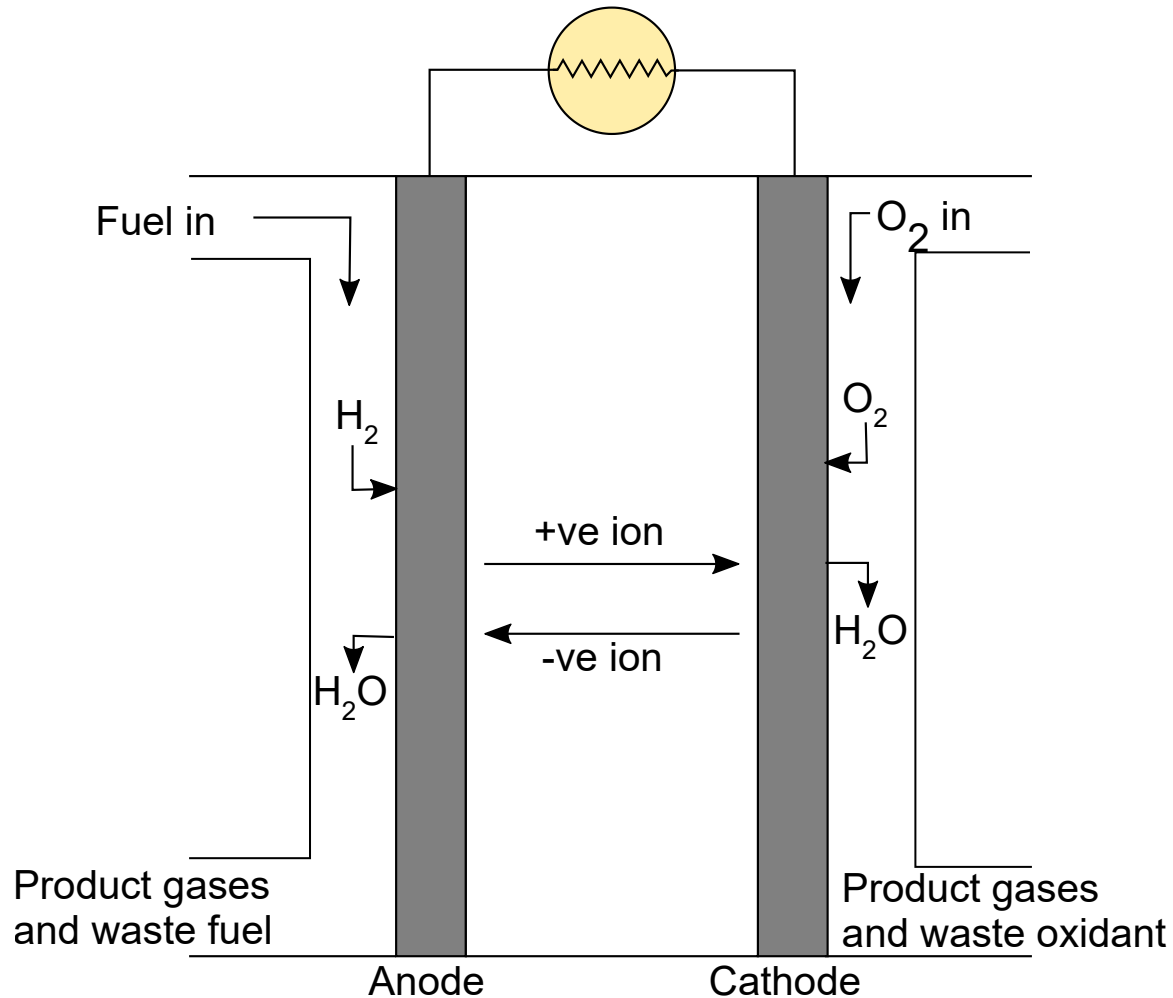


# Fuel Cells

# Fuel Cells

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



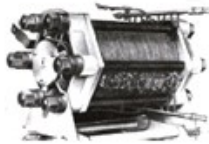
# Fuel cell history

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.

