#### **Chapter 20: Electrochemistry III**



#### Chem 102 Jussi Eloranta



#### **Batteries**

- Electrochemical cells convert chemical energy to electrical energy
- *Battery*: Arrangement of one or more electrochemical cells
- If cells are connected in *series*, the voltages of each cell add up:



Note: Connecting batteries in *parallel* does not increase voltage but the amperage.





#### **Dry-cell battery**

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- Want batteries to be portable, so we want an electrolyte without much water
- Alkaline battery (basic medium):

<u>Ox. (anode)</u>:  $Zn(s) + 2OH^{-}(aq) \rightarrow Zn(OH)_{2}(s) + 2e^{-}$ 

Red. (cathode):  $2MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow 2MnO(OH)(s) + 2OH^-(aq)$ 



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Recycle batteries!
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<u>Overall</u>:  $Zn(s) + 2MnO_2(s) + 2H_2O(I) \rightarrow Zn(OH)_2(s) + 2MnO(OH)(s)$ 



## Lead acid battery

- Car battery (12.6 V when fully charged)
- Oldest type of rechargeable battery (1859)
- Reliable, rechargeable
- Provide large surge of current in short time
- Heavy, acidic, Pb is bad



Old batteries must be recycled!

Cathode (red):PbO<sub>2</sub> (s) + 4H<sup>+</sup> (aq) + SO<sub>4</sub><sup>2-</sup> (aq) + 2e<sup>-</sup>  $\longrightarrow$  PbSO<sub>4</sub> (s) + 2H<sub>2</sub>O (/) Anode (ox): Pb (s) + SO<sub>4</sub><sup>2-</sup> (aq)  $\longrightarrow$  PbSO<sub>4</sub> (s) + 2e<sup>-</sup>  $E^0 = -0.31 \text{ V}$ Pb (s) + PbO<sub>2</sub> (s) + 4H<sup>+</sup> (aq) + 2SO<sub>4</sub><sup>2-</sup> (aq)  $\longrightarrow$  2PbSO<sub>4</sub> (s) + 2H<sub>2</sub>O (/)

$$E^{o}_{cell} = 2.1 \text{ V}$$



## Lead acid battery

- Usually 6 cells (2.1 V each)
- Total output 12.6 V (series)
- During usage  $Q \rightarrow K$ and  $E_{cell} \rightarrow 0 V$
- Rechargeable from the alternator in your car
- Reverses the reaction
  - Pb(s) and PbO<sub>2</sub>(s) form
  - PbSO<sub>4</sub>(*s*) reacts away

 $E^{0} = 1.70 V$ Cathode (red):PbO<sub>2</sub> (s) + 4H<sup>+</sup> (aq) + SO<sub>4</sub><sup>2-</sup> (aq) + 2e<sup>-</sup>  $\longrightarrow$  PbSO<sub>4</sub> (s) + 2H<sub>2</sub>O (/)

Anode (ox): Pb (s) + SO<sub>4</sub><sup>2-</sup> (aq)  $\longrightarrow$  PbSO<sub>4</sub> (s) + 2e<sup>-</sup>

 $E^0 = -0.31 \text{ V}$ 

 $Pb(s) + PbO_{2}(s) + 4H^{+}(aq) + 2SO_{4}^{2-}(aq) \longrightarrow 2PbSO_{4}(s) + 2H_{2}O(l)$ 





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#### **Rechargeable batteries**

- Lead-acid
- Nickel-cadmium (NiCad)
- Nickel-metal hydride (NiMH)
- Lithium ion



#### **Recycle batteries!**







If charging of Li-ion batteries is not properly regulated, they can overheat and even catch fire!



## NiCad (Nickel-Cadmium)



Oxidation (anode):  $Cd(s) + 2OH^{-}(aq) \rightarrow Cd(OH)_{2}(s) + 2e^{-}$ 

Reduction (cathode):  $2NiO(OH)_2(s) + 2H_2O(I) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$ 

- Cell voltage 1.30 V (Note: less than 1.5 V!)
- Recharge by applying a current in the opposite direction
- Possible problem: overcharging can produce H<sub>2</sub>(g) (flammable)
- Cd is toxic (recycle batteries!!!)



