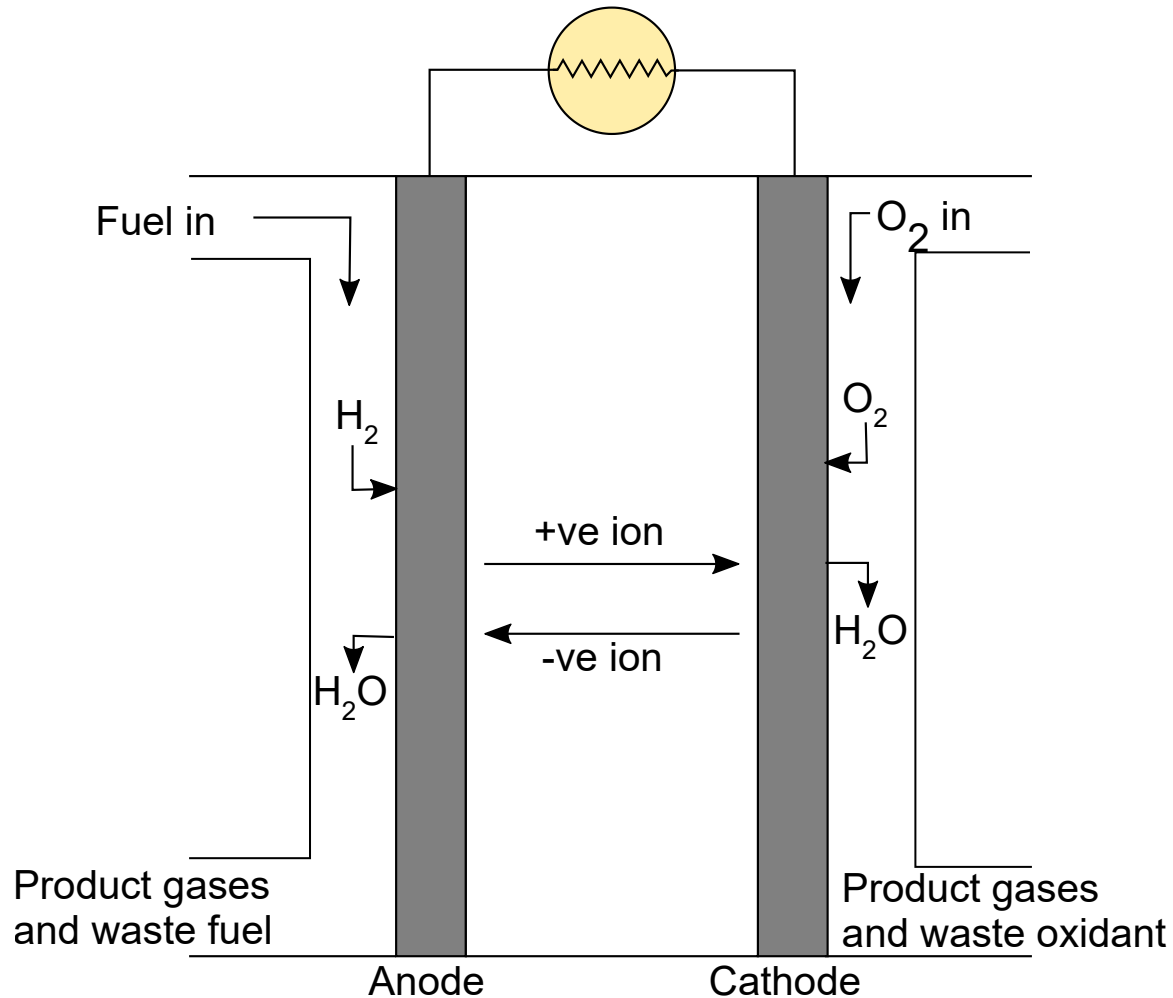


Fuel Cells

Fuel Cells

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



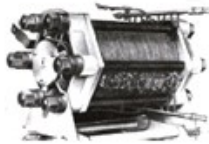
Fuel cell history

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.

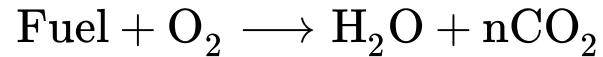


2009

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

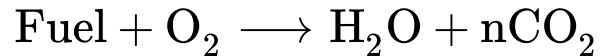


Fuel cell fundamentals



- Fuel cells are divided 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

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- H₂ is the preferred fuel
 - Particularly for LT devices.
 - Doesn't produce CO₂
- Other fuels (e.g. CH₃OH, CH₄, NH₃) can also be used, particularly for HT devices
 - e.g. for CH₄, steam reforming ($\text{CH}_4 + \text{H}_2\text{O} \xrightarrow{>700^\circ\text{C}} \text{CO} + 3\text{H}_2$) can be achieved in HT cells, but must be performed separately for LT cells.

