### Electrochemistry

Part Three: Electrochemical Cells (Batteries)





• The world's first truly handheld mobile phone was invented in 1973 by Martin Cooper of Motorola.

• The phone weighed 1.1 kg and measured 23 cm long, 13 cm deep and 4.45 cm wide.

 It was a prototype offering 30 minutes of talk time and took 10 hours to recharge.





 Many of the improvements that have been made to mobile phones since 1973 have only been possible due to developments in the batteries that they use.

 Scientists are constantly trying to develop batteries that are smaller, lighter, charge faster, last for longer, and are environmentally friendly.

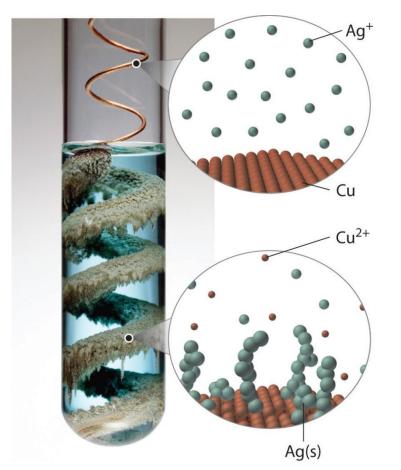


What happens in an electrochemical cell? How do they generate electricity?



 What would you observe when a piece of copper wire is placed in a test tube containing an aqueous solution of silver nitrate?

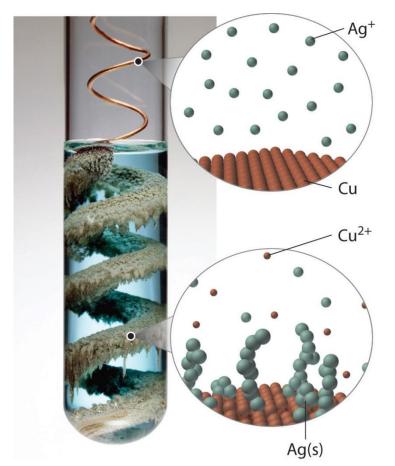




 Copper is more reactive than silver, and is therefore placed above silver in the reactivity series.

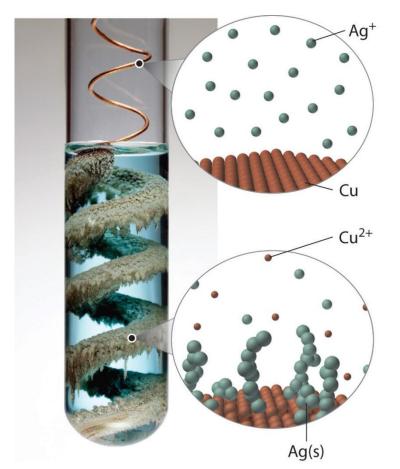
• Copper will displace silver from the silver nitrate.





- This is a redox reaction: Cu(s) + 2AgNO<sub>3</sub>(aq) ↓
  Cu(NO<sub>3</sub>)<sub>2</sub>(aq) + 2Ag(aq)
  - The ionic equation is: Cu(s) + 2Ag<sup>+</sup>(aq) ↓
    Cu<sup>2+</sup>(aq) + 2Ag(s)
- The ionic half-equations are:  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$  $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$

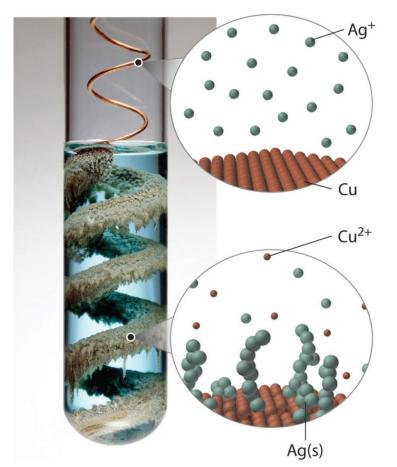




- Copper atoms are oxidised to copper(II) ions (loss of electrons, increase in oxidation state from 0 to +2).
  - Copper is the *reducing* agent, it reduces the silver ions to elemental silver.

• As copper(II) ions move into the aqueous solution, the solution turns *blue*.





- Silver ions are *reduced* to silver atoms (gain of electrons, decrease in oxidation state from +1 to 0).
- Silver is the oxidising agent. It oxidises the copper atoms to copper(II) ions.
- Crystals of silver form over the surface of the copper.



• Now imagine that the reaction for the copper, and the reaction for the silver, take place in *two separate beakers*.

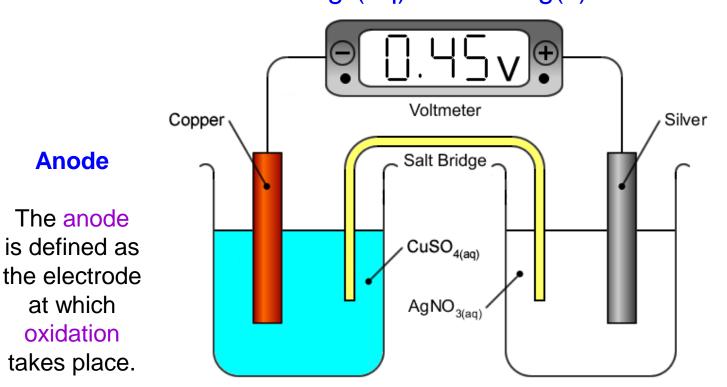
 Electrons can no longer be transferred directly from the copper atoms to the silver ions. Instead, the *electrons must travel through wires* to get from one metal to the other.

• This is a *simple battery*.



