Highlights of last lecture

Electrolysis...

CONCEPTS
- How does electrolysis work?
- Concept of over-potential,
- Chlor-alkali process
- Hall-Herault process
- Selecting which species are electrolysed

CALCULATIONS
- Minimum battery voltage required
- How much substance is deposited during electrolysis
- (or how much time to produce known amount of substance)
We will examine the operation, construction and chemistry of 3 classes of batteries:

- **Primary batteries**: These are non-reversible and once reactants converted to products the battery is “dead”.
- **Secondary batteries**: In these batteries the cell reaction can be reversed and the battery recharged.
- **Fuel cells**: Fuel (chemicals) pass through the battery, which converts chemical energy into electrical energy.
Primary Batteries

The Dry Cell

**Construction:**

A carbon rod acts as an inert or inactive cathode.

The rod is coated with MnO₂ (oxidant) and graphite powder (for electrical conductivity).

A paste of NH₄Cl and ZnCl₂ acts as an electrolyte (like the salt bridge), although the NH₄⁺ is also reduced.

The Zn metal can acts as the active anode.
Primary Batteries

Chemistry:

Anode: The anode reaction is the same as we have been using: the oxidation of zinc.

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E^0 = 0.76\text{V} \]

Cathode: The cathode reaction is complex, and not completely understood. The MnO_2 (O.N. = ___) is reduced to Mn_2O_3 (O.N. = ___) through a series of steps.

\[ 2\text{MnO}_2 + 2\text{NH}_4^+ + 2e^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \quad E^0 = 0.7\text{V} \]

* Different texts show different cathode reactions. This is an indication of the unknown cathode chemistry. The Cl^- probably plays a role in reacting with Zn to form crystalline \( \text{Zn(NH}_3\text{)}_2\text{Cl}_2 \). When dry cells get swollen it is due to build up of gases such as NH_3.
Primary Batteries

- Alkaline battery

The alkaline (e.g. “Duracell”) battery is an improved dry cell. It uses an alkaline environment which prevent the build up of gases, and preserves the zinc electrode:

Anode: \( \text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-; \quad E^0 = 1.25\text{V} \)

Cathode: \( 2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-; \quad E^0 = 0.12\text{V} \)

Overall: \( 2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-; \quad E^0 = ____ \text{V} \)
Primary Batteries

- Mercury or silver battery

\[ E^0(\text{silver}) = 1.6 \text{ V} \]
\[ E^0(\text{mercury}) = 1.3 \text{ V} \]

Anode: \[ \text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-; \quad E^0=1.25\text{V} \]

Cathode (Silver): \[ \text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ag} + 2\text{OH}^-; \quad E^0=0.34\text{V} \]

Cathode (Mercury): \[ \text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg} + 2\text{OH}^-; \quad E^0=0.05\text{V} \]

Overall: \[ \text{Zn} + \text{Ag}_2\text{O} \rightarrow \text{ZnO} + 2\text{Ag} \]
\[ \text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg} \]

\[ \Rightarrow \text{voltage is constant}!! \]
Secondary Batteries

- **Lead-acid battery**
  Probably the most familiar of all secondary batteries - this type of battery has started cars for 100 years.
  Large surface area of electrodes means that the battery can deliver very large currents.

  
  Anode: \( \text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \); \( E^0 = 0.30 \text{ V} \)
  
  Cathode: \( \text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \); \( E^0 = 1.63 \text{ V} \)

\[ E^0 = \text{______ V} \]

- 6 cells in series \( \rightarrow \) 12 V
Some features of the Pb-acid battery:

- Reactants are solids so the concentration of redox reactants never changes (solids don’t appear in Q), therefore the battery operates at relatively constant voltage; the voltage drops slightly as sulfuric acid is consumed and water is produced.
- The reaction is reversible so the battery can be recharged.

H$_2$SO$_4$ (electrolyte)
Discharge and recharge
Secondary Batteries

**Nickel-cadmium batteries**

Very popular replacement for primary batteries. The cell potential is the same so they can be used interchangably. They can be recharged hundreds of times.

