

KJM 3110 Electrochemistry

Chapter 5. Electrochemical power

With exercises

Electrochemical power

- Previous chapter: Electrical energy to chemical (Gibbs) energy

- Electrolysis

- Charging battery

- Secondary cells; Accumulators, rechargeable batteries)

- This chapter: Chemical (Gibbs) energy to electrical energy

- Fuel cell

electrochemical power source {
battery { primary cell
secondary cell
fuel cell

- Discharging battery

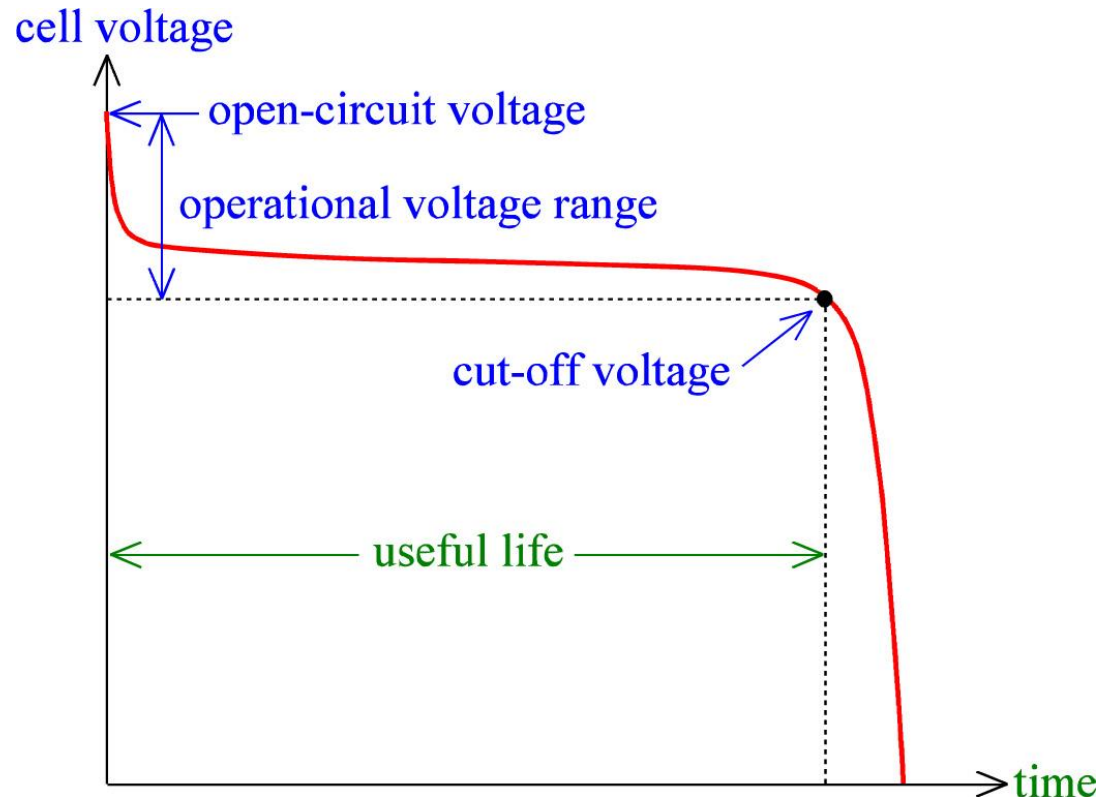
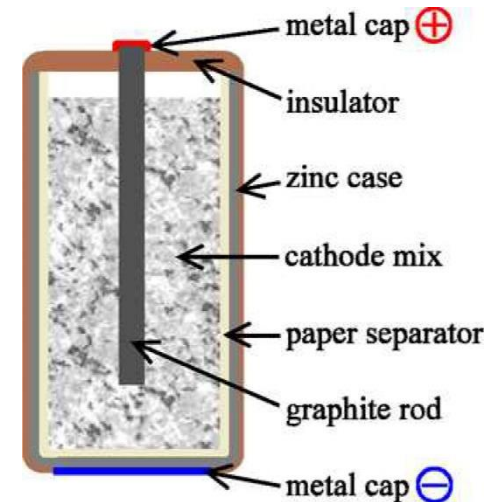
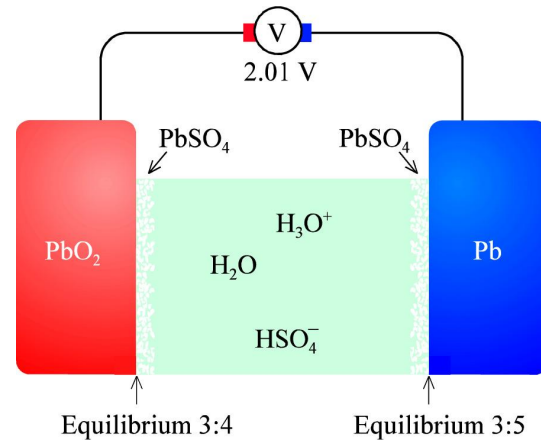
- Primary cells
 - Secondary cells; Accumulators, rechargeable battery