#### Combination of Copper and Silver Half-cells

- Atoms of the more reactive metal (copper) are oxidized: Cu(s) → Cu<sup>2+</sup>(aq) + 2e<sup>-</sup>
- lons of the less reactive metal (silver ions) are reduced:  $Ag^+(aq) + e^- \rightarrow Ag(s)$



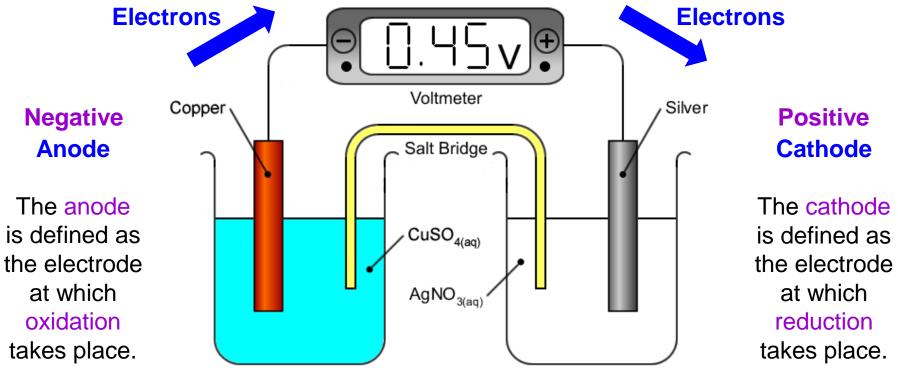
#### Cathode

The cathode is defined as the electrode at which reduction takes place.



#### **Combination of Copper and Silver Half-cells**

• Electrons flow through the external circuit from the more reactive metal (anode: site of oxidation) to the less reactive metal (cathode: site of reduction). Because negatively charged electrons will flow from negative to positive, this means that the anode is the negative electrode while the cathode is the positive electrode!

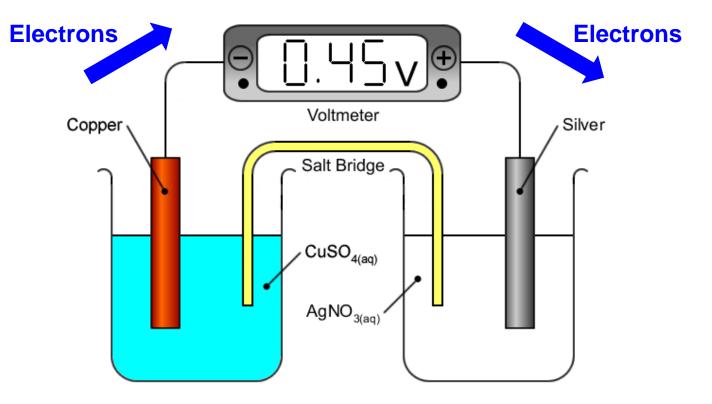




#### Combination of Copper and Silver Half-cells

 Note: The reactions that take place in an electrochemical cell are exothermic.

• Electrical energy is produced by the chemical system.



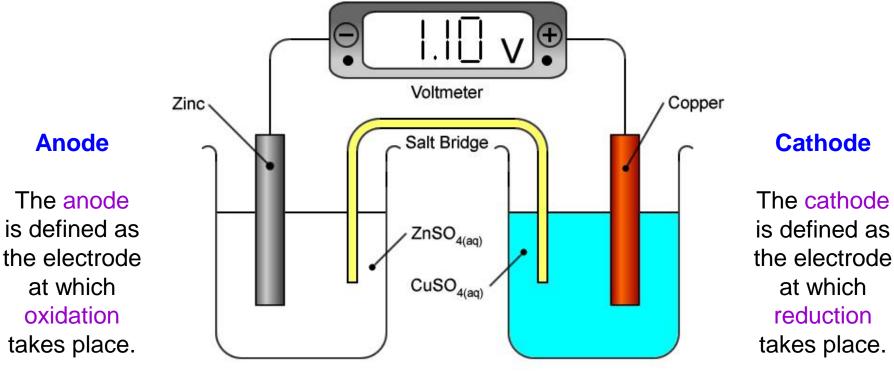


#### Combination of Zinc and Copper Half-cells

• Atoms of the more reactive metal (zinc) are oxidized:



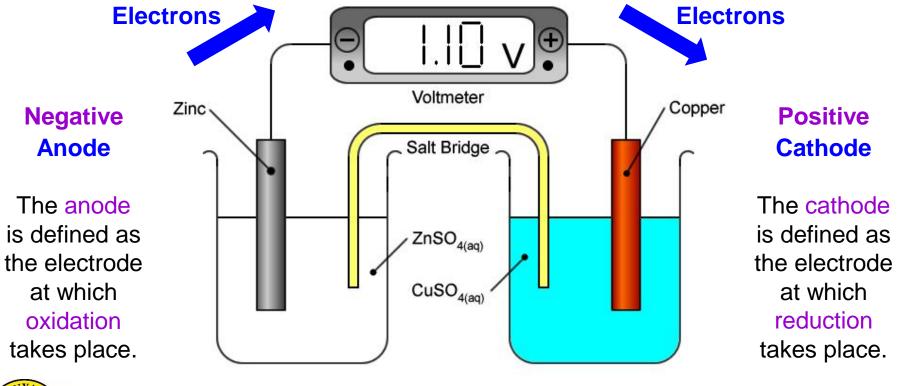
 lons of the less reactive metal (copper(II) ions) are reduced: Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> → Cu(s)





