

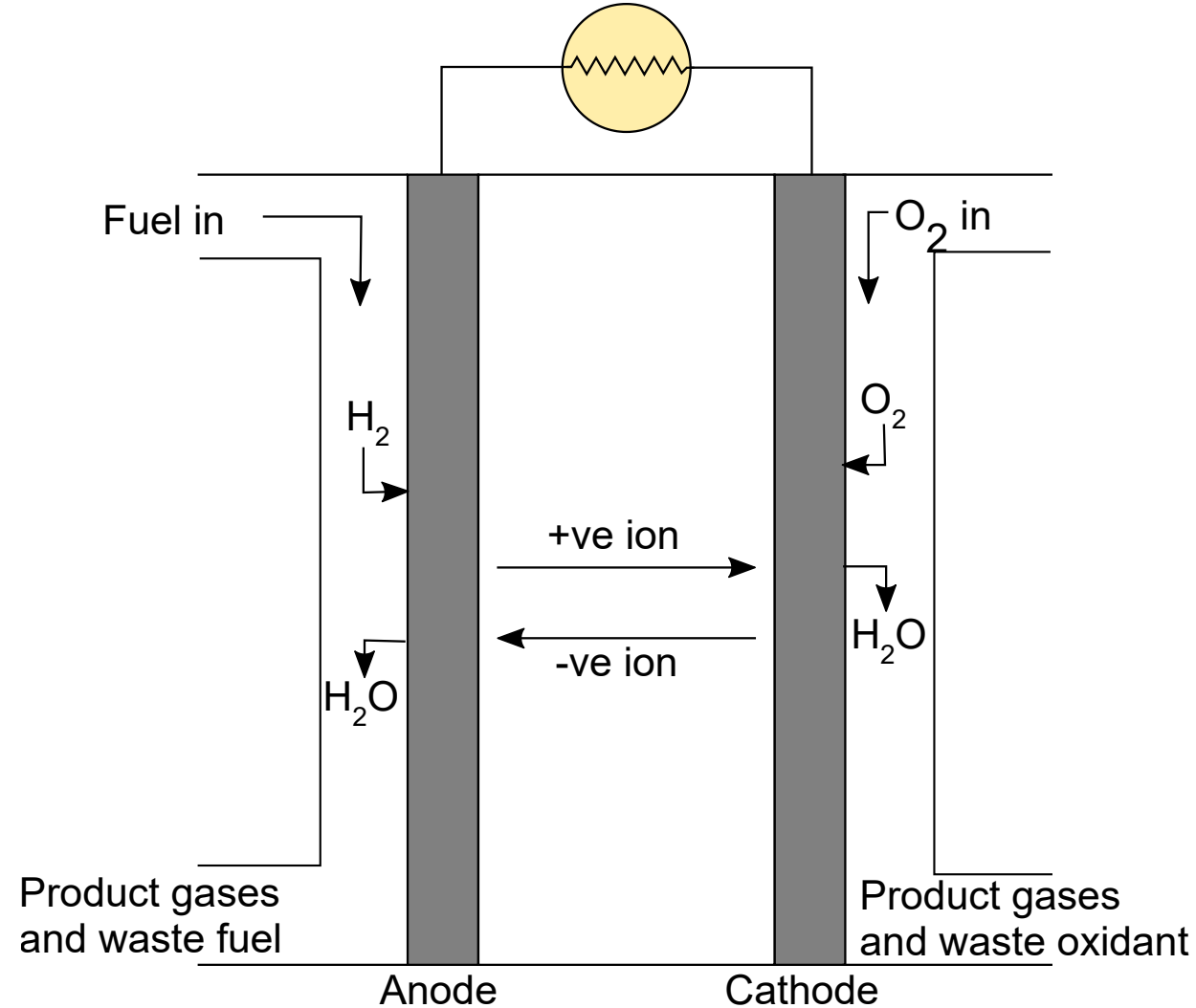
Lecture 6 - Fuel cells

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.

1889

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



1959

Francis Bacon demonstrates a 5 kW alkaline fuel cell.

1970s

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

1990s

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



2008

Honda begins leasing the FCX Clarity fuel cell electric vehicle.

1839

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



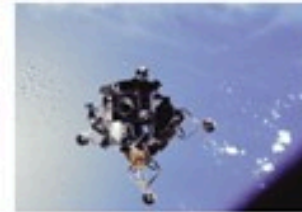
1950s

General Electric invents the proton exchange membrane fuel cell.



1960s

NASA first uses fuel cells in space missions.



1980s

US Navy uses fuel cells in submarines.

2007

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

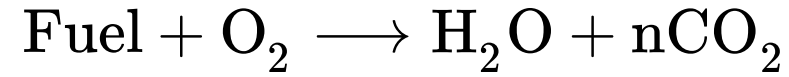


2009

Residential fuel cell micro-CHP units become commercially available in Japan. Also thousands of portable fuel cell battery chargers are sold.

