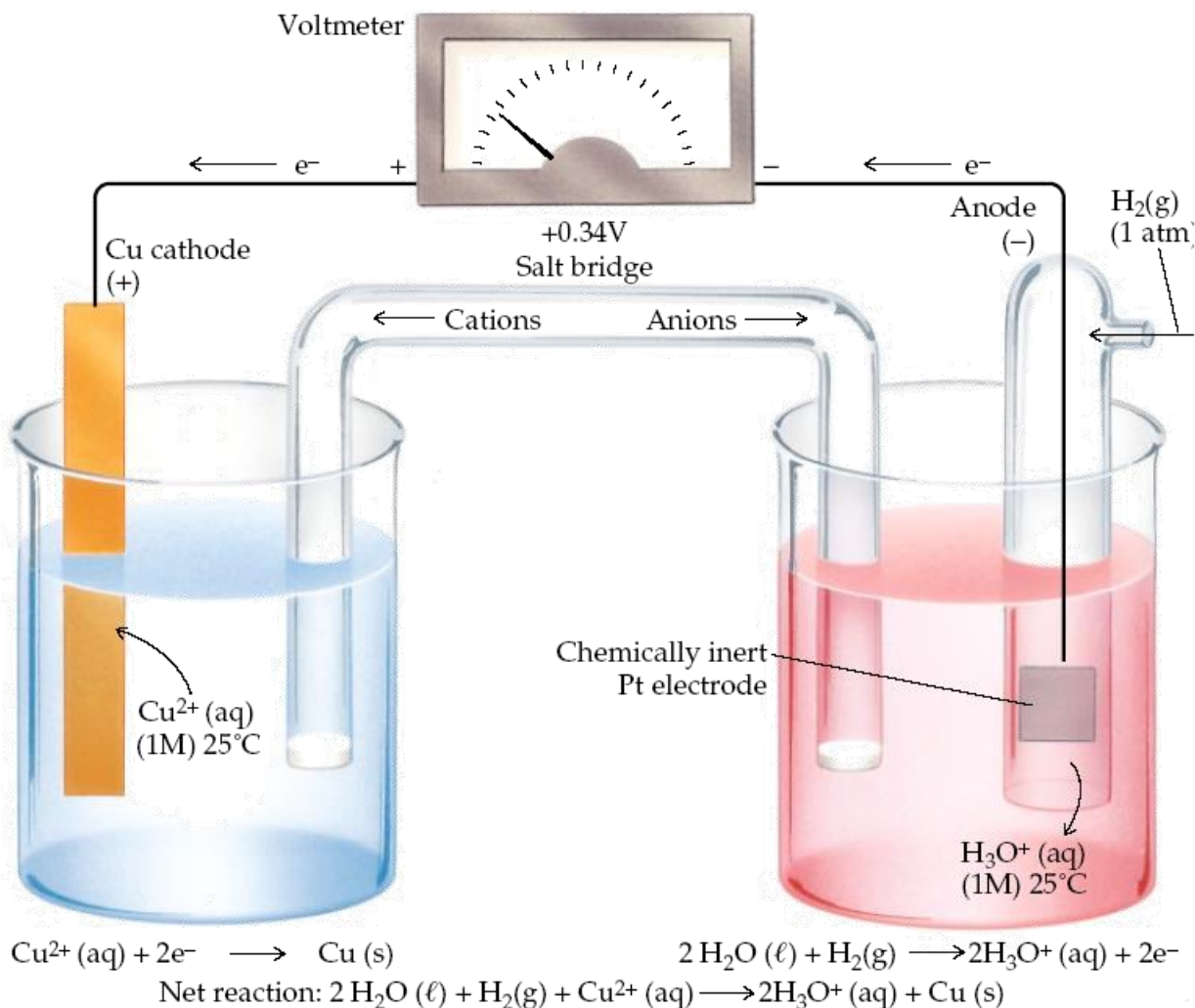
The Cu/Cu<sup>2+</sup> half cell has a **voltage** of +0.34 V against a SHE

**Combining** the two half-cell voltages gives  
 $+0.76 + +0.34 = +1.10 \text{ V}$

This is in **good agreement** with the measured voltage

These values have been compiled into a **general table**

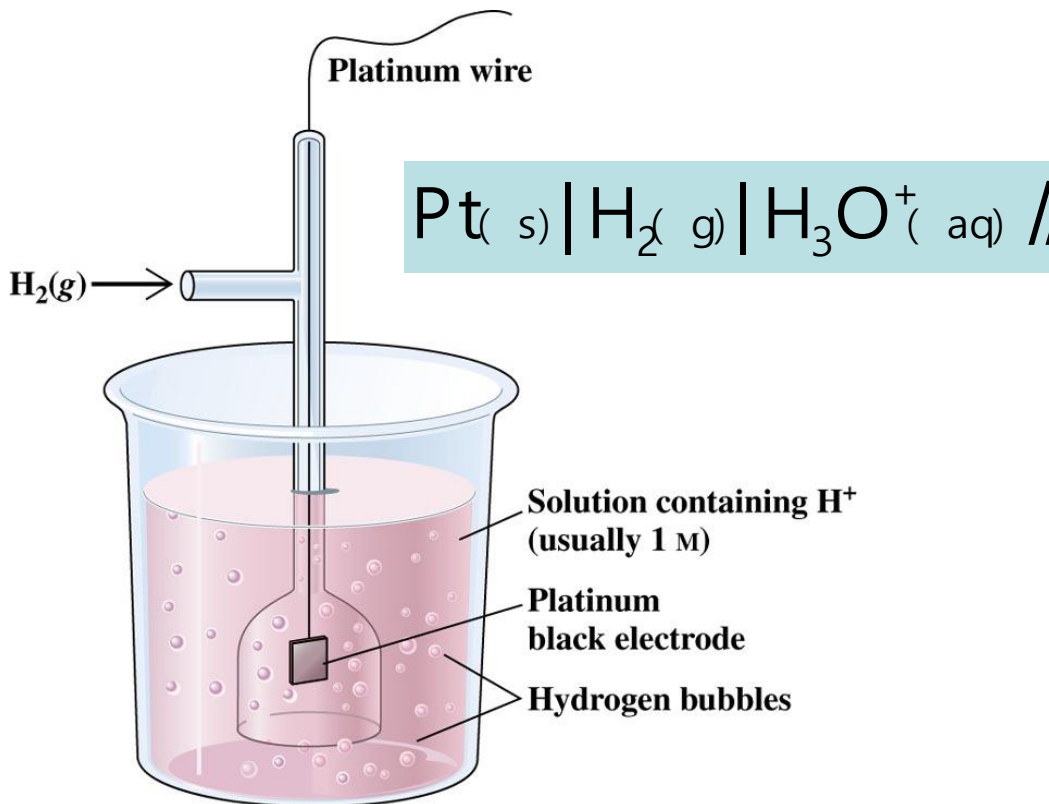
To account for the sign convention, the table is written only as **reduction reactions**





# Standard Hydrogen Electrode

The glass tube is a hydrogen electrode that can be used as real reference electrode  
The picture below is a diagram showing the function of this device.



