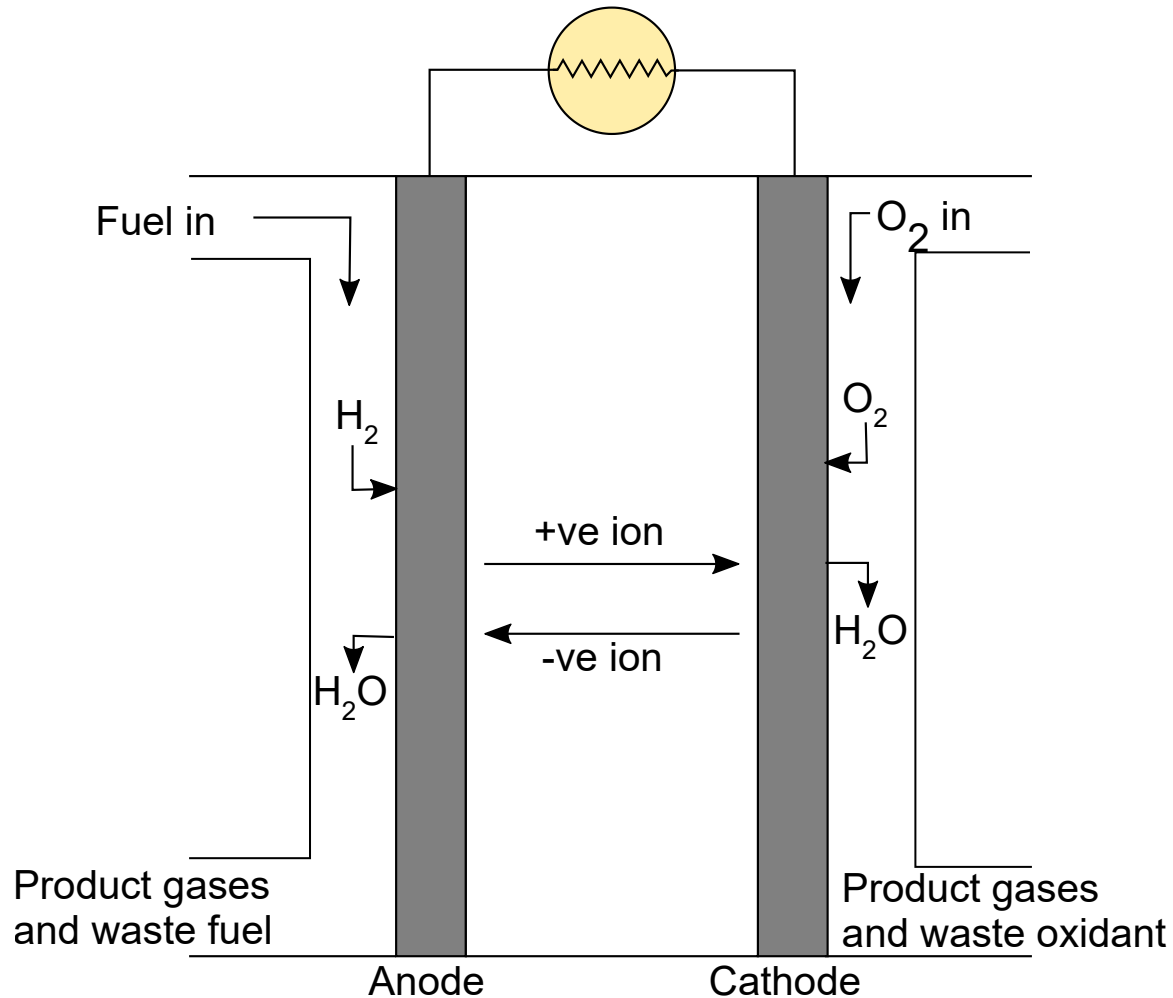


Fuel Cells

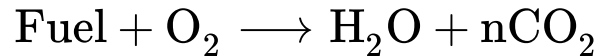
Fuel Cells

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



Fuel cell history

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
- 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.

