Lecture 6 - Fuel cells

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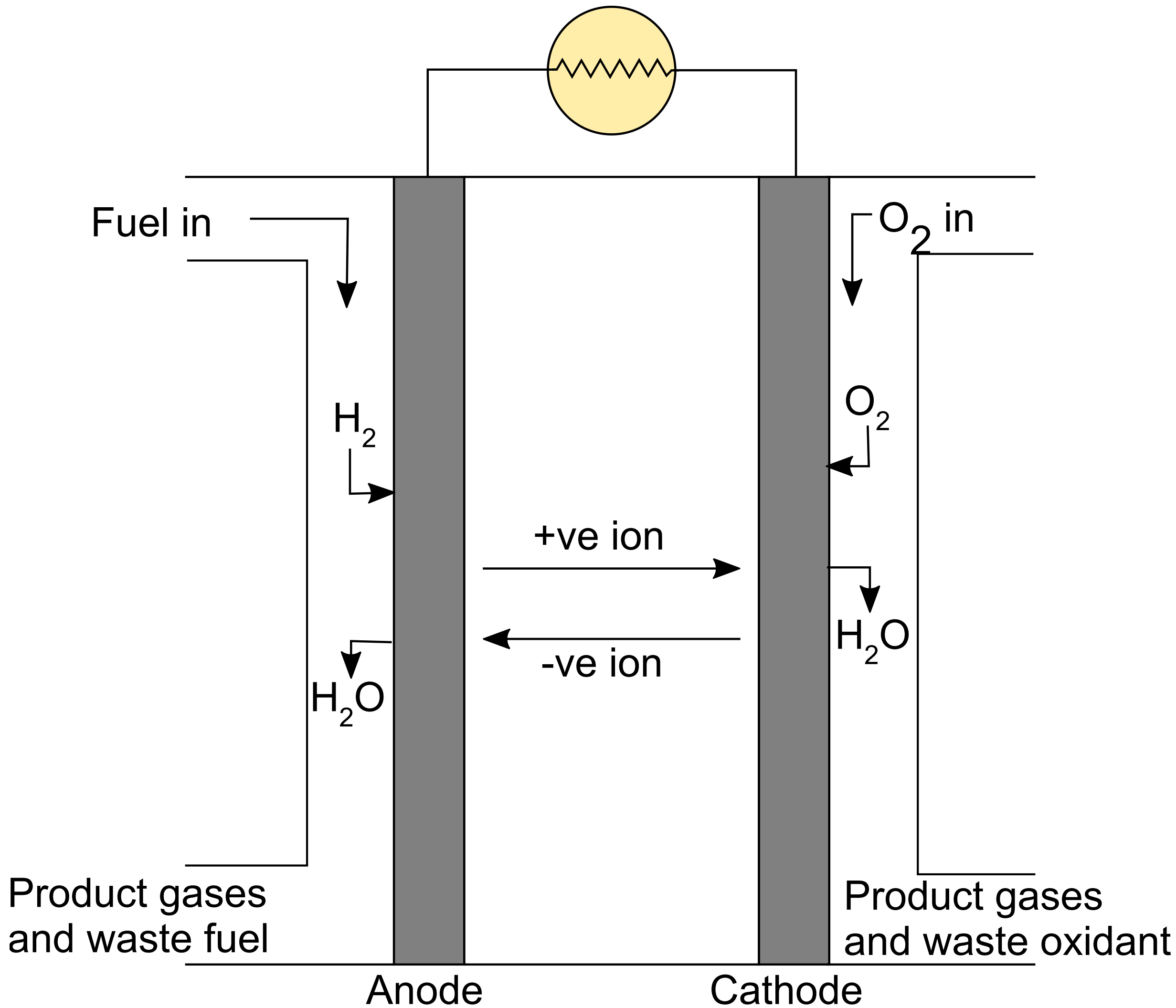
Lecture Summary

- Fuel cell introduction
- Types of fuel cells
  - Polymer cells
  - Solid oxide fuel cells (SOFCs)
- Materials requirements for SOFCs
  - example materials
- Defect ordering

Fuel Cells

Fuel cells are similar to batteries; they have a cathode, electrolyte and anode.



Electricity can be generated as long as fuel is supplied (they don't need to be recharged)

1801
Humphry Davy demonstrates the principle of what became fuel cells.

1839
William Grove invents the 'gas battery', the first fuel cell.

1889
Charles Langer and Ludwig Mond develop Grove's invention and name the fuel cell.

1950s
General Electric invents the proton exchange membrane fuel cell.

1959
Francis Bacon demonstrates a 5 kW alkaline fuel cell.

1960s
NASA first uses fuel cells in space missions.

1970s
The oil crisis prompts the development of alternative energy technologies including PAFC.

1980s
US Navy uses fuel cells in submarines.

1990s
Large stationary fuel cells are developed for commercial and industrial locations.

