

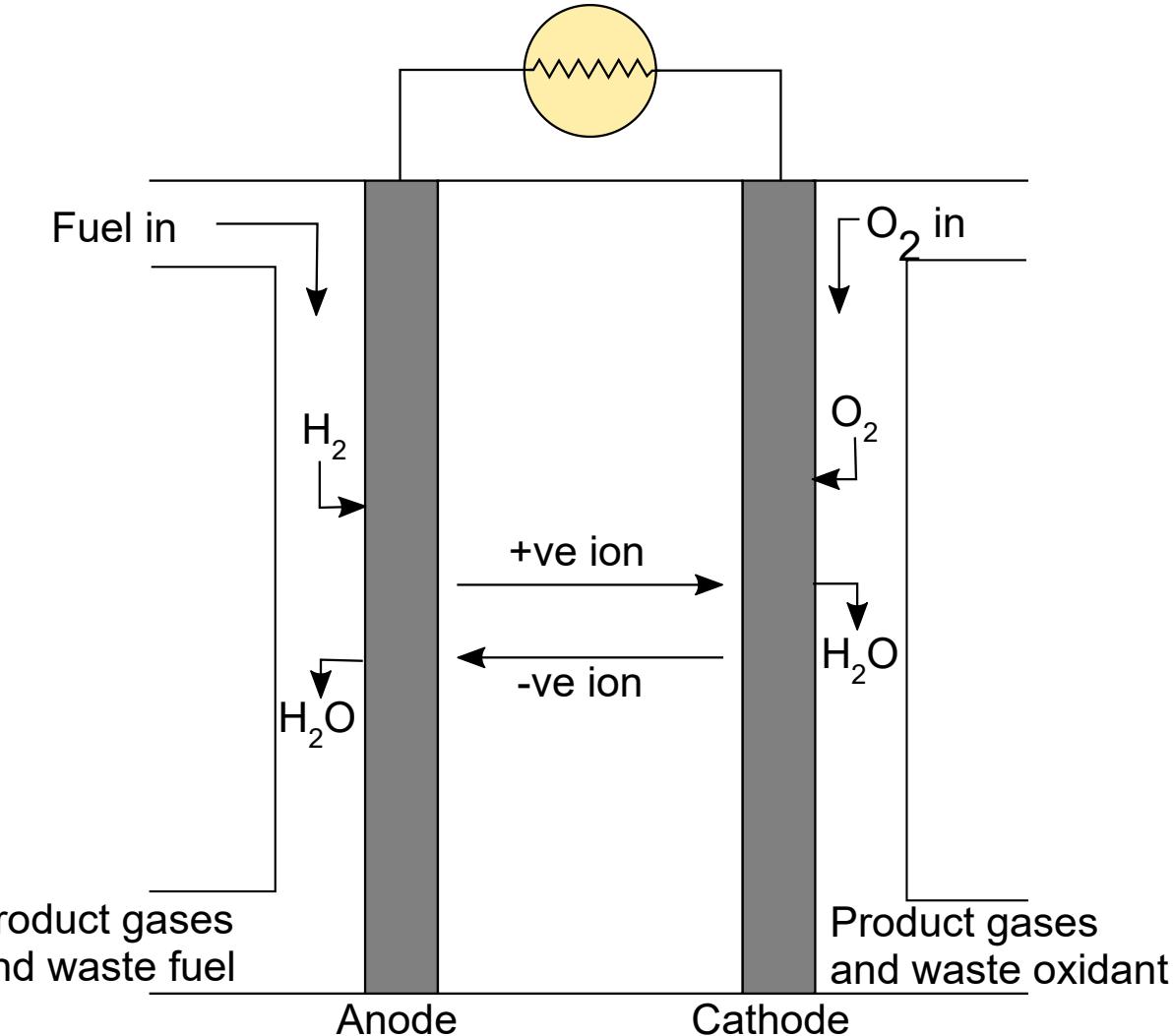
Lecture 6 - Fuel cells

Lecture Summary

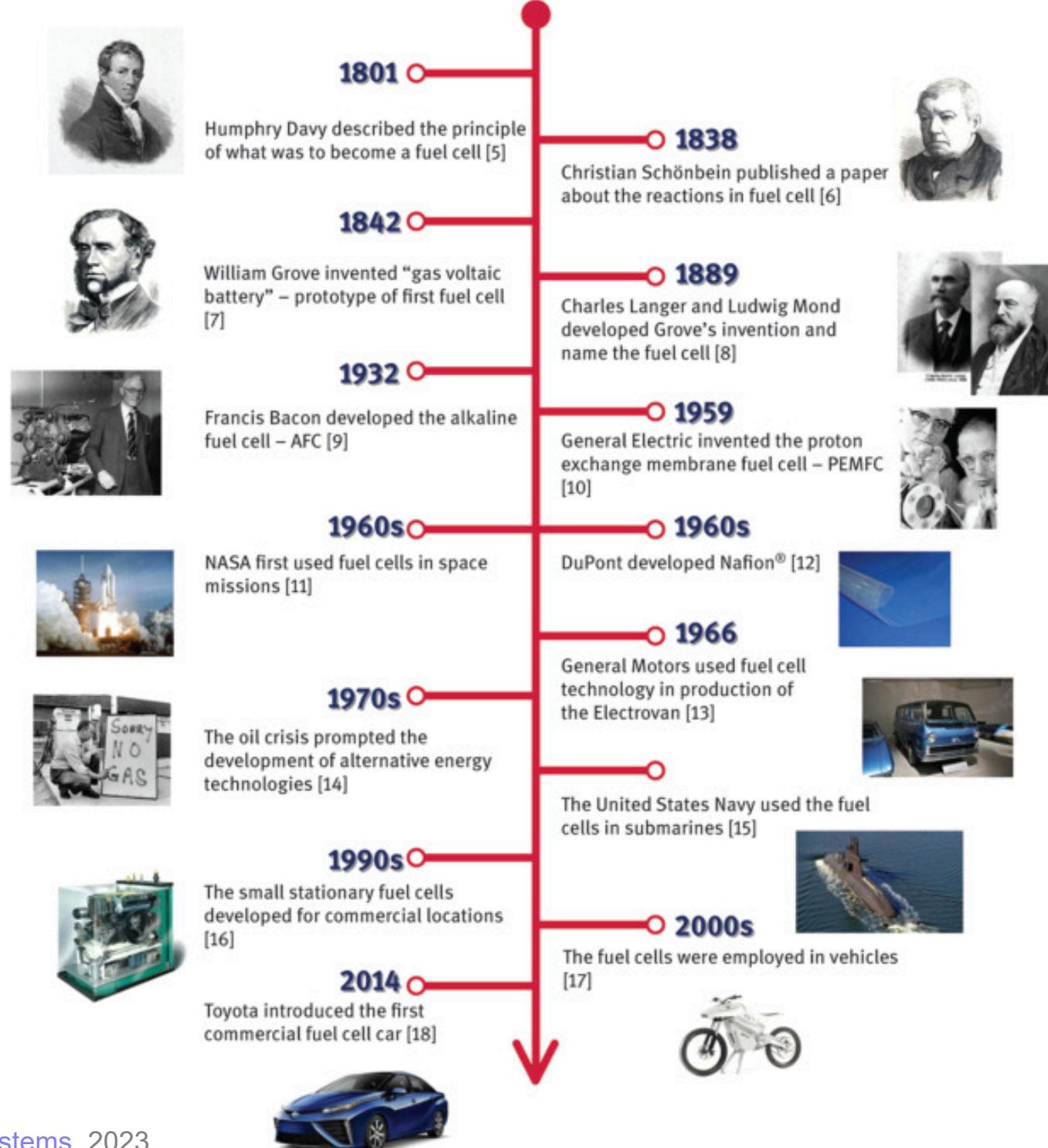
- Fuel cell introduction
- Types of fuel cells
 - Polymer cells
 - Solid oxide fuel cells (SOFCs)
- Materials requirements for SOFCs
 - example materials
- Defect ordering

Fuel Cells

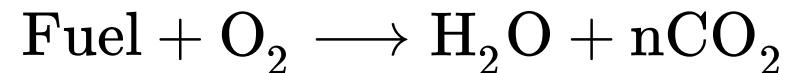
Fuel cells are similar to batteries; they have a cathode, electrolyte and anode.



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

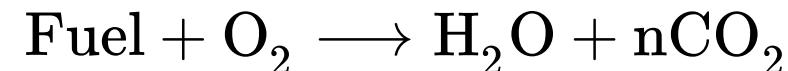


Fuel cell fundamentals

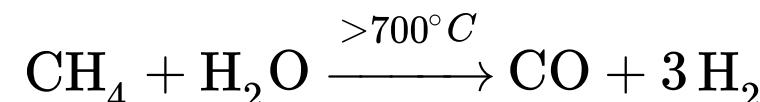


- Fuel cells grouped into *low-temperature* (LT, < 200 °C) and *high-temperature* (HT, > 450 °C).
- H₂ is the preferred fuel
 - Particularly for LT devices.