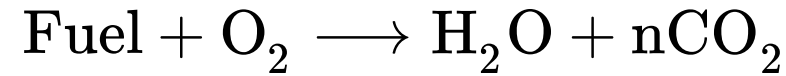


Fuel cell fundamentals

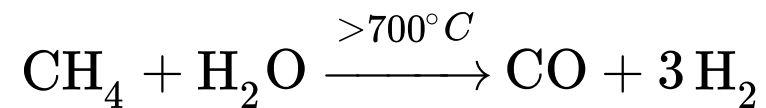


- Fuel cells grouped into *low-temperature* (LT, < 200 °C) and *high-temperature* (HT, > 450 °C).
- H₂ is the preferred fuel
 - Particularly for LT devices.
 - Doesn't produce CO₂

Fuel cell fundamentals



- Fuel cells grouped into *low-temperature* (LT, < 200 °C) and *high-temperature* (HT, > 450 °C).
- H₂ is the preferred fuel
 - Particularly for LT devices.
 - Doesn't produce CO₂
- Other fuels (e.g. CH₃OH, CH₄, NH₃) also possible
 - Steam reforming reaction converts fuels to H₂:



- can be achieved in-situ for HT cells, but must be separate for LT.

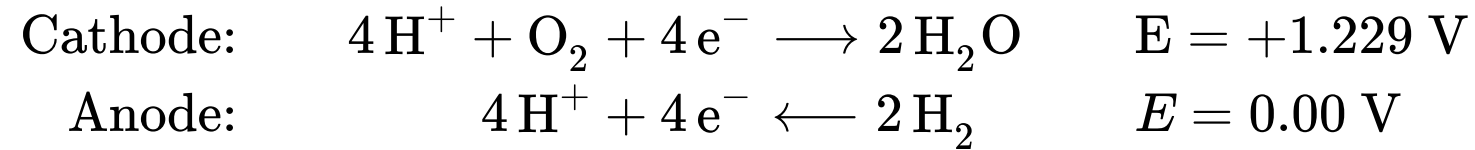
Fuel cell efficiency

Fuel cells are *very* efficient

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

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

e.g. for $2 \text{H}_2 + \text{O}_2 \longrightarrow 2 \text{H}_2\text{O}$ ($\Delta H = -571.6 \text{ kJ mol}^{-1}$):



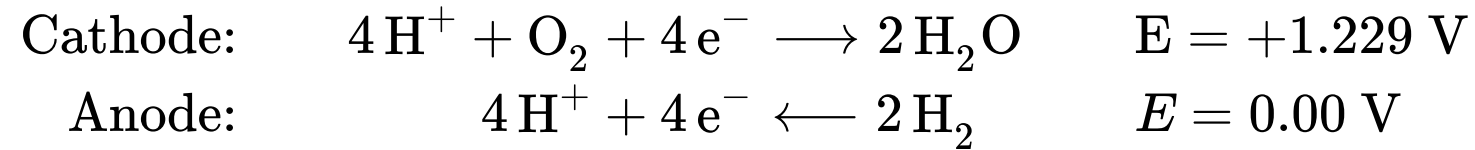
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$$\begin{aligned}\Delta G &= -nFE \\ &= -4 \times F \times 1.229 \\ &= -474.3 \text{ kJ mol}^{-1} \quad (\text{per mole O}_2)\end{aligned}$$

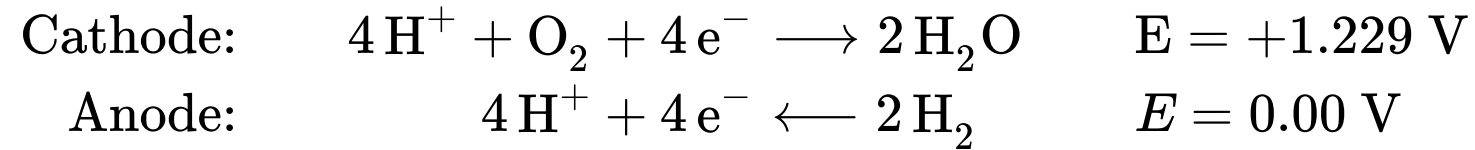
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$$\text{Efficiency} = \eta = -474.3 / 571.6 = \mathbf{83\%}$$

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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For 'ideal' combustion engine (heat engine) the maximum efficiency is the Carnot limit:

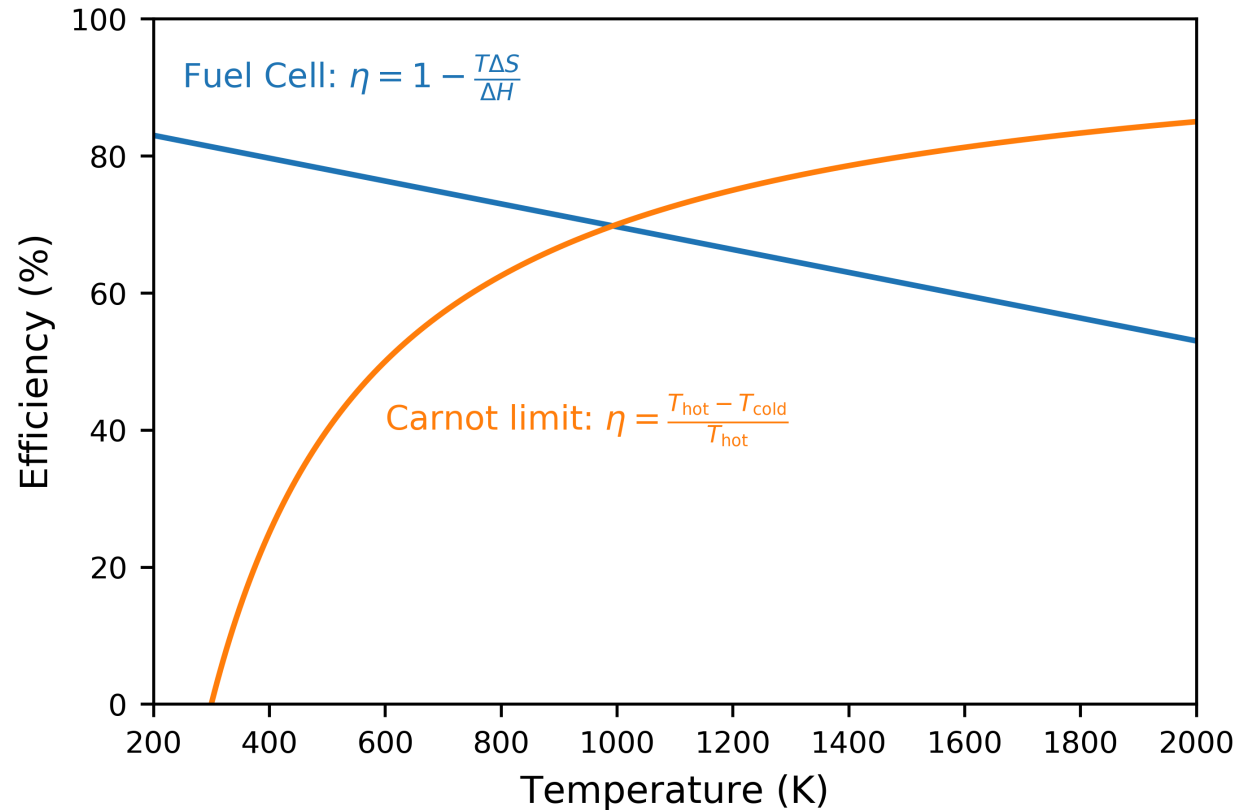
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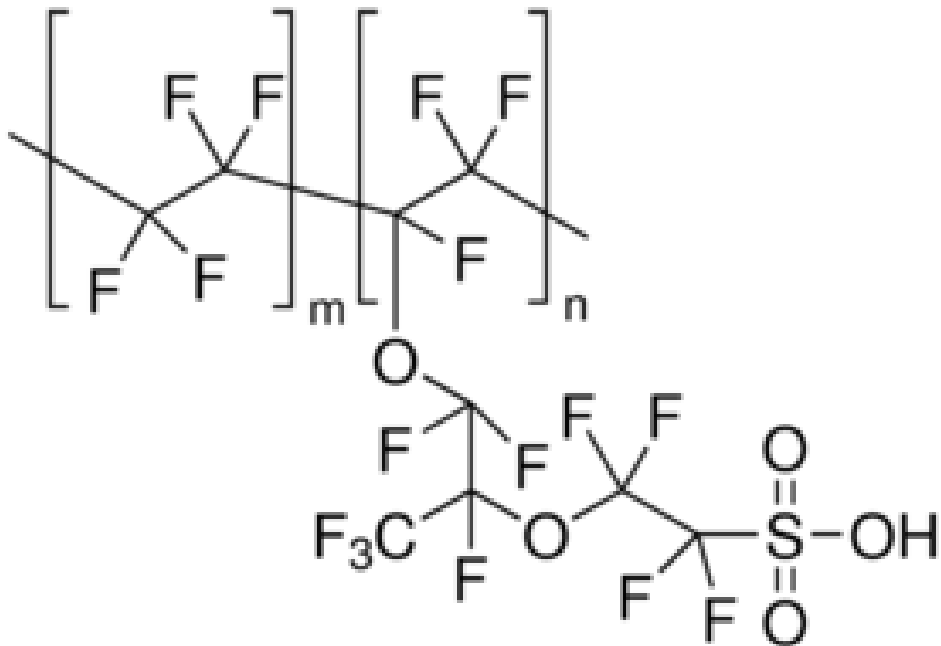


Types of fuel cell

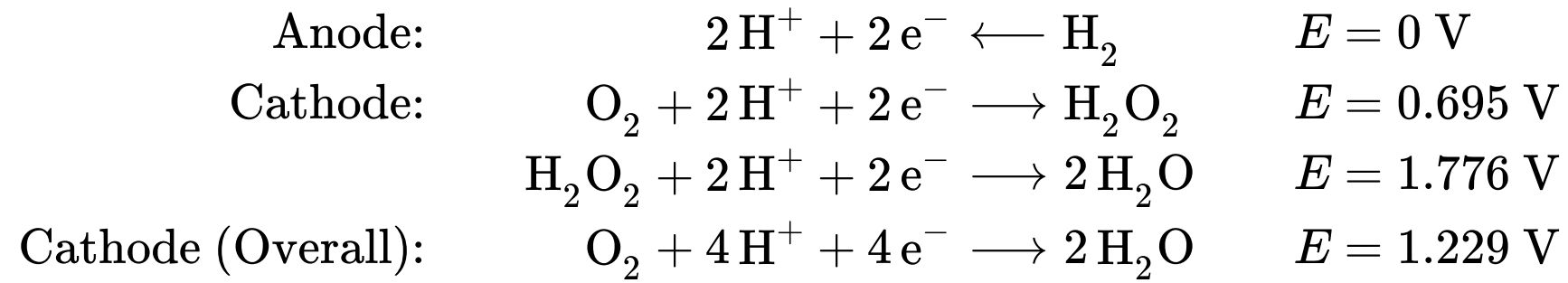
Type	Mobile ion	Temperature (°C)	Applications
Alkaline	OH^-	50-100	Stationary power, space missions
Polymer	H^+ or OH^-	50-100	Portable devices, transport
Phosphoric acid (PAFC)	H^+	220	Medium to large scale combined heat and power (CHP) systems
Molten Carbonate (MCFC)	CO_3^{2-}	650	:
Solid Oxide (SOFC)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