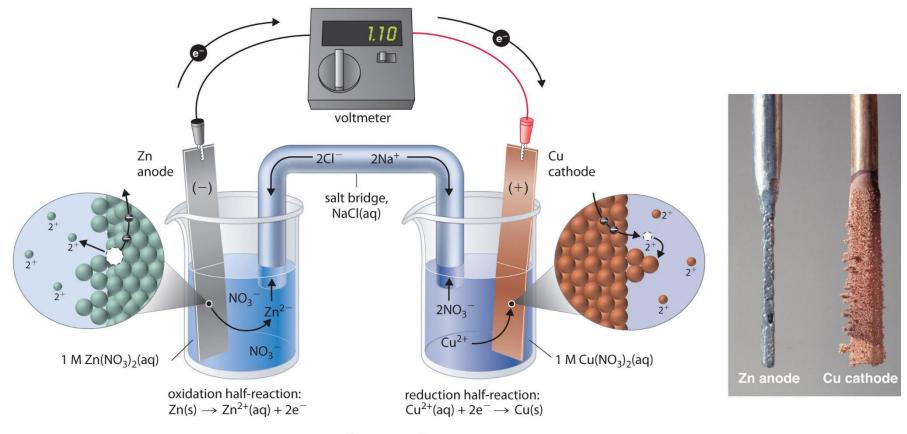
#### **Combination of Zinc and Copper Half-cells**

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#### **Combination of Zinc and Copper Half-cells**

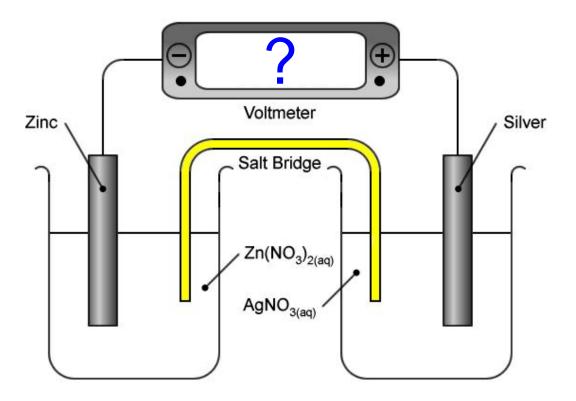


overall reaction:  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ 

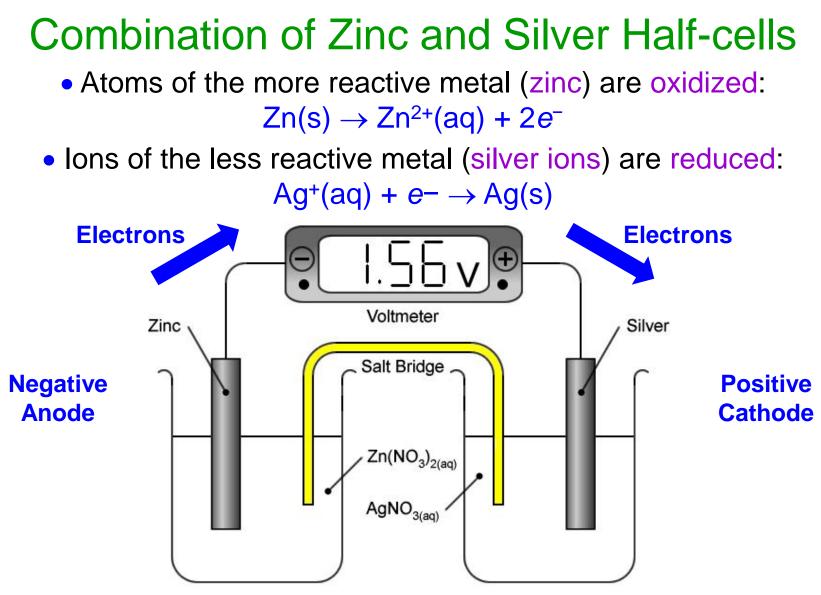


#### **Combination of Zinc and Silver Half-cells**

• The greater the separation of the metals in the electrochemical series, the greater the potential difference that is generated between their half-cells, and vice-versa.









- Potassium K / K<sup>+</sup>
- Sodium Na / Na<sup>+</sup>
- Calcium Ca / Ca<sup>2+</sup>
- Magnesium Mg / Mg<sup>2+</sup>
  - Aluminium Al / Al<sup>3+</sup>
    - Zinc Zn / Zn<sup>2+</sup>
    - Iron Fe / Fe<sup>2+ / 3+</sup>
    - Lead Pb / Pb<sup>2+</sup>
  - Copper Cu / Cu<sup>2+</sup>



• Silver – Ag / Ag<sup>+</sup>

• The greater the separation of the two metals in the electrochemical series, the greater the potential difference generated by the cell.

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- Sodium Na / Na<sup>+</sup>
- Calcium Ca / Ca<sup>2+</sup>
- Magnesium Mg / Mg<sup>2+</sup>
  - Aluminium Al / Al<sup>3+</sup>
    - Zinc Zn / Zn<sup>2+</sup>
    - Iron Fe / Fe<sup>2+ / 3+</sup>
      - Lead Pb / Pb<sup>2+</sup>
  - Copper Cu / Cu<sup>2+</sup>

Silver – Ag / Ag<sup>+</sup>



separation of the two metals in the electrochemical series, the greater the potential difference generated by the cell.