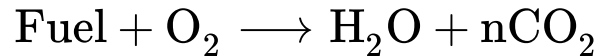


2009

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).
- H<sub>2</sub> is the preferred fuel
  - Particularly for LT devices.
  - Doesn't produce CO<sub>2</sub>
- Other fuels (e.g. CH<sub>3</sub>OH, CH<sub>4</sub>, NH<sub>3</sub>) can also be used, particularly for HT devices
  - e.g. for CH<sub>4</sub>, 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.

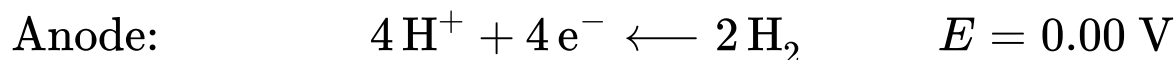
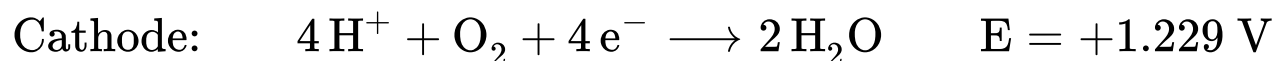
# Fuel cell efficiency

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



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

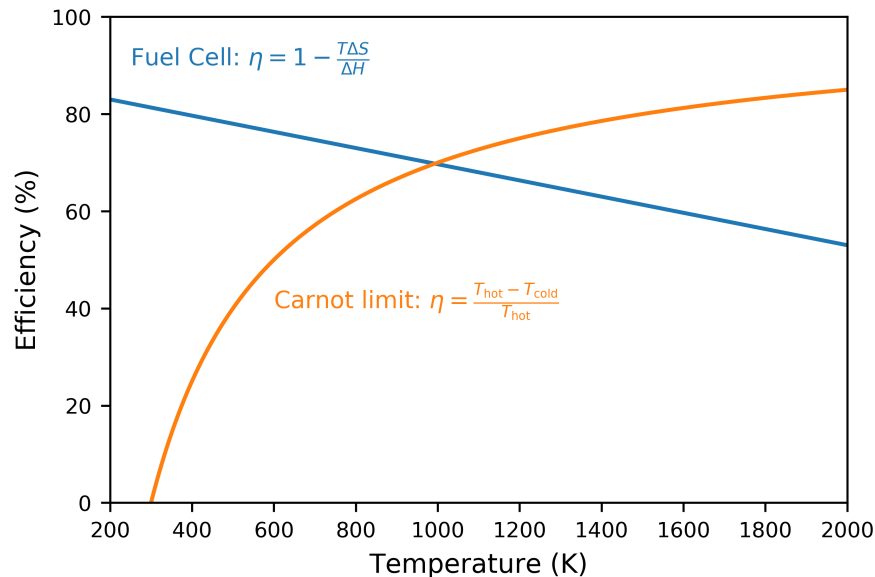
$$\text{Efficiency} = \eta = -474.3 / 571.6 = \mathbf{83\%}$$

# 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:

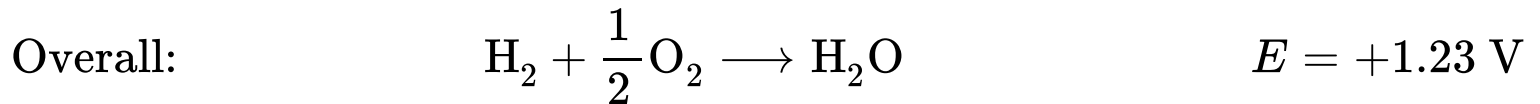
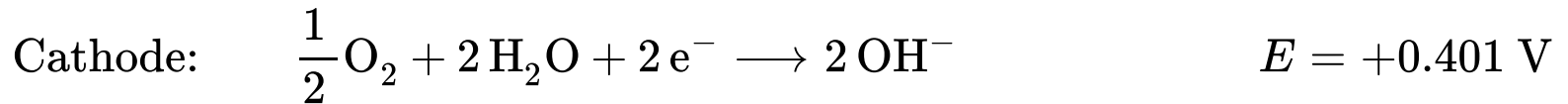
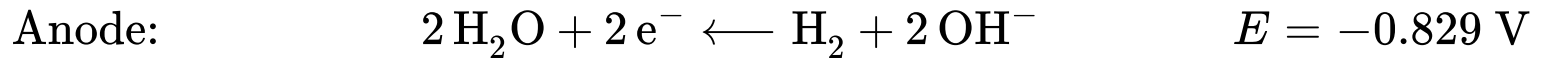
$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$