Main low temperature device: Proton exchange membrane fuel cell (PEMFC)

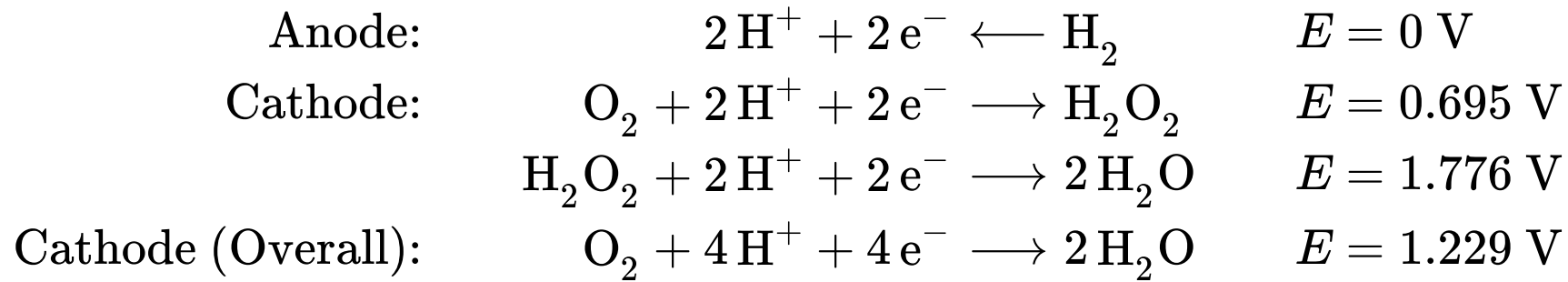
- Carbon electrodes with precious metal catalysts (Pt, Pd, Ru)
- Requires acidic proton-conducting polymer
 - e.g. Nafion
- Use H₂ as fuel, but can work with MeOH (less efficiently)



PEMFC + H₂



PEMFC + H₂



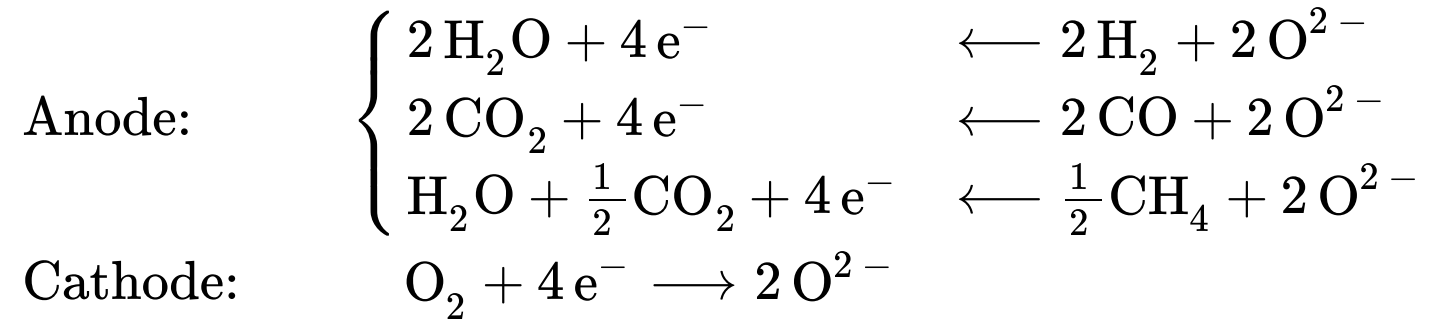
- Good Low-temperature (< 100 °C) operation ✓
 - Quick to start/stop
 - Suitable for portable applications
- H₂O₂ forms when acidic ✗
 - Corrodes carbon-containing electrodes
 - Lowers cell voltage
 - Requires expensive Pt or Pd catalysts to decompose H₂O₂
- Need careful hydration to ensure H⁺ conduction ✗

Main high temperature chemistry: Solid Oxide (SOFC)

