Batteries and Electrolysis

A battery is classified as any self-contained device that produces an electrical current.

We have seen how a common car battery is made from a series of voltaic cells:

\[ (-) \text{ Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2e^- \]
\[ E^\circ_{\text{red}} = -0.356 \]

\[ (+) \text{ PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \]
\[ E^\circ_{\text{red}} = 1.685 \]

Putting the half reactions together:

\[ \text{Pb} + \text{PbO}_2 + 2\text{HSO}_4^- + 2\text{H}^+ + 2e^- \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \]

\[ E^\circ_{\text{cell}} = E^\circ_{\text{red}} (\text{cathode}) - E^\circ_{\text{red}} (\text{anode}) \]
\[ E^\circ_{\text{cell}} = (1.685 \text{ V} - (-0.126 \text{ V})) \]
\[ E^\circ_{\text{cell}} = 2.041 \text{ V} \]

As this voltage is produced by the LSB, lead (II) sulfate is deposited on the lead and lead(II) oxide electrodes.

What if we wanted to know how much lead or lead oxide was consumed when a certain voltage was drained from the battery. Or, what if we wanted to calculate the mass of lead sulfate formed on the electrodes as the battery was used?

Remember, that the voltage produced is associated with electron transfer, and Faraday’s constant describes the charge on one mole of electrons.

Let’s investigate the relationship

For any half reaction, the amount of substance that is reduced or oxidized in an electronic cell is directly proportional to the number of electrons passed across the cell.

In our LSB, 1 mol of lead produces 2 moles of electrons.

\[ 1F = 96,485 \text{ C/mol} = 96,485 \text{ J/V-mol} \]

So, what is the link between these facts and voltage?
None that we can apply without fully describing the physics of the circuit. Therefore, we must find some other measurement to connect electrons to molar quantities of reactants or products.

Voltage only describes the difference in potential across the cell. We want to measure the current, or flow of electrons across the cell.

\[
\text{Current} = \frac{\text{charge passing}}{\text{time}}
\]

To do this, we will use amperes (amps).

An ampere is defined as one coulomb of charge per second, or:

\[
i (\text{amps}) = \frac{\text{coulombs}}{\text{seconds}}
\]

So, if 1200 amps are passed through the battery for 10 seconds, we can now calculate the mass of PbSO\(_4\) deposited.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{1200 C} & \text{10 sec} & \text{1 mol e}^- & \text{2 mol PbSO}_4 & \text{303.25 g PbSO}_4 \\
\hline
\text{1 sec} & \text{96 500 C} & \text{2 mol e}^- & \text{1 mol PbSO}_4 \\
\hline
\end{array}
\]

\[= 37.7 \text{ g PbSO}_4 \text{ produced}\]

You should identify that in the previous example that there was a 2:2 ratio of electrons to PbSO\(_4\) produced. One mole of lead sulfate came from the oxidation of lead and the other mole from the reduction of lead nitrate.

This buildup of lead sulfate should eventually render the battery useless, however, the process can be reversed.

1. Our Cu/Ag cell ran 0.05 amps for 15 min before we disconnected the circuit. How many grams of silver were “plated” on the silver electrode during that time? How many atoms of copper were dissolved into solution?

Keep in mind, the forward oxidation of lead and reduction of lead oxide is spontaneous but the reverse is not.

To reverse the reaction, the cell potential for the reverse reaction must be increased for the reaction to be driven backward.

The process of using electrical current to drive a non-spontaneous reaction is called electrolysis.

Common uses for electrolysis

- Electroplating
- Metal and gas production
- “Recharging” batteries
- Corrosion prevention

Charles Hall (1863-1914) developed electrolysis process. Founded Alcoa.
Types of Electrolysis

Electrolysis of molten salts

2Na\(^{+}(l)\) + 2e\(^{-}\) → 2Na\(^{0}(l)\)

2Cl\(^{-}(l)\) → Cl\(^2(g)\) + 2e\(^{-}\)

Remember, to drive the electrolysis, the energy input must be greater than the spontaneous cell potential.

Down’s Cell

Sodium ions migrate to cathode
Reduced to sodium metal
Chloride ions migrate to anode
Oxidized to chlorine

Aqueous solution with an inert electrode

Here we have the galvanic cell created by forcing H\(_2\) and O\(_2\) into a basic solution across inert electrodes to produce water.

Reactions follow

Reduction

4e\(^{-}\) + O\(_2(g)\) + 2 H\(_2\)O → 4OH\(^{-}\) \hspace{1cm} E^o_{\text{red}} = 1.23 \text{V}

Oxidation

2H\(_2(g)\) + 4OH\(^{-}\) → 4H\(_2\)O + 4e\(^{-}\) \hspace{1cm} E^o_{\text{red}} = -0.86\text{V}

The net reaction:

\[ 2H\(_2(g)\) + O\(_2(g)\) → 2H\(_2\)O \]

\[ E^o_{\text{cell}} = 2.06 \]

By introducing a current greater than the voltage equivalent of 2.06, we can drive the reverse reaction, or the non-spontaneous electrolysis of water (DEMO)

Aqueous solution with an Active electrode

Examine the following electrolytic cell:

From the SRP table, we see that the reduction of nickel is less favored than the reduction of water. Likewise, the oxidation of nickel is more favored than the oxidation of water.

So, Nickel naturally oxidizes in water to form nickel oxide.

If we could somehow prevent the reduction of water, we could simply transfer the nickel metal from the anode to an active cathode.
By introducing a current, the spontaneous reduction of water can be reversed resulting in the oxidation - reduction of only nickel.

This is the process of electroplating.

Impure copper is oxidized to Cu$^{2+}$ at the anode. The aqueous Cu$^{2+}$ ions are reduced to Cu metal at the cathode.

2. The electroplating of a silver teapot requires the use of 15.0 grams of silver.

A. Draw the electrolytic cell labeling cathode, anode, showing electron/ion movement and write both half cell reactions.

B. Determine how long it will take to electroplate the teapot if the cell runs at 2.00 amps.

3. Sodium metal and chlorine gas are prepared industrially in a Down’s cell from the electrolysis of molten sodium chloride. What mass of metal and volume of gas can be made per day if the cell operates at 4.0 x 10$^4$ amps and 75% efficiency?