• The greater the

**e.g.** Fe / Cu = 0.80 V

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- Sodium Na / Na<sup>+</sup>
- Calcium Ca / Ca<sup>2+</sup>
- Magnesium Mg / Mg<sup>2+</sup>
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    - Zinc Zn / Zn<sup>2+</sup>
    - Iron Fe / Fe<sup>2+ / 3+</sup>
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  - Aluminium Al / Al<sup>3+</sup>
    - Zinc Zn / Zn<sup>2+</sup>
    - Iron Fe / Fe<sup>2+ / 3+</sup>
    - Lead Pb / Pb<sup>2+</sup>
  - Copper Cu / Cu<sup>2+</sup>

Silver – Ag / Ag<sup>+</sup>

• The greater the separation of the two metals in the electrochemical series, the greater the potential difference generated by the cell.

e.g. Mg / Cu = 2.70 V



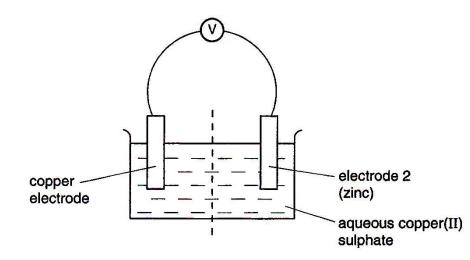
Electrochemistry • Simple batteries in a nutshell...  $\rightarrow$  The more reactive metal is oxidised. This is the anode.  $\rightarrow$  lons of the less reactive metal are reduced. This is the cathode.  $\rightarrow$  Electrons flow through the external circuit from the more reactive metal to the less reactive metal.  $\rightarrow$  The further apart the metals are in the

electrochemical series, the greater the voltage.



Could I please have some questions to check my understanding of electrochemical cells?



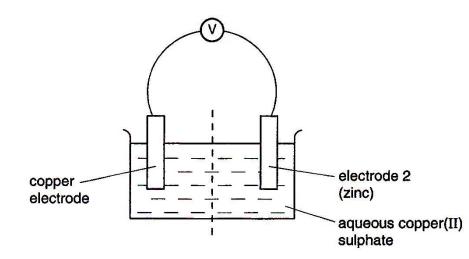


#### **Question.**

 The voltage of the cell was measured when the following metals were used for electrode 2.
Copper Iron Lead Zinc Complete the table by entering the metals in the correct order.

| Meter Reading / V | Metal |
|-------------------|-------|
| 1.10              |       |
| 0.78              |       |
| 0.21              |       |
| 0.00              |       |



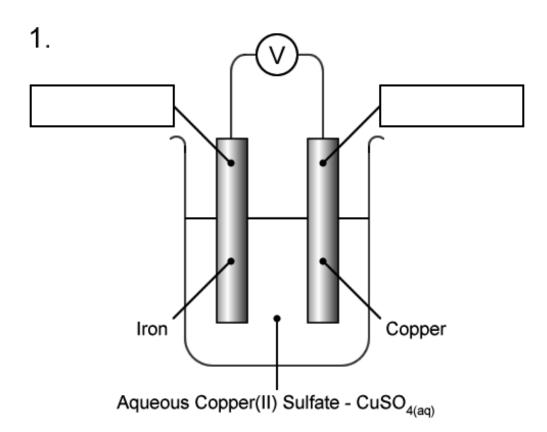


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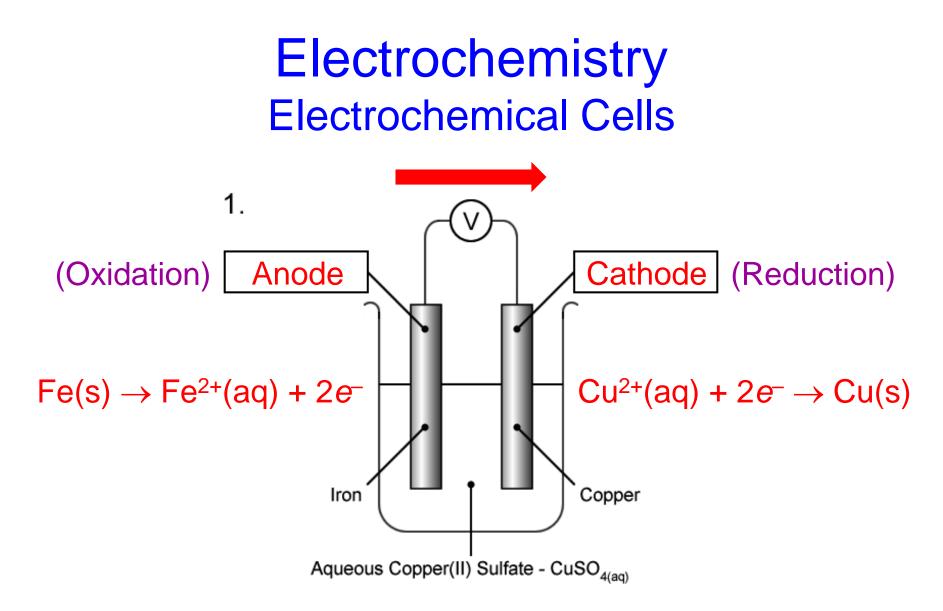
| Meter Reading / V | Metal  |
|-------------------|--------|
| 1.10              | Zinc   |
| 0.78              | Iron   |
| 0.21              | Lead   |
| 0.00              | Copper |





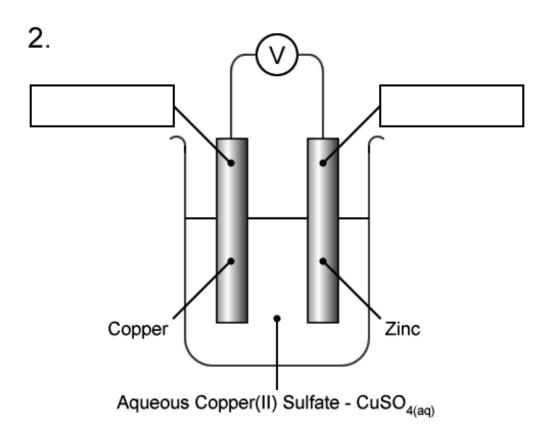


(a) Label the anode and the cathode.