© 2003 Thomson-Brooks/Cole



## Strongest oxidizers

	Reduction Half-Reaction	$E^\circ$ (V)
$\text{F}_2(g) + 2 e^-$	$\rightarrow 2 \text{F}^-(aq)$	+2.87
$\text{H}_2\text{O}_2(aq) + 2 \text{H}_3\text{O}^+(aq) + 2 e^-$	$\rightarrow 4 \text{H}_2\text{O}(l)$	+1.77
$\text{PbO}_2(s) + \text{SO}_4^{2-}(aq) + 4 \text{H}_3\text{O}^+(aq) + 2 e^-$	$\rightarrow \text{PbSO}_4(s) + 6 \text{H}_2\text{O}(l)$	+1.685
$\text{MnO}_4^-(aq) + 8 \text{H}_3\text{O}^+(aq) + 5 e^-$	$\rightarrow \text{Mn}^{2+}(aq) + 12 \text{H}_2\text{O}(l)$	+1.52
$\text{Au}^{3+}(aq) + 3 e^-$	$\rightarrow \text{Au}(s)$	+1.50
$\text{Cl}_2(g) + 2 e^-$	$\rightarrow 2 \text{Cl}^-(aq)$	+1.360
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}_3\text{O}^+(aq) + 6 e^-$	$\rightarrow 2 \text{Cr}^{3+}(aq) + 21 \text{H}_2\text{O}(l)$	+1.33
$\text{O}_2(g) + 4 \text{H}_3\text{O}^+(aq) + 4 e^-$	$\rightarrow 6 \text{H}_2\text{O}(l)$	+1.229
$\text{Br}_2(l) + 2 e^-$	$\rightarrow 2 \text{Br}^-(aq)$	+1.08
$\text{NO}_3^-(aq) + 4 \text{H}_3\text{O}^+(aq) + 3 e^-$	$\rightarrow \text{NO}(g) + 6 \text{H}_2\text{O}(l)$	+0.96
$\text{OCl}^-(aq) + \text{H}_2\text{O}(l) + 2 e^-$	$\rightarrow \text{Cl}^-(aq) + 2 \text{OH}^-(aq)$	+0.89
$\text{Hg}^{2+}(aq) + 2 e^-$	$\rightarrow \text{Hg}(l)$	+0.855
$\text{Ag}^+(aq) + e^-$	$\rightarrow \text{Ag}(s)$	+0.80
$\text{Hg}_2^{2+}(aq) + 2 e^-$	$\rightarrow 2 \text{Hg}(l)$	+0.789
$\text{Fe}^{3+}(aq) + e^-$	$\rightarrow \text{Fe}^{2+}(aq)$	+0.771
$\text{I}_2(s) + 2 e^-$	$\rightarrow 2 \text{I}^-(aq)$	+0.535
$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 e^-$	$\rightarrow 4 \text{OH}^-(aq)$	+0.40
$\text{Cu}^{2+}(aq) + 2 e^-$	$\rightarrow \text{Cu}(s)$	+0.337
$\text{Sn}^{4+}(aq) + 2 e^-$	$\rightarrow \text{Sn}^{2+}(aq)$	+0.15
$2 \text{H}_3\text{O}^+(aq) + 2 e^-$	$\rightarrow \text{H}_2(g) + 2 \text{H}_2\text{O}(l)$	<b>0.00</b>

Reduction Half-Reaction		$E^\circ$ (V)
$2 \text{H}_3\text{O}^+ (aq) + 2 \text{e}^-$	$\rightarrow \text{H}_2(g) + 2 \text{H}_2\text{O}(l)$	<b>0.00</b>
$\text{Sn}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Sn}(s)$	-0.14
$\text{Ni}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Ni}(s)$	-0.25
$\text{V}^{3+} (aq) + \text{e}^-$	$\rightarrow \text{V}^{2+} (aq)$	-0.255
$\text{PbSO}_4(s) + 2 \text{e}^-$	$\rightarrow \text{Pb}(s) + \text{SO}_4^{2-} (aq)$	-0.356
$\text{Cd}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Cd}(s)$	-0.40
$\text{Fe}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Fe}(s)$	-0.44
$\text{Zn}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Zn}(s)$	-0.763
$2 \text{H}_2\text{O}(l) + 2 \text{e}^-$	$\rightarrow \text{H}_2(g) + 2 \text{OH}^- (aq)$	-0.8277
$\text{Al}^{3+} (aq) + 3 \text{e}^-$	$\rightarrow \text{Al}(s)$	-1.66
$\text{Mg}^{2+} (aq) + 2 \text{e}^-$	$\rightarrow \text{Mg}(s)$	-2.37
$\text{Na}^+ (aq) + \text{e}^-$	$\rightarrow \text{Na}(s)$	-2.714
$\text{K}^+ (aq) + \text{e}^-$	$\rightarrow \text{K}(s)$	-2.925
$\text{Li}^+ (aq) + \text{e}^-$	$\rightarrow \text{Li}(s)$	-3.045

**Strongest  
reducing  
agents**

† In volts (V) versus the standard hydrogen electrode.

# Examples

## Copper/Lithium cell

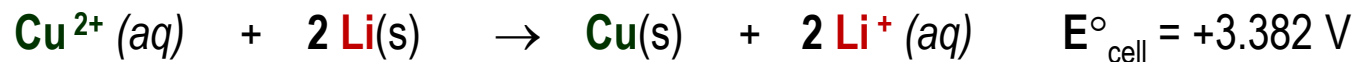
The **standard reduction potentials** of the half-reactions from the table:



We now **combine** them *in such a way as to get a **positive overall cell potential***. This means we must reverse the **lithium** equation, making it the **anode** (where the **oxidation** will take place.)



cell potential for the overall reaction:



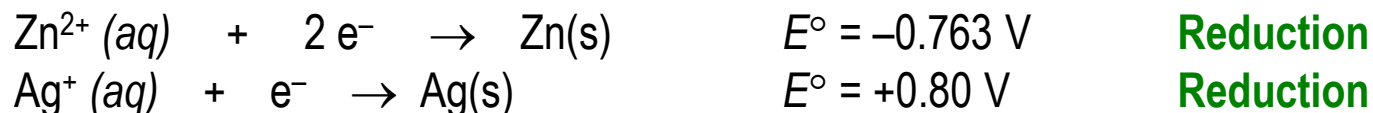
Note: The **voltage** was **not doubled** when the coefficients are **doubled**.  
However,  $n$  for this reaction = 2.

**Cell voltages** are therefore **independent of stoichiometry**. The stoichiometric information is stored in the value of  $n$ .

# Examples

## Silver/zinc cell

The **standard reduction potentials** for the half-reactions from the table:

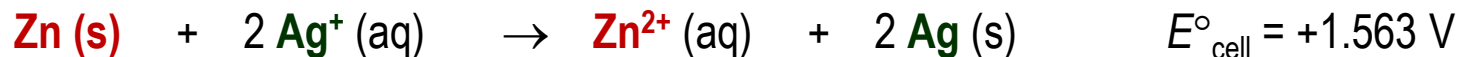


We now **combine** them *in such a way as to get a **positive overall cell potential***.

This means we must reverse the **zinc** equation, making it the **anode** (where the **oxidation** will take place.)



the cell potential for the overall reaction:



# Nernst Equation - Cells Non-Standard Conditions

**Voltaic cells** eventually get **depleted** and **stop** producing a voltage.

As the **reactants** are **consumed** the voltage produced decreases.