2007
Fuel cells begin to be sold commercially as APU and for stationary backup power.

2008
Honda begins leasing the FCX Clarity fuel cell electric vehicle.

2009
Residential fuel cell micro-CHP units become commercially available in Japan.

Fuel cell fundamentals

$$\mathrm{Fuel} + \mathrm{O_2} \longrightarrow \mathrm{H_2O} + \mathrm{nCO_2}$$

- Fuel cells classed as *low-temperature* (LT, < 200 °C) and *high-temperature* (HT, > 450 °C).
- H_2 is the preferred fuel
  - Particularly for LT devices.
  - Doesn't produce CO_2

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- H_2 is the preferred fuel
  - Particularly for LT devices.
  - Doesn't produce CO_2
- Other fuels (*e.g.* CH_3OH, CH_4, NH_3) also possible
  - Steam reforming (e.g. $\mathrm{CH_4} + \mathrm{H_2O} \xrightarrow{>700^\circ C} \mathrm{CO} + 3\,\mathrm{H_2}$) can convert fuels to $\mathrm{H_2}$
    - achieved in-situ for HT cells, but must be separate for LT.

Fuel cell efficiency

Fuel cells are *very* efficient

- Convert fuel → electricity directly, rather than fuel → heat → electricity (as in combustion)

$$\text{Thermodynamic efficiency} = \frac{\Delta G}{\Delta H}$$

e.g. for $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ $(\Delta H = -571.6\ \mathrm{kJ\ mol^{-1}})$:

$$\begin{array}{rlr} \text{Cathode:} & 4\,\mathrm{H^+} + \mathrm{O_2} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} & \mathrm{E} = +1.229\ \mathrm{V} \\ \text{Anode:} & 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longleftarrow 2\,\mathrm{H_2} & E = 0.00\ \mathrm{V} \end{array}$$

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$$\begin{aligned} \Delta G &= -nFE \\ &= -4 \times F \times 1.229 \\ &= -474.3\ \mathrm{kJ\ mol^{-1}} \qquad (\text{per mole } O_2) \end{aligned}$$

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Efficiency = η = -474.3 / 571.6 = **83%**

Efficiency with temperature

$$\Delta G = \Delta H - T\Delta S, \quad \therefore \quad \frac{\Delta G}{\Delta H} = \eta = 1 - \frac{T\Delta S}{\Delta H}$$

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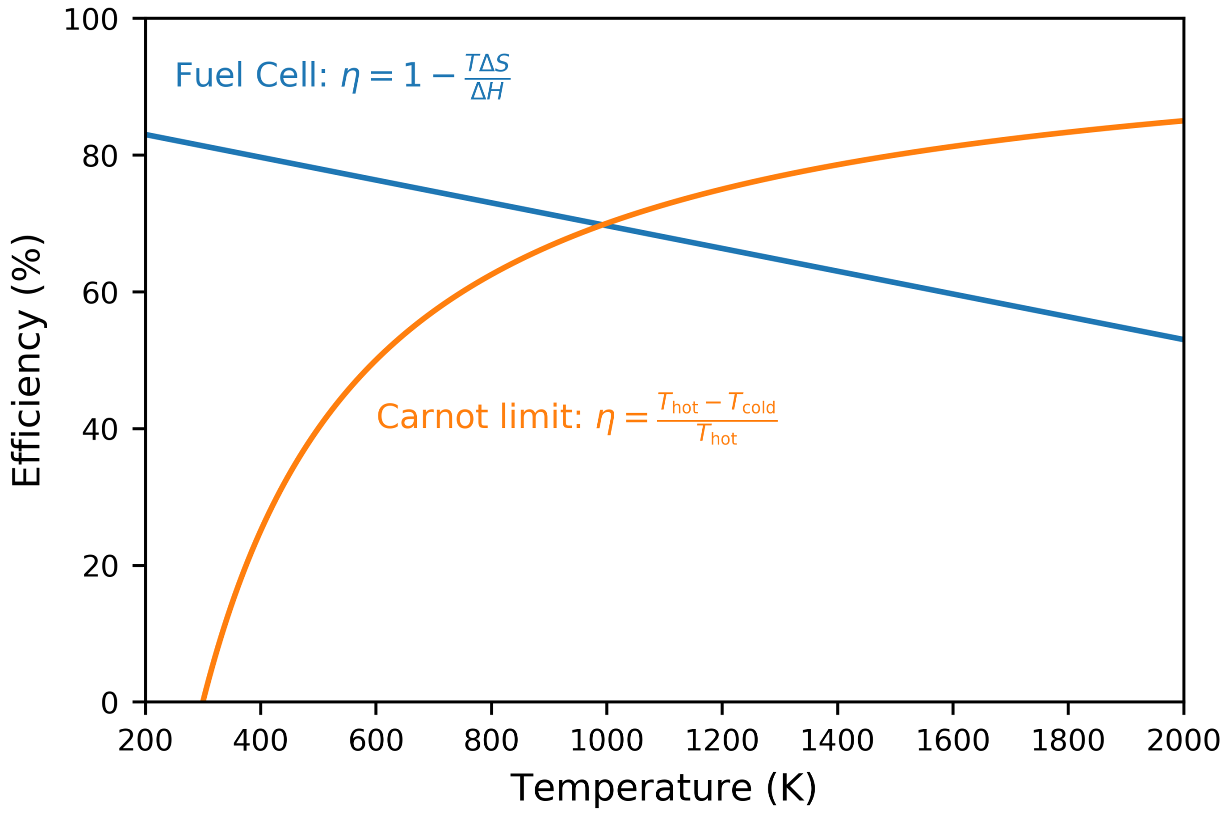