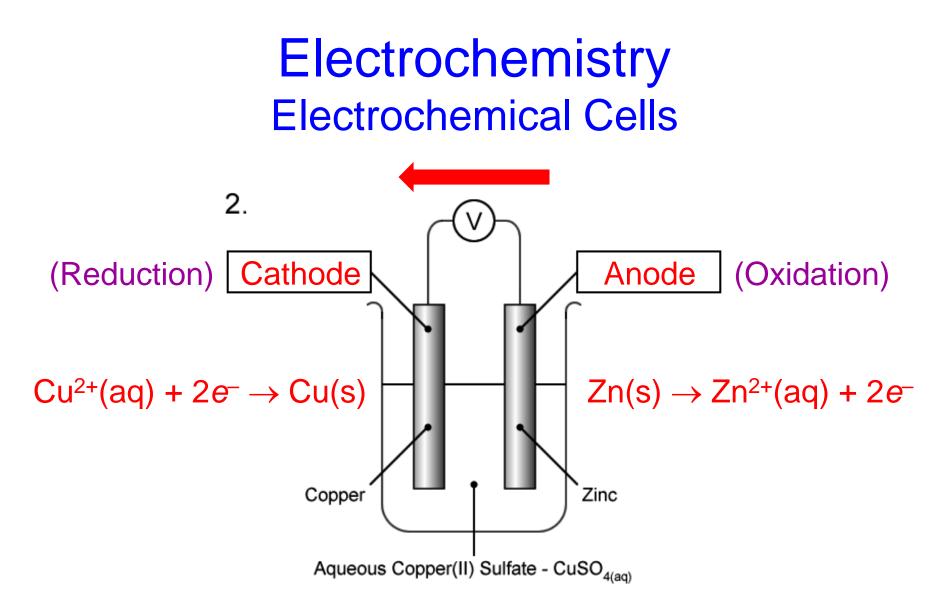


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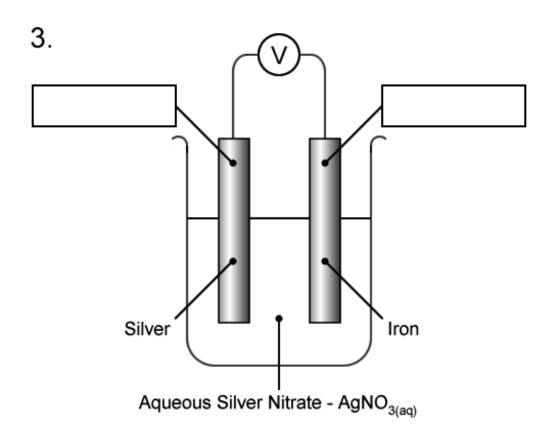


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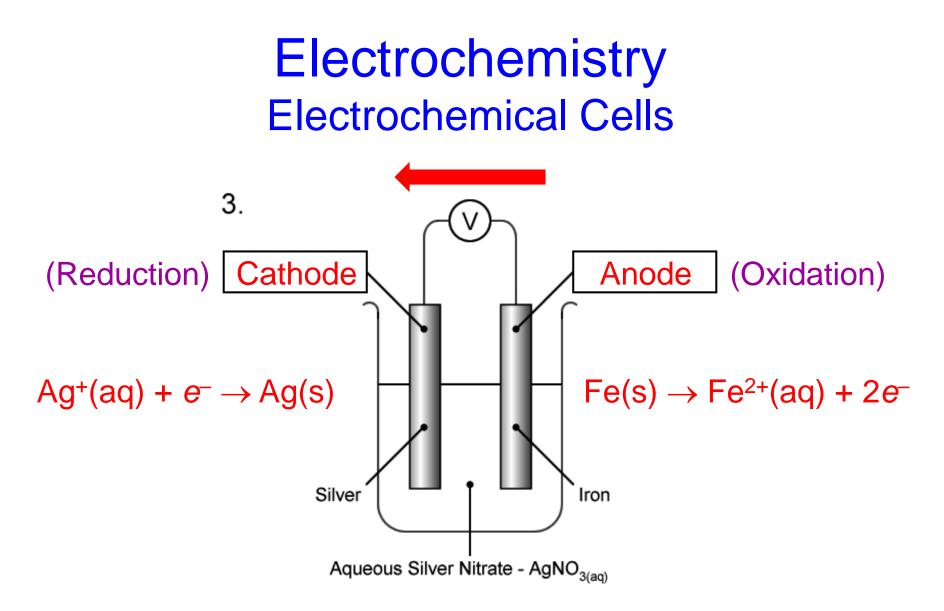


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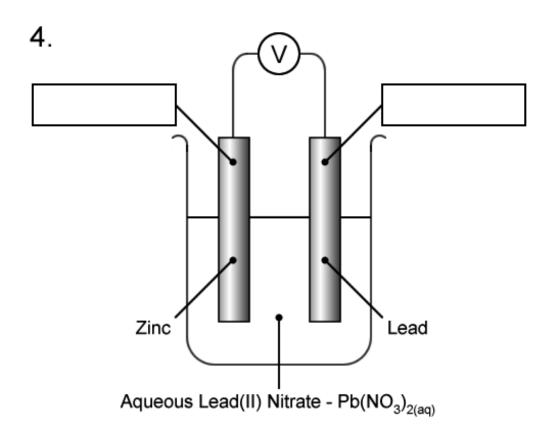