 - Doesn't produce CO₂

Fuel cell fundamentals



- Fuel cells grouped into *low-temperature* (LT, $< 200^\circ\text{C}$) and *high-temperature* (HT, $> 450^\circ\text{C}$).
- 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 reaction converts fuels to H_2 :



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

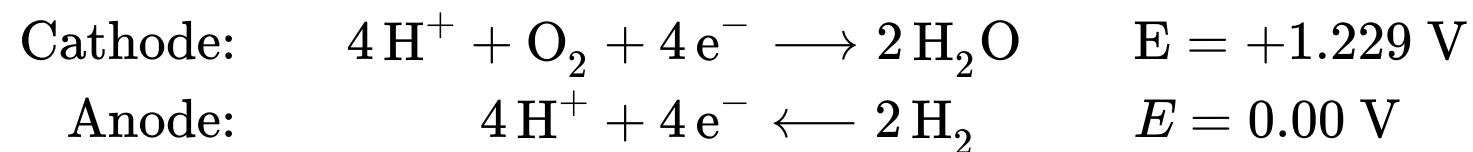
Fuel cell efficiency

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 $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ ($\Delta H = -571.6 \text{ kJ mol}^{-1}$):



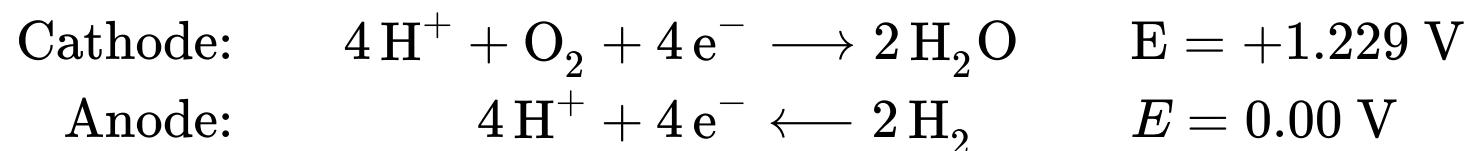
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$$\begin{aligned}\Delta G &= -nFE \\ &= -4 \times F \times 1.229 \\ &= -474.3 \text{ kJ mol}^{-1} \quad (\text{per mole O}_2)\end{aligned}$$