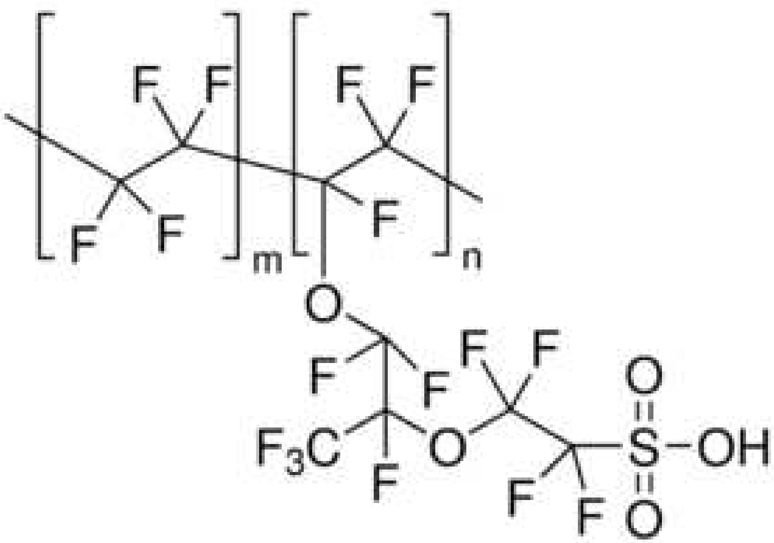
Types of fuel cell

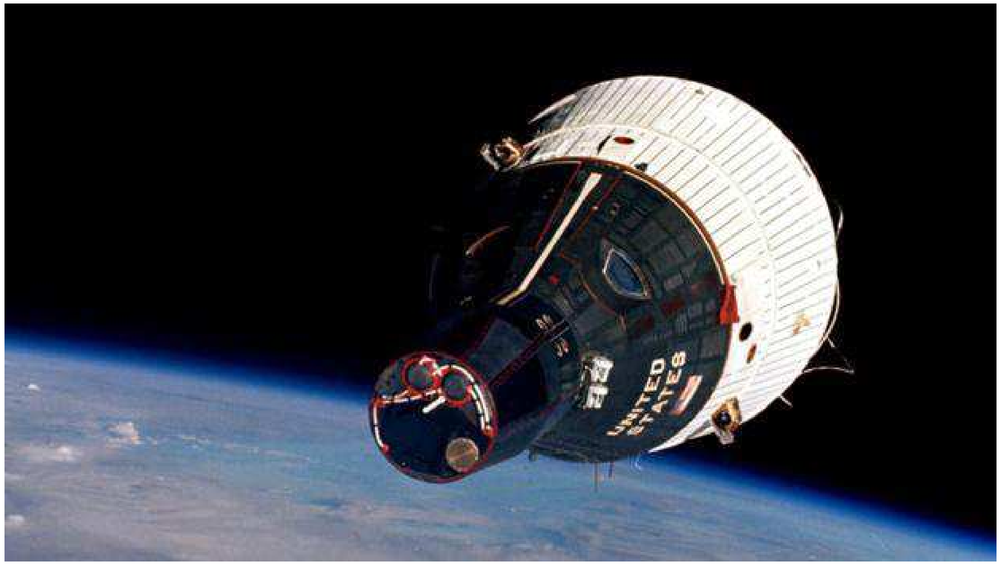
Type	Mobile ion	Temperature (°C)	Applications
Alkaline	OH^-	50-100	Stationary power, space missions
Polymer	H^+ or OH^-	50-100	Portable devices, transport
Phosphoric acid (PAFC)	H^+	220	Medium to large scale combined heat and power (CHP) systems
Molten Carbonate (MCFC)	CO_3^{2-}	650	⋮
Solid Oxide (SOFC)	O^{2-}	500 - 1000	⋮

L. Carrette, *Fuel Cells*, 2001, 5.

Polymer - Proton exchange membrane fuel cell (PEMFC)

- First developed for the Gemini space vehicle
- Based on acidic proton-conducting polymer
  - *e.g.* Nafion
- Use H_2 as fuel, but can work with MeOH (less efficiently)