**Temperature** effects cell potential – the potential is **reduced** upon **cooling**.

**Walter Nernst** developed an expression, the **Nernst equation**, defined for the general equilibrium equation:



$$E = E^\circ - [RT/nF] \ln Q$$

$$= E^\circ - [RT/nF] \ln [a_C^c a_D^d / a_A^a a_B^b]$$

Frequently the equation is given for  $T = 298.15\text{K}$  as:

$$E = E^\circ - [0.0257/n] \ln Q$$

# Electrochemical Cells and Equilibrium Constants

We have already seen that  $\Delta G^\circ$  and  $E^\circ$  are related:  $\Delta G^\circ = -n F E^\circ$

We also know that  $\Delta G^\circ$  and  $K$  are related:  $\Delta G^\circ = -RT \ln K$

So it stands to reason that  $E^\circ$  and  $K$  are related, and you already *know* the relationship:

***An electrochemical reaction is at equilibrium when the cell voltage is zero***

So using the Nernst equation:

$$E = E^\circ - [RT/nF] \ln Q \quad \text{when } E = 0 \text{ V} \quad 0 = E^\circ - [RT/nF] \ln K$$

Gives the relationship between cell potential and equilibrium constant

$$\ln K = nFE^\circ/RT$$

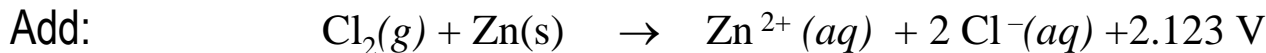
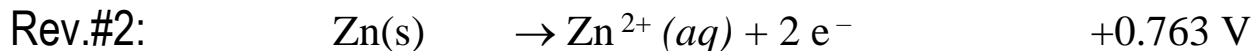
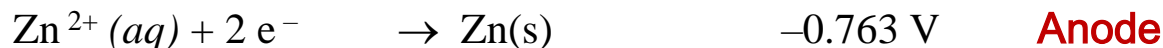
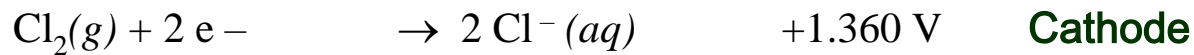
Note that “nF” is on top in this equation!

Many equilibria are actually determined in this way

# Electrochemistry Example Problems

1. Calculate the  $E_{\text{cell}}$  of a cell formed from a  $\text{Zn}^{2+}/\text{Zn}$  half-cell in which  $[\text{Zn}^{2+}] = 0.0500 \text{ M}$  and a  $\text{Cl}_2/\text{Cl}^-$  half cell in which the  $[\text{Cl}^-] = 0.0500 \text{ M}$  and  $P(\text{Cl}_2) = 1.25 \text{ bar}$  at  $25^\circ\text{C}$ .
2. In addition, provide a cell notation.

From the **Standard Reduction Potentials** Table:



$$E = E^\circ - [RT/nF] \ln[a_{\text{Zn}^{2+}} a_{\text{Cl}^-}^2 / a_{\text{Cl}_2} a_{\text{Zn}}]$$

$$= 2.123 \text{ V} - [(8.314 \text{ J/molK}) * (298.15 \text{ K}) / 2 * (96485 \text{ C/mol})] \ln [0.050 * (0.050)^2 / 1.25]$$

$$= 2.123 \text{ V} + 0.118 \text{ V} = 2.241 \text{ V}$$

Voltage *higher* than standard!





# Electrochemistry Example Problems

More oxidizing

3. Consider the following half-reactions:

Half-Reaction	$E^\circ$ (V)
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+ 1.61
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+ 0.80
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2 \text{Hg}(\text{l})$	+ 0.79
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	- 0.14
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	- 0.25
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	- 1.66

More reducing

- Which is the weakest oxidizing agent in the list?
- Which is the strongest oxidizing agent?
- Which is the strongest reducing agent?
- Which is the weakest reducing agent?
- Does Sn(s) reduce  $\text{Ag}^+(\text{aq})$  to Ag(s)?
- Does Hg(l) reduce  $\text{Sn}^{2+}(\text{aq})$  to Sn(s)?
- Name the ions that can be reduced by Sn(s).
- What metals can be oxidized by  $\text{Ag}^+(\text{aq})$ ?

$\text{Al}^{3+}$

$\text{Ce}^{4+}$

Al

$\text{Ce}^{3+}$

$+0.80 \text{ V} + 0.14 \text{ V} = +0.94 \text{ V}$ : YES

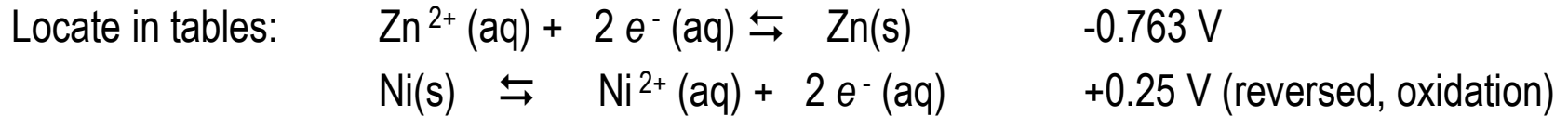
$-0.79 \text{ V} + -0.14 \text{ V} = -0.93 \text{ V}$ : NO

$\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ce}^{4+}$

Hg, Sn, Ni, Al

# Electrochemistry Example Problems

4. Calculate equilibrium constant for the following reaction:



So  $E_{\text{cell}} = -0.763 + 0.25 = -0.51$  V (two sig. fig. from the subtraction)

We use the equation:  $\ln K = nFE^{\circ}/RT$

which becomes:  $K = \exp[nFE^{\circ}/RT]$

$$\begin{aligned} K &= \exp[2 \cdot (96485 \text{ C/mol}) \cdot (-0.51 \text{ V}) / (8.314 \text{ J/molK}) \cdot (298.15 \text{ K})] \\ &= 5.7 \cdot 10^{-18} \end{aligned}$$

# pH meter: the glass electrode

A “pH meter” is actually a sensitive voltmeter attached to a **glass electrode**

The electrode response to changes in  $[\text{H}_3\text{O}^+]$  by altering its voltage as described by the Nernst equation

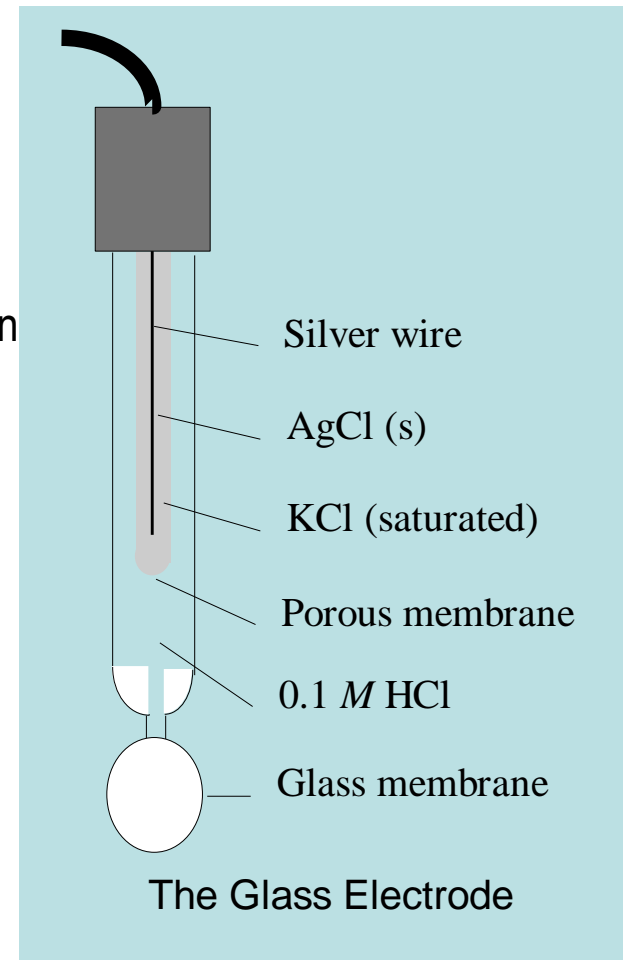
The key to its function as a meter is the very thin and fragile glass membrane made of special materials that allow  $[\text{H}_3\text{O}^+]$  but not other cations or anions to be sensed on the outer surface of the membrane