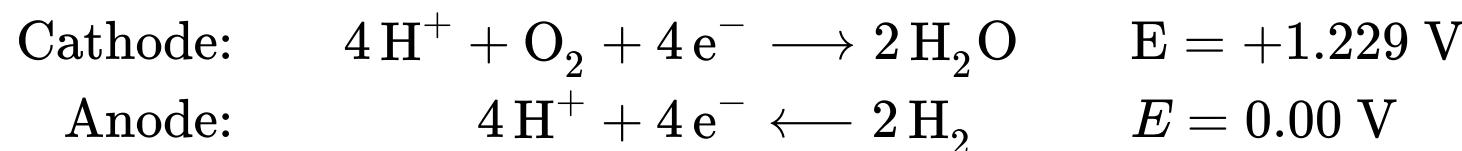
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$$\text{Efficiency} = \eta = -474.3 / 571.6 = 83\%$$

Thermodynamic Efficiency

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

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

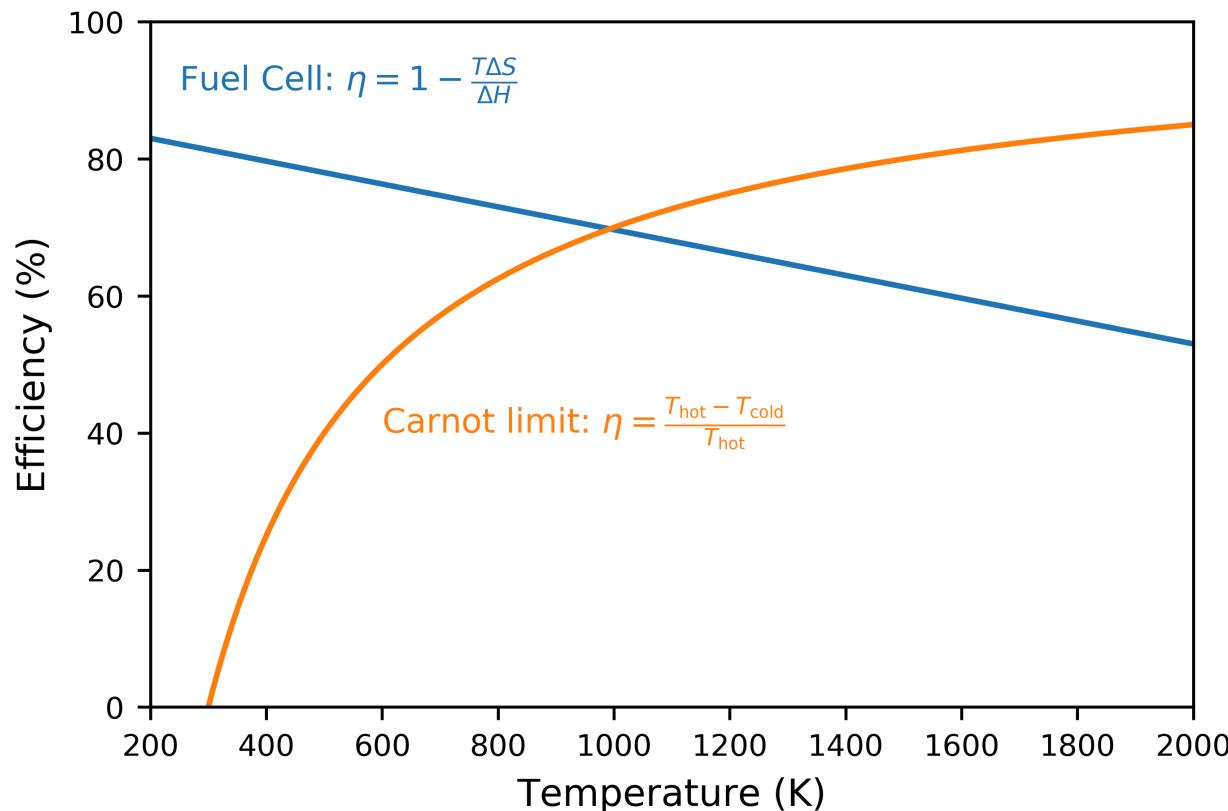
- $\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$

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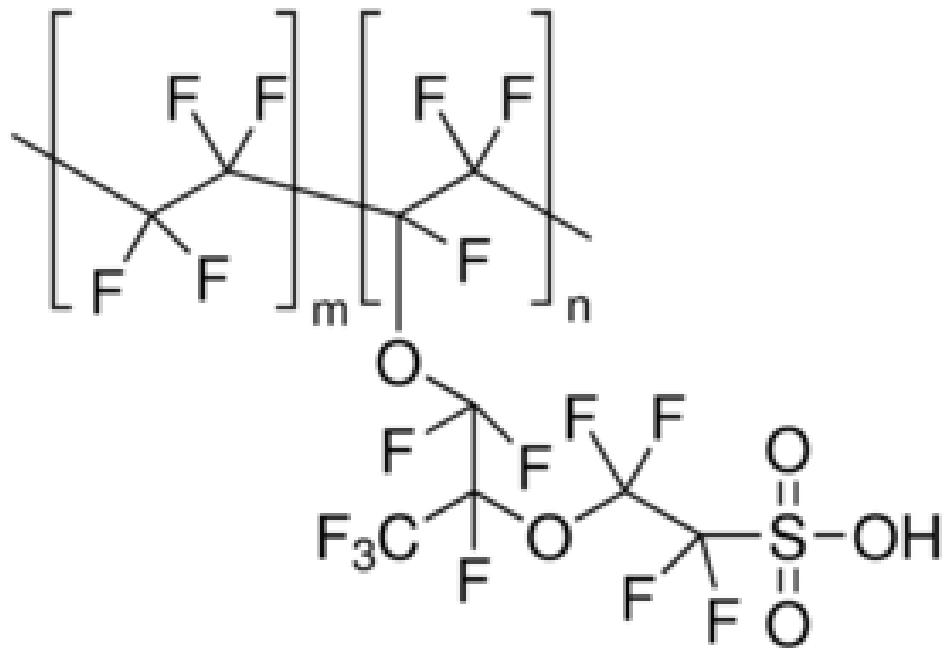