Nafion

Gemini spacecraft

PEMFC + H_2

$$\begin{aligned}
\text{Anode:} \quad & 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longleftarrow \mathrm{H_2} & E &= 0\ \mathrm{V} \\
\text{Cathode:} \quad & \mathrm{O_2} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2O_2} & E &= 0.695\ \mathrm{V} \\
& \mathrm{H_2O_2} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} & E &= 1.776\ \mathrm{V} \\
\text{Cat. (Overall):} \quad & \mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} & E &= 1.229\ \mathrm{V}
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$$

- Good Low-temperature (< 100 °C) operation ✓
  - Quick to start/stop
  - Suitable for portable applications
- H_2O_2 forms when acidic ✗
  - Corrodes carbon-containing electrodes
  - Lowers cell voltage
  - Requires expensive Pt or Pd catalysts to decompose H_2O_2
- Need careful hydration to ensure H^+ conduction ✗

PEMFC + Methanol

Methanol easier to store/transport than H_2

- Readily oxidised, does not require C-C bond breaking

$$\begin{aligned}
&\text{An.:} && \mathrm{CO_2 + 6\,H^+ + 6\,e^- \longleftarrow CH_3OH + H_2O} && E = 0.046\ \mathrm{V} \\
&\text{Cat.:} && \mathrm{\frac{3}{2}O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O} && E = 1.229\ \mathrm{V} \\
&\text{Overall:} && \mathrm{CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2\,H_2O} && E = 1.183\ \mathrm{V}
\end{aligned}$$

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\text{Overall:} & CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2\,H_2O & E = 1.183\ \text{V}
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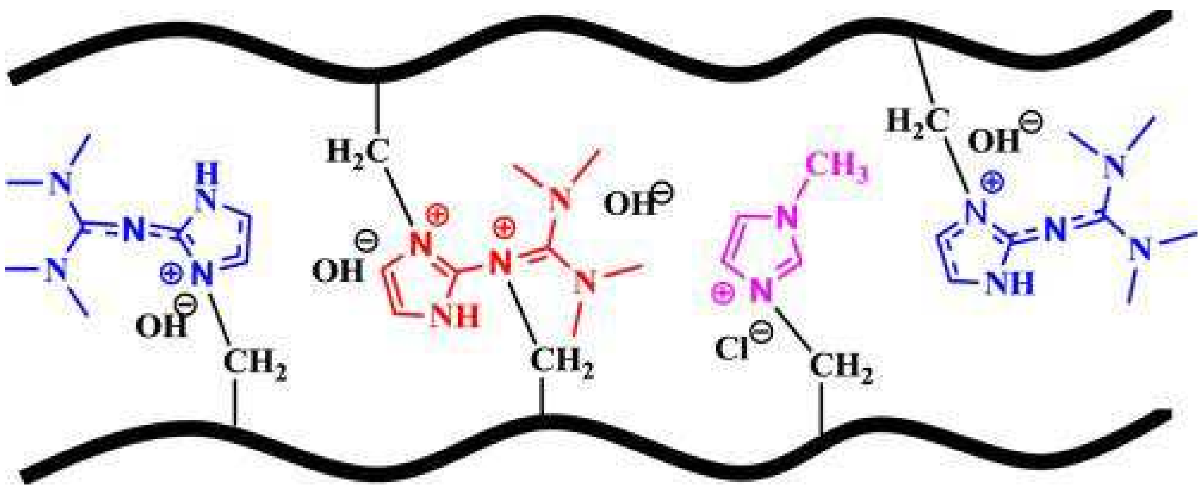
Problems

- MeOH crosses from anode to cathode ✗
  - Reduces cell voltage to ~0.5 V
- CO formed in side-reaction, blocking reaction sites ✗
  - requires more Pt catalyst!

Alkaline polymers?

- OH^- as mobile ion prevents H_2O_2 formation ✓
- pH change alters redox energies, allowing Ni catalysts to replace Pt ✓
- Attaching counter-cation to the polymer reduces electrode poisoning ✓



- Current OH^- polymers have low ionic conductivity! ✗

Y-J. Wang et al., *Chem. Soc. Rev.* **2013**, 42, 5768-5787.

Solid Oxide (SOFC)

- All-solid-state system (*i.e.* solid electrolyte)
- Two sub-groups:
  - High-temperature (HT) SOFC: 800 - 1000 °C
  - Intermediate temperature (IT) SOFC: 500 - 700 °C

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$$\text{Anode:} \quad \begin{cases} 2\,\mathrm{H_2O} + 4\,\mathrm{e^-} & \longleftarrow 2\,\mathrm{H_2} + 2\,\mathrm{O^{2\,-}} \\ 2\,\mathrm{CO_2} + 4\,\mathrm{e^-} & \longleftarrow 2\,\mathrm{CO} + 2\,\mathrm{O^{2\,-}} \\ \mathrm{H_2O} + \frac{1}{2}\mathrm{CO_2} + 4\,\mathrm{e^-} & \longleftarrow \frac{1}{2}\mathrm{CH_4} + 2\,\mathrm{O^{2\,-}} \end{cases}$$

$$\text{Cathode:} \quad \mathrm{O_2} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{O^{2\,-}}$$

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\end{array}
$$

- High temperature allows internal steam reforming; many fuels
- No precious metal catalysts
- Excess heat can be used to increase efficiency (to ~90%)
  - drive an electricity turbine or combined heat and power (CHP)

SOFC Limitations

High temperatures:

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Delicate balance between:

- optimum temperature for redox and/or ionic conductivity
- thermal expansion, reactivity and device construction
- Intermediate-temperature (IT) SOFCs are the current optimum.