The meter is calibrated in pH units by rewriting the Nernst equation logarithms

$$\begin{aligned} E &= 0 - [0.0257/n] \ln [a(\text{H}^+_{\text{inside}})/a(\text{H}^+_{\text{outside}})] \\ &= - 0.0592 [\log a(\text{H}^+_{\text{inside}}) - \log(\text{H}^+_{\text{outside}})] \\ &= - 0.0592 \text{ pH} - 0.0592 \log[a(\text{H}^+_{\text{inside}})] \end{aligned}$$

$$\text{pH} = E/0.0592 + \text{constant}$$

Note that *calibration* is required to determine the constant

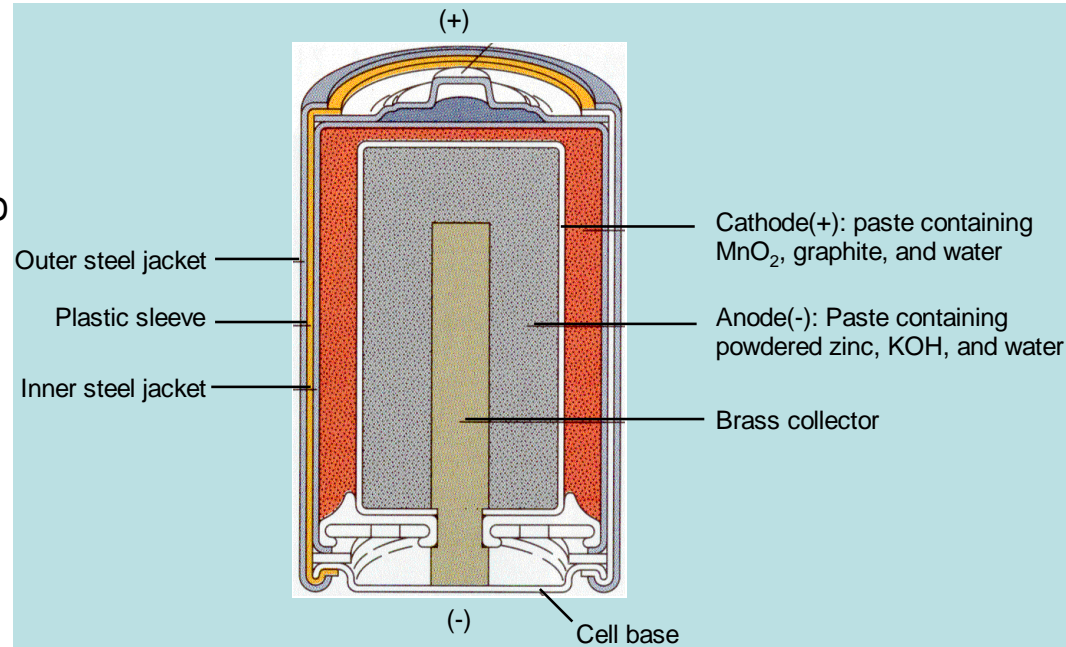


# Alkaline (Zinc/MnO<sub>2</sub> in KOH)

CATEGORY: Primary (Throwaway) Zinc Family

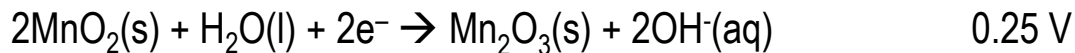
## CONSTRUCTION:

The alkaline dry cell. The anode is a paste of zinc, KOH, and water, which donates electrons to cell base via a brass collector. The cathode is a paste of MnO<sub>2</sub>, graphite, and water, which takes electrons from the inner steel case. A plastic sleeve separates the inner steel case from the outer steel jacket.

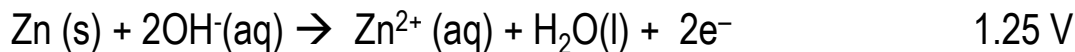


## REDOX REACTIONS

Positive terminal:



Negative terminal:



**Nominal cell voltage = +1.5 V**

The alkaline dry cell is more expensive than the Leclanché cell, but it is also more efficient. Again, zinc is the anode and manganese dioxide the oxidizing agent. The electrolyte is 40% KOH saturated with zinc oxide (ZnO).

# Lead Acid (PbO<sub>2</sub>/Pb)

CATEGORY: Secondary/Rechargeable

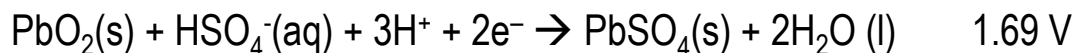
## CONSTRUCTION:

Shown in the picture is a 6-V (i.e. motorcycle) battery, which contains 3 individual cells in series. The anode (negative terminal) consists of a lead grid filled with spongy lead, and the cathode (positive terminal) is a lead grid filled with lead dioxide. The cell also contains 38% (by mass) sulfuric acid.

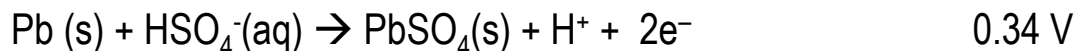
## REDOX REACTIONS

Nominal cell voltage = +2.0 V

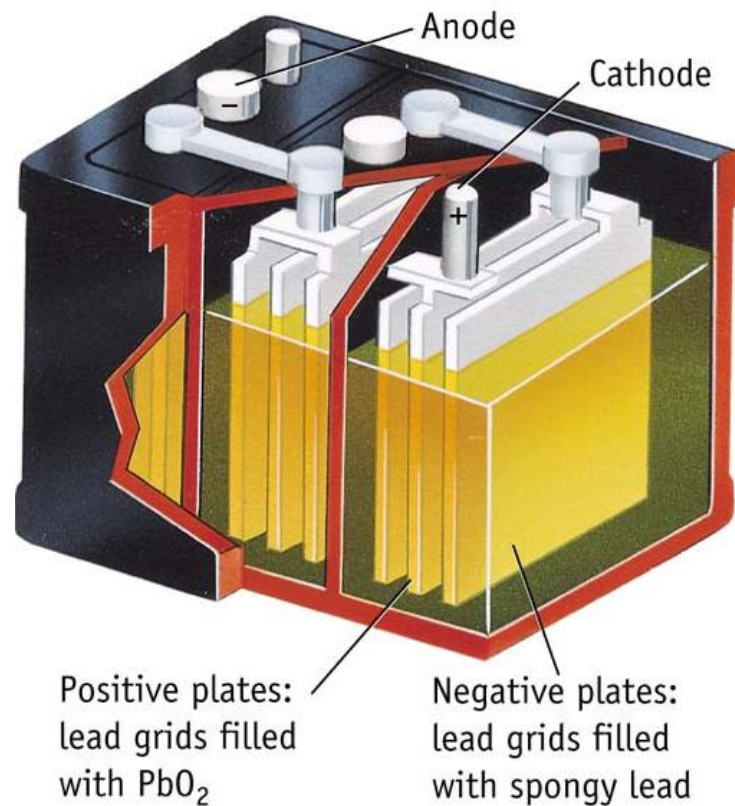
Positive terminal:



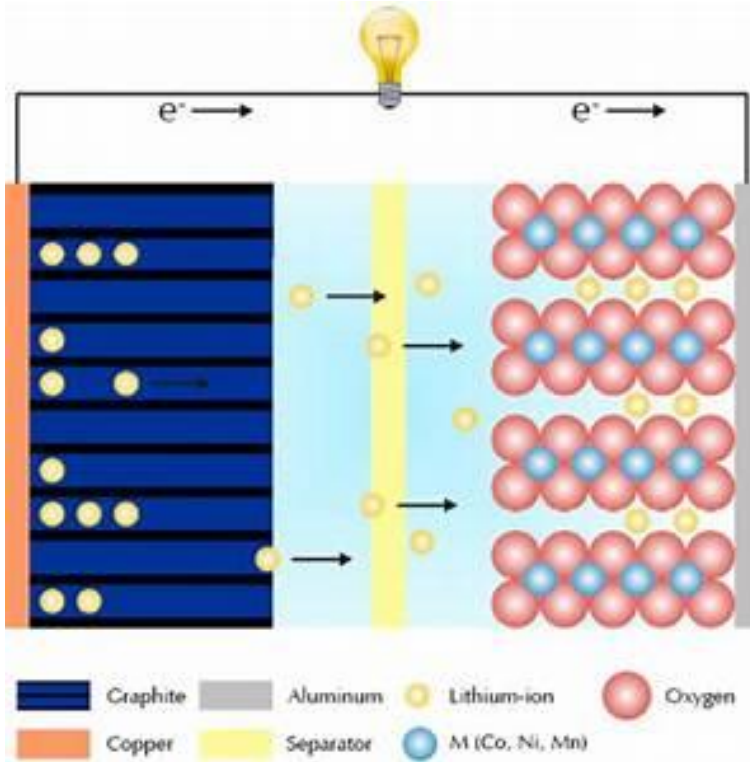
Negative terminal:



The cell equations shows that discharging depletes the sulfuric acid electrolyte and deposits solid lead sulfate on both electrodes. The electrolyte density can be measured by a hydrometer; it is charged when  $d = 1.28$  (37% H<sub>2</sub>SO<sub>4</sub>) and discharged when it is below 1.15 g/mL (21% H<sub>2</sub>SO<sub>4</sub>). The lead acid battery is extremely reliable, but heavy. Electrical cars using such batteries are too inefficient.



# Lithium Ion



E-bike

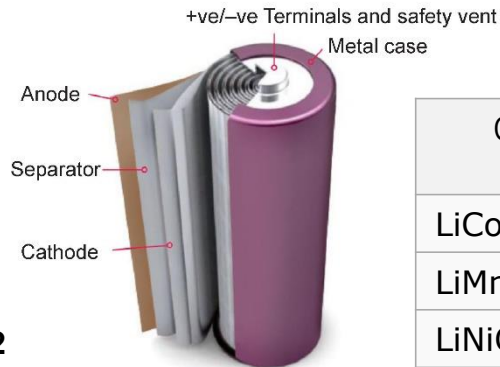


Anode	Voltage	Capacity
Graphite (LiC <sub>6</sub> )	0.1-0.2 V	372 mA·h/g
Titanate (Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> )	1-2 V	160 mA·h/g
Si (Li <sub>4.4</sub> Si) <sup>[26]</sup>	0.5-1 V	4212 mA·h/g
Ge (Li <sub>4.4</sub> Ge) <sup>[27]</sup>	0.7-1.2 V	1624 mA·h/g

**Anode:**



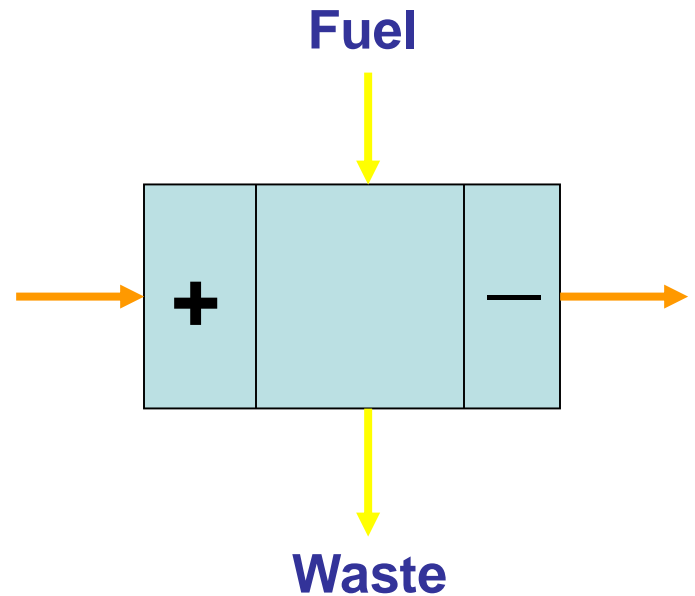
**Cathode:**



Cathode	Voltage	Capacity
LiCoO <sub>2</sub>	3.7 V	140 mA·h/g
LiMn <sub>2</sub> O <sub>4</sub>	4.0 V	100 mA·h/g
LiNiO <sub>2</sub>	3.5 V	180 mA·h/g

# Fuel Cells

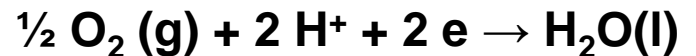
- o electrochemical reactor in which continuously supplied fuel and oxidant is converted directly to electrical energy
- o Most fuel cells involve the reaction of hydrogen with oxygen to form water, however new systems are coming that use alcohol
- o There are many different fuel cell designs that depend on their application. Size, operation temperature and power output are the major considerations.