- All-solid-state system (*i.e.* solid electrolyte)
- Most work at 800 - 1000 °C

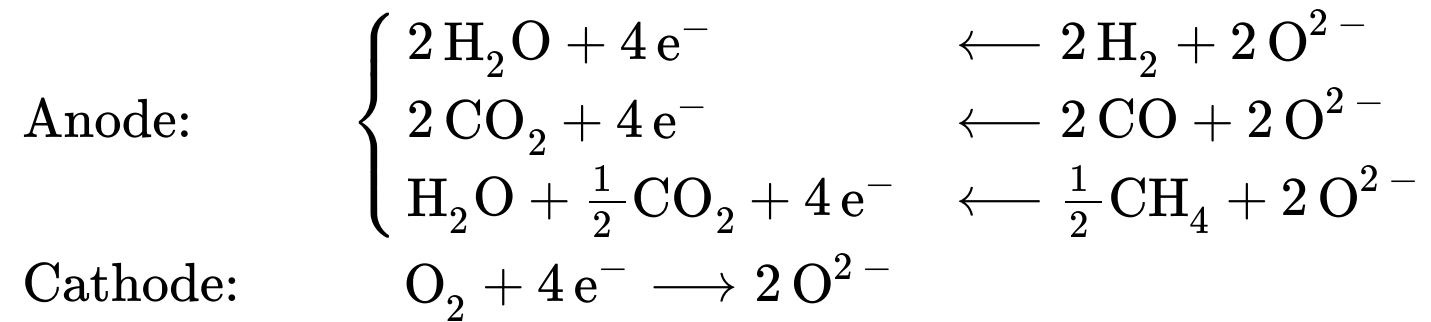
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- All-solid-state system (*i.e.* solid electrolyte)
- Most work at 800 - 1000 °C
- Based around redox and conduction of O^{2-} :



- 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:

- prevent rapid start/stop
- cause reactivity between electrolyte and electrodes
- make thermal expansion important

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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

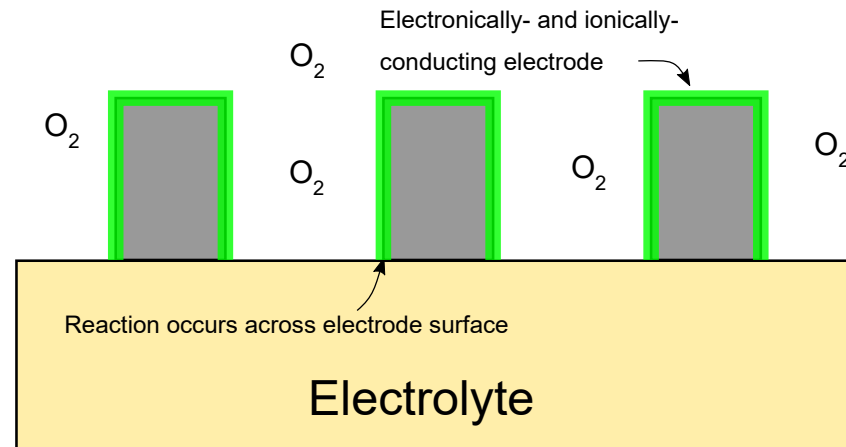
Property	Anode	Electrolyte	Cathode
Electronic conductivity	High	Low	High
Ionic Conductivity	High	High	High
Chemical stability	reducing conditions	oxidising and reducing conditions	oxidising conditions
Catalytic activity	Fuel oxidation	O ₂ reduction	O ₂ reduction

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

'Perfect' electrodes

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

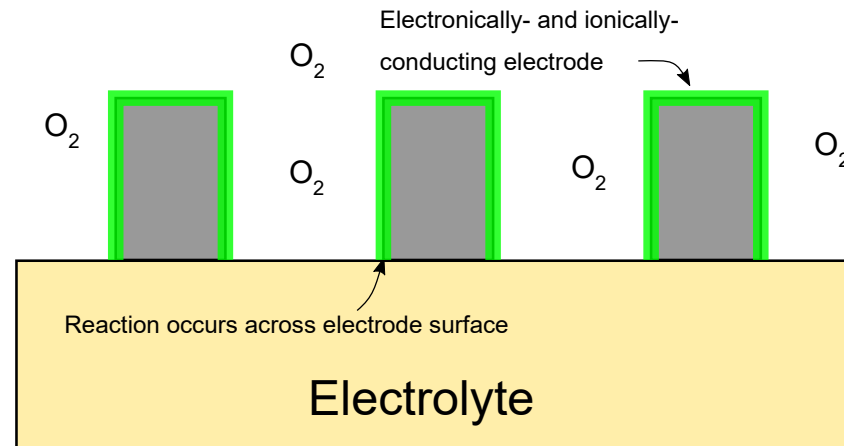
- fuel/oxygen reactions would occur at the electrode surface



'Perfect' electrodes

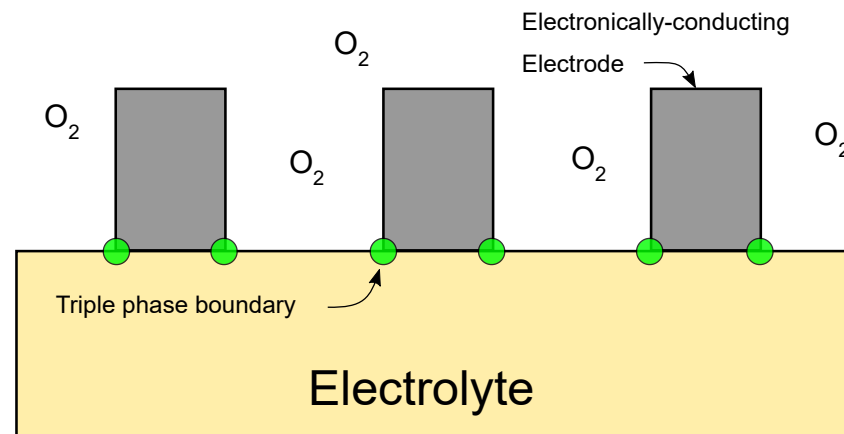
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- fuel/oxygen reactions would occur at the electrode surface