Recap from Ch. 4 Electrosynthesis - Summary

- We have seen some industrial examples of electrolytic operation of electrochemical cells for production of high-energy fuels and chemicals
 - Some important
 - Hall-Hèrault for aluminium
 - Chlor-alkali for chlorine products
 - Electrolysis for H₂
 - Some new trends
 - Organic electrosynthesis
- Applications of high-temperature solid electrolytes pursued at UiO
- Ion-selective membranes give additional possibilities
- In electrosynthesis, otherwise impossible reactions become possible
 - The electronic energy adds to or – more typically – overpowers the chemical energy
 - Thermodynamic
 - Kinetic (can also give unique selectivities)
- “Control chemistry by controlling electrons”

Batteries

- Positive and negative electrodes
- Positrode and negatrode
- Cathode and anode
- Nominal voltage
 - = OCV full charged
- Cut-off voltage
- Capacity
 - Coulomb, or A s
 - $1\text{ C} = \text{A} \cdot \text{s}$
 - $1\text{ A h} = 3600\text{ A s}$
- Energy
 - Unit?
 - Specific energy
 - Energy density
- Power
 - Unit?
 - Specific power
 - Power density

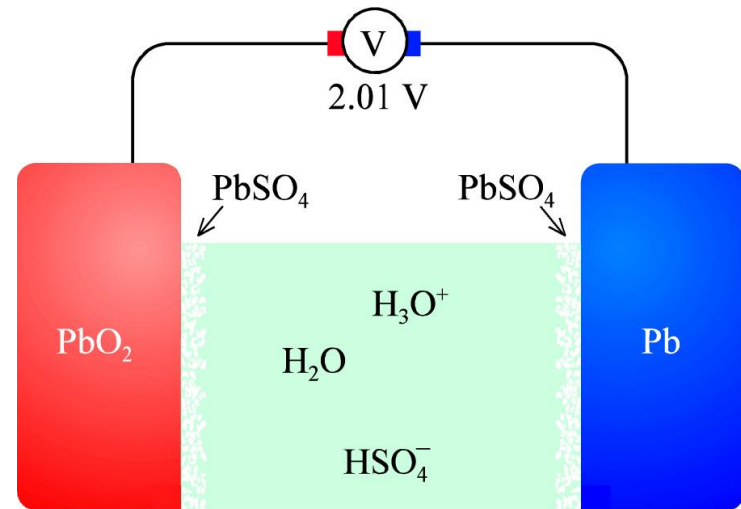


Storage

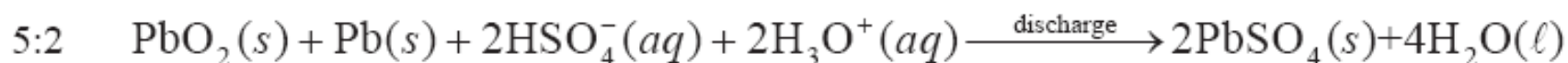
- Battery: Chemistry
- Ultracapacitor: Chemistry + electrode interface
- Supercapacitor: Electrode interface
- Capacitor: Dielectric

| | energy density / W h L^{-1} | power density / kW L^{-1} | discharge time / s | cycle life |
|-------------------|---|---------------------------------------|-----------------------|------------|
| secondary battery | 100 | 0.1 | 10^4 | 100 |
| ultracapacitor | 10 | 1 | 10 | 10^5 |
| supercapacitor | 1 | 10 | 1 | 10^6 |
| capacitor | 0.1 | 10^5 | 0.01 | ∞ |

Lead acid battery



The theoretical capacity and specific power of a battery are rather easily calculated when simplifying assumptions are made. For example, in a fully charged lead-acid cell (diagramed and discussed on pages 56–57), 0.239 kg of PbO_2 at the positive and 0.207 kg of Pb at the negative (one mole of each) would theoretically require only 0.385 liters (weighing 0.499 kg) of 5.2 molar aqueous sulfuric acid to permit the cell reaction



to proceed to completion. This galvanic process would produce⁵⁰⁸

$$5:3 \quad (2.00 \text{ mol}) \times (96485 \text{ C mol}^{-1}) = 1.93 \times 10^5 \text{ C} = 53.6 \text{ Ah}$$

of electricity, so that our ideal lead-acid cell would have a capacity of 53.6 ampere hours and a mass of $(0.239 + 0.207 + 0.499) \text{ kg} = 0.945 \text{ kg}$. With a cell voltage of 2.01 V, as calculated in equation 3:10, we compute a specific energy of