#### NiMH (Nickel-Metal Hydride)



Oxidation (anode):  $M \cdot H(s) + OH^{-}(aq) \rightarrow M(s) + H_2O(l) + e^{-l}$ 

Reduction (cathode): NiO(OH)<sub>2</sub>(s) + H<sub>2</sub>O(/) +  $e^{-} \rightarrow$ Ni(OH)<sub>2</sub>(s) + OH<sup>-</sup>(aq)

- M = metal alloy
- More environmentally friendly than NiCad
- Better energy density (energy per battery mass)

| <b>TABLE 19.2</b> Energy Density and Overcharge Tolerance of Several<br>Rechargeable Batteries |                          |                      |  |  |  |  |
|--|--------------------------|----------------------|--|--|--|--|
| Battery Type   | Energy Density(W · h/kg) | Overcharge Tolerance |  |  |  |  |
| NiCad  | 45–80                    | Moderate             |  |  |  |  |
| NiMH   | 60–120                   | Low                  |  |  |  |  |
| Li ion   | 110–160                  | Low                  |  |  |  |  |
| Pb storage   | 30–50                    | High                 |  |  |  |  |



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## Lithium ion

- Even better energy density
- Li is least dense metal
- Very little charge loss (5% per month) when not in use
- Hundreds of charge/discharge cycles
- 2-3 year life
- Sensitive to high temperatures
- Needs extra circuitry to manage the charging/discharging of the battery
- Fire hazard when improperly charged

|   | Rechargeable Batteries         |                          |                      |  |
|---|--------------------------------|--------------------------|----------------------|--|
| ) | Battery Type                   | Energy Density(W · h/kg) | Overcharge Tolerance |  |
|   | NiCad                          | 45–80                    | Moderate             |  |
|   | NiMH                           | 60–120                   | Low                  |  |
|   | Li ion                         | 110–160                  | Low                  |  |
|   | Pb storage                     | 30–50                    | High                 |  |
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**TABLE 19.2** Energy Density and Overcharge Tolerance of Several



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## Lithium ion



- Thin layers of cathode and anode kept apart by separator
- Output is 3.7 V per cell



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#### WHY LITHIUM-ION BATTERIES CATCH FIRE

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Lithium-ion batteries have been in the news recently with reports of some of Samsung's phones unexpectedly catching fire. Here, we examine how the batteries work and what can make them ignite.



http://cen.acs.org/articles/94/i45/Periodic-graphics-Li-ion-batteries.html?utm\_source=Newsletter&utm\_medium=Newsletter&utm\_campaign=CEN

## Fuel cells

- Major problem with batteries: Reactants become depleted over time
- Fuel cell: Reactants continuously flow through system
- Hydrogen/Oxygen fuel cell
- Product is <u>water</u>

Anode:

Cathode:



 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad E_{cell}^0 = 1.23V$ 







#### **Fuel cells**

#### Problem: Hydrogen is scarce











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### **Electrolysis**

- **Remember:** For a voltaic cell ( $E_{cell}^o > 0$  V), spontaneous when not in equilibrium,  $E_{cell} > 0$  V
- Electrolysis: Drive a non-spontaneous reaction with an external voltage source (like charging a battery)
- Forces the reaction go in the (normally) non-spontaneous direction
- e<sup>-</sup> are drawn from the anode and connected to the positive terminal of the external voltage source
- e<sup>-</sup> are forced to the cathode and connected to the negative terminal of the external voltage source









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Spontaneous (produces current in a voltaic cell):  $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$ 

Non-spontaneous (consumes electrical current in an electrolytic cell):  $2H_2O(I) \rightarrow 2H_2(g) + O_2(g)$ 

Need a salt (electrolyte) to carry current through the water!



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- If  $E_{cell} = 1.10$  V, need a power supply with > 1.10 V to drive reverse *rxn*
- Note that the anode and cathode swap positions (oxidation still occurs at the anode, reduction still occurs at the cathode)
- Anode of the battery is applied to the former anode of the cell to make it a cathode



#### **Products of electrolysis**



- Can form pure metal on surface of another metal
- Application: electroplating
- Very energy intensive process on large scale





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#### Summary of electrochemical cells

#### • In all electrochemical cells:

- oxidation occurs at the anode
- reduction occurs at the cathode

#### • In voltaic cells:

- anode is the source of electrons and has a negative charge (anode -)
- cathode draws electrons and has a positive charge (cathode +)

#### In electrolytic cells

- electrons drawn from anode, which must be connected to positive terminal of external power source (anode +)
- electrons forced to cathode, which must be connected to the negative terminal of the external power source (cathode -)



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### Predicting products of electrolysis



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## Predicting products of electrolysis

Mixtures of cations or anions in a molten salt:

- For example: NaCl with KCl
- Anion is oxidized and cation is reduced
- Which will be reduced first, Na<sup>+</sup> or K<sup>+</sup>?