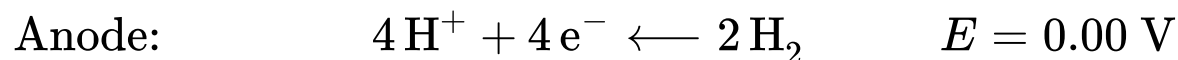
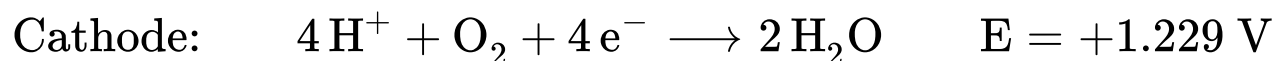
Fuel cell efficiency

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



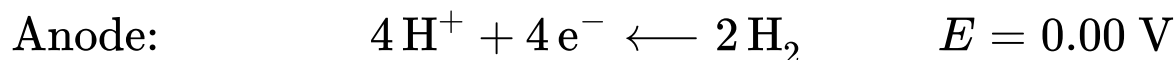
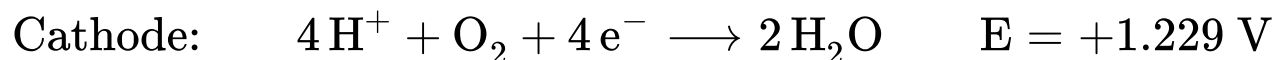
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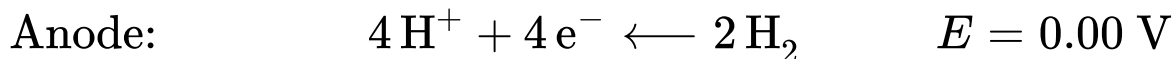
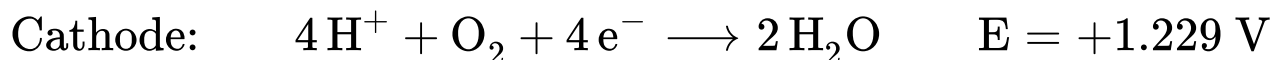
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$$\text{Efficiency} = \eta = -474.3 / 571.6 = \mathbf{83\%}$$

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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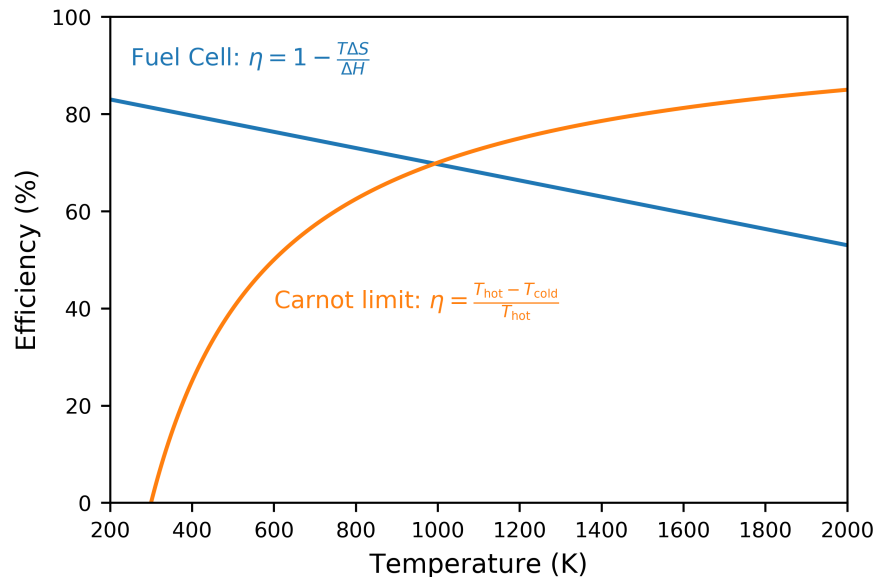
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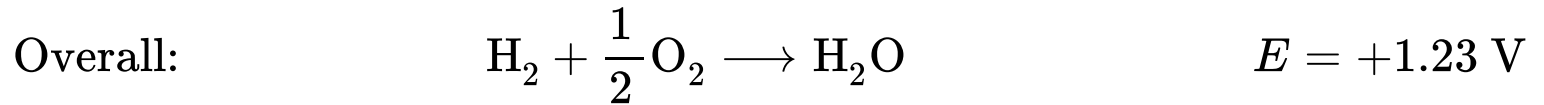
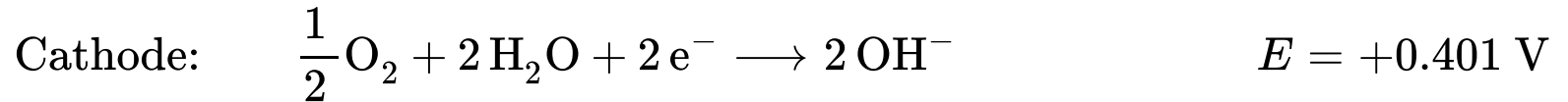
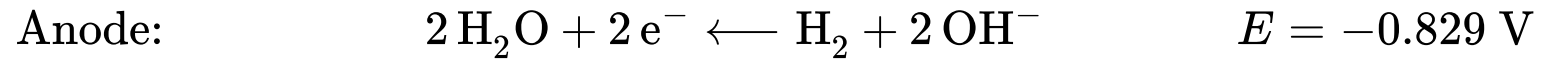
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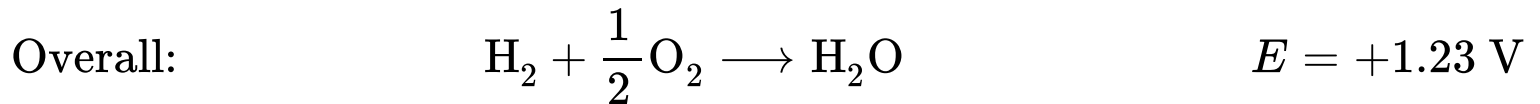
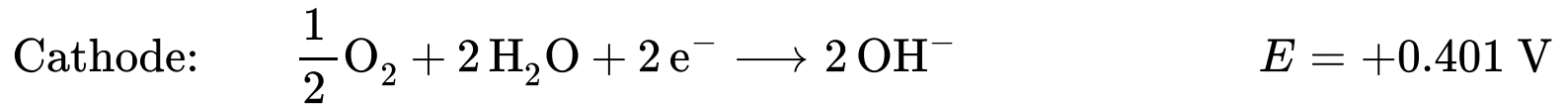
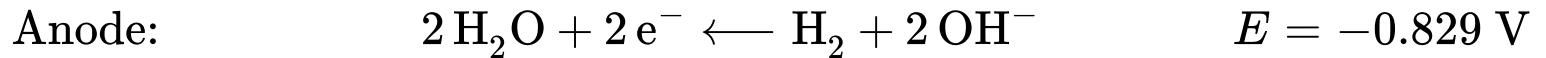
Types of fuel cell