Types of fuel cell

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	:

Low temperature: Proton exchange membrane fuel cell (PEMFC)

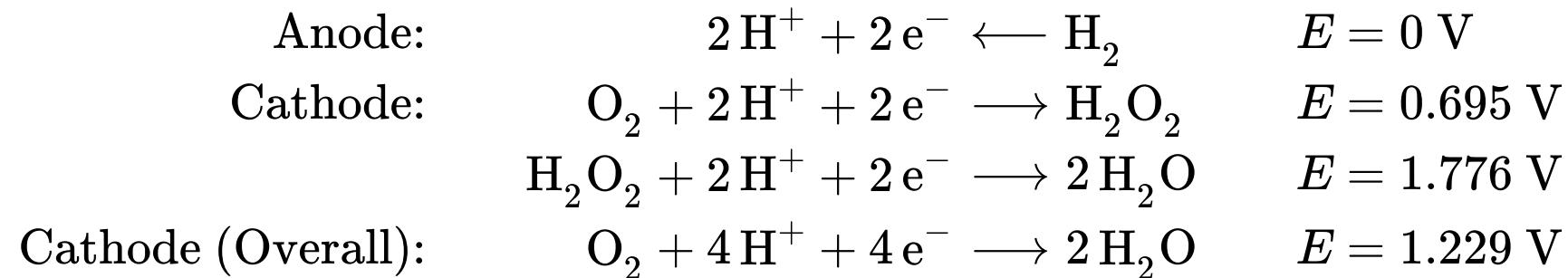
- Carbon electrodes with precious metal catalysts (Pt, Pd, Ru)
- Requires acidic proton-conducting polymer
 - e.g. Nafion
- Use H₂ as fuel, but can work with MeOH (less efficiently)



Nafion

Gemini spacecraft

PEMFC + H₂



PEMFC + H₂

Anode:	$2 \text{H}^+ + 2 \text{e}^- \leftarrow \text{H}_2$	$E = 0 \text{ V}$
Cathode:	$\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2$	$E = 0.695 \text{ V}$
	$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}$	$E = 1.776 \text{ V}$
Cathode (Overall):	$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}$	$E = 1.229 \text{ V}$

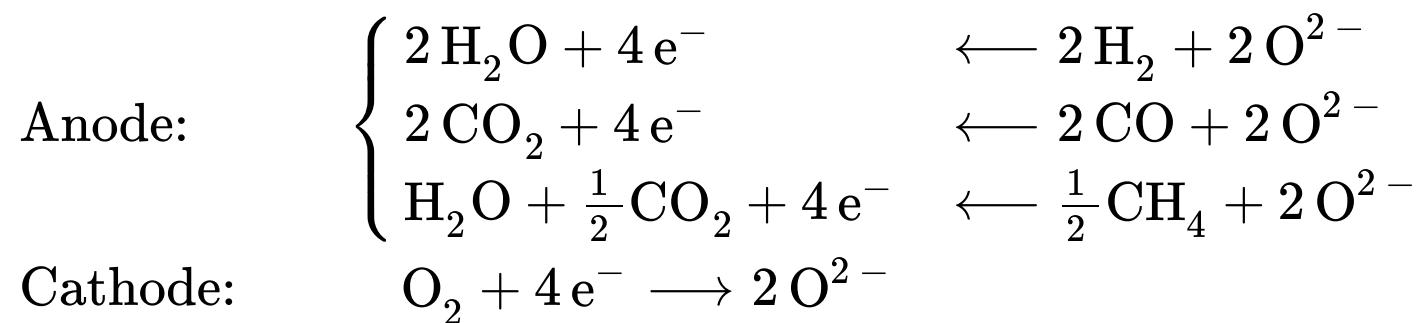
- Good Low-temperature (< 100 °C) operation ✓
 - Quick to start/stop
 - Suitable for portable applications
- H₂O₂ forms when acidic X
 - Corrodes carbon-containing electrodes
 - Lowers cell voltage
 - Requires expensive Pt or Pd catalysts to decompose H₂O₂
- Need careful hydration to ensure H⁺ conduction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

High temperature: Solid Oxide (SOFC)