| eduction Half-Rea         | ction  |   | E      | _              |
|---------------------------|--|---|--------|----------------|
| <i>C</i> 1                | F <sub>2</sub> (g) + 2 e <sup>-</sup>  |   |        | _              |
| oxidizing agent           | H <sub>2</sub> O <sub>2</sub> (aq) + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>                        | → 2 H <sub>2</sub> O( <i>l</i> )  |        | _              |
| -                         | PbO <sub>3</sub> (s) + 4 H <sup>+</sup> (ag) + SO <sub>2</sub> <sup>2-</sup> (ag) + 2 e <sup>-</sup> | > PbSO <sub>4</sub> (s) + 2 H <sub>2</sub> O(l)                             |        | _              |
|                           | MnO <sub>4</sub> -(ag) + 4 H <sup>+</sup> (ag) + 3 e <sup>-</sup>                                    | > Mn0 <sub>2</sub> (s) + 2 H <sub>2</sub> 0(/)                              |        | _              |
|                           | MnO <sub>4</sub> <sup>-(ag)</sup> + 8 H <sup>+</sup> (ag) + 5 e <sup>-</sup>                         | $\longrightarrow$ Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(l)             |        | _              |
|                           | Au <sup>3+</sup> (aq) + 3 e <sup>-</sup>   | → Au(s)   |        | _              |
|                           | PbO <sub>2</sub> (s) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup>                                      | > Pb2+(aq) + 2 H₂O(/)   |        | _              |
|                           | Cl <sub>2</sub> (g) + 2 e <sup>-</sup>   |   |        | _              |
|                           | Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> (aq) + 14 H <sup>+</sup> (aq) + 6 e <sup>-</sup>        | $\longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l)$   |        | _              |
|                           | $O_2(g) + 4 H^+(aq) + 4 e^-$   | $\longrightarrow 2 H_2O(l)$   |        | _              |
|                           | MnO <sub>2</sub> (s) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup>                                      | $\longrightarrow$ Mn <sup>2+</sup> (aq) + 2 H <sub>2</sub> O(l)             |        | _              |
|                           | IO3 <sup>-(aq)</sup> + 6 H <sup>+</sup> (aq) + 5 e <sup>-</sup>                                      | $\longrightarrow \frac{1}{2}I_2(aq) + 3 H_2O(l)$                            |        | _              |
|                           | Br <sub>2</sub> ( <i>l</i> ) + 2 e <sup>-</sup>  | → 2 Br <sup>-</sup> (aq)  |        | _              |
|                           | V02+(aq) + 2 H+(aq) + e-   | $\longrightarrow$ VO <sup>2+</sup> (aq) + H <sub>2</sub> O(I)               |        |                |
|                           | NO3 <sup>-</sup> (aq) + 4 H <sup>+</sup> (aq) + 3 e <sup>-</sup>                                     | $\longrightarrow$ NO(g) + 2 H <sub>2</sub> O(l)                             |        | 347 1.         |
|                           | $ClO_2(g) + e^-$   | $\longrightarrow ClO_2^{-}(aq)$   |        | weaker         |
|                           | $Ag^+(aq) + e^-$   | $\longrightarrow Ag(s)$   |        |                |
|                           | $Fe^{3+}(aq) + e^{-}$  | $\longrightarrow$ Fe <sup>2+</sup> (aq)                                     |        | ovidizing agon |
|                           | O <sub>2</sub> (g) + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>  | $\longrightarrow$ H <sub>2</sub> O <sub>2</sub> (aq)                        |        | oxidizing agen |
|                           | MnO <sub>4</sub> -(aq) + e <sup>-</sup>  | $\longrightarrow$ MnO <sub>4</sub> <sup>2-</sup> (aq)                       |        | 00             |
|                           | I <sub>2</sub> (s) + 2 e <sup>-</sup>  | > 2 I <sup>-</sup> (aq)   | 0.54   |                |
|                           | Cu <sup>+</sup> (aq) + e <sup>-</sup>  | $\longrightarrow$ Cu(s)   | 0.52   |                |
|                           | $O_2(g) + 2 H_2O(l) + 4 e^{-1}$  | $\longrightarrow$ 4 OH (aq)   | 0.40   |                |
|                           | Cu <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | → Cu(s)   | 0.34   |                |
|                           | SO <sub>4</sub> <sup>2-</sup> (aq) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup>                        | $\longrightarrow$ H <sub>2</sub> SO <sub>3</sub> (aq) + H <sub>2</sub> O(l) | 0.20   |                |
|                           | $Cu^{2+}(aq) + e^{-}$  | → Cu <sup>+</sup> (aq)  | 0.16   |                |
|                           | Sn <sup>4+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow$ Sn <sup>2+</sup> (aq)                                     | 0.15   | _              |
|                           | 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow H_2(g)$  | 0      |                |
|                           | Fe <sup>3+</sup> (aq) + 3 e <sup>-</sup>   | $\longrightarrow$ Fe(s)   | -0.036 |                |
|                           | Pb <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | > Pb(s)   | -0.13  |                |
|                           | Sn <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | → Sn(s)   | -0.14  |                |
|                           | Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow$ Ni(s)   | -0.23  |                |
|                           | Cd <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow Cd(s)$   | -0.40  |                |
|                           | Fe <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow$ Fe(s)   | -0.45  |                |
|                           | Cr <sup>3+</sup> (aq) + e <sup>-</sup>   | $\longrightarrow Cr^{2+}(aq)$   | -0.50  |                |
|                           | Cr <sup>3+</sup> (aq) + 3 e <sup>-</sup>   | → Cr(s)   | -0.73  |                |
|                           | Zn <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | → Zn(s)   | -0.76  |                |
|                           | 2 H <sub>2</sub> 0(/) + 2 e <sup>-</sup>   | $\longrightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)               | -0.83  |                |
|                           | Mn <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow$ Mn(s)   | -1.18  |                |
|                           | Al <sup>3+</sup> (aq) + 3 e <sup>-</sup>   | $\longrightarrow Al(s)$   | -1.66  |                |
|                           | Mg <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | $\longrightarrow$ Mg(s)   | -2.37  |                |
|                           | Na <sup>+</sup> (aq) + e <sup>-</sup>  | → Na(s)   | -2.71  |                |
|                           | Ca <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | → Ca(s)   | -2.76  |                |
|                           | Ba <sup>2+</sup> (aq) + 2 e <sup>-</sup>   | Ba(s)   | -2.90  |                |
| Maskar                    | K <sup>+</sup> (aq) + e <sup>-</sup>   | $\longrightarrow$ K(s)  | -2.92  | Stronger       |
| weaker<br>oxidizing agent | Li*(aq) + e-   | → Li(s)   | -3.04  | reducing agent |