# Types of fuel cell

Type	Mobile ion	Operating temperature (°C)	Applications
Alkaline	$\text{OH}^-$	50-100	Stationary power, space missions
Polymer	$\text{H}^+$ or $\text{OH}^-$	50-100	Portable devices, transport
Phosphoric acid (PAFC)	$\text{H}^+$	220	Medium to large scale combined heat and power (CHP) systems ⋮ ⋮
Molten Carbonate (MCFC)	$\text{CO}_3^{2-}$	650	
Solid Oxide (SOFC)	$\text{O}^{2-}$	500 - 1000	

# Alkaline Fuel cell (AFC)



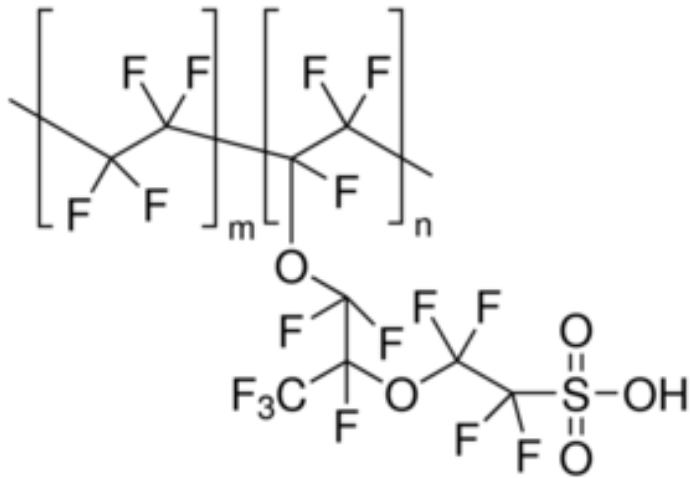
- First developed for the Apollo missions
  - Updated version still used in current space shuttle
- Based around concentrated KOH electrolyte with Ni anode and catalytic cathode (such as Pt, Pd or Ag)
- Cheap fuel cell to produce ✓
- Susceptible to CO<sub>2</sub> poisoning: ✗
  - $2 \text{KOH} + \text{CO}_2 \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$
  - K<sub>2</sub>CO<sub>3</sub> goes on to block electrode
- Requires pure H<sub>2</sub> and O<sub>2</sub> ✗





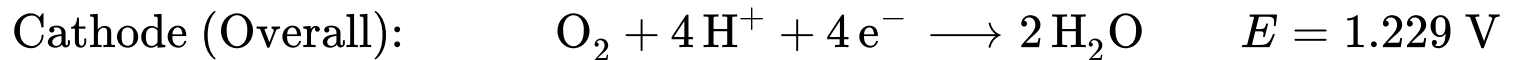
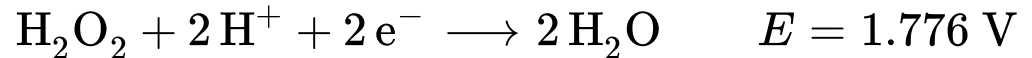
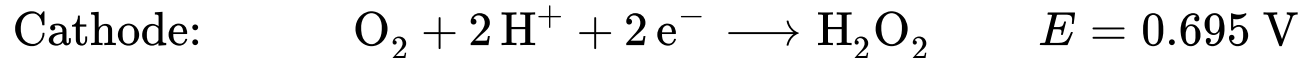
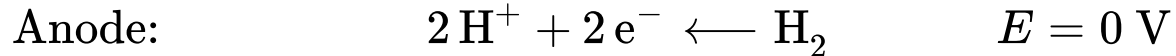
# Proton exchange membrane fuel cell (PEMFC)

