Chemistry 2000 Slide Set 16: Batteries and fuel cells

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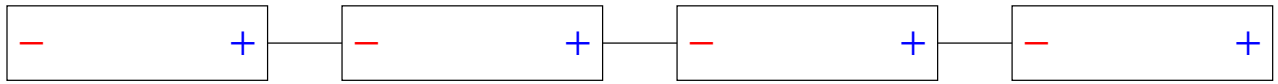
Cells and batteries

- We have already seen that electrochemical cells can produce a voltage, i.e. they can be used to power electrical devices.
- The voltage generated by a cell is determined by a number of factors:
  - thermodynamics of the reaction
  - concentrations of reactants and products
  - temperature
- The physical size of a cell only determines the amount of reactants stored, i.e. how long it can run, and sometimes the current that can be drawn.

- Typical useful cell voltages are around 1 V.
- If we need a higher voltage, we have to connect a number of cells in series:



  This is called a battery.
- The voltage generated by a battery is the sum of the voltages of the cells.

Recharging batteries

- In principle, all batteries can be recharged by forcing electrons in the opposite direction to that in which the battery normally pushes them.
- This is done by using an opposing overvoltage (i.e. a voltage larger than that generated by the battery pushing electrons toward the anode).
- In practice, some batteries can't easily (or safely) be recharged:
  - The electrodes can be damaged during the discharge process.
  - The electrodes can become coated with resistive products that cause excessive heating when current is passed through them.
  - Different reactions can occur when recharging is attempted than the reverse of the cell reaction, e.g. electrolysis of water.

Alkaline cells

Anode: $\mathrm{Zn_{(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e^-}$

$E^\circ = 1.246\,\mathrm{V}$

Cathode: $\mathrm{2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}}$

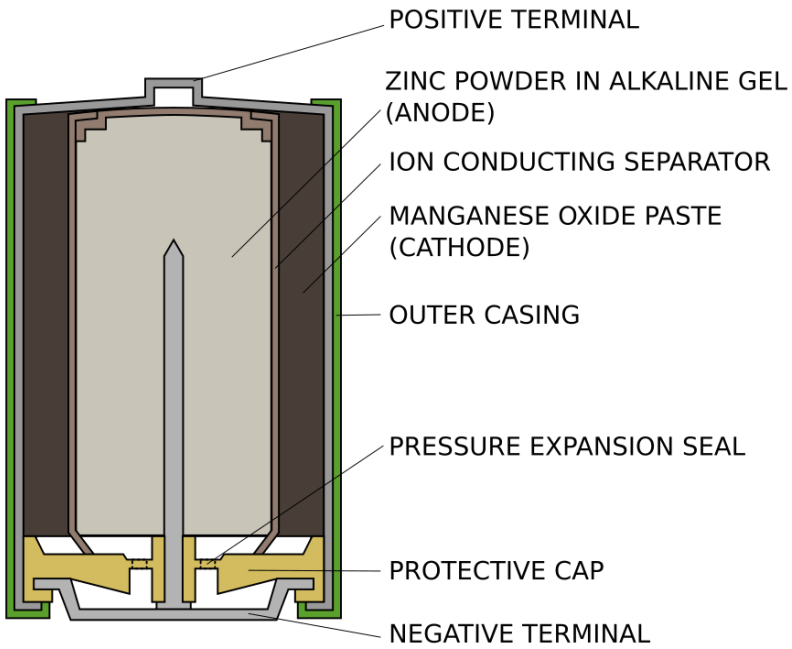
$E^\circ = 0.118\,\mathrm{V}$

Overall: $\mathrm{Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}}$

$E^\circ = 1.364\,\mathrm{V}$

- Note the absence of any solutes in the overall reaction.
- Water would be present in significant excess, so its activity would be approximately constant.
- E should therefore remain roughly constant as the cell discharges.

Alkaline cells (continued)



$$Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \rightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$$

Adapted from `https://commons.wikimedia.org/wiki/File:Alkaline-battery-english.svg`

- Recharging a normal alkaline cell results in the growth of zinc crystals, which can puncture the separator.
- Recharging can also cause the formation of hydrogen gas by water electrolysis, which is an obvious safety hazard.
- Rechargeable alkaline cells contain additional chemical ingredients to prevent both of these effects.