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

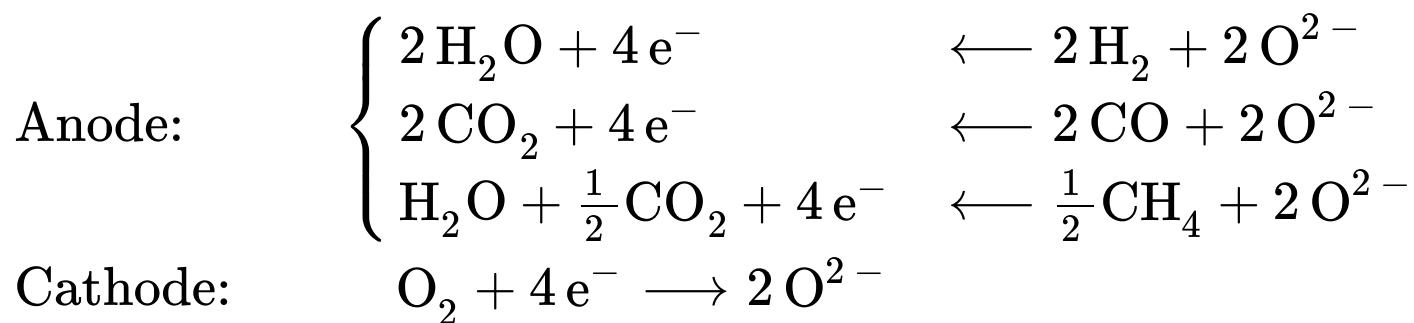
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- Based around redox and conduction of O²⁻:



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- All-solid-state system (*i.e.* solid electrolyte)
- Most work at 800 - 1000 °C
- Based around redox and conduction of O²⁻:



- 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.

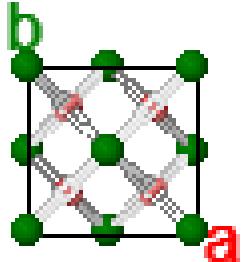


Ideal requirements for fuel cell materials

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	(Fuel ox ⁿ and O ₂ red ⁿ)	O ₂ reduction

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

Top Trumps - Fuel cell version

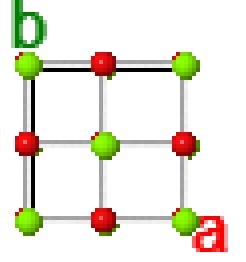
$\text{Bi}_{1.6}\text{Gd}_{0.4}\text{O}_3$	
	JSmol
Electronic Conductivity	Low
Ionic Conductivity	High
Oxidation Stability	Mid
Reduction Stability	Low



Which is the better SOFC electrolyte?

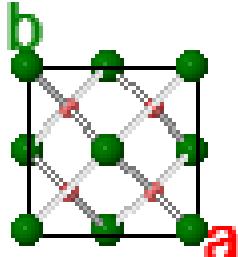
$\text{Bi}_{1.6}\text{Gd}_{0.4}\text{O}_3$

MgO

MgO	
	JSmol
Electronic Conductivity	Low
Ionic Conductivity	Low
Oxidation Stability	High
Reduction Stability	High

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Top trumps #2

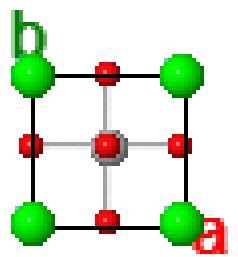
$\text{PrO}_{1.833}$	
	JSmol
Electronic Conductivity	High
Ionic Conductivity	Mid
Oxidation Stability	??
Reduction Stability	??



Which is the better SOFC anode?

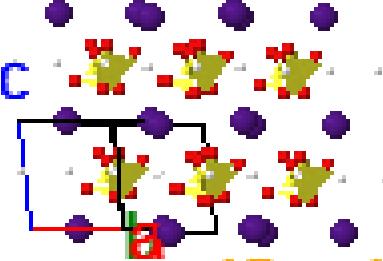
Pr $O_{1.833}$

Sr $_{0.89}Y_{0.07}\text{TiO}_{2.995}$

$\text{Sr}_{0.89}Y_{0.07}\text{TiO}_{2.995}$	
	JSmol
Electronic Conductivity	High
Ionic Conductivity	Mid
Oxidation Stability	Low
Reduction Stability	High

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Top trumps #3

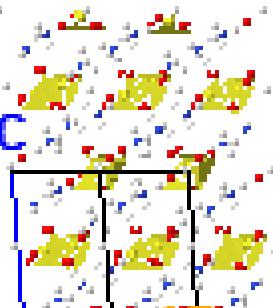
$\text{CsH}(\text{SO}_4)$	
	JSmol
Electronic Conductivity	Low
Ionic Conductivity	???
Oxidation Stability	Mid
Reduction Stability	Low



Which is the better proton-conducting electrolyte?

CsH(SO₄)

(NH₄)₃H(SO₄)₂

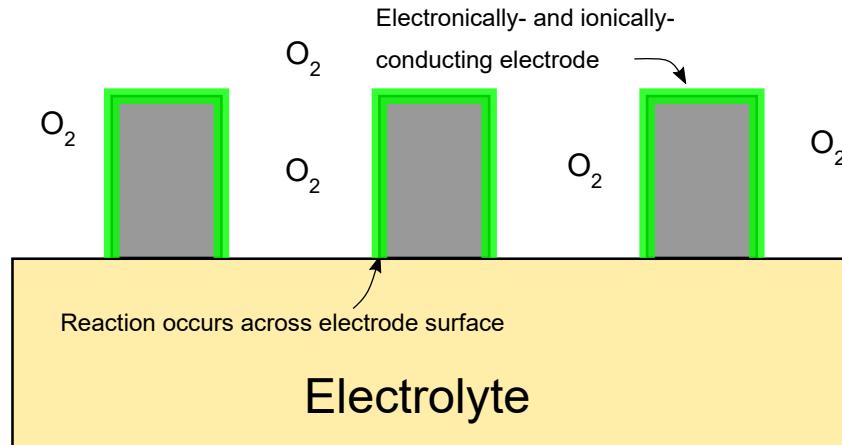
$(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$	
	JSmol
Electronic Conductivity	Low
Ionic Conductivity	???
Oxidation Stability	Mid
Reduction Stability	Low