Requirements for SOFC materials

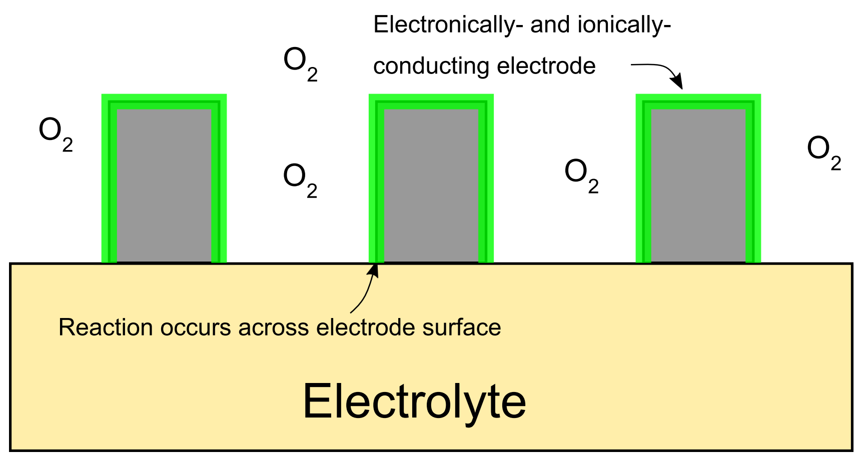
Property	Anode	Electrolyte	Cathode
Electronic conductivity	High	Low	High
Ionic Conductivity	High	High	High
Chemical stability	reducing conditions	oxidising **and** reducing conditions	oxidising conditions
Catalytic activity	Fuel oxidation	O_2 reduction	O_2 reduction

Also: chemical compatibility between materials, similar thermal expansion, low cost, ...

'Perfect' electrodes

Ideally, electrodes should be good electronic *and* ionic conductors!

- fuel/oxygen reactions would occur at the electrode surface



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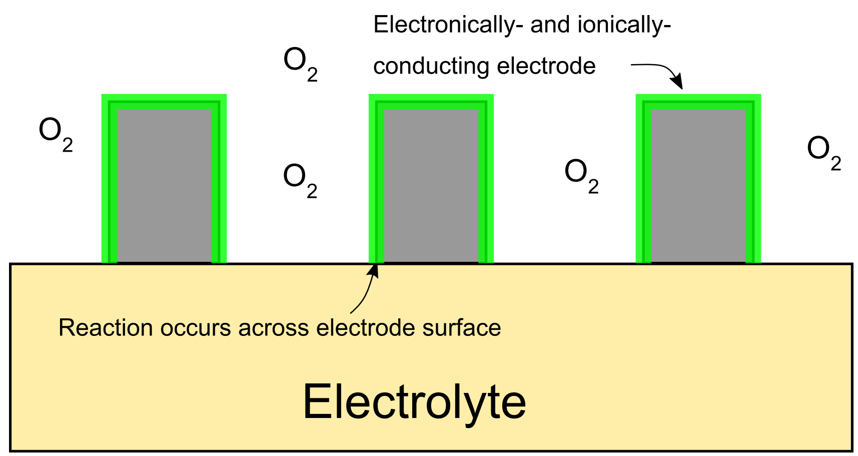
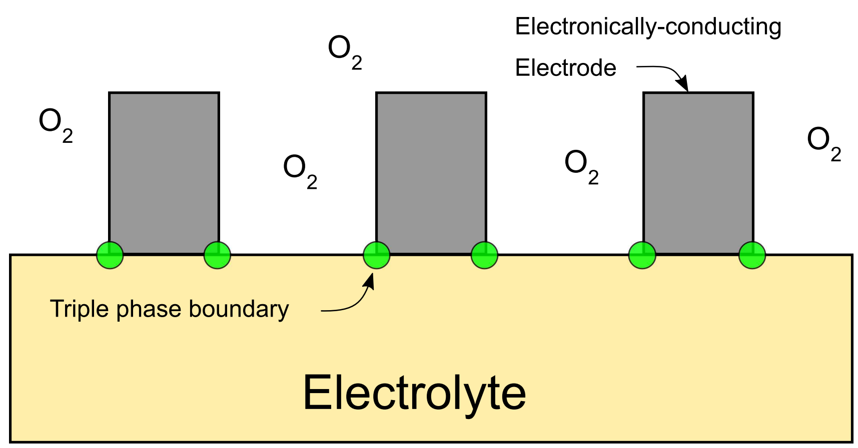


In reality, use a mixture of good ionic and electronic conductors.