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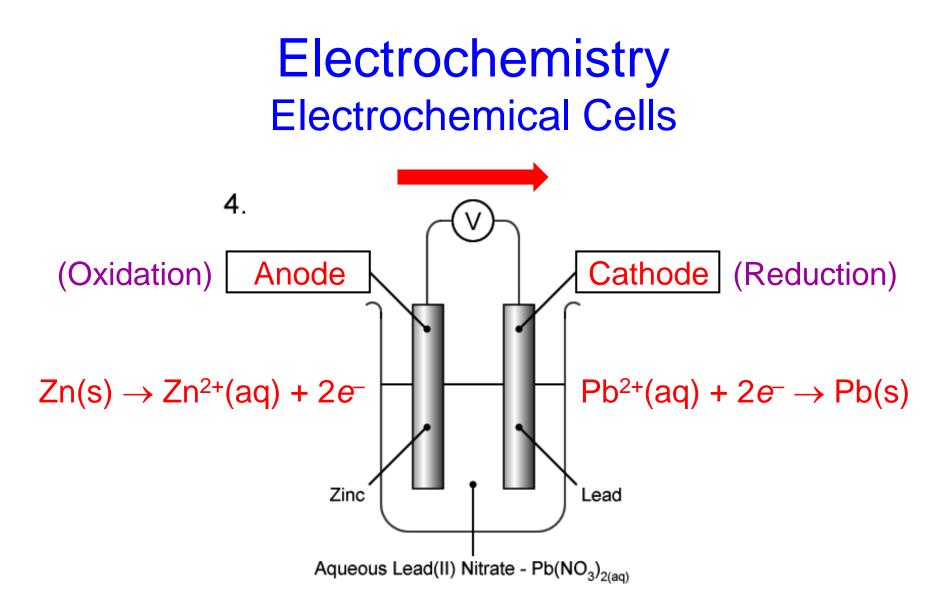


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(a) Label the anode and the cathode.

### Electrochemistry

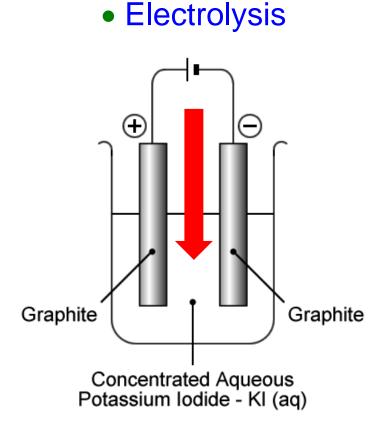
• Enduring understanding in a nutshell...

→ If a circuit diagram contains a battery, then the system is electrolysis. Electrical energy is used to decompose a chemical (endothermic).

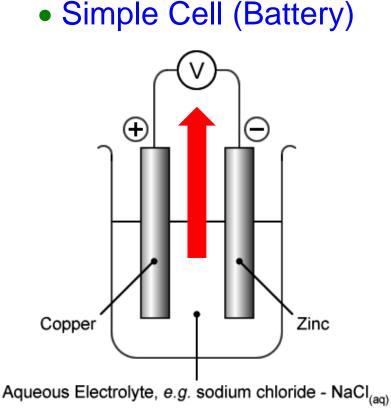
→ If a circuit diagram does not contain a battery, but does contain two different metals connected to a voltmeter, then the system is a simple cell. The chemical system produces electricity (exothermic).



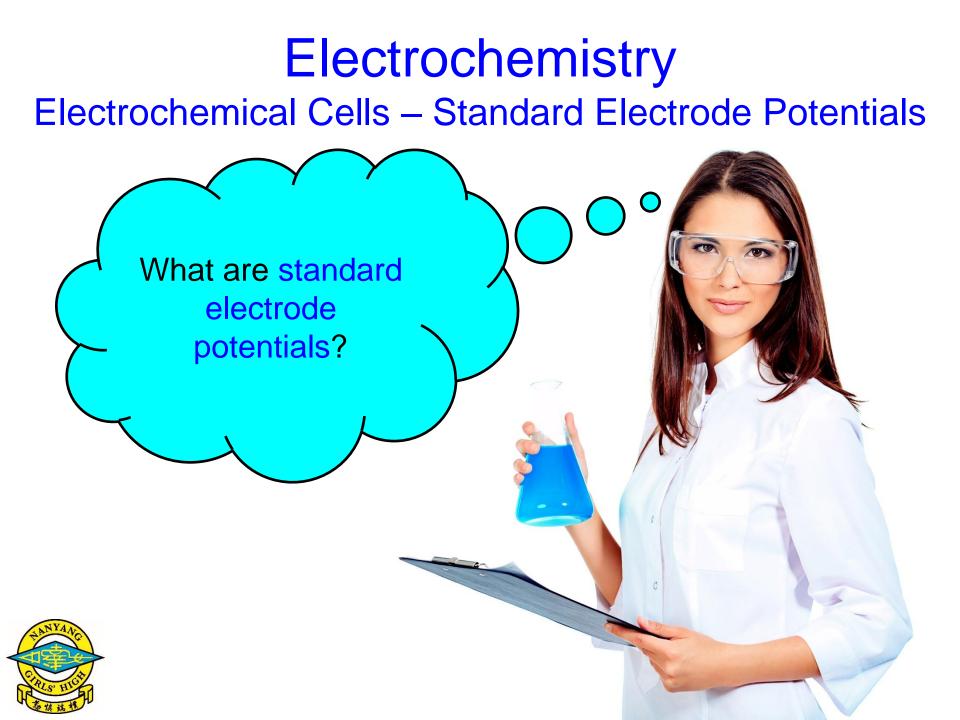
### Electrochemistry



Electrical energy goes into the system (endothermic). Electrical energy causes a chemical change.



The system produces electrical energy (exothermic). A chemical change produces electrical energy.