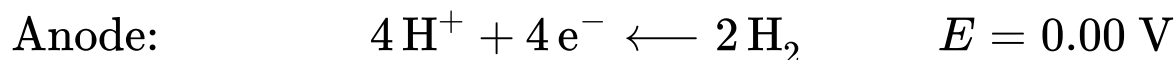
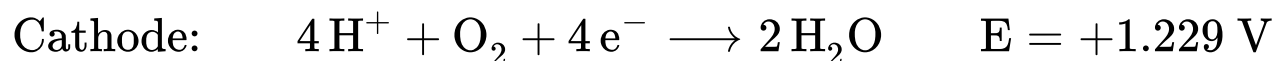
Fuel cell efficiency

Fuel cells are *very* efficient

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

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

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



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

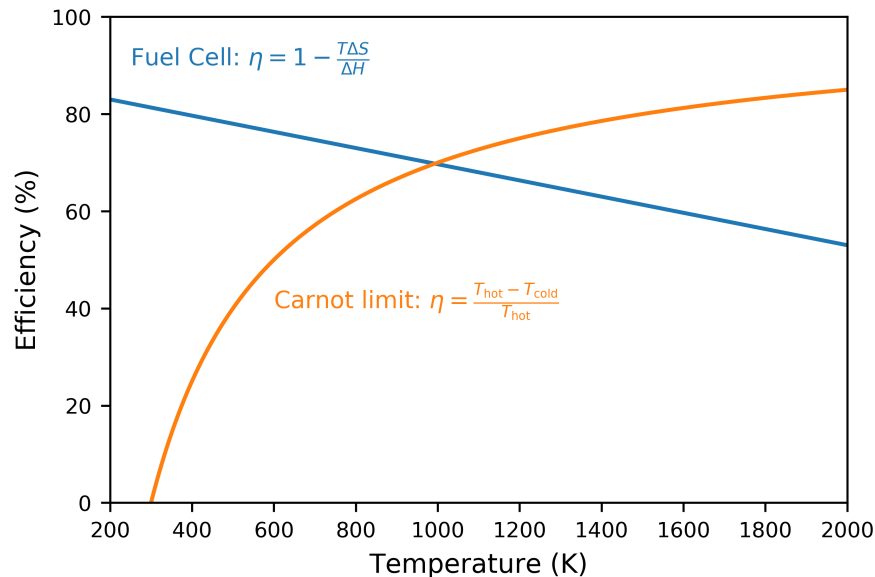
$$\text{Efficiency} = \eta = -474.3 / 571.6 = \mathbf{83\%}$$

Efficiency with temperature

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

For an 'ideal' heat engine (a perfectly efficient combustion engine) the maximum efficiency is determined by the Carnot limit:

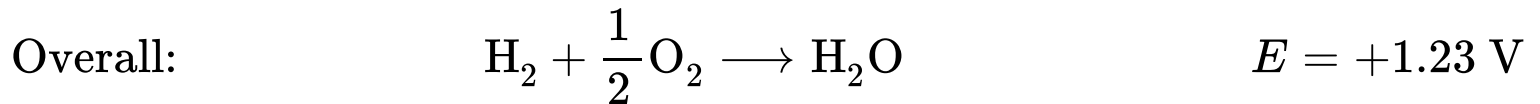
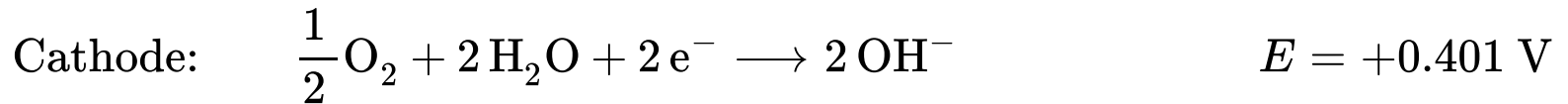
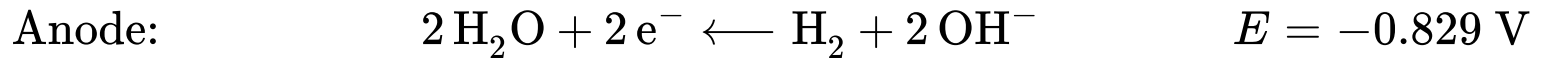
$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$



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)