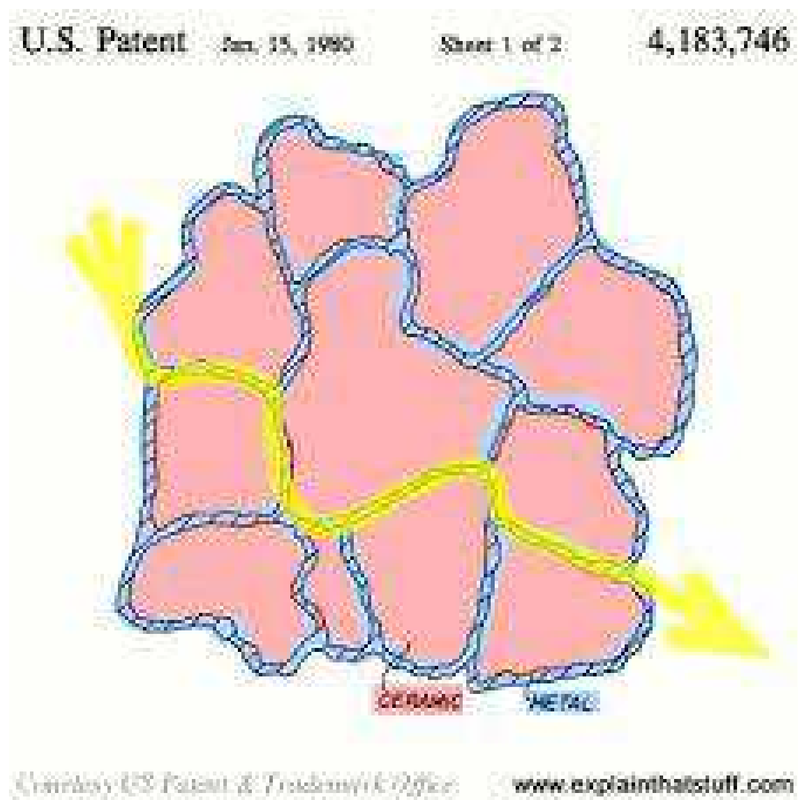
- reactions occur at the **triple phase boundary**



Typical anode materials

Usually a cermet (*i.e.* mixture) of Ni and electrolyte

- Ni → high e⁻ conductivity and catalytic activity
    - but susceptible to poisoning by S (forming stable NiS)
- High ionic conductivity from electrolyte



Typical cathode materials

Composite of $\mathrm{La_{1-x}Sr_xMnO_3}$ perovskite (LSMO) and electrolyte

- LSMO gives e⁻ conduction and high catalytic activity
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- poor performance below 700 °C ✗

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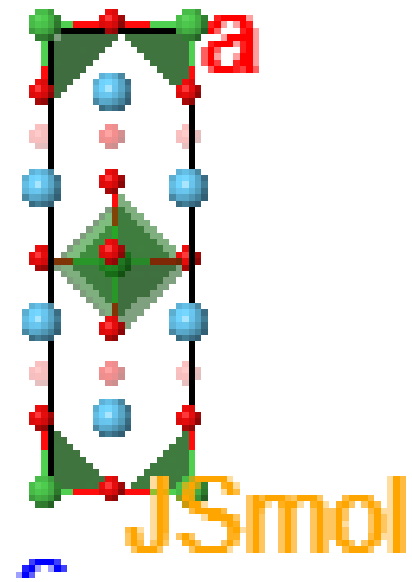
Interest in mixed-conductors:

- $\mathrm{La_{1-x}Sr_xCoO_{3-y}}$
  (perovskite with $\mathrm{V_O}$)
  - good ionic/electronic conduction
  - high thermal expansion
- $\mathrm{La_2NiO_{4+x}}$
  - 'layered' $\mathrm{O_i}$ conductor
  - $2\,\mathrm{Ni_{Ni}} + \frac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{O_i''} + 2\,\mathrm{Ni_{Ni}^{\bullet}}$



Electrolyte materials

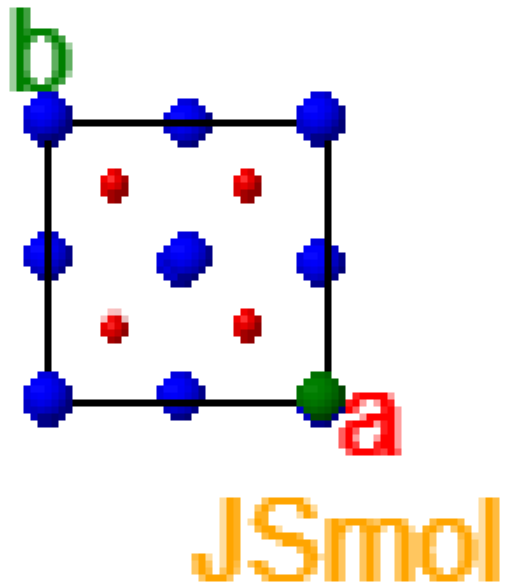
Most studied electrolyte is $\mathrm{Y_{0.15}Zr_{0.85}O_{1.925}}$ (yttrium-stabilised zirconia, YSZ)