|  |         |       | _                          |
|--|---------|-------|----------------------------|
| Na <sup>+</sup> (aq) + e <sup>-</sup>    | → Na(s) | -2.71 |                            |
| Ca <sup>2+</sup> (aq) + 2 e <sup>-</sup> | → Ca(s) | -2.76 | Stronger<br>reducing agent |
| Ba <sup>2+</sup> (aq) + 2 e <sup>-</sup> | → Ba(s) | -2.90 |                            |
| $K^{+}(aq) + e^{-}$                      | → K(s)  | -2.92 |                            |
| $Li^+(aq) + e^-$                         | → Li(s) | -3.04 |                            |

Na<sup>+</sup> is easier to reduce, so Na(s) will form more easily (at cathode)

For mixed anions, the one that is more easily oxidized is oxidized first (at anode)



## **Stoichiometry of electrolysis**

How much product will form?

- Current: 1 A = 1 C / s
- Amount of charge: Current (A) x time (s) = Charge (C)
- F = 96495 C / mol (here mol corresponds to mol of  $e^{-}$ )
- Calculate the moles of electrons transferred for a given current passing in a given amount of time
- Don't forget that more than one mole of electrons may be required to make one mole of product





#### Example



Gold can be plated out of a solution containing Au<sup>3+</sup> according to: Au<sup>3+</sup>(*aq*) + 3e<sup>-</sup>  $\rightarrow$  Au(*s*). What mass of gold is plated by 25 minutes of 5.5 A electrolysis?

**Solution.** 25 min. = 1500 s. To get the number of charges:  $5.5 \text{ A} \times 1500 \text{ s} = 8250 \text{ C}$ . Convert this to moles of e-: 8250 C / (96495 C / mol) = 0.0855 mol. Since 3 electrons are involved, we must divide this by 3 ti get the number of moles of Au: 0.0855 mol / 3 = 0.0285 mol. Finally, convert moles of Au to grams by using the molar mass:  $0.0285 \text{ mol} \times 196.9665 \text{ g/mol} = 5.6 \text{ g of Au(s)}$ .

Oxidation of metals is usually spontaneous when exposed to  $O_2(g)$ :

Requires water

Corrosion

- Electrolytes promote corrosion (enhance current flow; e.g. salt water)
- Acids promote corrosion because O<sub>2</sub>(g) is reduced at an even more positive potential in the presence of additional H<sup>+</sup>







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### **Corrosion of iron**





The Rusting of Iron

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Rust forms a protective layer that can prevent further oxidation.

#### **Preventing corrosion**

- Aluminum forms aluminum oxide (white) outside (patina)
- Copper forms copper carbonate
- Paint (cars)
- Galvanization: addition of zinc to steel, which will oxidize before the iron underneath









#### **Tips for this section**

- General idea of how batteries work (do not memorize the reactions)
- General idea of how fuel cells work (do not memorize the reactions)
- Electrolysis

(describe electrolysis cell)

Corrosion

(do not memorize the reactions)