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

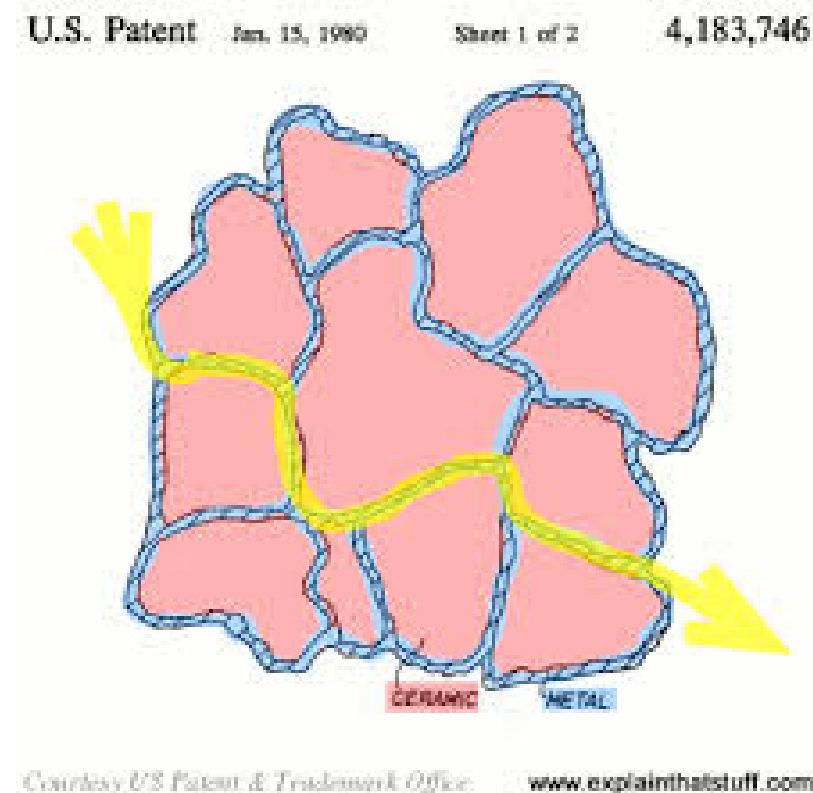
- reactions occur at the **triple phase boundary**



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 $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ perovskite (LSMO) and electrolyte

- LSMO gives e^- conduction and high catalytic activity
 - Sr^{2+} substitution generates holes in valence band
- poor performance below 700 °C **X**

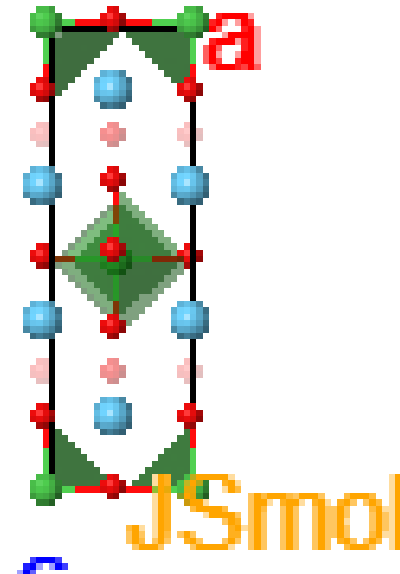
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Interest in mixed-conductors:

- $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$
(perovskite with V_{O})
 - good ionic/electronic conduction
 - high thermal expansion
- $\text{La}_2\text{NiO}_{4+x}$
 - 'layered' O_i conductor
 - $2\text{Ni}_{\text{Ni}} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{O}_i'' + 2\text{Ni}_{\text{Ni}}^\bullet$



Electrolyte materials

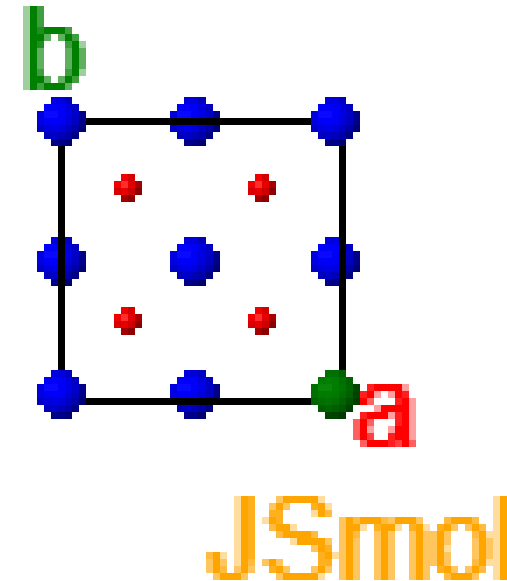
Most studied electrolyte is $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.925}$ (yttrium-stabilised zirconia, YSZ)

- defective fluorite structure
- $\text{Y}_2\text{O}_3 + 2\text{Zr}_{\text{Zr}} + \text{O}_{\text{O}} \rightleftharpoons 2\text{Y}'_{\text{Zr}} + \text{V}_{\text{O}}^{\bullet\bullet}$
- Sc-doping also effective (but expensive)