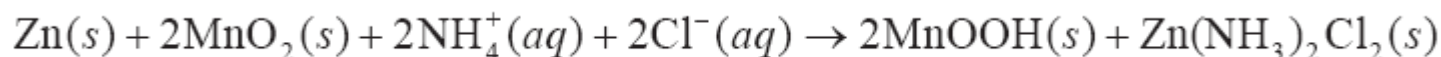
$$5:4 \quad \frac{(53.6 \text{ Ah}) \times (2.01 \text{ V})}{0.945 \text{ kg}} = 114 \text{ Wh kg}^{-1}$$

Primary batteries

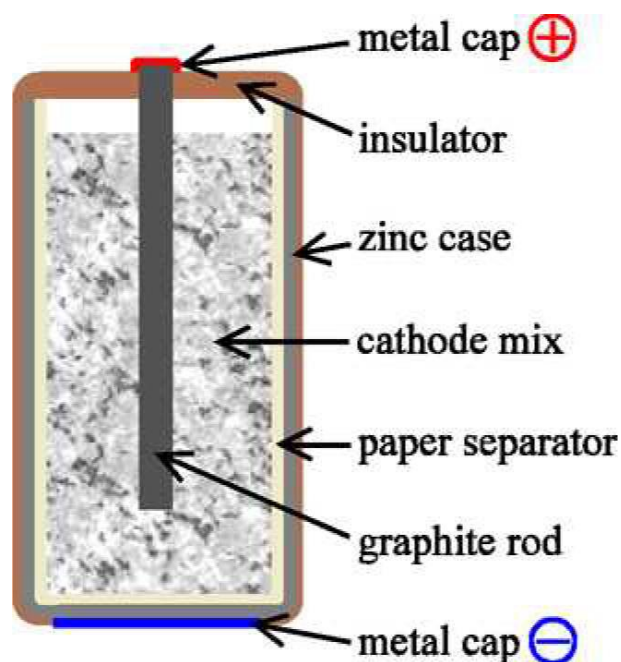
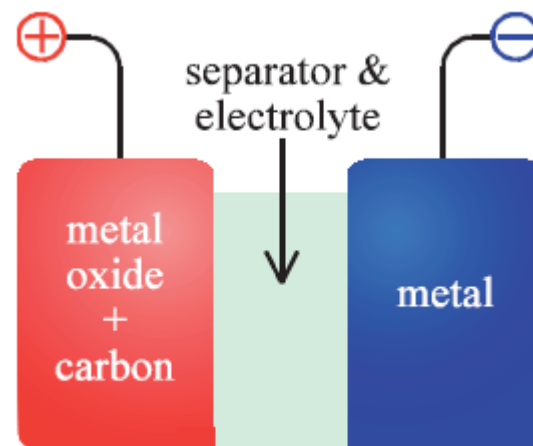
- Volta pile
- Daniell cell
- Leclanché wet cell with $\text{NH}_4\text{Cl}(aq)$

negative: $\text{Zn}(s) \rightarrow 2e^- + \text{Zn}^{2+}(aq)$

positive: $\text{MnO}_2(s) + \text{NH}_4^+(aq) + e^- \rightarrow \text{MnOOH}(s) + \text{NH}_3(aq)$

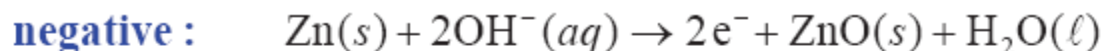


- Dry cell
 - $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ paste
 - C powder composite cathode