- defective fluorite structure
- $\mathrm{Y_2O_3 + 2\,Zr_{Zr} + O_O \rightleftharpoons 2\,Y'_{Zr} + V_O^{\bullet\bullet}}$
- Sc-doping also effective (but expensive)

Another commercial material is $\mathrm{Gd_{0.1}Ce_{0.9}O_{1.95}}$ (CGO)

- Better for lower temperature
  - e^- conductor above 600 °C

Many other materials, but issues with cost, stability, manufacturing...



Improving Ionic conduction

As $\sigma = nq\mu$, so as [defects] $\uparrow$, $\sigma \uparrow$

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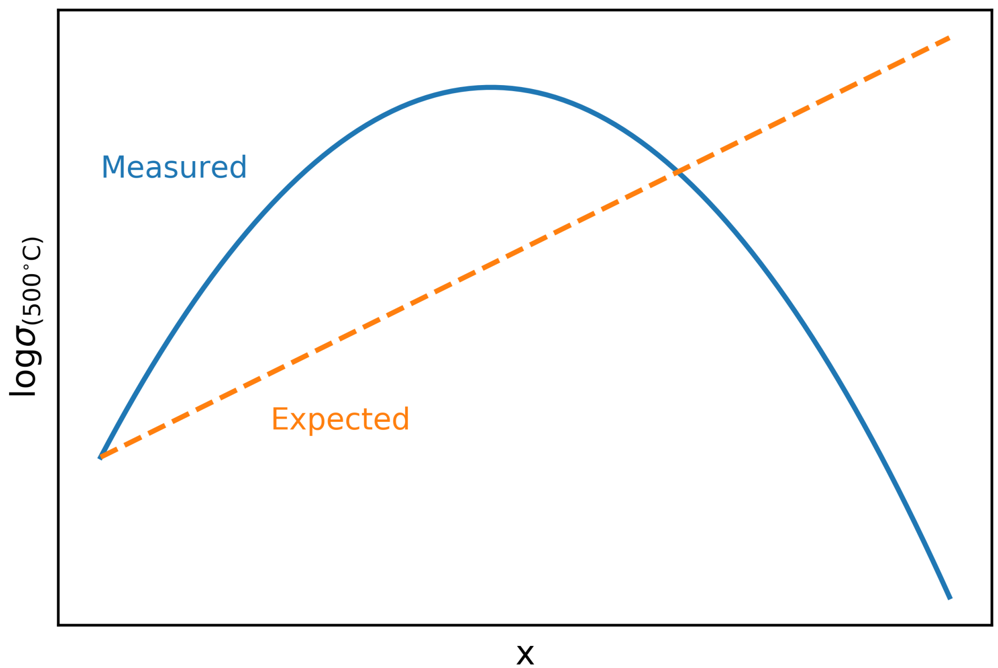
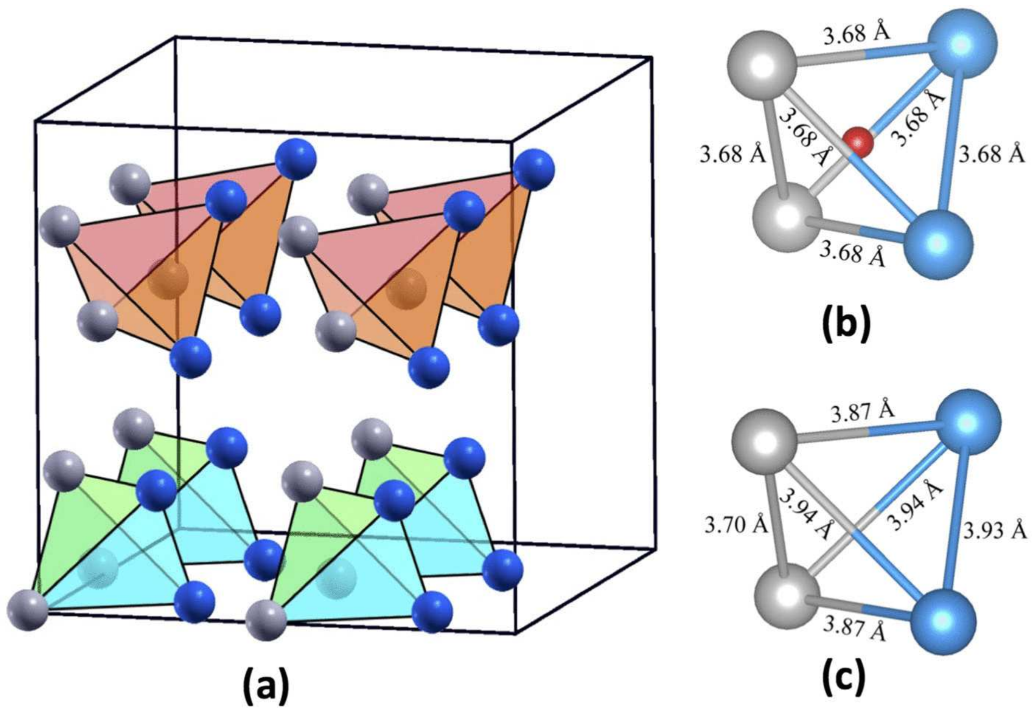
e.g. in YSZ: $((1 - \mathrm{x})\mathrm{ZrO_2} + \frac{\mathrm{x}}{2}\mathrm{Y_2O_3} \longrightarrow \mathrm{Y_xZr_{1-x}O_{2-\frac{x}{2}}})$