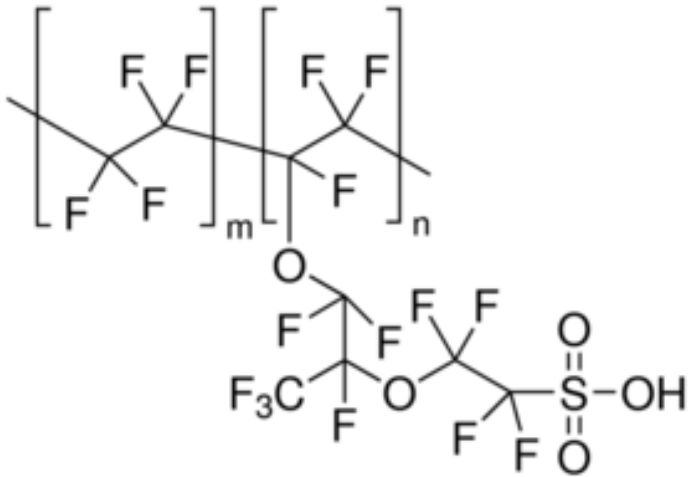


- First developed for the Apollo missions
 - Updated version still used in current space shuttle
- Based around concentrated KOH electrolyte with Ni anode and catalytic cathode (such as Pt, Pd or Ag)
- Cheap fuel cell to produce ✓
- Susceptible to CO₂ poisoning: ✗
 - $2 \text{KOH} + \text{CO}_2 \longrightarrow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



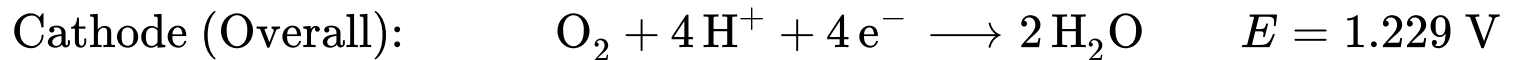
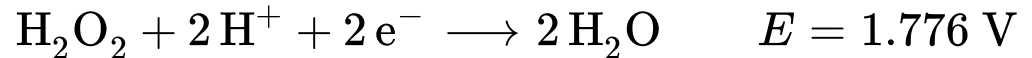
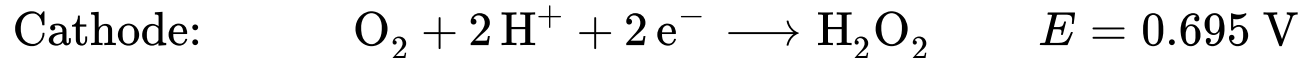
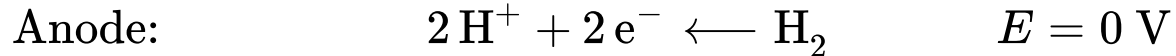
Proton exchange membrane fuel cell (PEMFC)

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



- Use H₂ as fuel, but can work with MeOH (less efficiently)

PEMFC + H₂

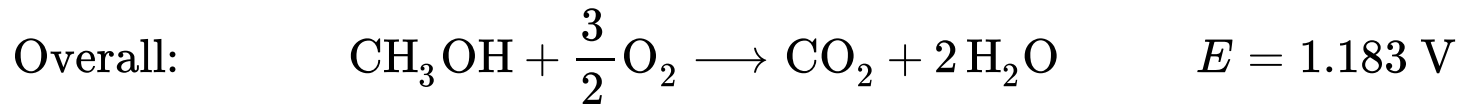
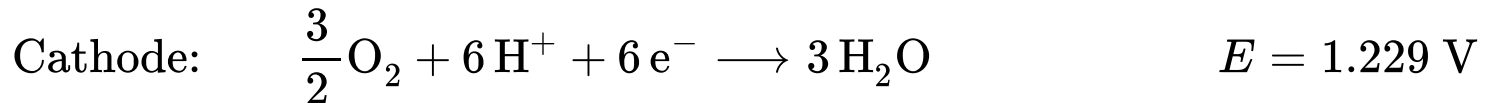
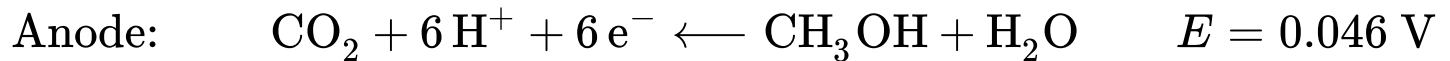


- PEMFCs give good Low-temperature (< 100 °C) operation ✓
 - Quick to start/stop
 - Suitable for portable applications
- In acidic conditions, H₂O₂ forms ✗
 - Corrodes carbon-containing electrodes
 - Lowers cell voltage
 - Requires Pt or Pd catalysts to promote H₂O₂ decomposition
 - ~0.5 mg cm⁻³
 - Expensive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