Another commercial material is $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (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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However, at high defect concentrations we can get **defect clusters**

- Local ordering of defects reduces mobility

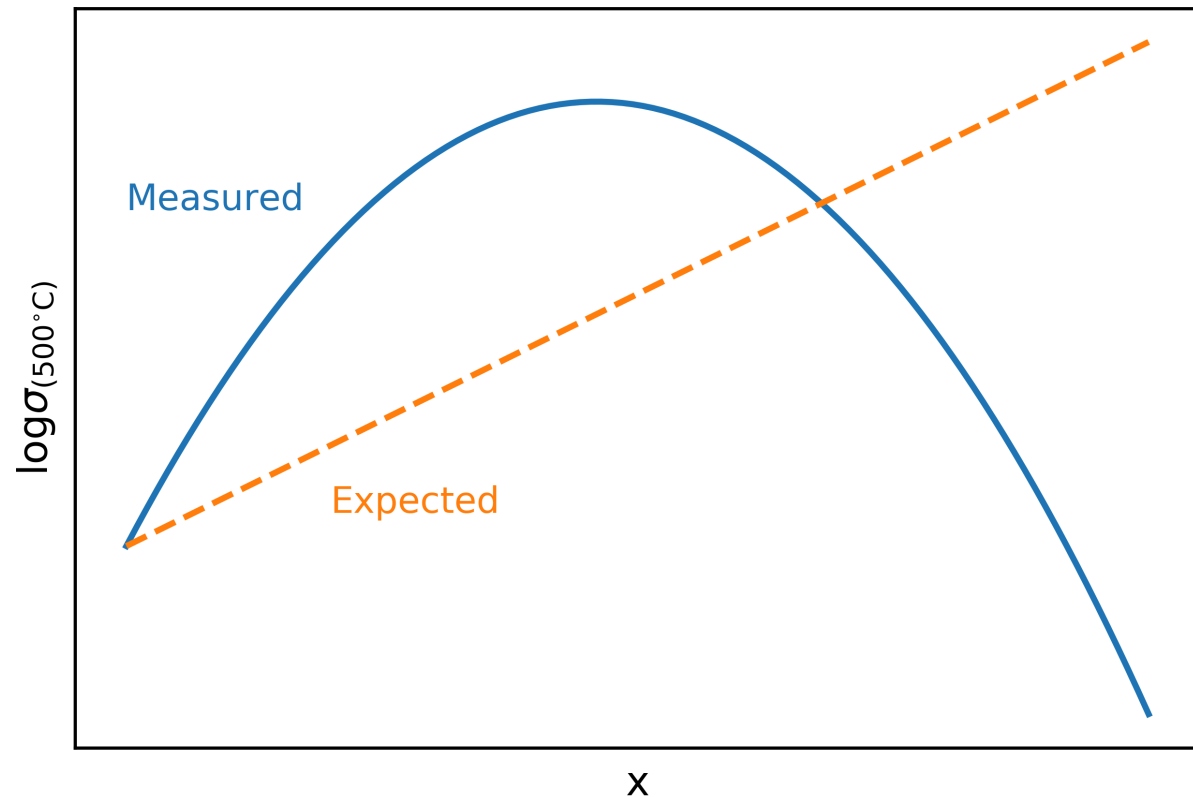
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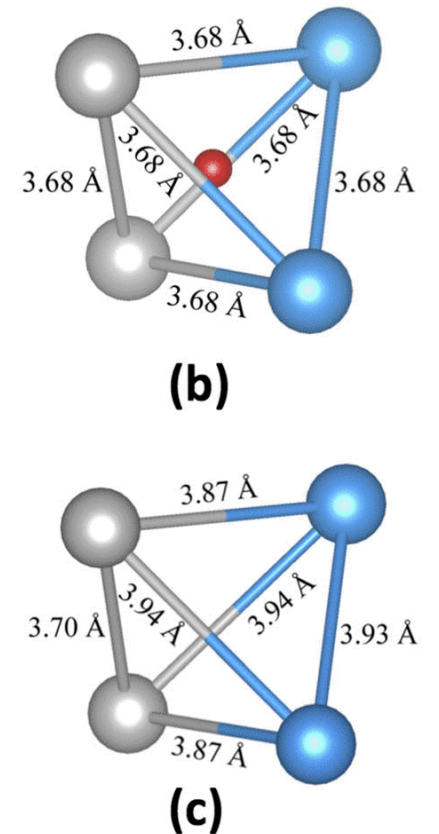
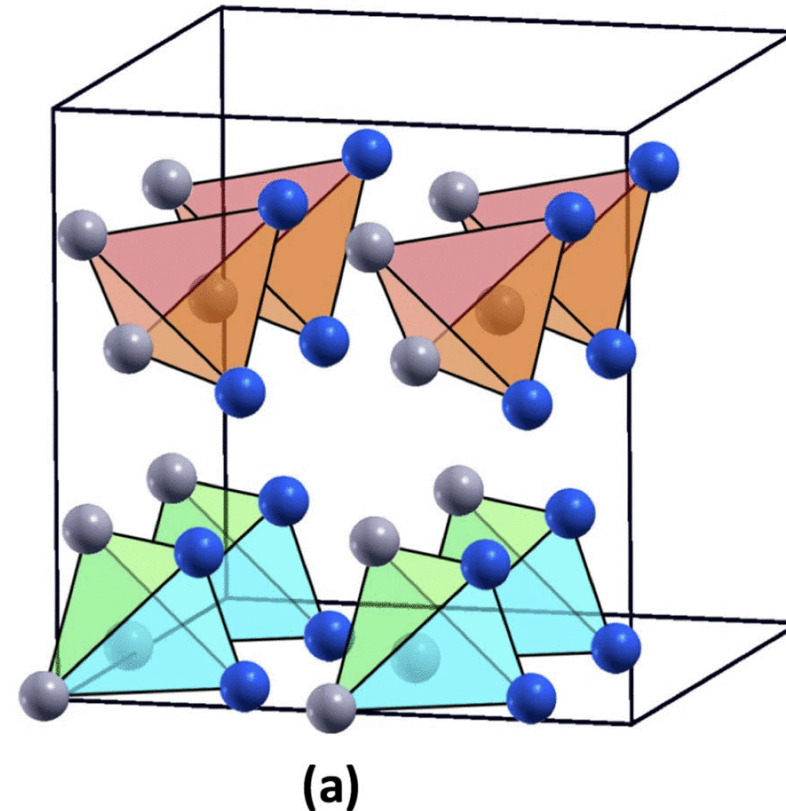
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e.g. in YSZ: $((1-x)\text{ZrO}_2 + \frac{x}{2}\text{Y}_2\text{O}_3 \longrightarrow \text{Y}_x\text{Zr}_{1-x}\text{O}_{2-\frac{x}{2}})$