Type	Mobile ion	Operating 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	

Alkaline Fuel cell (AFC)



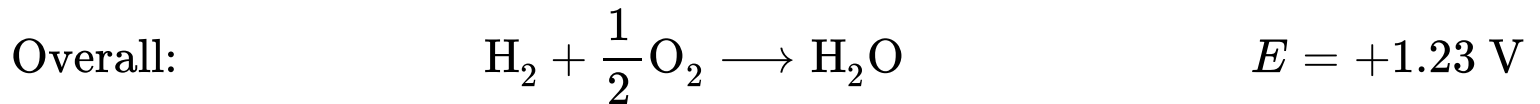
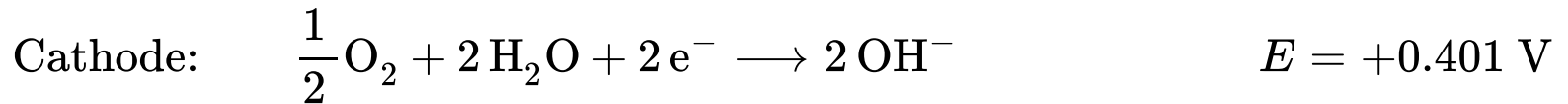
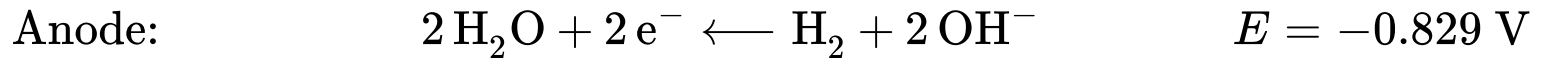
Alkaline Fuel cell (AFC)



- First developed for the Apollo missions
 - Updated version still used in current space shuttle
- Based around concentrated KOH electrolyte with Ni anode and catalytic cathode (such as Pt, Pd or Ag)
- Cheap fuel cell to produce ✓



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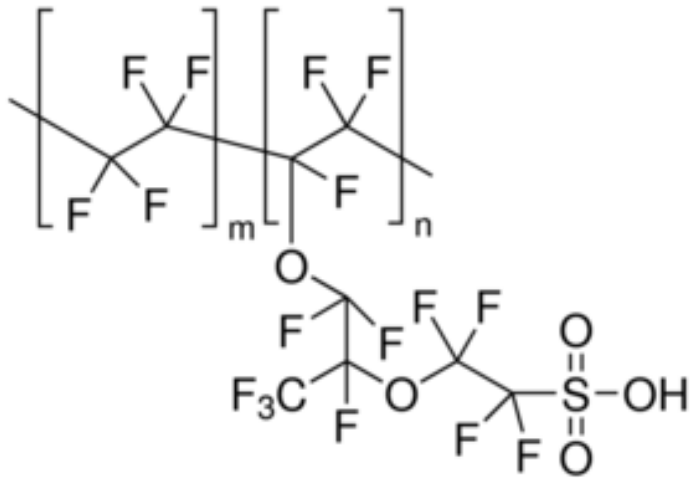


- First developed for the Apollo missions
 - Updated version still used in current space shuttle
- Based around concentrated KOH electrolyte with Ni anode and catalytic cathode (such as Pt, Pd or Ag)
- Cheap fuel cell to produce ✓
- Susceptible to CO₂ poisoning: ✗
 - $2 \text{KOH} + \text{CO}_2 \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$
 - K₂CO₃ goes on to block electrode
- Requires pure H₂ and O₂ ✗