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



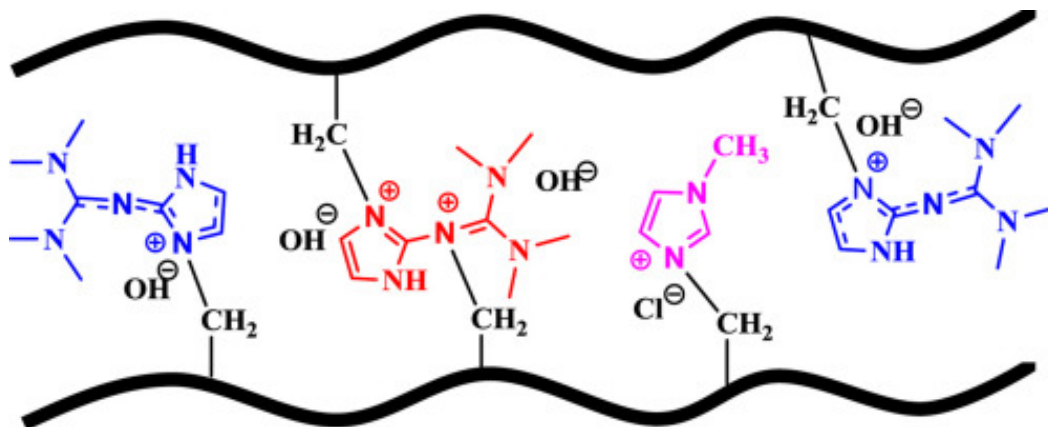
Problems:

- 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)

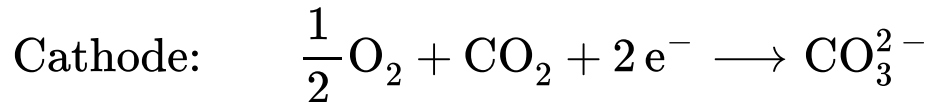
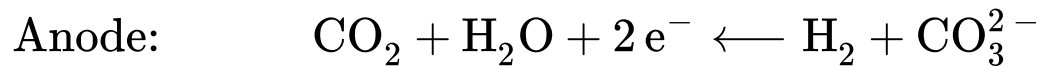
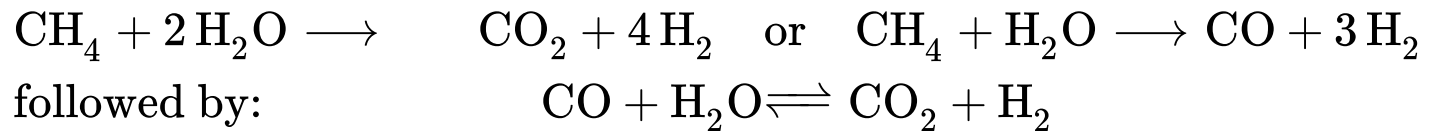
Operates at 200 °C

- 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
 - High temperature allows steam reforming (water-gas shift reaction) to generate H₂:

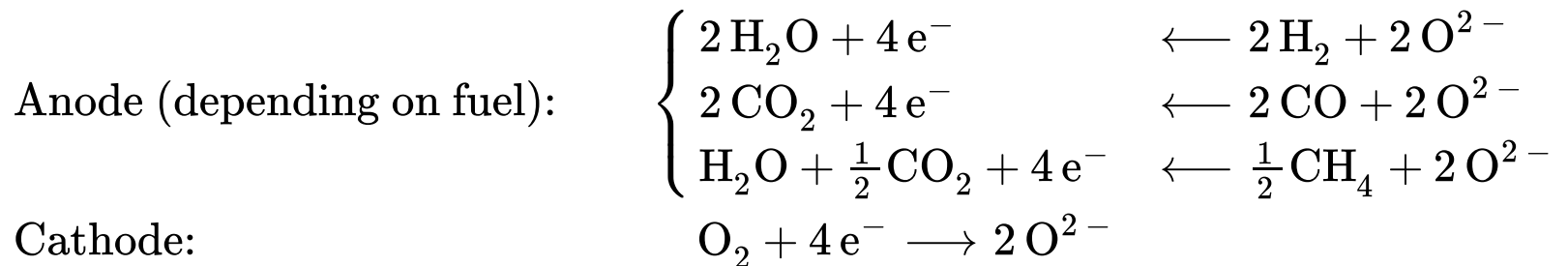


- Cathode - porous NiO
- Anode - porous Ni
- No need for expensive catalyst materials
- Molten alkali-metal carbonates are highly corrosive
 - Conductivity is also limited
- Ni electrodes are sensitive to sulfur contaminants