#### **Electrochemical Cells – Standard Electrode Potentials**

| Electrode Reaction                                   | Standard Electrode<br>Potential (E <sup>e</sup> ) / V |
|--|---|
| K+(aq) + <i>e</i> ⁻ ≓ K(s)                           | -2.92   |
| Na⁺(aq) + <i>e</i> ⁻ ≓ Na(s)                         | -2.71   |
| Mg²+(aq) + 2 <i>e</i> ⁻ ≓ Mg(s)                      | -2.38   |
| Zn²+(aq) + 2 <i>e</i> ⁻ ≓ Zn(s)                      | -0.76   |
| $H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$ | 0.00  |
| Cu²+(aq) + 2 <i>e</i> ⁻ ≓ Cu(s)                      | +0.34   |
| $Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$        | +0.80   |



**Electrochemical Cells – Standard Electrode Potentials** 

| Electrode Reaction                                   | Standard Electrode<br>Potential ( $E^{\theta}$ ) / V |
|--|--|
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| $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$      | +0.34  |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$            | +0.80  |

 The standard electrode potential is defined as the *potential* or tendency of a redox system to lose, or gain, electrons when compered to the *standard hydrogen electrode* (SHE) – which is assigned a value of 0.00 V.



#### **Electrochemical Cells – Standard Electrode Potentials**

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| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$            | +0.80   |

 The ⇒ symbol is used in place of the → symbol to show that the reaction is reversible.

• The ionic half-equations that are used to describe standard electrode potentials are always written showing the species on the left-hand-side being *reduced*, *i.e.* gaining electrons.



**Electrochemical Cells – Standard Electrode Potentials** 

| Electrode Reaction                                   | Standard Electrode<br>Potential ( $E^{\theta}$ ) / V |
|--|--|
| K⁺(aq) + <i>e</i> ⁻ ≓ K(s)                           | -2.92  |
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| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$            | +0.80  |

 Redox systems with the reduced side (right-hand-side) more reactive than hydrogen have a negative electrode potential, *i.e.* they lose electrons more readily than hydrogen.



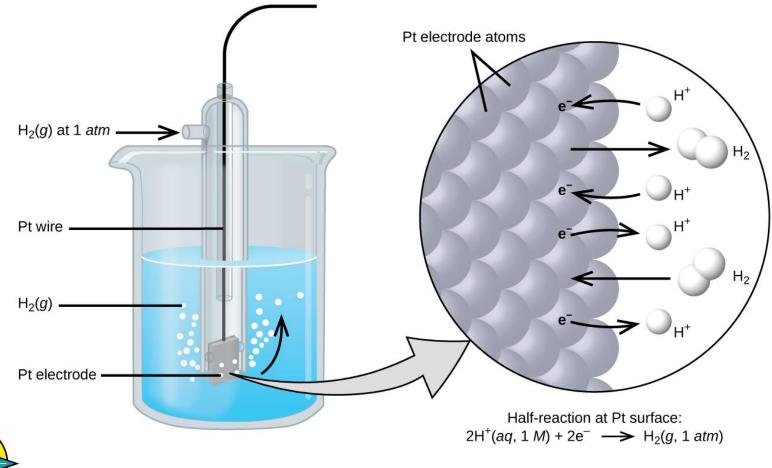
**Electrochemical Cells – Standard Electrode Potentials** 

| Electrode Reaction                                   | Standard Electrode<br>Potential (E <sup>e</sup> ) / V |
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| $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$      | -0.76   |
| $H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$ | 0.00  |
| $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$      | +0.34   |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$            | +0.80   |

 Redox systems with the reduced side (right-hand-side)
*less reactive* than hydrogen have a *positive* electrode potential, *i.e.* they lose electrons *less readily* than hydrogen.

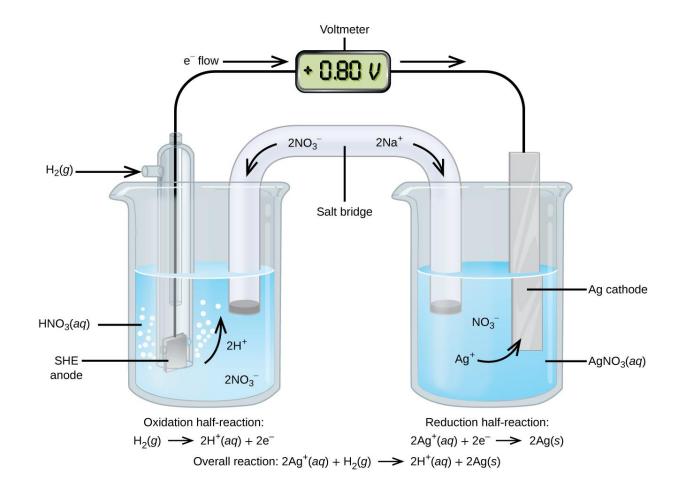


Electrochemical Cells – Standard Electrode Potentials The Standard Hydrogen Electrode (SHE)





Electrochemical Cells – Standard Electrode Potentials Measuring the Potential of a Silver Half-Cell Relative to the Standard Hydrogen Electrode





**Electrochemical Cells – Standard Electrode Potentials** 

- Calculate the potential difference between a zinc half-cell and a copper half-cell:
- → Write the ionic half-equations for the two half-cells, the equation for the half-cell with the less positive (more negative) value being written above the equation for the half-cell with the more positive (less negative) value.