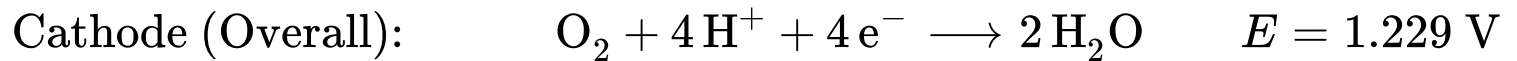
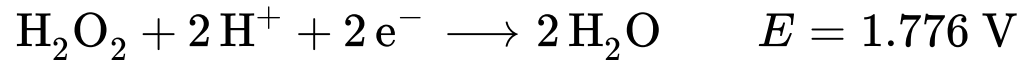
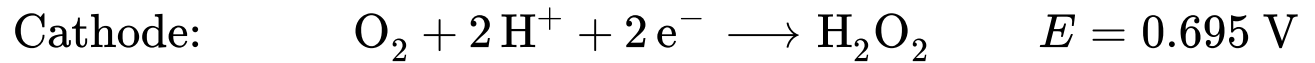
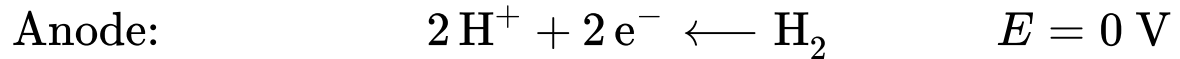
Proton exchange membrane fuel cell (PEMFC)

- First developed for the Gemini space vehicle
- Based around an acidic proton-conducting polymer
 - *e.g.* Nafion

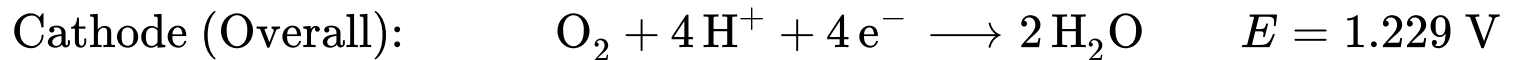
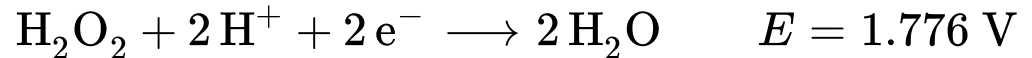
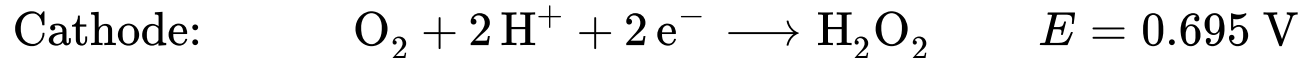
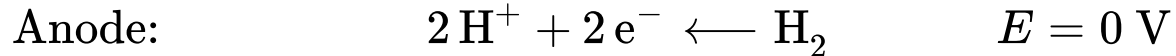


- Use H_2 as fuel, but can work with MeOH (less efficiently)

PEMFC + H₂



PEMFC + H₂

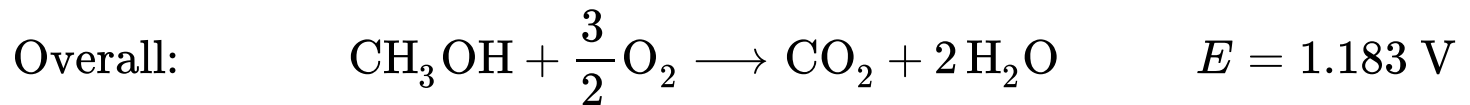
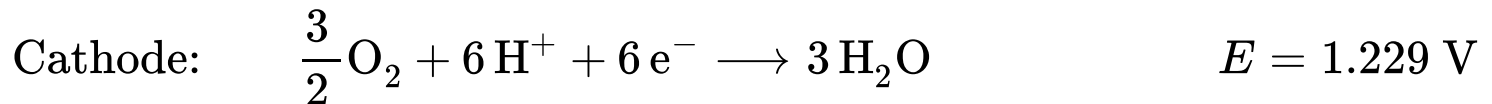
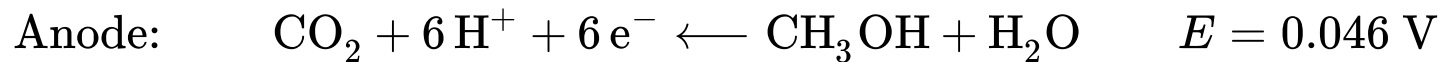


- PEMFCs give good Low-temperature (< 100 °C) operation ✓
 - Quick to start/stop
 - Suitable for portable applications
- In acidic conditions, H₂O₂ forms ✗
 - Corrodes carbon-containing electrodes
 - Lowers cell voltage
 - Requires Pt or Pd catalysts to promote H₂O₂ decomposition
 - ~0.5 mg cm⁻³
 - Expensive
 - Poor tolerance to CO or NH₃
- Require careful hydration to ensure H⁺ conduction ✗