Lead-acid battery

Anode: $\mathrm{Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^-}$

$E^\circ = 0.3588\,\mathrm{V}$

Cathode: $\mathrm{PbO_{2(s)} + 3H^+_{(aq)} + HSO^-_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}}$

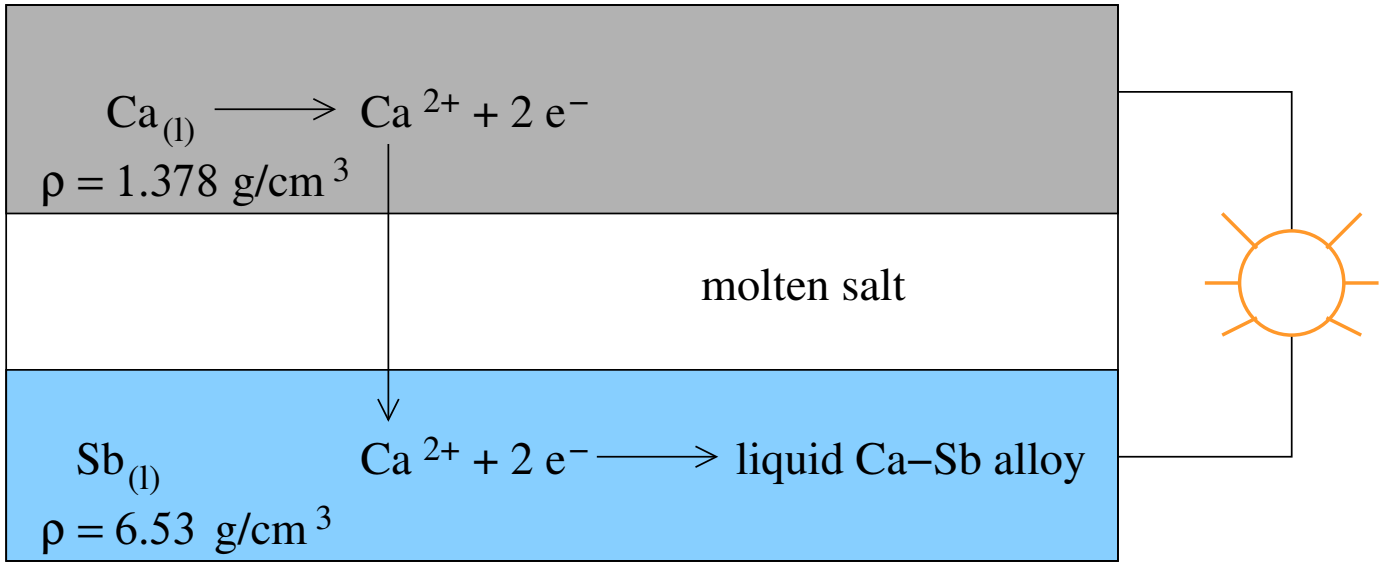
$E^\circ = 1.6913\,\mathrm{V}$

Overall: $\mathrm{Pb_{(s)} + PbO_{2(s)} + 2H^+_{(aq)} + 2HSO^-_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}}$

$E^\circ = 2.0501\,\mathrm{V}$

- The voltage will depend somewhat on the solute concentrations, but is typically around 2 V for each cell.
- To get the usual 12 V, six cells would be connected in series.