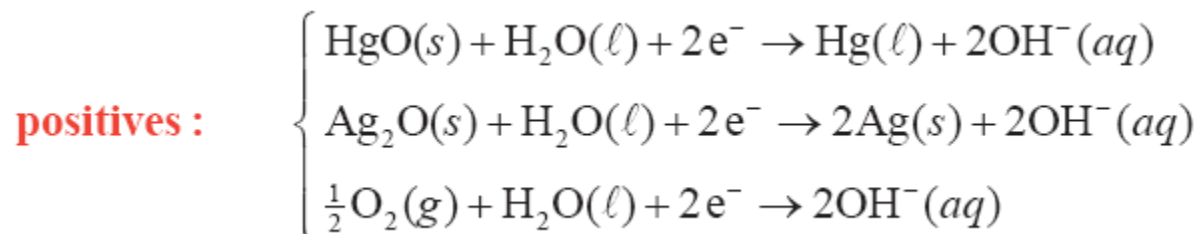


Alkaline batteries

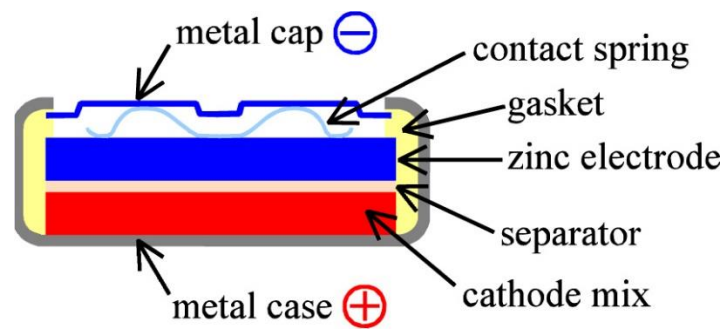
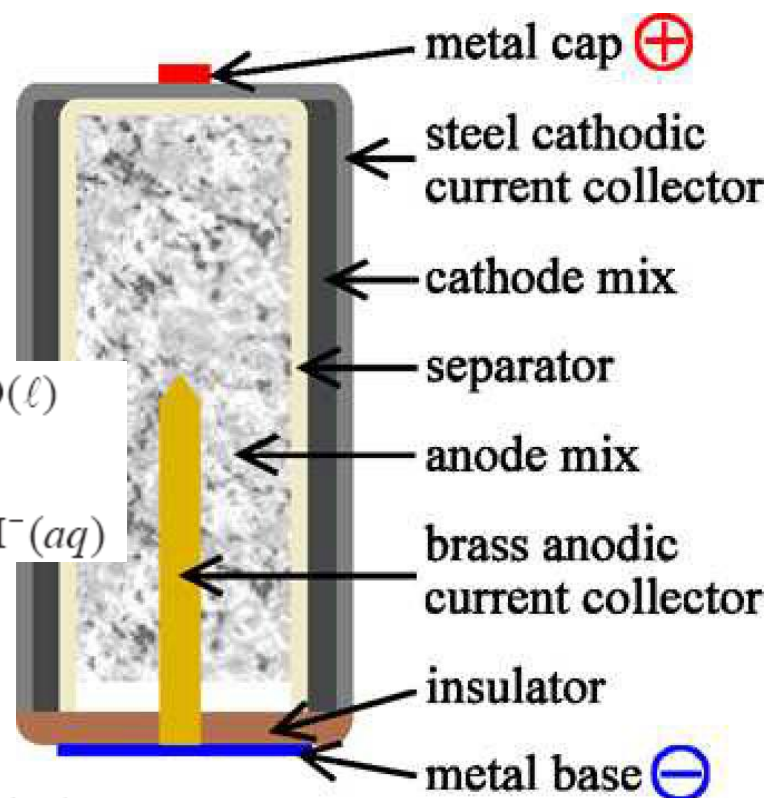
- In some ways an inversed design...



- Other alkaline positrodes



- Air battery



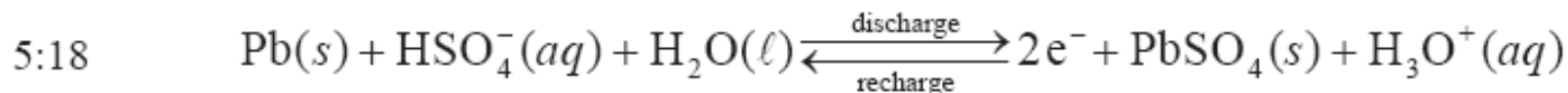
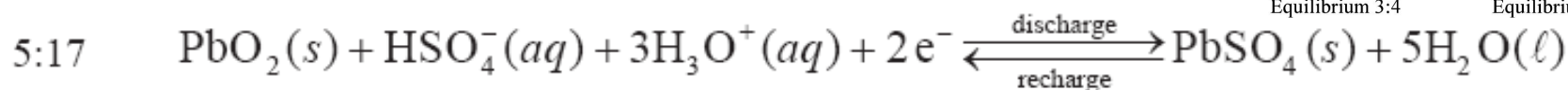
Exercise

- Write full cell reactions and Gibbs energy expressions for each of the four alkaline cells in the previous slide

Secondary (rechargeable) batteries (accumulators)

- Most widespread: Lead-acid battery.
- Repeat from Ch. 3:

To review, the **positive**, **negative** and net **cell** reactions are⁵²⁶



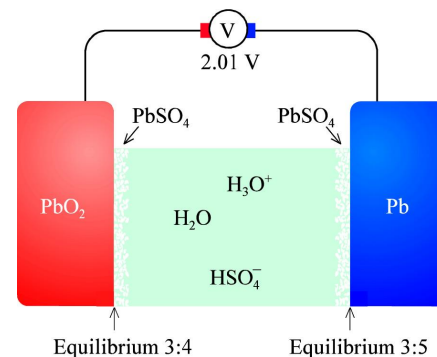
and



The standard cell voltage, as calculated on page 59, is 1.925 V, but the Nernst equation

$$5:20 \quad \Delta E_n = (1.925 \text{ V}) - \frac{RT}{2F} \ln \left\{ \frac{a_{\text{H}_2\text{O}}^4}{a_{\text{H}_3\text{O}^+}^2 a_{\text{HSO}_4^-}^2} \right\}$$

shows the null voltage to depend on the sulfuric acid concentration. For a fully-charged concentration of 5.2 M, the voltage is about 2.13 V at 25°C, but this declines on discharge as the ions are consumed to reach a cut-off voltage of about 1.8 V.

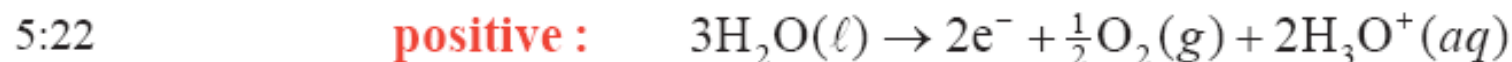


Lead acid batteries: Extraneous reactions

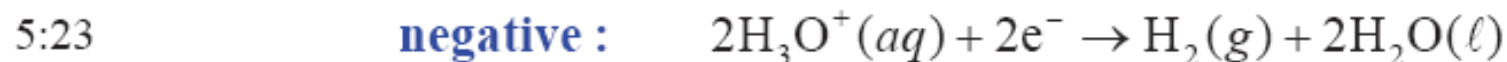
There are four extraneous reactions that concern designers of lead-acid batteries:
corrosion of the positive electrode



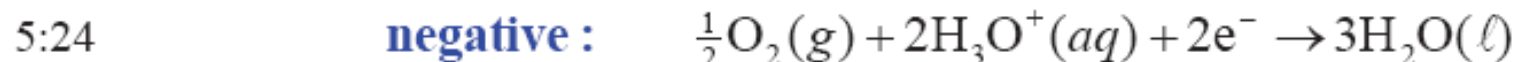
oxygen evolution from the positive electrode



hydrogen evolution at the negative electrode



and oxygen reduction at the negative electrode



Reactions 5:22 and 5:23 compete with the charging reactions 5:17 and 5:18 and these competitive processes take over completely when recharge is complete, leading to loss of water from the cell and necessitating periodic “topping up” of the cells with pure water.

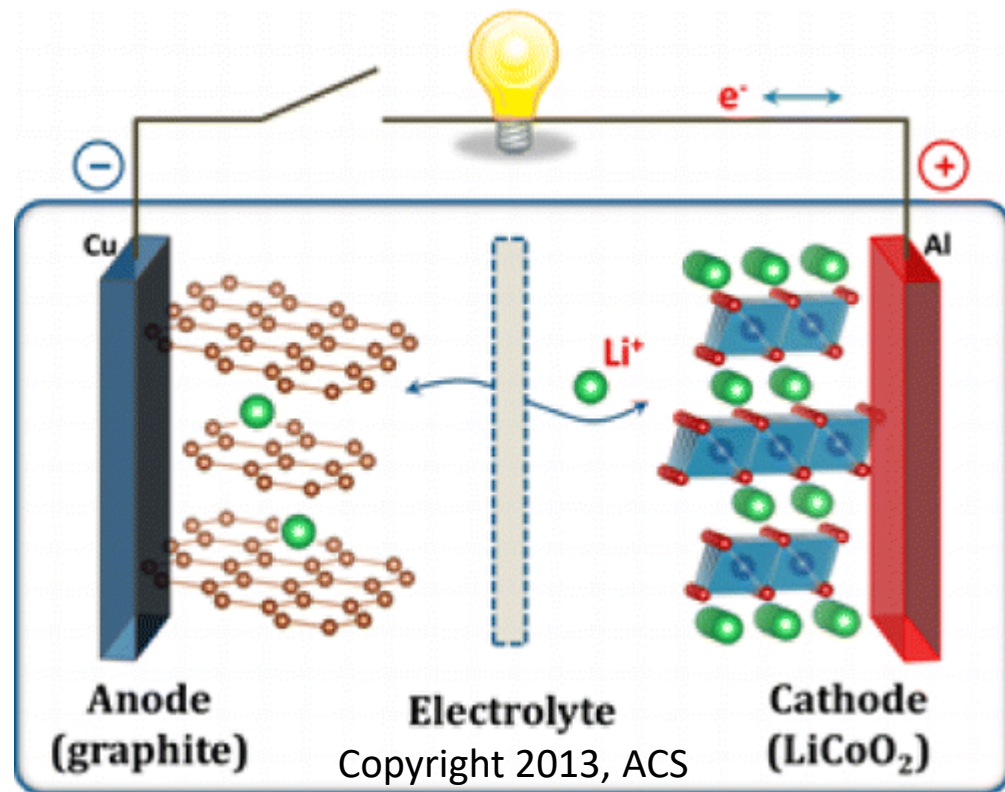
- In modern, sealed batteries, diffusion of O_2 + reaction 5.24 replenishes the water.