PEMFC + Methanol

Methanol is easier to store/transport than H_2 and almost as efficient

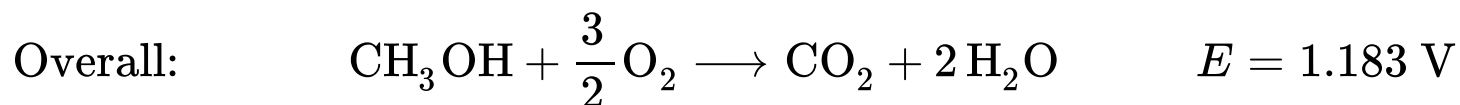
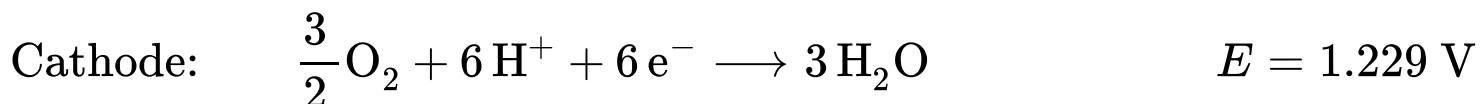
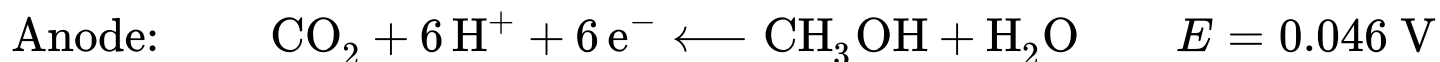
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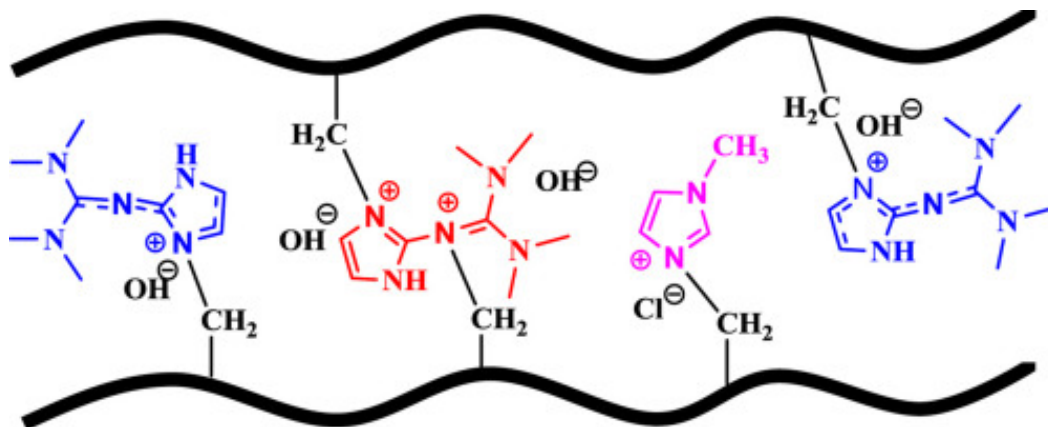
Problems:

- MeOH is fairly soluble in membrane, crossing from anode to cathode **X**
 - Reduces cell voltage to $\sim 0.5 \text{ V}$
- CO is formed in a side-reaction, blocking reaction sites **X**
 - Improved by adding more Pt catalyst ($\sim 3 \text{ mg cm}^{-2}$)



Towards alkaline polymers?

- OH^- conduction removes the problems associated with H_2O_2 formation
- Attaching the counter-cation to the polymer reduces the risk of electrode poisoning
- pH change also modifies redox energies, allowing Ni catalysts to replace Pt



Unfortunately, current OH^- conducting polymers currently have low ionic conductivity at practical temperatures!

Phosphoric Acid (PAFC)

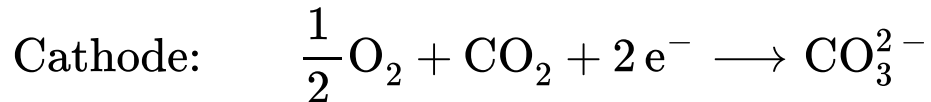
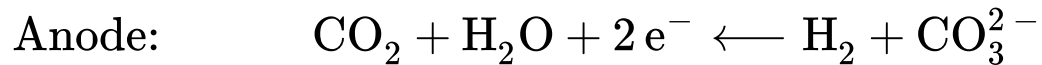
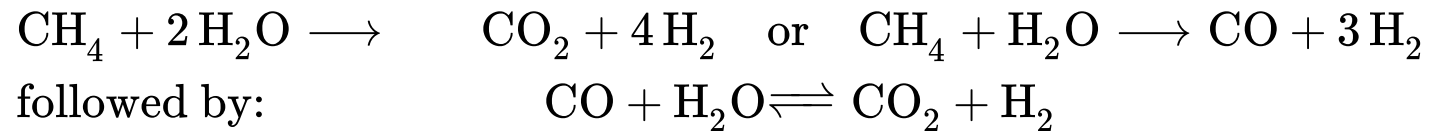
Operates at 200 °C

- High temperature acid prevents build up of H_2O_2 ✓
- Temperature makes cell more tolerant to CO_2 impurities ✓
- Below 150 °C conductivity is low ✗
- Above 200 °C H_3PO_4 decomposes into a range of acids ✗
- Hot H_3PO_4 is highly corrosive! ✗
 - Materials stability challenge