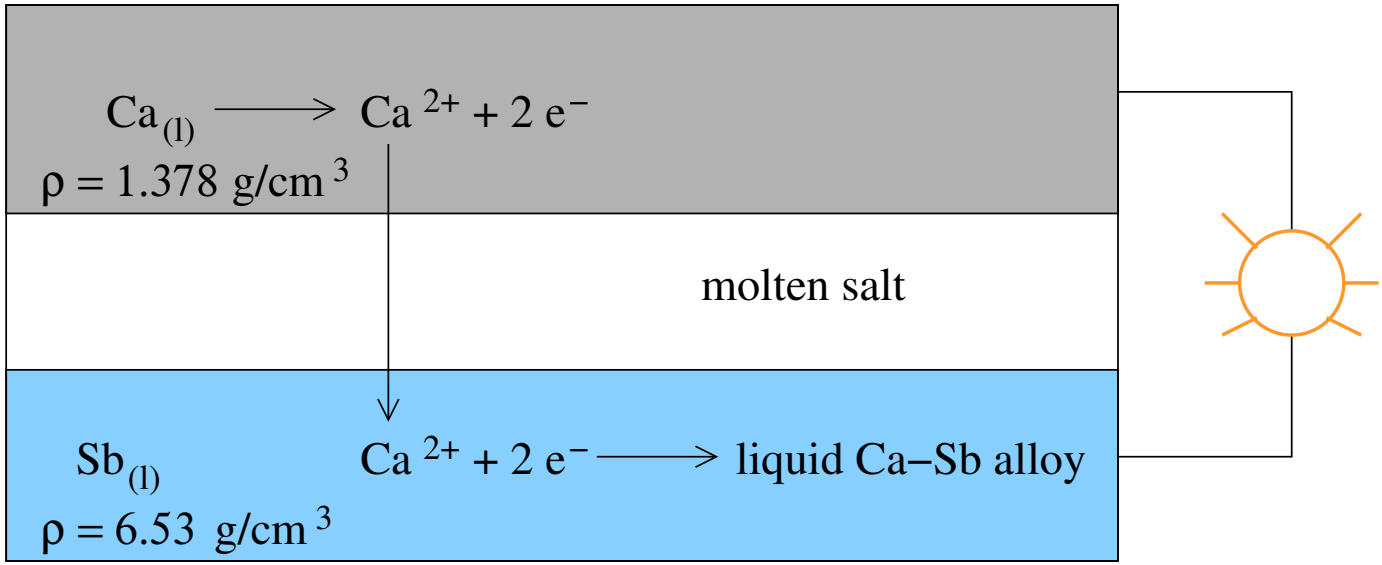
The Ambri liquid-metal cell



- Rechargeable cell developed by Professor Donald Sadoway of MIT.
- Overall reaction:

$$Ca_{(l)} + Sb_{(l)} \rightarrow \text{Ca-Sb alloy(l)} \qquad E = 0.95\,V$$

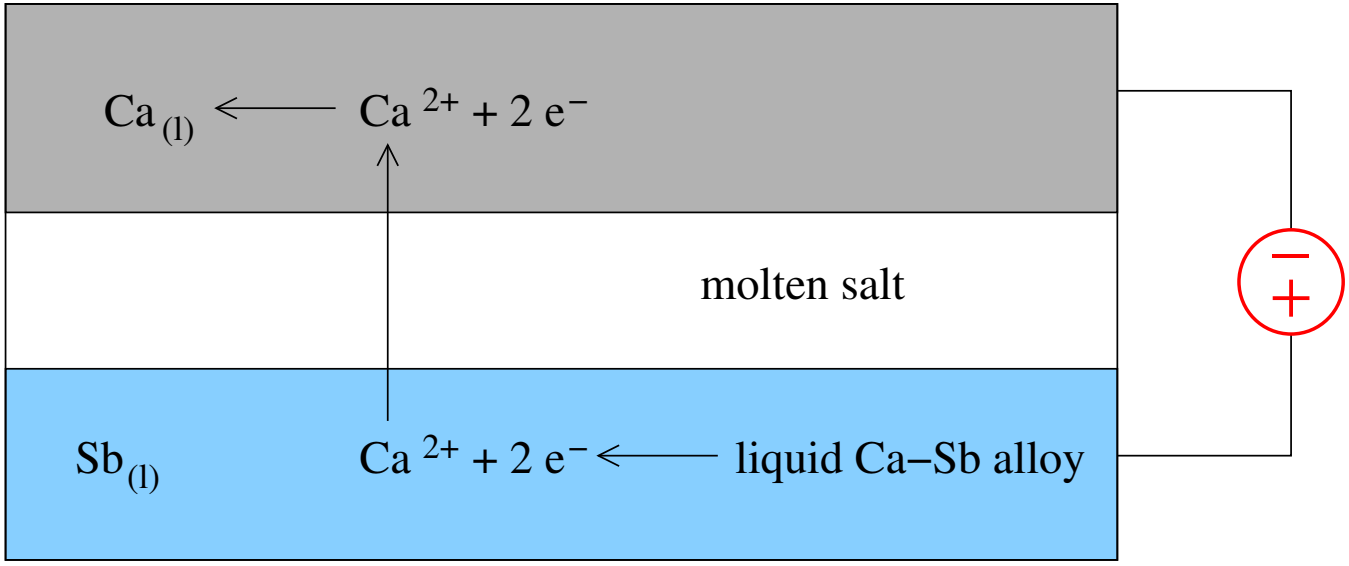
The Ambri liquid-metal cell



- While operating, the cell generates enough heat to keep all the components in the liquid state.
- No solid electrodes to degrade, so low-maintenance and long-lasting.
- NEC currently developing large-scale energy storage systems using Ambri cells