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
- Based around redox and conduction of O^{2-} :



- 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:

- Prevent rapid start/stop. SOFCs are limited to stationary power applications
- Cause problems in terms of reactivity between electrolyte and electrodes
- Make sealing the cell difficult

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

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

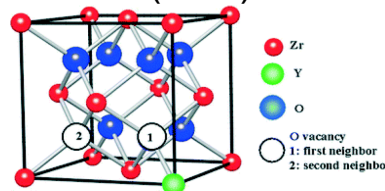
- Ni has high electronic conductivity and catalytic activity
- High ionic conductivity from electrolyte

Electrolyte

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

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
- Stable in HT oxidising conditions

- $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$: a good mixed conductor, but with high thermal expansion
- $\text{La}_2\text{NiO}_{4+x}$: an interstitial oxide ion conductor

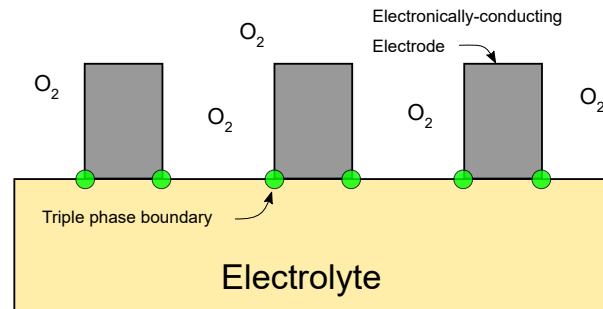
As well as: Chemical stability, similar thermal expansion, cost, ...

Improving electrodes

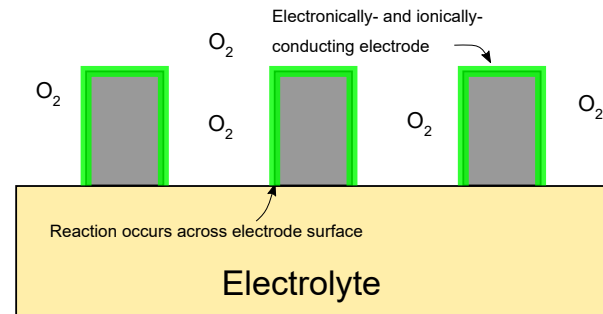
Ideally want a perfect mixed electronic/ionic conductor, with high chemical stability, high catalytic activity etc...