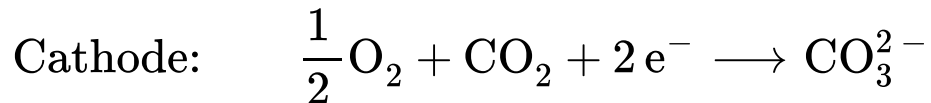
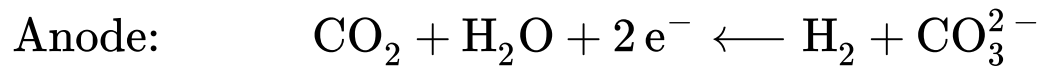
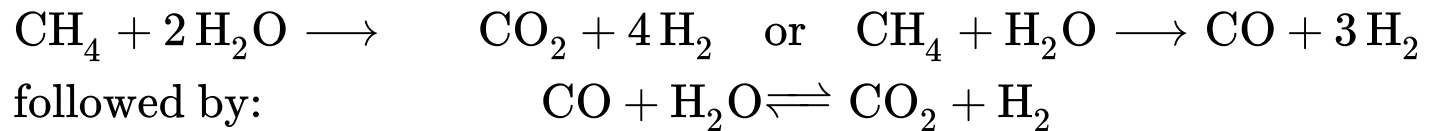
Molten Carbonate (MCFC)

- Optimum temperature 560 °C
- Range of fuel choices
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- Cathode - porous NiO
- Anode - porous Ni
- No need for expensive catalyst materials
- Molten alkali-metal carbonates are highly corrosive
 - Conductivity is also limited
- Ni electrodes are sensitive to sulfur contaminants

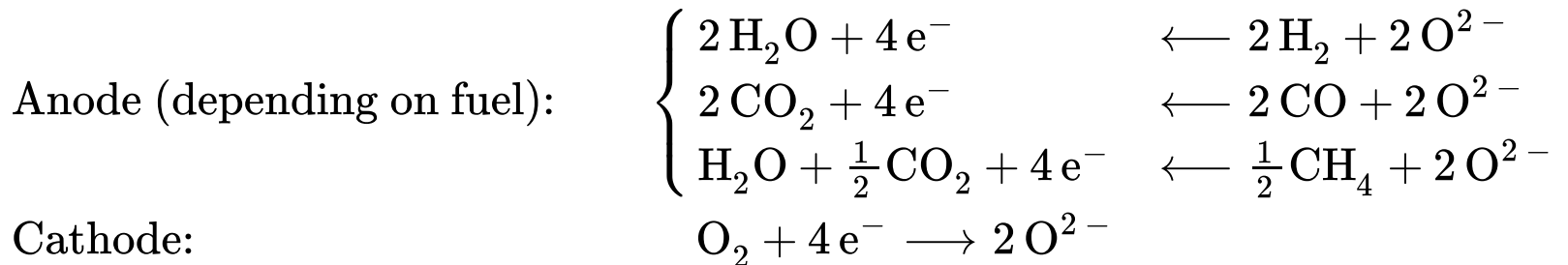


Solid Oxide (SOFC)

- 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

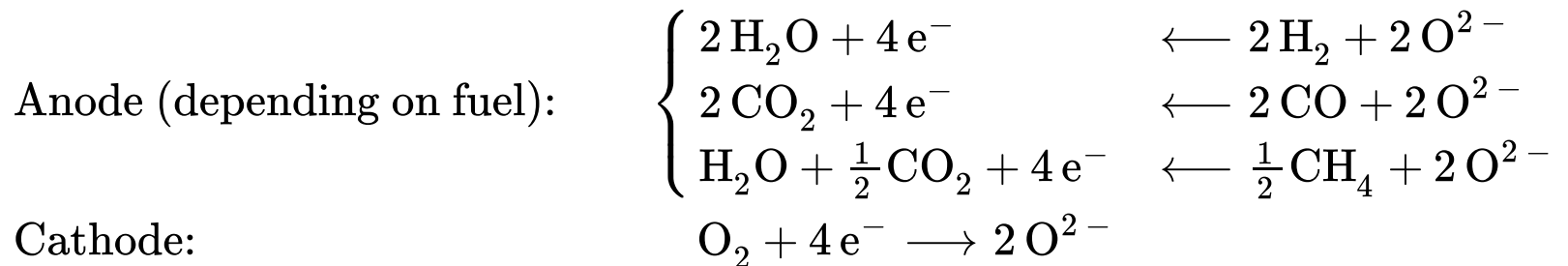
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- The high temperature operation means that internal steam reforming occurs readily
 - a wide range of fuels can be used
- No precious metal catalysts are required
- Excess heat from exhaust gas can be used to increase efficiency (can reach ~90%)
 - *e.g.* drive a turbine to generate extra electricity
 - Combined heat and power (CHP)

SOFC Limitations

High temperatures:

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- Cause problems in terms of reactivity between electrolyte and electrodes
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There is a delicate balance between optimum temperature for redox and/or ionic conductivity, and issues with thermal expansion, reactivity and device construction

- Intermediate-temperature (IT) SOFCs are the current optimum.



Requirements for SOFC materials

Anode

- High electronic conductivity
- High catalytic activity for fuel oxidation
- High ionic conductivity
- High stability under HT reducing conditions

Electrolyte

- High ionic conductivity
- Negligible electronic conductivity
- High stability in oxidising *and* reducing environments

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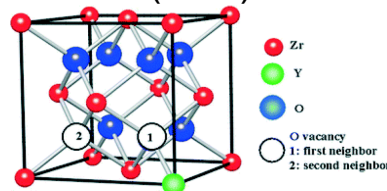
- Ni has high electronic conductivity and catalytic activity
- High ionic conductivity from electrolyte

Electrolyte

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e.g.