Conductivity vs x in YSZ



Ideal arrangement for $x = 0.5$, $\text{Y}_2\text{Zr}_2\text{O}_7$

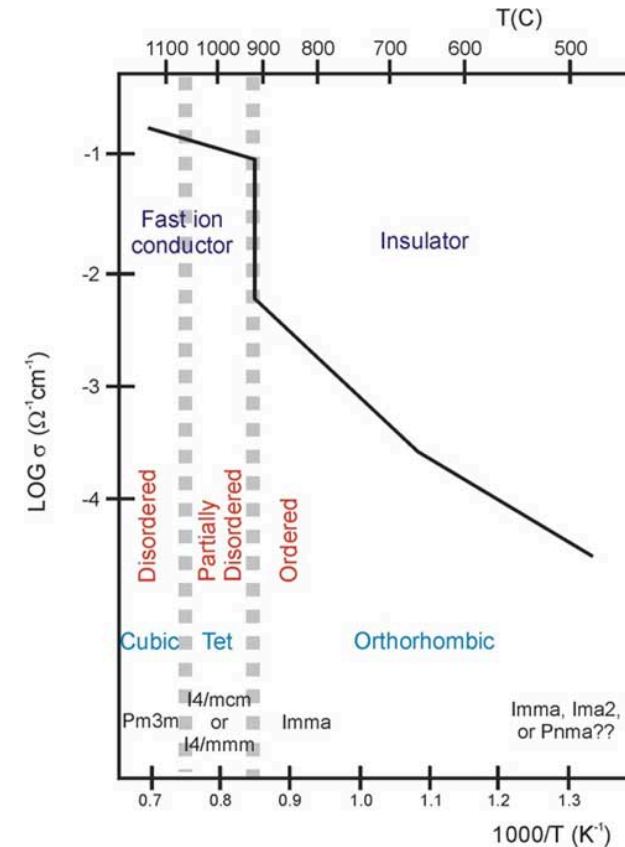
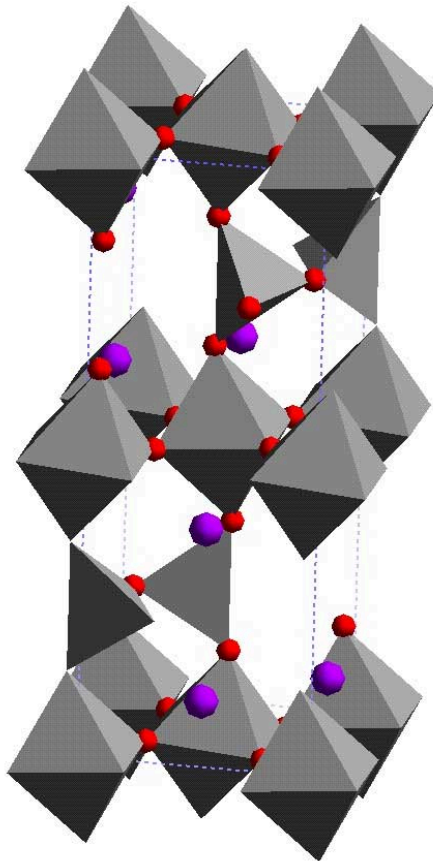
Long-range defect ordering

In some cases defects can form long-range order

- Many show order-disorder phase transition with T

Example: $\text{Ba}_2\text{In}_2\text{O}_5$

- Brownmillerite structure ($\text{ABO}_{2.5}$ perovskite with ordered $\text{V}_\text{O}^{\bullet\bullet}$)
- Large increase in σ at phase transition



Lecture recap

- fuel cells operate like a battery with continuous '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

Feedback



What did you like or dislike about lecture 6 (or the course as a whole)?

Write your answer...



 **Submit**