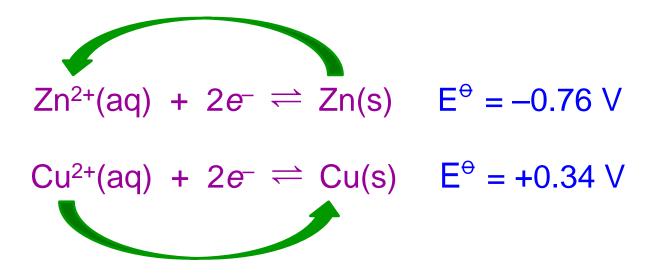
 $Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s) \quad E^{\Theta} = -0.76 V$ 

 $Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s) \quad E^{\Theta} = +0.34 \text{ V}$ 



**Electrochemical Cells – Standard Electrode Potentials** 

- Calculate the potential difference between a zinc half-cell and a copper half-cell:
- → Cycle through the two ionic-half equations in an anti-clockwise direction:





**Electrochemical Cells – Standard Electrode Potentials** 

- Calculate the potential difference between a zinc half-cell and a copper half-cell:
- → The reaction for the *zinc* moves from *right-to-left* and the reaction for the *copper* moves from *left-to-right*.

$$Zn^{2+}(aq) + 2e^{-} \leftarrow Zn(s) \quad E^{\Theta} = -0.76 \text{ V}$$
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^{\Theta} = +0.34 \text{ V}$$



**Electrochemical Cells – Standard Electrode Potentials** 

 Calculate the potential difference between a zinc half-cell and a copper half-cell:

 $\rightarrow$  Re-write the ionic half-equation for zinc so that the reaction takes place in the correct direction. Change the sign of E<sup> $\Theta$ </sup> for zinc from *negative* to *positive* to reflect that the reaction is now taking place in the opposite direction.

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} E^{\Theta} = +0.76 V$ 

 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^{\Theta} = +0.34 \text{ V}$ 



**Electrochemical Cells – Standard Electrode Potentials** 

 Calculate the potential difference between a zinc half-cell and a copper half-cell:

→ Combine the ionic half-equations for the two half-cells together to produce the overall reaction that takes place in the cell.

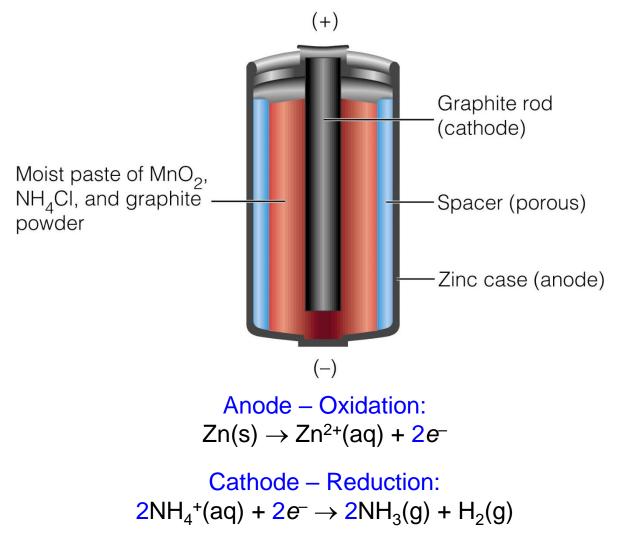
#### $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

 $\rightarrow$  The sum of the E<sup> $\Theta$ </sup> values for the two half-cells gives the overall potential difference (voltage) produced by the cell:

(+0.76) + (+0.34) = 1.10 V

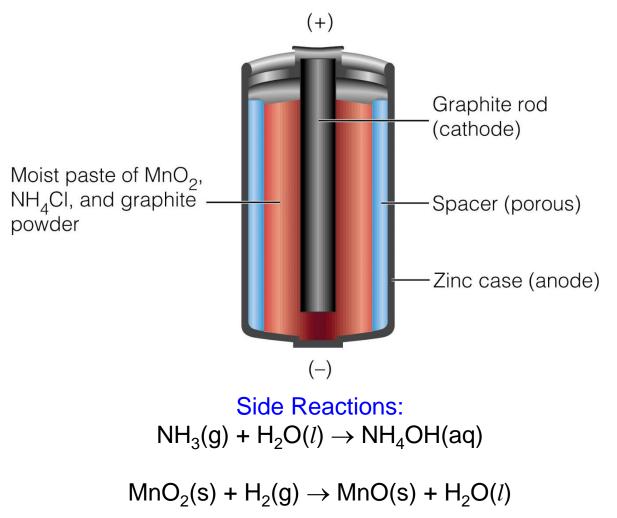


#### Electrochemistry Electrochemical Cells – Zinc Carbon Battery



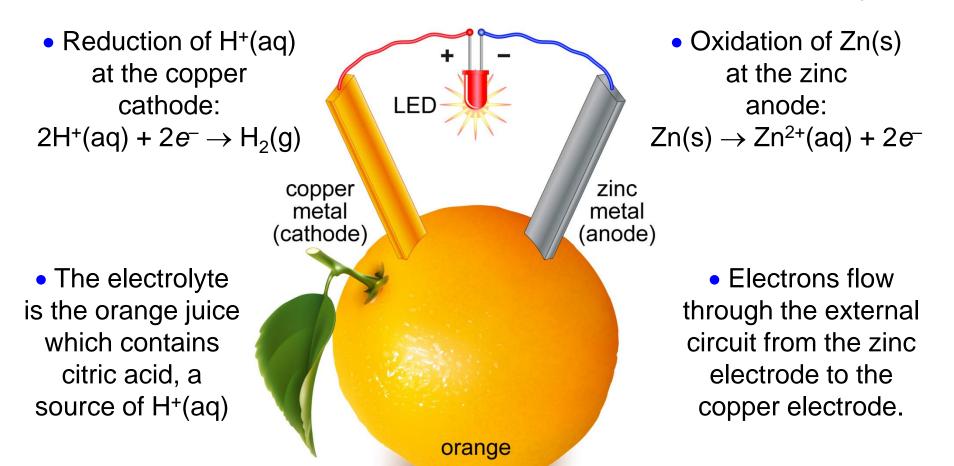


#### Electrochemistry Electrochemical Cells – Zinc Carbon Battery





#### Electrochemistry Electrochemical Cells – Citrus Fruit Battery





#### Presentation on Electrochemical Cells (Batteries) by Dr. Chris Slatter christopher\_john\_slatter@nygh.edu.sg

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#### 8<sup>th</sup> February 2016