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



- Use H<sub>2</sub> as fuel, but can work with MeOH (less efficiently)

# PEMFC + H<sub>2</sub>

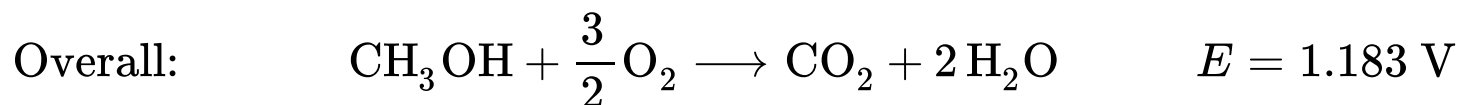
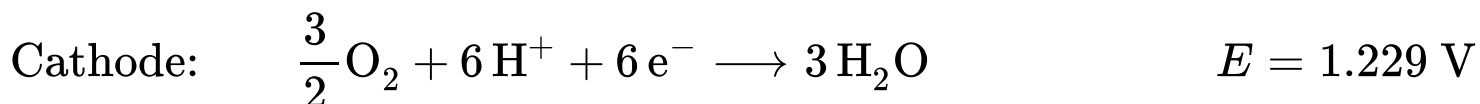
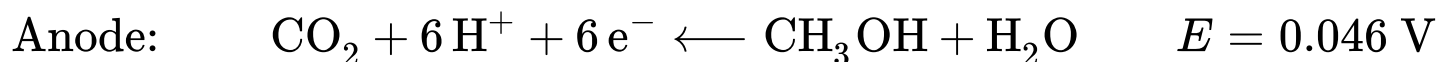


- PEMFCs give good Low-temperature (< 100 °C) operation ✓
  - Quick to start/stop
  - Suitable for portable applications
- In acidic conditions, H<sub>2</sub>O<sub>2</sub> forms ✗
  - Corrodes carbon-containing electrodes
  - Lowers cell voltage
  - Requires Pt or Pd catalysts to promote H<sub>2</sub>O<sub>2</sub> decomposition
    - ~0.5 mg cm<sup>-3</sup>
    - Expensive
    - Poor tolerance to CO or NH<sub>3</sub>
- Require careful hydration to ensure H<sup>+</sup> 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



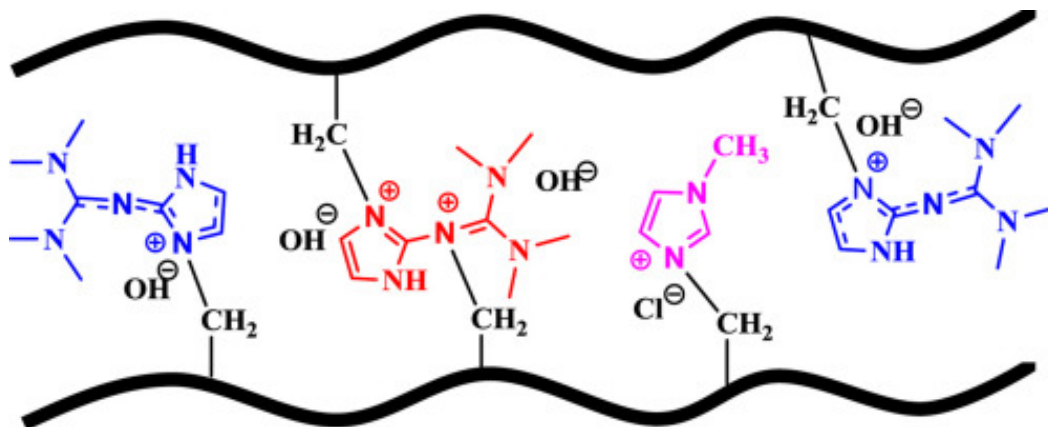
Problems:

- 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?