Conductivity vs x in YSZ

Ideal arrangement for $x = 0.5, \mathrm{Y_2Zr_2O_7}$

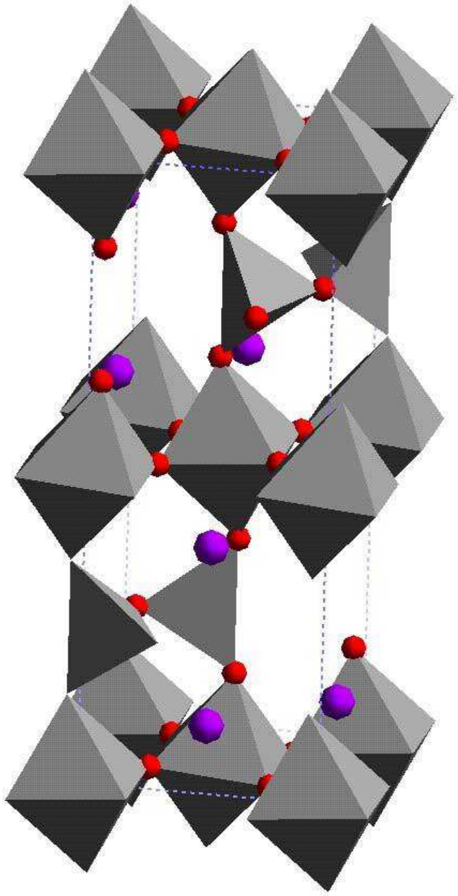
Long-range defect ordering

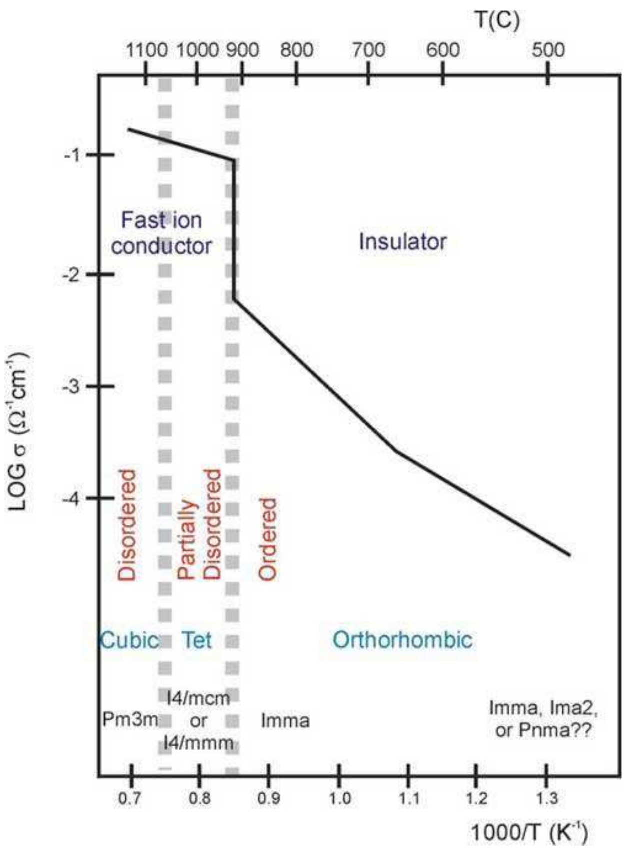
In some cases defects can form long-range order

- Many show order-disorder phase transition with T

Example: $Ba_2In_2O_5$

- Brownmillerite structure ($ABO_{2.5}$ perovskite with ordered $V_O^{\bullet\bullet}$)
- Large increase in σ at phase transition





Lecture recap

- fuel cells operate like a battery with continous 'charge' supply
  - Many similar materials properties required
- different technologies work at different temperatures
  - advantages and disadvantages for both
- properties of electrolyte, cathode and anode must be optimised
- ideal electrodes would be ionically *and* electronically conducting
  - more commonly a mixture of materials is used
- Ionic conduction reaches a maximum with defect concentration
  - defect ordering occurs
- Defect ordering can give rise to new structure types