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'Perfect' electrodes

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

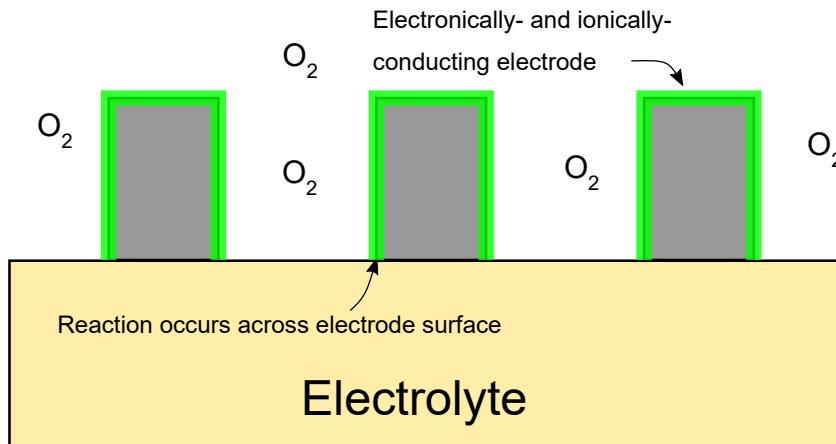
- fuel/oxygen reactions would occur at the electrode surface



'Perfect' electrodes

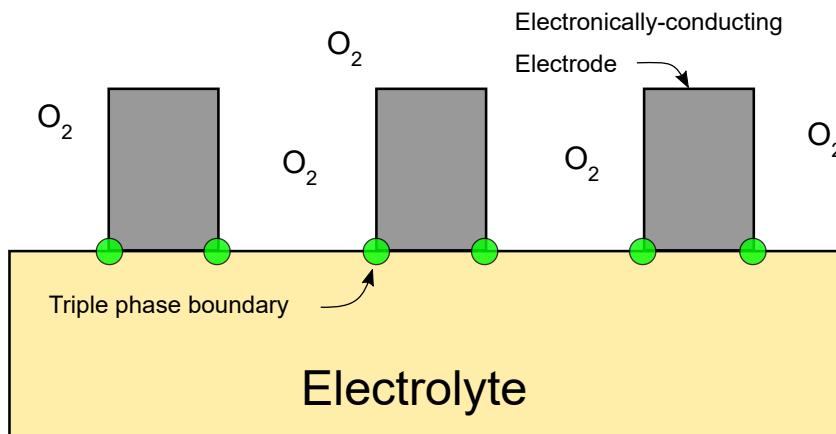
Ideally, electrodes should be good electronic *and* ionic conductors!

- fuel/oxygen reactions would occur at the electrode surface



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

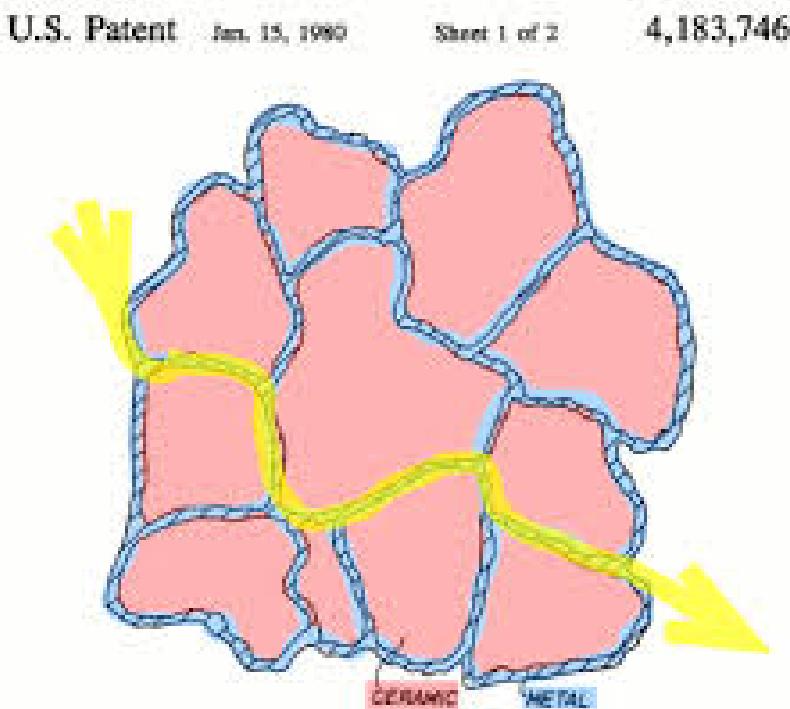
- reactions occur at the **triple phase boundary**



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**

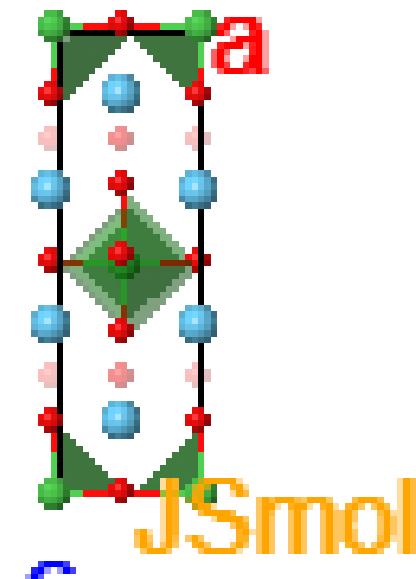
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- poor performance below 700 °C $\textcolor{red}{X}$