Exercise: Ni-Cd and Ni-H cells

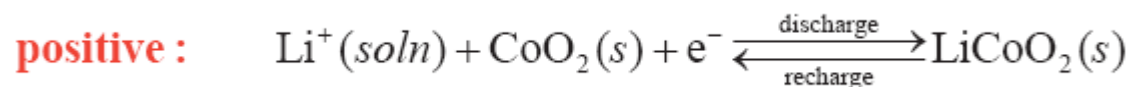
- Write full cell reactions for these cells (se half cell reactions in the book) and Gibbs energy expressions

Li-ion batteries

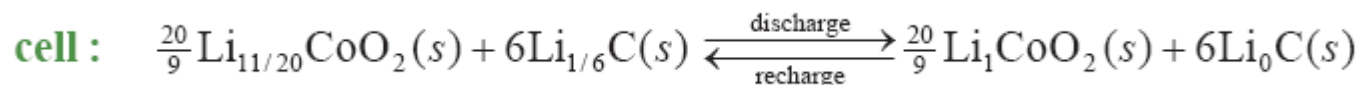
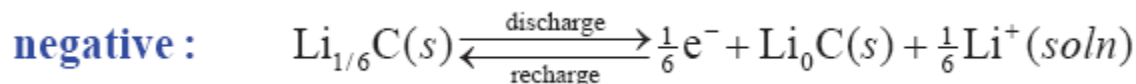
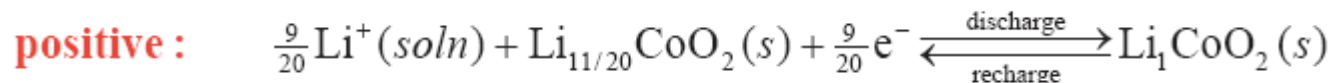
The electrolyte used in most lithium-ion cells is a solution of LiClO_4 or LiAsF_6 in organic carbonates, absorbed in microporous polyolefin separator.