- $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (CGO)
- $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.925}$ (YSZ)



Cathode

- High electronic conductivity
- High catalytic activity for O_2 reduction
- High ionic conductivity
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- $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$: a good mixed conductor, but with high thermal expansion
- $\text{La}_2\text{NiO}_{4+x}$: an interstitial oxide ion conductor

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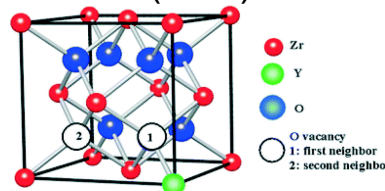
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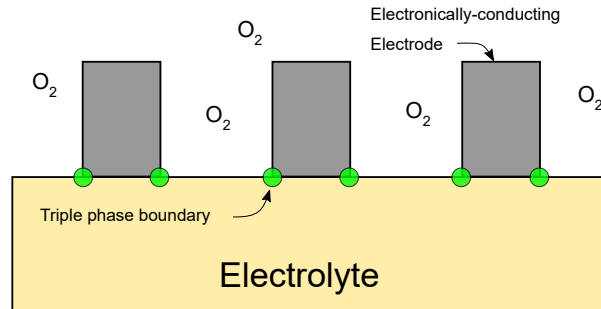
As well as: Chemical stability, similar thermal expansion, cost, ...

Improving electrodes

Ideally want a perfect mixed electronic/ionic conductor, with high chemical stability, high catalytic activity etc...

In reality, we can use a mixture of good (and chemically-stable) ionic and electronic conductors. Reactions will then occur at the **triple phase boundary**

Electronic Conductor

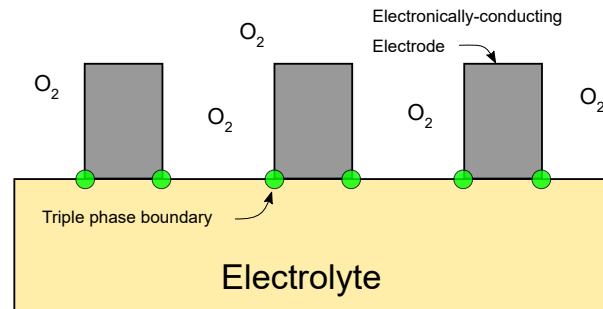


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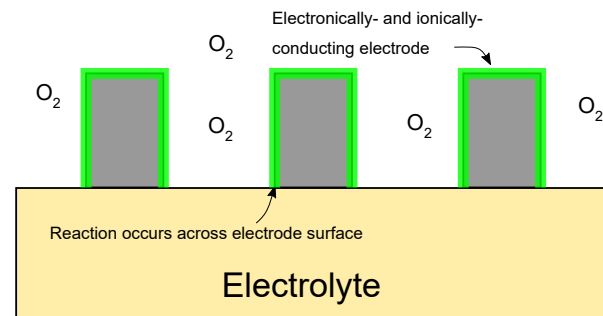
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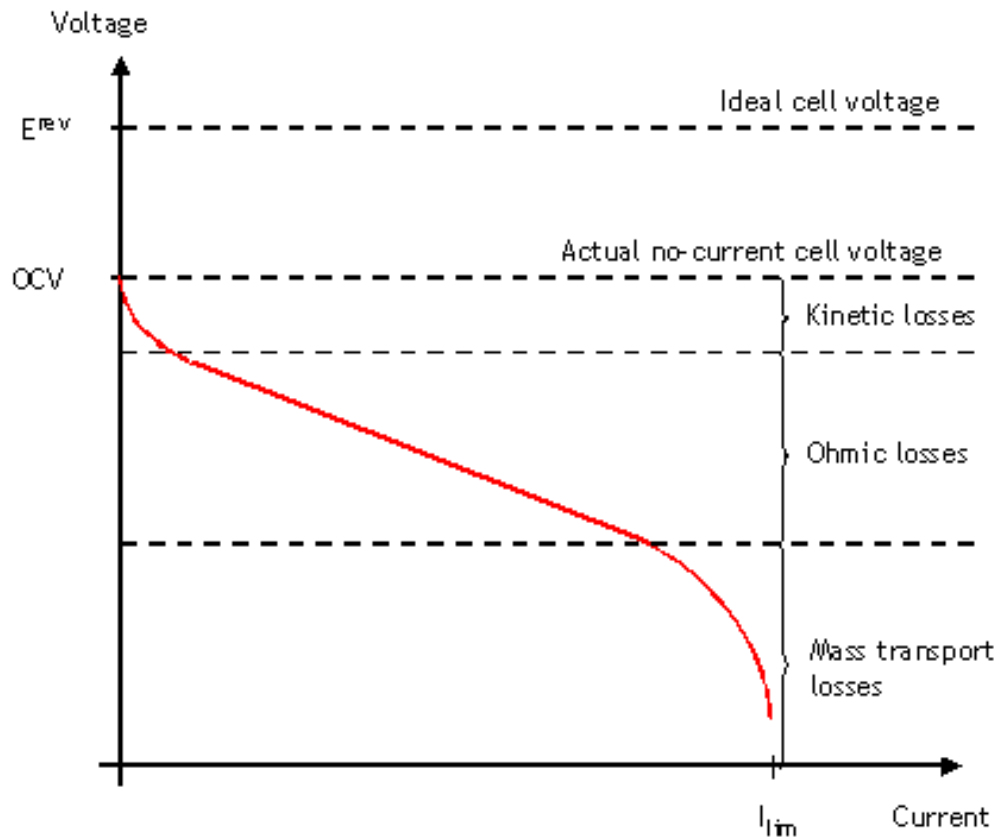
Mixed conductor



Practical efficiency

We can calculate maximum thermodynamic efficiencies, but how do realistic efficiencies compare?