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

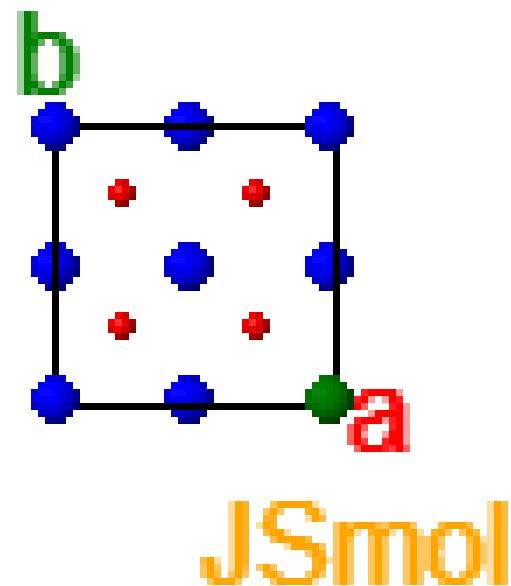
Most studied electrolyte is $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.925}$ (yttrium-stabilised zirconia, YSZ)

- defective fluorite structure
- $\text{Y}_2\text{O}_3 + 2 \text{Zr}_{\text{Zr}} + \text{O}_{\text{O}} \rightleftharpoons 2 \text{Y}'_{\text{Zr}} + \text{V}^{\bullet\bullet}_{\text{O}}$
- 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**

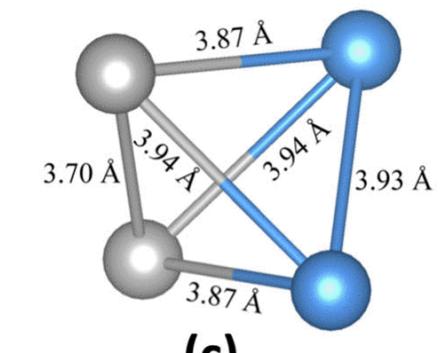
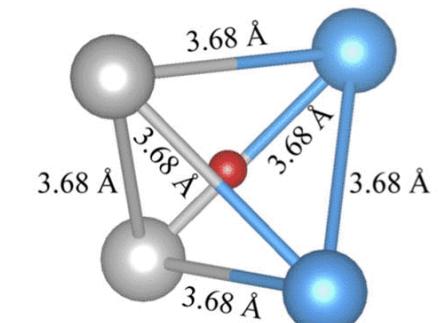
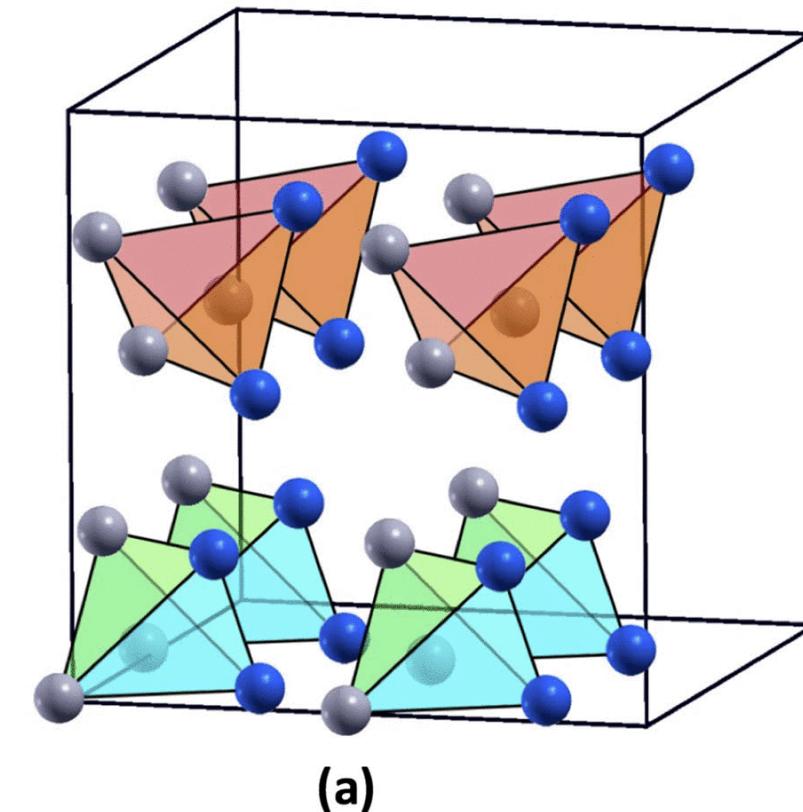
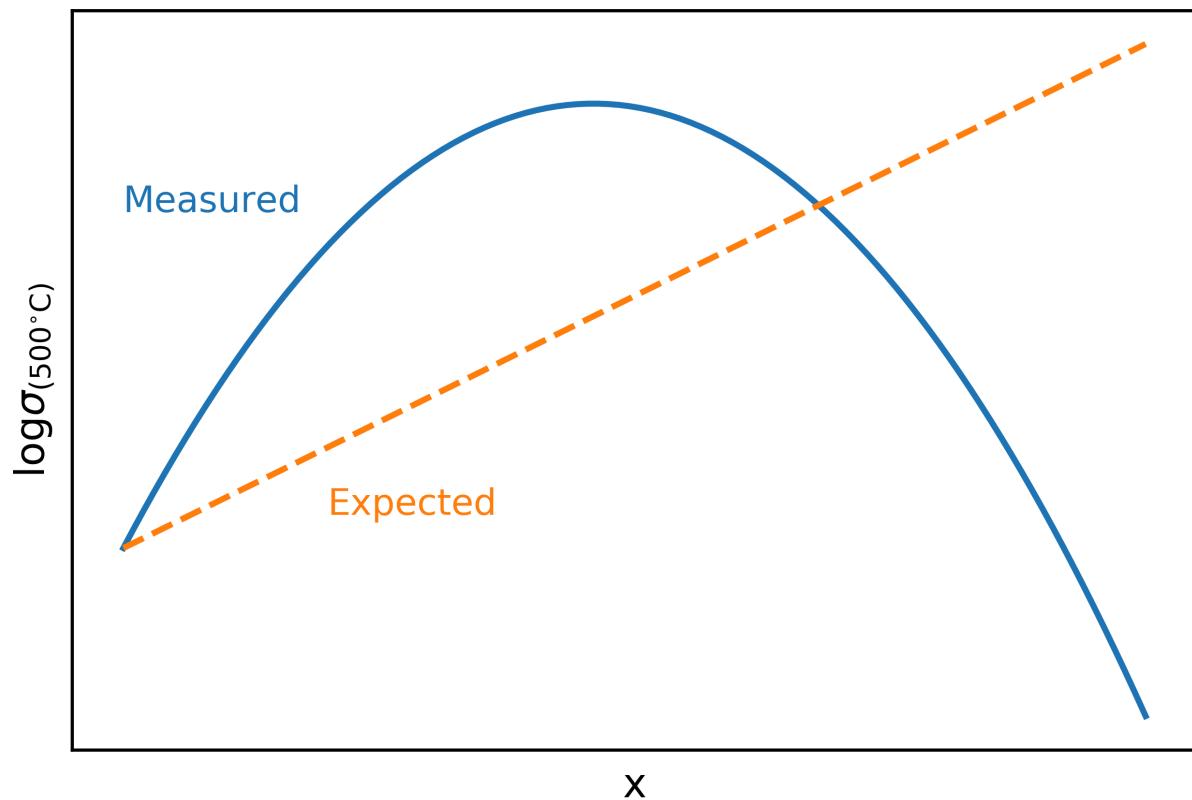
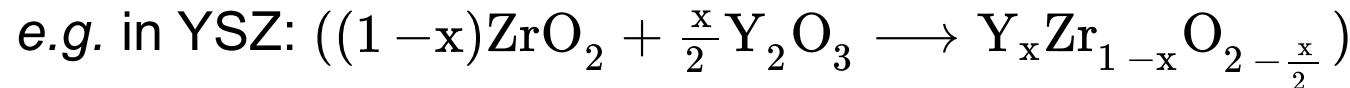
- Local ordering of defects reduces mobility