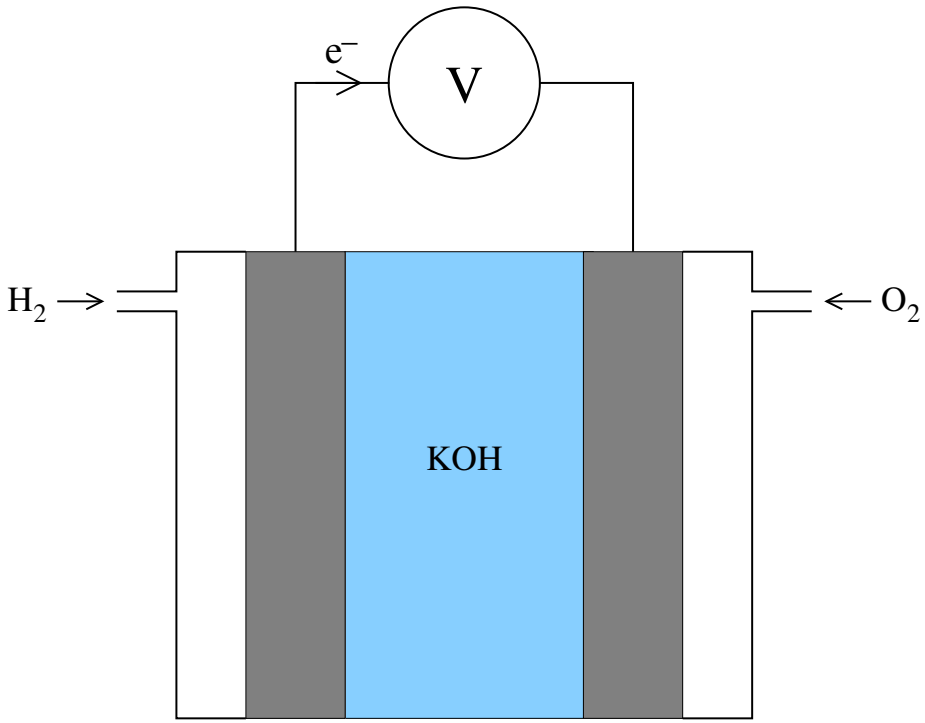
The Ambri liquid-metal cell

Recharge cycle



Fuel cells

- Fuel cells oxidize a fuel in an electrochemical cell to produce a current.
- This is more efficient than burning a fuel to turn an engine, and less polluting as well.



Methane-oxygen fuel cell

- In a previous lecture, we found that the half-reactions of this fuel cell were

$$\begin{aligned} \mathrm{CH_{4(g)}} + 8\mathrm{OH^-_{(aq)}} &\rightarrow \mathrm{CO_{2(g)}} + 6\mathrm{H_2O_{(l)}} + 8\mathrm{e^-} \\ 2\mathrm{O_{2(g)}} + 4\mathrm{H_2O_{(l)}} + 8\mathrm{e^-} &\rightarrow 8\mathrm{OH^-_{(aq)}} \end{aligned}$$

  with overall reaction

$$\mathrm{CH_{4(g)}} + 2\mathrm{O_{2(g)}} \rightarrow \mathrm{CO_{2(g)}} + 2\mathrm{H_2O_{(l)}}$$

  and $\nu_e = 8$.
- We can easily calculate $\Delta_r G^\circ_m = -818.1\,\mathrm{kJ/mol}$.
- $E^\circ = -\Delta_r G^\circ_m/(\nu_e F) = 1.060\,\mathrm{V}$
- Say that $P_{\mathrm{CH_4}} = 1\,\mathrm{bar}$, $P_{\mathrm{O_2}} = 0.2\,\mathrm{bar}$ and $P_{\mathrm{CO_2}} = 0.1\,\mathrm{bar}$.
- Using the Nernst equation, we find $E = 1.057\,\mathrm{V}$.
- To make a 12 V battery, we would have to connect 12 of these cells in series.

Fuel cells

Continued

- The cathode reaction in a fuel cell is always either

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

or

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$$

- Either way, there are 4 electrons for every O_2.
- We can therefore figure out ν_e from the balanced reaction by simply multiplying the number of oxygen molecules by 4.

Direct formic acid fuel cell

- Gaseous reactants require complicated and expensive high-pressure regulation systems.
- Liquid reactants like methanol often permeate through the electrodes, which in practical fuel cells are often made of a polymer. This reduces the efficiency of the fuel cell.
- Formic (methanoic) acid (HCOOH, m.p. 8.4 °C, b.p. 100.8 C) is nonflammable under typical storage/operating conditions and does not permeate typical fuel cell membranes.
- So far, formic acid fuel cells are a tantalizing but unproven technology.

Direct formic acid fuel cell

Continued

Calculate the voltage generated by this cell at 25 °C with $p_{O_2} = 0.20\,\text{bar}$, $p_{CO_2} = 1.1\,\text{mbar}$ and $a_{H_2O} = 0.82$ if pure formic acid is supplied at the anode.

Species	$\Delta_f G^\circ / \text{kJ mol}^{-1}$
$CO_{2(g)}$	-394.37
$HCOOH_{(l)}$	-362.56
$H_2O_{(l)}$	-237.140

Answer: 1.4750 V