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



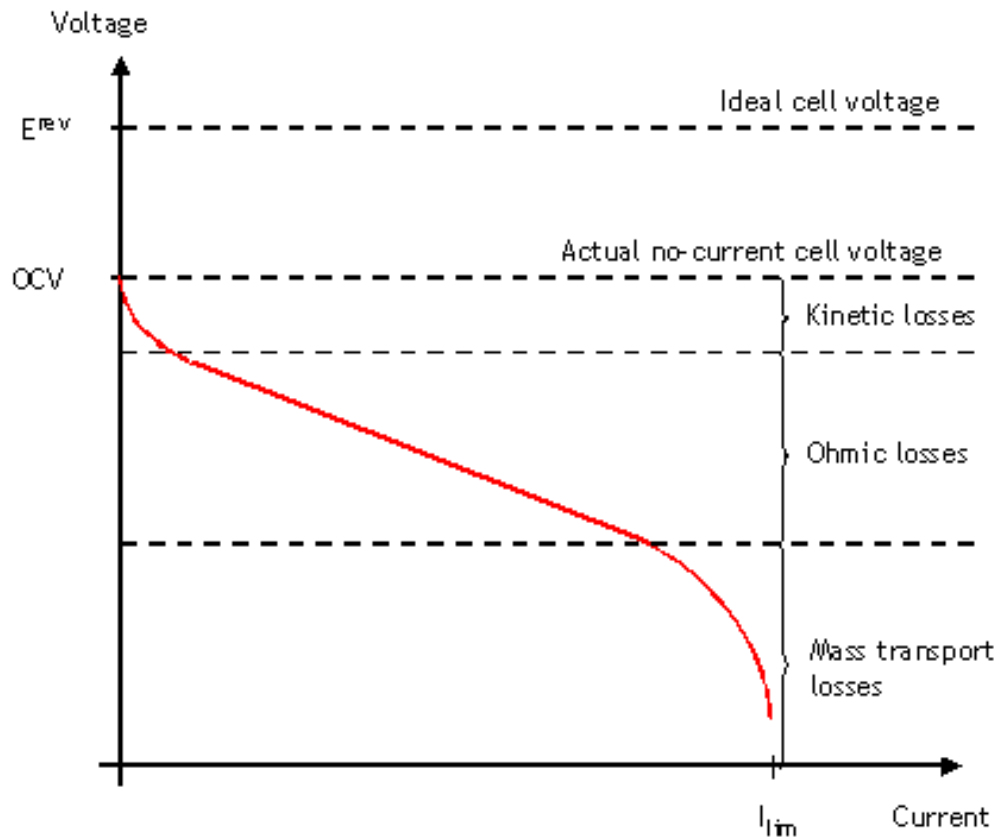
Mixed conductor



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:

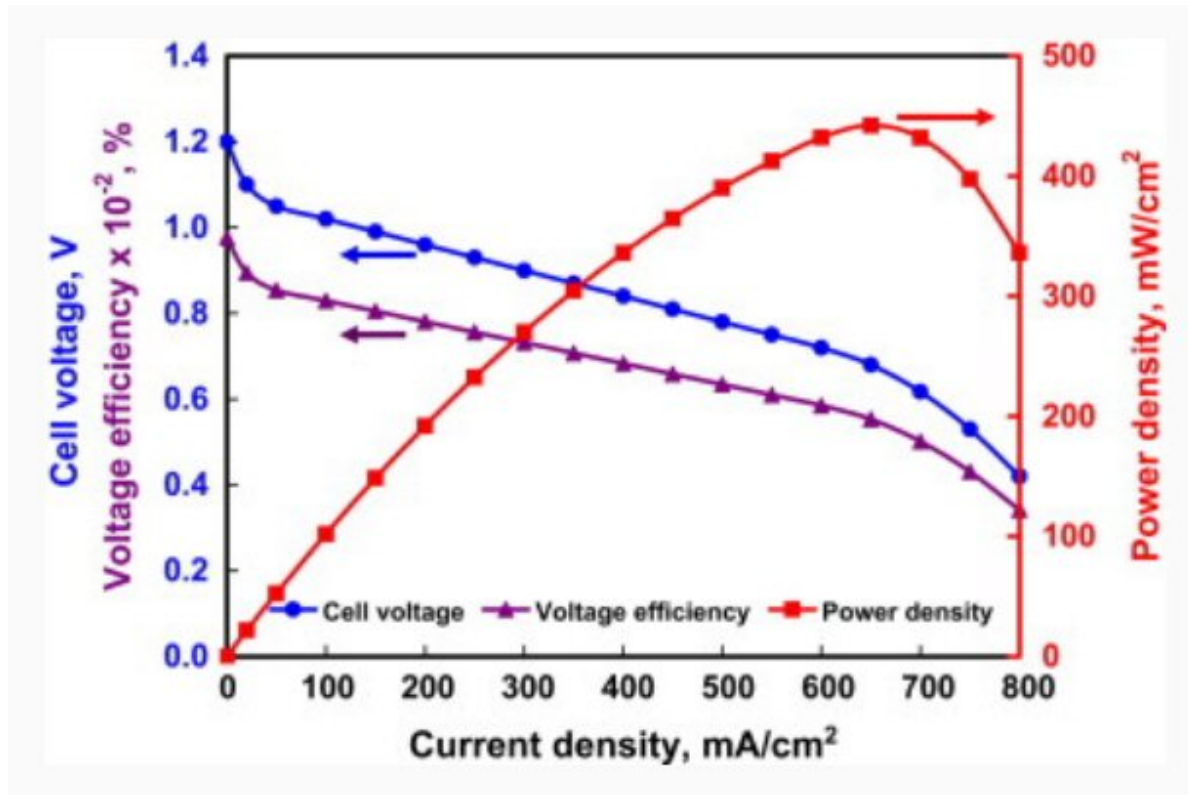


Practical efficiency

- 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
- 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