Like batteries, the obtainable voltage (and efficiency) depends on the current rate:



Practical efficiency

- The difference between theoretical and **zero-current** voltage is due to issues such as small electronic conductivity of electrolyte and crossover of fuel
 - More pronounced for LT than HT cells

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- At low currents, **kinetic (or activation) losses** cause a rapid drop in voltage
 - O₂ reduction is kinetically slow
 - Improved by higher temperatures or presence of catalysts

Practical efficiency

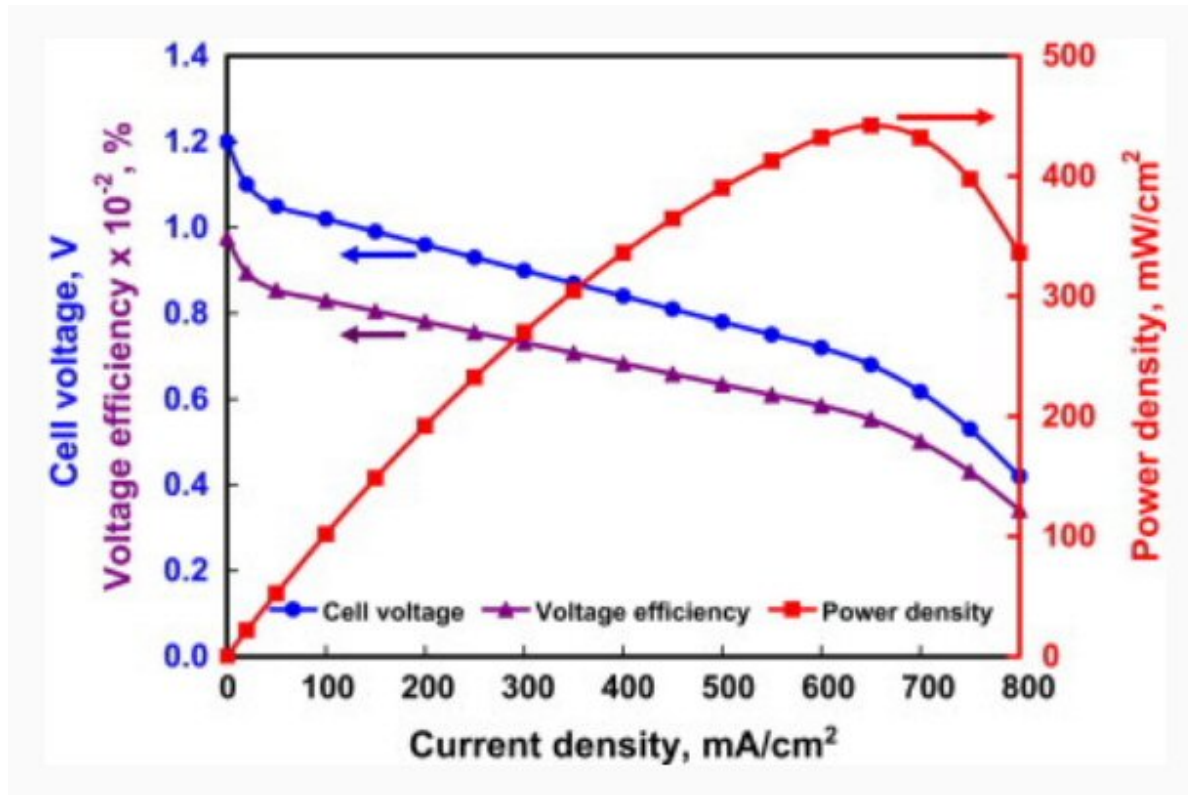
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 - Improved by higher temperatures or presence of catalysts
- At intermediate currents, **Ohmic losses** dominate
 - Caused by the resistance of ionic motion in the electrolyte
 - R constant with T, so voltage varies linearly with current ($V = IR$)
 - Major loss in both HT and LT cells
 - Can be decreased by thinner electrolyte layers

Practical efficiency

- The difference between theoretical and **zero-current** voltage is due to issues such as small electronic conductivity of electrolyte and crossover of fuel
 - More pronounced for LT than HT cells
- At low currents, **kinetic (or activation) losses** cause a rapid drop in voltage
 - O₂ reduction is kinetically slow
 - Improved by higher temperatures or presence of catalysts
- At intermediate currents, **Ohmic losses** dominate
 - Caused by the resistance of ionic motion in the electrolyte
 - R constant with T, so voltage varies linearly with current ($V = IR$)
 - Major loss in both HT and LT cells
 - Can be decreased by thinner electrolyte layers
- At high currents, **Mass transport** causes rapid voltage drop
 - At high rates, the concentration of fuel and/or O₂ at the electrode surface gets depleted
 - Occurs for both HT and LT cells
 - Higher rates can be achieved by better controlling gas flow

Power limits

Because voltage \downarrow as current \uparrow , power ($= IV$) will show a peak:



Typically, these peak powers are lower than batteries