- May be represented simple



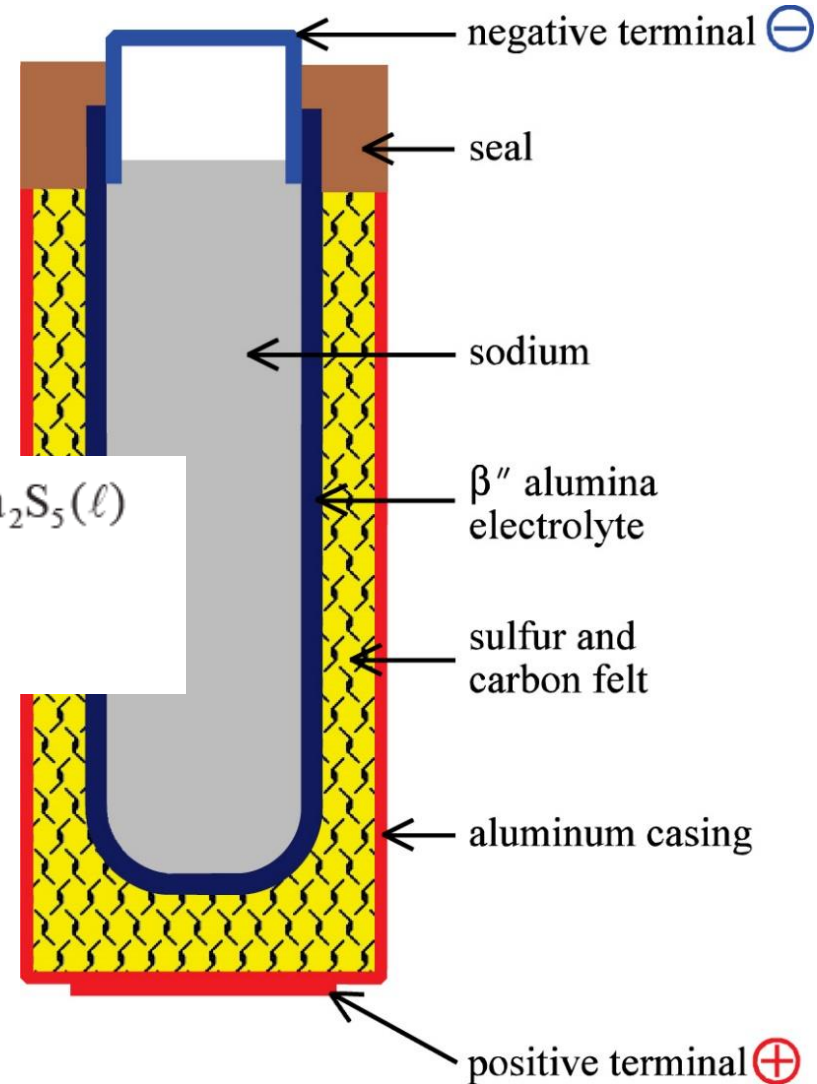
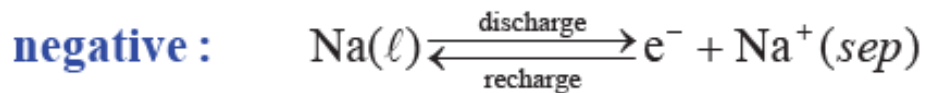
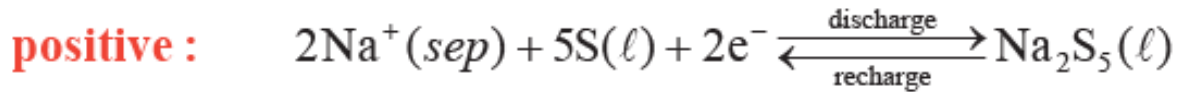
- or more realistic



Exercise

- The previous slide shows a realistic, complex example. Write a simple one and the Gibbs energy expression.

Na-S battery



- **Exercise:** What is the total reaction and Gibbs expression?

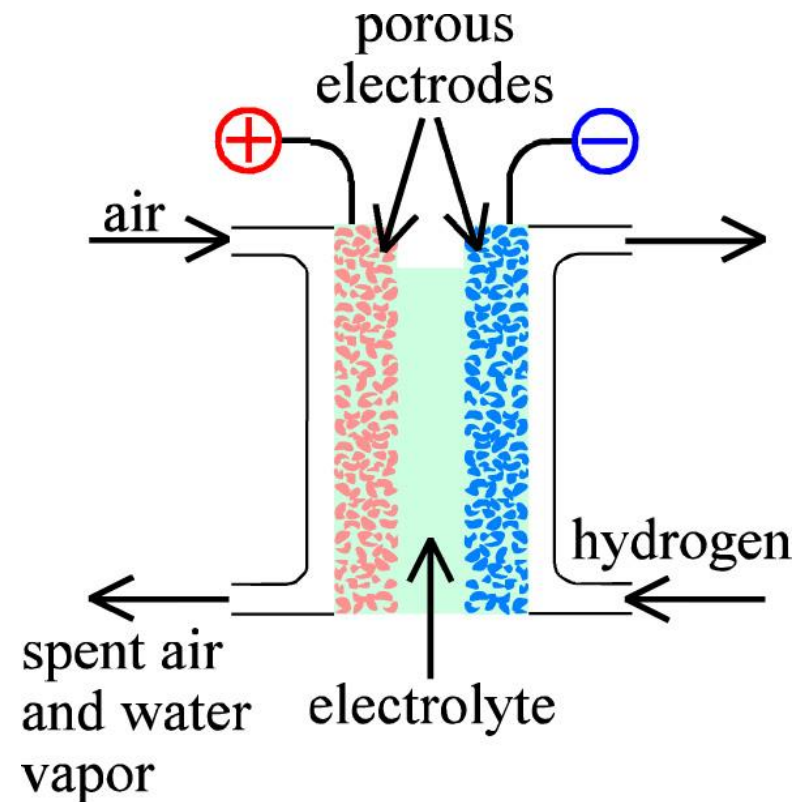
Fuel cells; continuous supply of fuel and oxidant air

- Fuels:

- H_2
- Reformed CH_3OH
- Reformed CH_4

- Electrolytes:

- Alkaline
- Acid (Phosphoric acid and PEM)
- Molten carbonate
- Solid oxide
- Proton ceramic

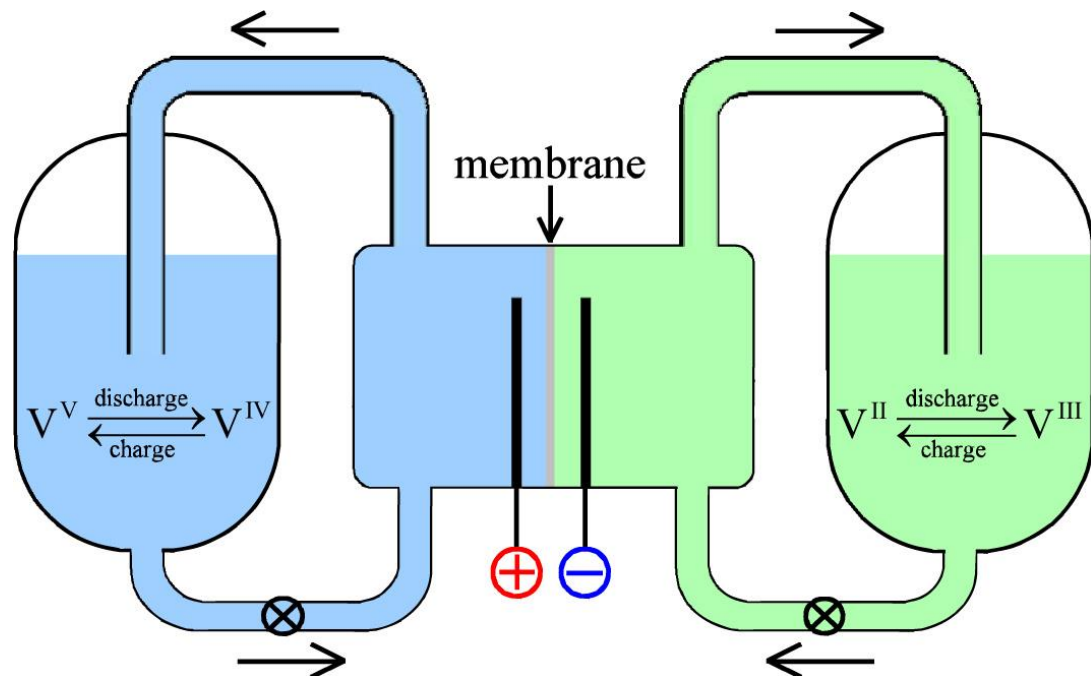


Exercise

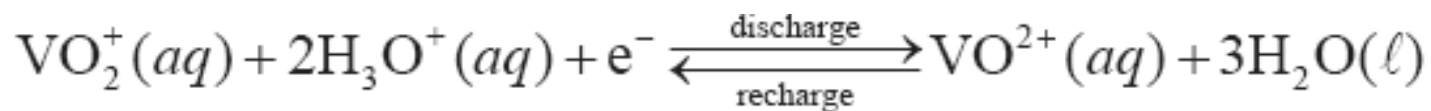
- What is reforming? Write reactions for CH_3OH and CH_4 .
- What is shift?
- What is external vs internal reforming?

- Write half and full cell reactions as well as an expression for ΔG for H_2 and O_2 for the different electrolytes on the previous slide

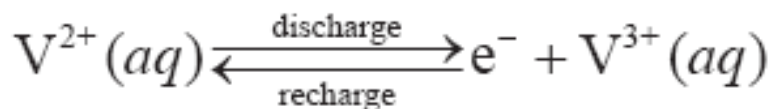
Redox flow battery



positive :



negative :



Exercise

- Write the total reaction and Gibbs energy expression
- What are the electrodes?
- What goes on in the membrane?

Ch. 5 Summary

All three categories of electrochemical power source – primary cells, secondary batteries, and fuel cells – are rapidly developing fields of electrochemical technology.

Notwithstanding the hyperbole from environmentalists and battery fabricators – and, of late, from governments and car manufacturers – it is most unlikely that electrochemical power sources will ever rival the internal combustion engine in power density. Nevertheless, it seems certain that environmental and economic constraints will increasingly force the replacement of many internal combustion engines by rechargeable power sources. At the time of writing, the lead-acid, nickel-metal-hydride, and lithium-ion secondary batteries are all competing for the potentially lucrative electric car market. All have disadvantages, as have other contending secondary batteries and fuel cells. Sadly, the paragon secondary battery remains elusive.

- **Exercise:** Discuss each sentence, not least the last one. When was this written?