Anode: \( \text{Cd} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 + 2\text{e}^-; \quad E^0=0.82 \text{ V} \)

Cathode: \( \text{NiO(OH)} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^-; \quad E^0=0.6 \text{ V} \)

\( \text{Cd(s)} + 2\text{NiO(OH)} + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2; \quad E^0=1.4 \text{ V} \)

**Lithium batteries**

Perhaps the batteries of the future because Li is so light, and the cell potential is one the highest of common batteries. Lithium has the highest oxidation potential of all, so little Li is needed.

Anode: \( \text{Li} \rightarrow \text{Li}^+ + \text{e}^-; \quad E^0=3.0 \text{ V} \)

Cathode: \( \text{MnO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiMnO}_2; \quad E^0=0.0 \text{ V} \)

\( \text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2; \quad E^0=3.0 \text{ V} \)
Fuel Cells

A fuel cell is a voltaic cell where the reactants are a fuel, e.g. H\(_2\), CH\(_4\). The fuel undergoes a normal (overall) combustion reaction, however the two half-reaction are separated and the electrons harnessed. Fuel cells are still in the experimental stage, and their most notable success is probably in space.

| Anode:   | H\(_2\) → 2H\(^+\) + 2e\(^-\); | E\(^0\)=0.0 V |
| Cathode: | \(\frac{1}{2}\)O\(_2\) + 2H\(^+\) + 2e\(^-\) → H\(_2\)O; | E\(^0\)=1.23 V |
|          |                              | E\(^0\)=______ V |
| Anode:   | CH\(_4\) + 2H\(_2\)O → CO\(_2\) + 8H\(^+\) + 8e\(^-\); | E\(^0\)=-0.3 V |
| Cathode: | 4 x \{\(\frac{1}{2}\)O\(_2\) + 2H\(^+\) + 2e\(^-\) → H\(_2\)O\}; | E\(^0\)=1.23 V |
|          |                              | E\(^0\)=______ V |
Fuel cells

- $H_2 / O_2$ fuel cell

H$_2$O(g)

Anode (-)

(+ ) Cathode

$H_2$ O$_2$

Pt catalyst surrounding graphite electrode

Electrolyte: Teflon (CF$_2$)$_n$ with RSO$_3^-$ groups
Fuel Cell Efficiency

[Graph: Efficiency versus Power Plant Capacity]

- SOFC
- PAFC
- Diesel Generator
- Petrol Engine
- Gas Turbine
- ST + GT Combined Cycle Plant
- SOFC Combined Cycle Plant

Source: Siemens
Fuel Cell Emissions

Emissions from Stationary Power Sources

- Coal
- Oil
- Gas

Pollutants:
- Sulphur dioxide
- Nitrogen Oxide
- Hydrocarbons
- Particulates

Source: IEC
Corrosion: Unwanted voltaic cells

We have already examined the process of converting a metal oxide to a metal (L.28). We saw that it required reducing the oxide and a lot of heat energy. This means that the reverse, oxidation of a metal to its oxide will be exothermic, and likely to be spontaneous.

- Economically, the most important corrosion process is iron or steel.
Corrosion

Corrosion occurs commonly in our environment. It is considered a product-favoured reaction. That is, $E^o$ for the reaction is positive (a spontaneous process).

- Such reactions are undesirable because the corrosion results in loss of structural strength.
- For instance, rust holes in cars, corrosion of structural supports in bridges.
1) Oxidation of Fe at active anode forms a pit and yields e\textsuperscript{-} which travel through the metal;
2) Electrons at the Fe (inactive) cathode reduce O\textsubscript{2} to H\textsubscript{2}O;
3) The Fe\textsuperscript{2+} migrates through the drop and reacts with O\textsubscript{2} to form rust.