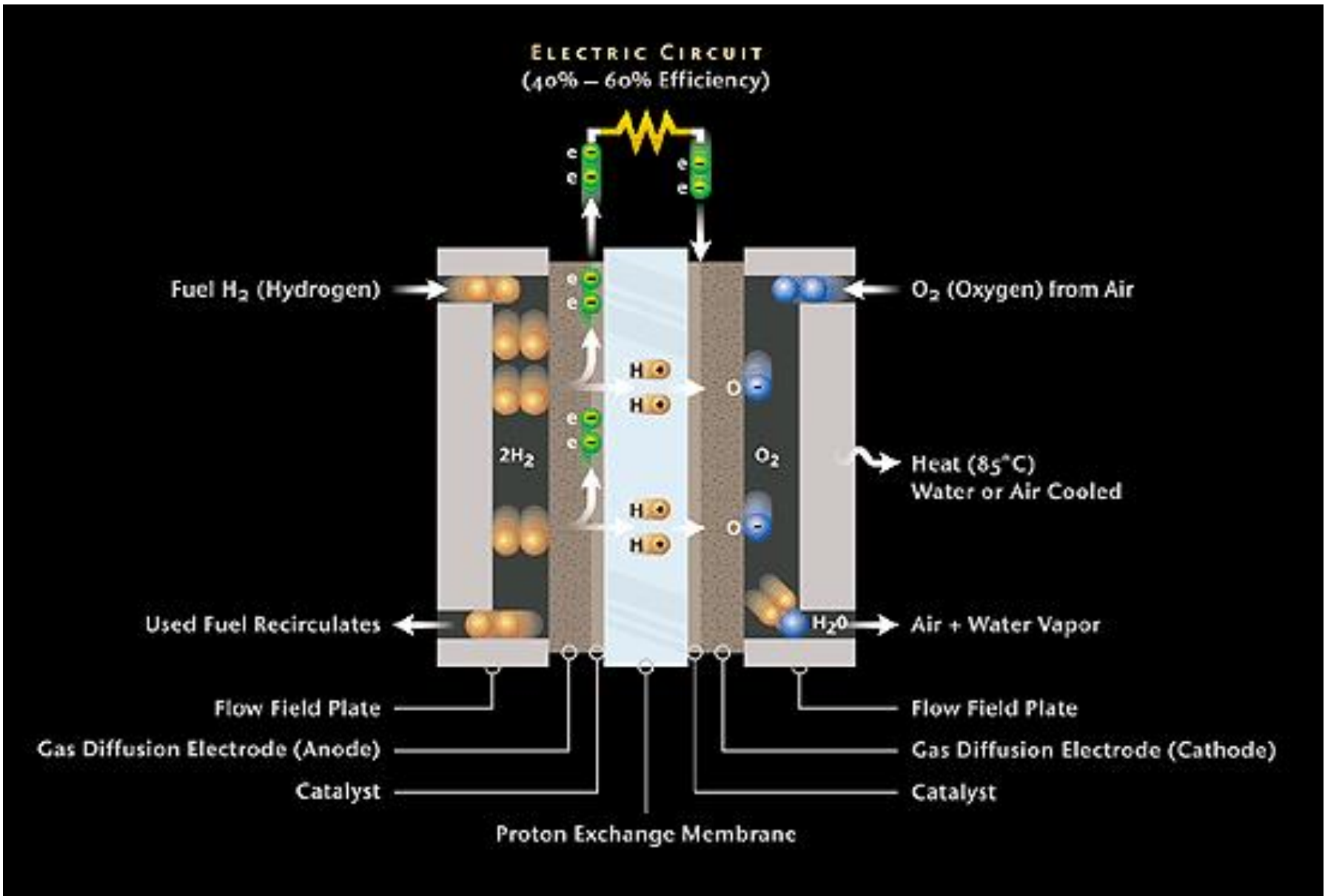
**Anode:**



**Cathode:**



# PEM FUEL CELL



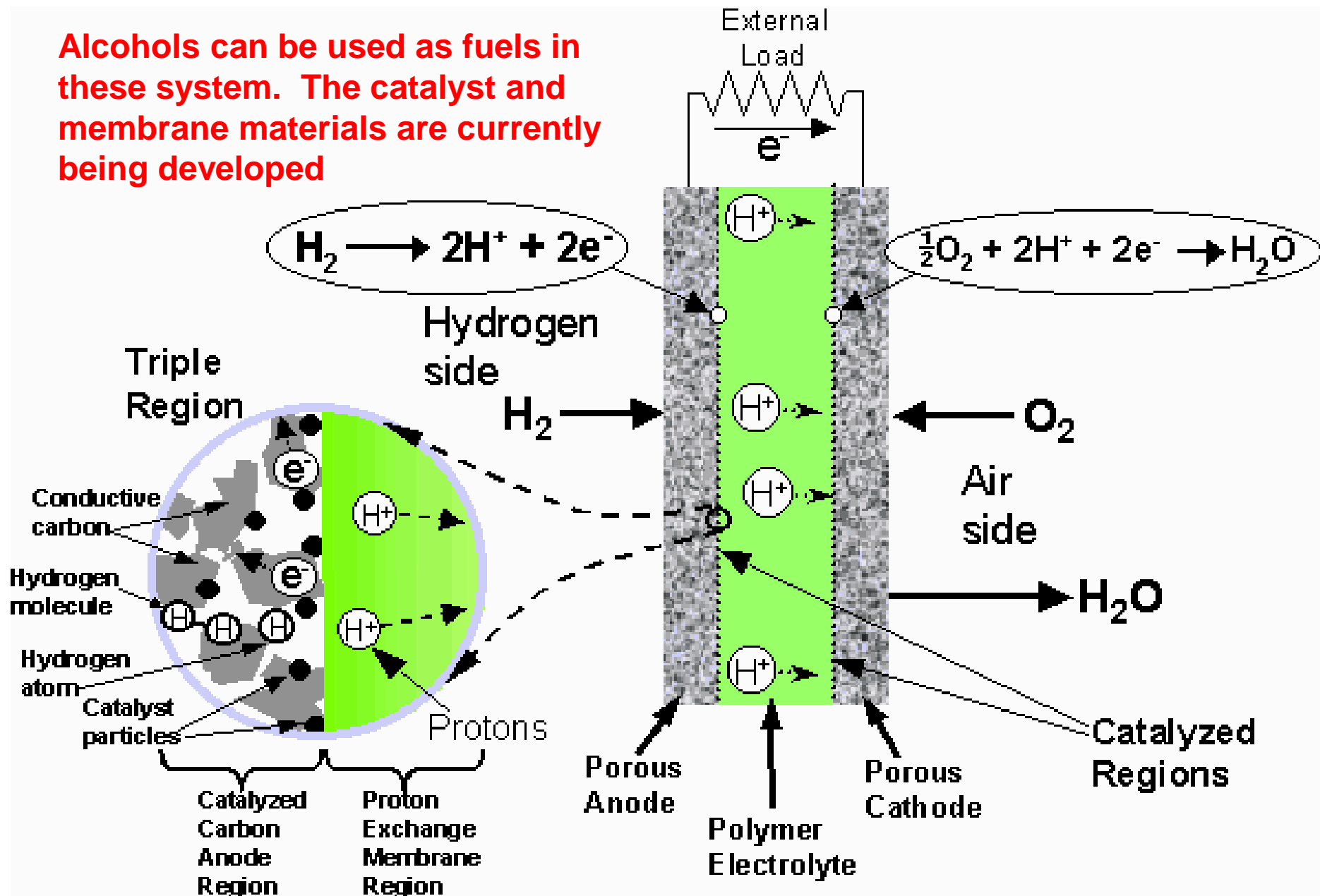


# Comparison of Five Fuel Cell Technologies

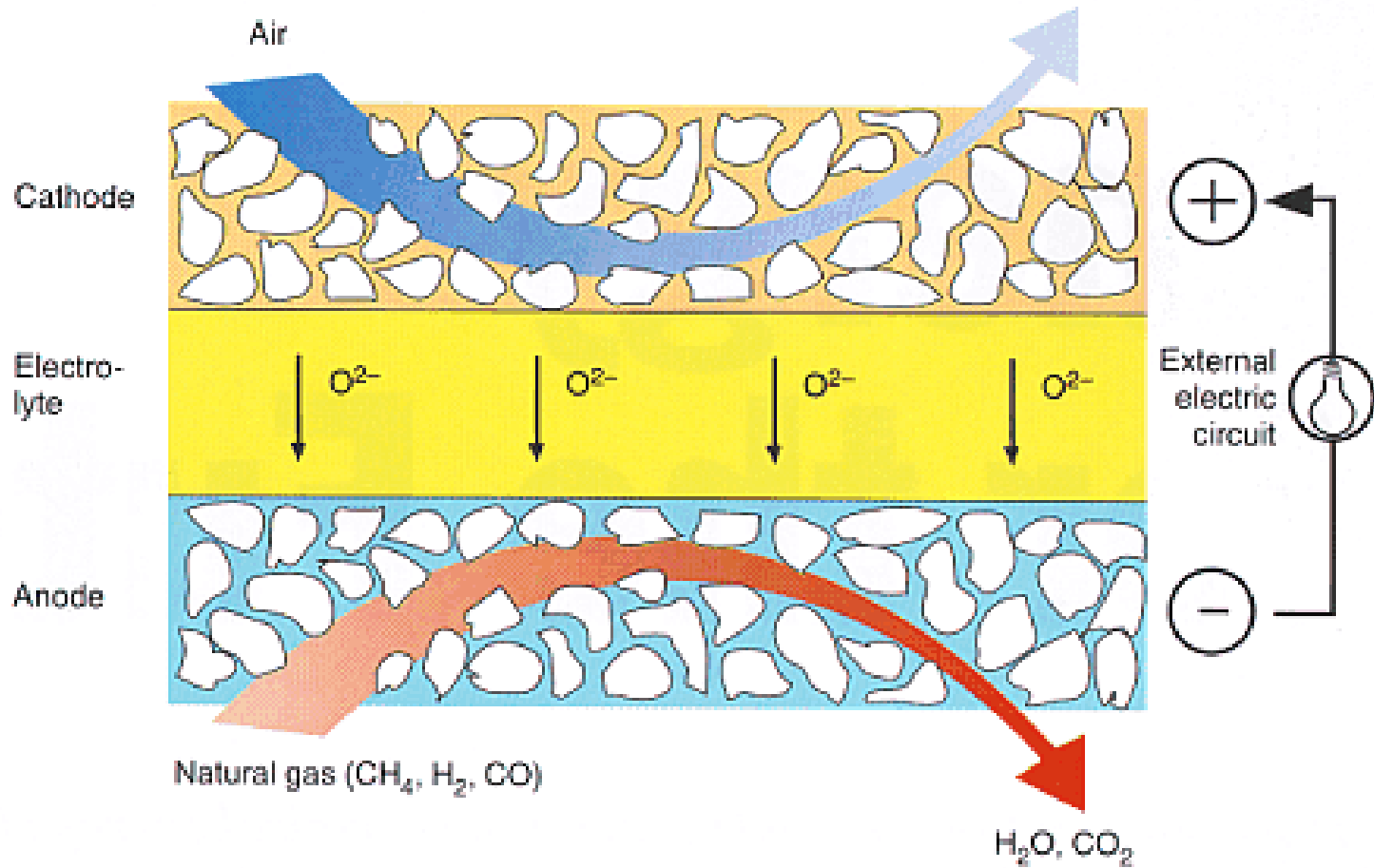
Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte/ Membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60 - 100	<b>Anode:</b> $H_2 \rightarrow 2H^+ + 2e^-$ <b>Cathode:</b> $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$ <hr/> <b>Cell:</b> $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100	<b>Anode:</b> $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$ <b>Cathode:</b> $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ <hr/> <b>Cell:</b> $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	175 - 200	<b>Anode:</b> $H_2 \rightarrow 2H^+ + 2e^-$ <b>Cathode:</b> $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$ <hr/> <b>Cell:</b> $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium and/or potassium carbonates, soaked in a matrix	600 - 1000	<b>Anode:</b> $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ <b>Cathode:</b> $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ <hr/> <b>Cell:</b> $H_2 + \frac{1}{2} O_2 + CO_2 \rightarrow H_2O + CO_2$  (CO <sub>2</sub> is consumed at cathode and produced at anode)