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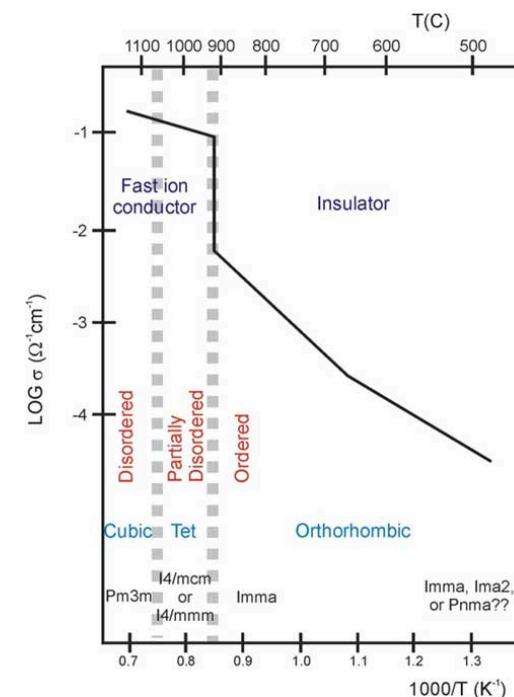
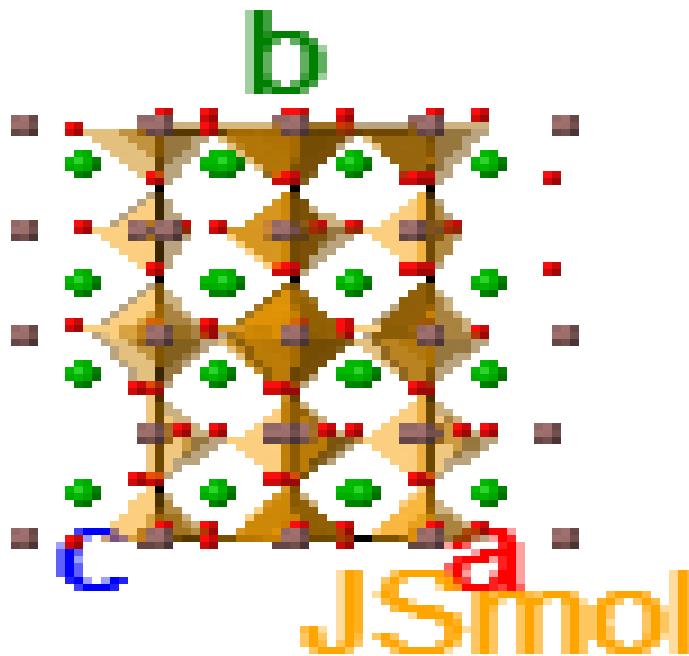
Long-range defect ordering

As discussed in Lecture 2, defects can undergo long-range order

- Temperature can induce order-disorder phase transition

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...



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