\textbf{Corrosion}

\[ \text{Rust} \quad \text{Fe}_2\text{O}_3 \cdot n \text{H}_2\text{O} \]
Redox chemistry of corrosion

The rusting of iron involves two (or more) redox reactions:

**Anode:**  
\[ 2 \times \{ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \}; \quad E^0=0.44 \text{ V} \]

**Cathode:**  
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{H}_2\text{O}; \quad E^0=1.23 \text{ V} \]

\[ 2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \rightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}(l); \quad E^0=1.67 \text{ V} \]

The \( \text{Fe}^{2+} \) is further oxidised at the edges of the droplet, where \([\text{O}_2]\) is highest:

**Anode:**  
\[ 2 \times \{ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \}; \quad E^0=0.77 \text{ V} \]

**Cathode:**  
\[ \frac{1}{2} \times \{ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{H}_2\text{O} \}; \quad E^0=1.23 \text{ V} \]

\[ 2\text{Fe}^{2+}(aq) + \frac{1}{2}\text{O}_2(g) + 2\text{H}^+(aq) \rightarrow 2\text{Fe}^{3+}(aq) + \text{H}_2\text{O}(l); \quad E^0=2.00 \text{ V} \]

Iron (III) forms a very insoluble oxide, so rust is deposited at the edge:

\[ 2\text{Fe}^{3+}(aq) + (3+n)\text{H}_2\text{O}(l) \rightarrow \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}(s) + 6\text{H}^+(aq) \]

**Overall:**

\[ H^+ \text{ is a catalyst!} \]
You should now be able to explain some of the known features of rusting:

- Iron does not rust in dry air;
- Iron does not rust in oxygen-free water, such as ocean depths;
- Iron rusts more quickly in acidic environments;
- Iron rusts more quickly at the seaside.
Presence of other metals

A) Enhanced corrosion

1. Fe gives up electrons to Cu cathode
2. Electrons from Fe reduce O₂ to H₂O

B) Cathodic protection

1. Zn gives up electrons to Fe cathode
2. Electrons from Zn reduce O₂ to H₂O
Protection against corrosion

Iron acts as both an active anode and inactive cathode. Anything that gives up electrons more readily will instead act as anode and the iron will not oxidise. These sacrificial anodes can be made of any metal that is more active than iron. If you remember the “Activity Series of Metals” lecture experiment, you will recall that both zinc and magnesium are more active than iron. This is called “cathodic protection”, and is used frequently in large iron structure such as ships, pipes, bridges, etc.

Galvanising:

\[
\begin{align*}
\text{Mg rod} & \quad \text{Fe pipe} \\
\text{Zinc} & \quad \text{Iron} \\
\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 & \rightarrow \text{4OH}^- \\
2e^- & \rightarrow \text{Zn} \rightarrow \text{Zn}^{2+}
\end{align*}
\]
Corrosion Protection

- An example of anodic inhibition would be to prevent oxygen from reaching the metal. This could be achieved by greasing (oiling the surface) or allowing a thin film (metal oxide) film to form on the surface.

- A common method is the treatment of a surface with a solution of sodium chromate. 
  \[2Fe(s) + 2Na_2CrO_4(aq) + 2H_2O(l) \rightarrow Fe_2O_3(s) + Cr_2O_3(s) + 4NaOH(aq)\]

- The surface of the iron is oxidised by the chromate salt to give Fe(III) and Cr(III) oxides. These form a coating that cannot be penetrated by oxygen and water, which inhibits further oxidation.
Corrosion Protection

This was the approach used by PG&E in the small town of Hinkley in US. Cr(VI) was used to prevent corrosion of the power plant’s cooling towers.

- Unfortunately, the company then disposed of the Cr(VI) containing water into unlined ponds leading to environmental disaster.
- The result was numerous reports of cancer, in excess of 648 law suits and >$10M of payouts.
Summary

CONCEPTS

- Difference between primary and secondary batteries
- How common batteries work
- Chemical reactions for common batteries
- Fuel cells and how they work
- Corrosion and corrosion protection

CALCULATIONS

- None specifically, except redox calculations involving batteries.