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of yttria is added	600 - 1000	<b>Anode:</b> $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ <b>Cathode:</b> $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$ <hr/> <b>Cell:</b> $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

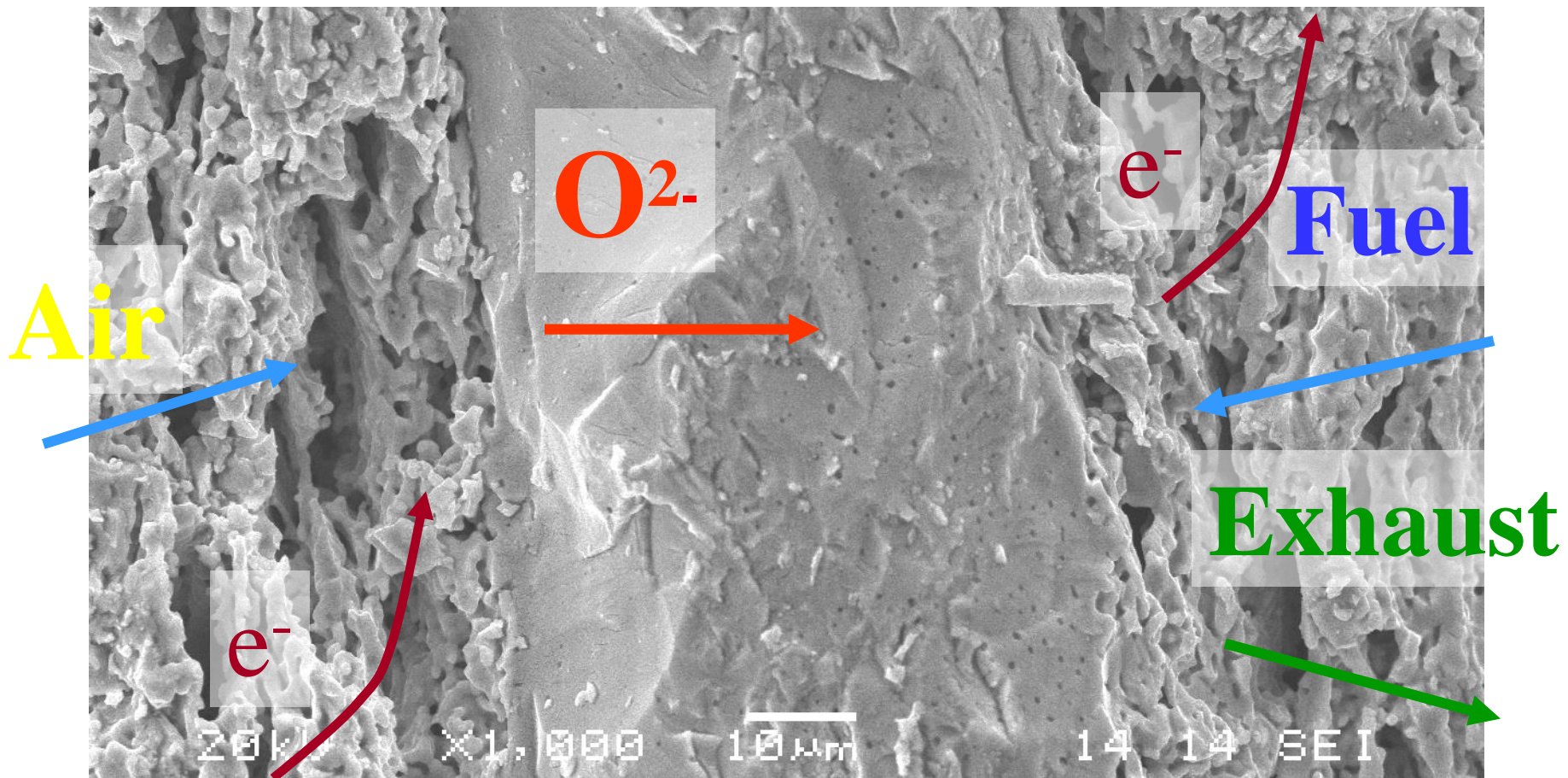
# Polymer Electrolyte Membrane Fuel Cell

Alcohols can be used as fuels in these system. The catalyst and membrane materials are currently being developed



# Solid Oxide Fuel Cell





# Fuel Cells for Motive Power in Vehicles

## Demonstrated

- o >3000 miles in 12 days - Range
- o 100 mph - Speed/power
- o -1 -> 35°C – Operating temperature range
- o World Record Fuel efficiency 25 km for 1 g H<sub>2</sub>.
- o A conventional car has fuel efficiency ranging between 7 to 20 km/l (18 to 50 MPG), or 14 to 5 L/100km
- o This translates to 6 to 18 m for 1 g of fuel
- o This is a difference of 1400 to 4000 fold.



## Key Targets

- Cost \$120/kW
- Lifetime, reliability

# Liquid Fuels

■ Energy Technology & Environmental Science

## High-Selectivity Electrochemical Conversion of CO<sub>2</sub> to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode

Yang Song,<sup>[a]</sup> Rui Peng,<sup>[a]</sup> Dale K. Hensley,<sup>[a]</sup> Peter V. Bonnesen,<sup>[a]</sup> Liangbo Liang,<sup>[a]</sup> Zili Wu,<sup>[a, b]</sup> Harry M. Meyer, III,<sup>[c]</sup> Miaofang Chi,<sup>[a]</sup> Cheng Ma,<sup>[a]</sup> Bobby G. Sumpter,<sup>[a, d]</sup> and Adam J. Rondinone<sup>\*[a]</sup>

Though carbon dioxide is a waste product of combustion, it can also be a potential feedstock for the production of fine and commodity organic chemicals provided that an efficient means to convert it to useful organic synthons can be developed. Herein we report a common element, nanostructured catalyst for the direct electrochemical conversion of CO<sub>2</sub> to ethanol with high Faradaic efficiency (63% at -1.2 V vs RHE) and high selectivity (84%) that operates in water and at ambient temper-

ature and pressure. Lacking noble metals or other rare or expensive materials, the catalyst is comprised of Cu nanoparticles on a highly textured, N-doped carbon nanospine film. Electrochemical analysis and density functional theory (DFT) calculations suggest a preliminary mechanism in which active sites on the Cu nanoparticles and the carbon nanospikes work in tandem to control the electrochemical reduction of carbon monoxide dimer to alcohol.

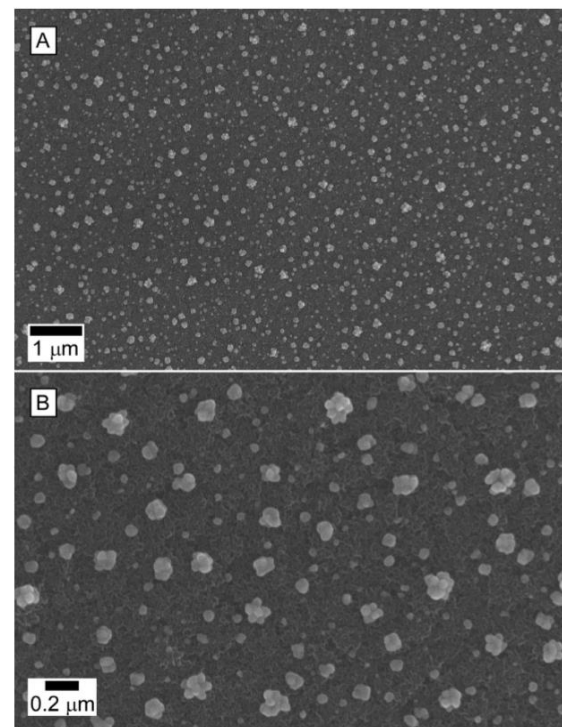
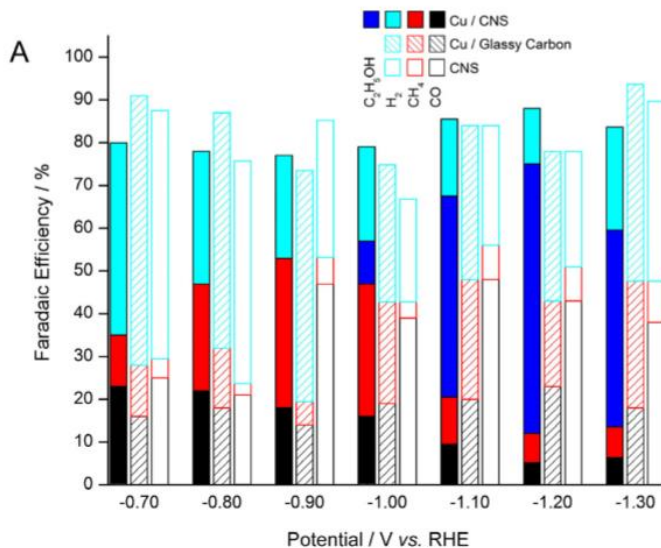
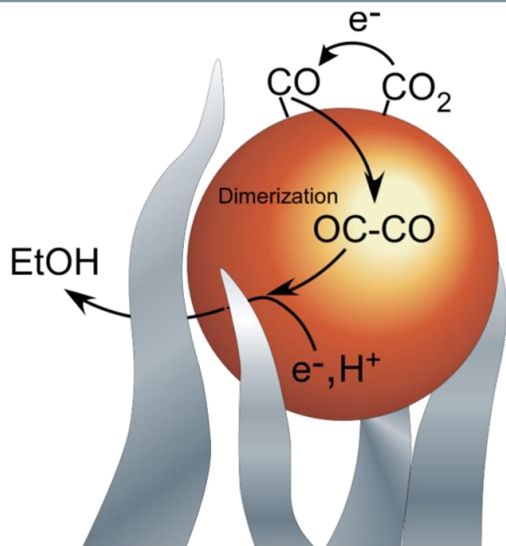
### Introduction

Closing the carbon cycle by utilizing CO<sub>2</sub> as a feedstock for currently used commodities, in order to displace a fossil feedstock, is an appropriate intermediate step towards a carbon-free future. Direct electrochemical conversion of CO<sub>2</sub> to useful products has been under investigation for a few decades. Metal-based catalysts, such as copper,<sup>[1]</sup> platinum,<sup>[2]</sup> iron,<sup>[3]</sup> tin,<sup>[4]</sup> silver,<sup>[5]</sup> and gold,<sup>[6]</sup> along with carbons such as g-C<sub>3</sub>N<sub>4</sub><sup>[7]</sup> have been the primary focus for CO<sub>2</sub> reduction, with some very high Faradaic efficiencies for methane conversion. Copper is argu-

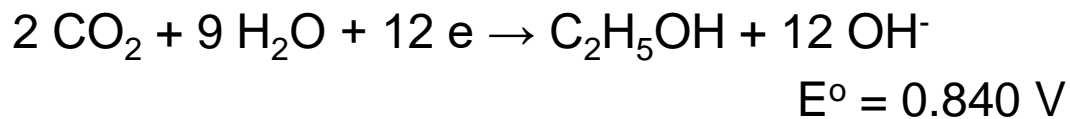
ably the best-known metal catalyst for electrochemical CO<sub>2</sub> reduction,<sup>[8]</sup> capable of electrochemically converting CO<sub>2</sub> into more than 30 different products,<sup>[9]</sup> including carbon monoxide (CO), formic acid (HCOOH), methane (CH<sub>4</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) or ethane (C<sub>2</sub>H<sub>6</sub>), but efficiency and selectivity for any product heavier than methane are far too low for practical use.<sup>[10]</sup> Competing reactions limit the yield of any one liquid product to single-digit percentages.<sup>[8]</sup>

Polycrystalline Cu foil produces a mixture of compounds in CO<sub>2</sub>-saturated aqueous solutions that are dominated either by H<sub>2</sub> at low overpotential, or by CO and HCOO<sup>-</sup> at high overpotential, or by hydrocarbons and multi-carbon oxygenates at

# Electrochemical ETOH production



Cathode



Anode