- $\text{OH}^-$  conduction removes the problems associated with  $\text{H}_2\text{O}_2$  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  $\text{OH}^-$  conducting polymers currently have low ionic conductivity at practical temperatures!

# Phosphoric Acid (PAFC)

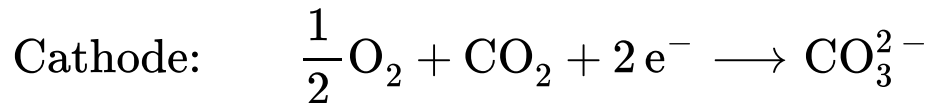
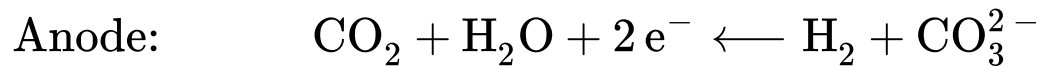
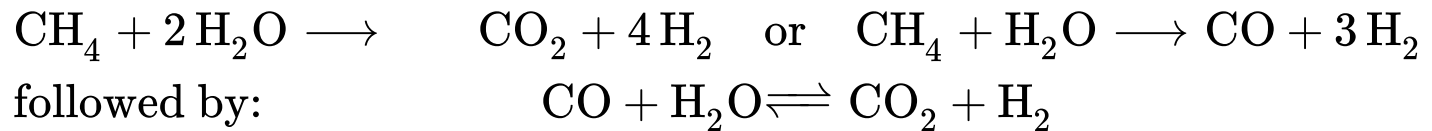
Operates at 200 °C

- High temperature acid prevents build up of  $\text{H}_2\text{O}_2$  ✓
- Temperature makes cell more tolerant to  $\text{CO}_2$  impurities ✓
- Below 150 °C conductivity is low ✗
- Above 200 °C  $\text{H}_3\text{PO}_4$  decomposes into a range of acids ✗
- Hot  $\text{H}_3\text{PO}_4$  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 H<sub>2</sub>:

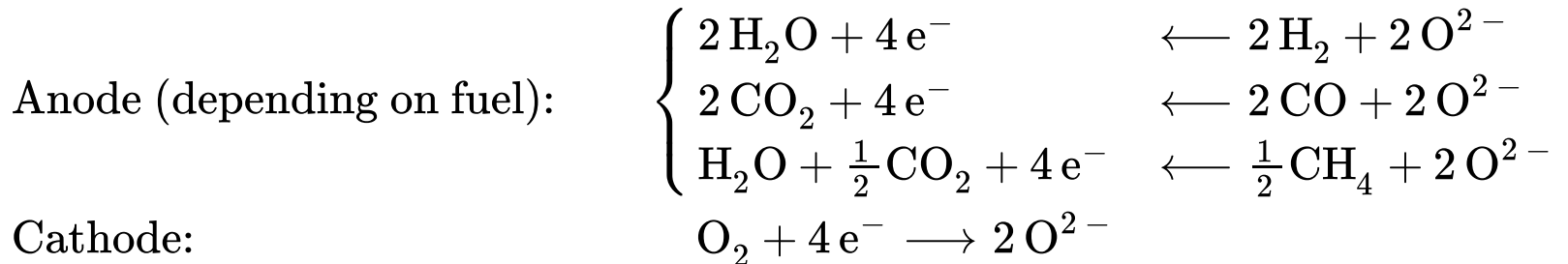


- Cathode - porous NiO
- Anode - porous Ni
- No need for expensive catalyst materials
- Molten alkali-metal carbonates are highly corrosive
  - Conductivity is also limited
- Ni electrodes are sensitive to sulfur contaminants



# 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

# 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

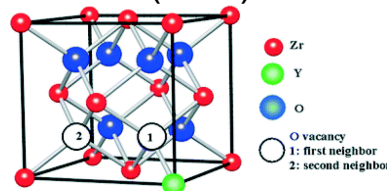
- Ni has high electronic conductivity and catalytic activity
- High ionic conductivity from electrolyte

## 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  $\text{O}_2$  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

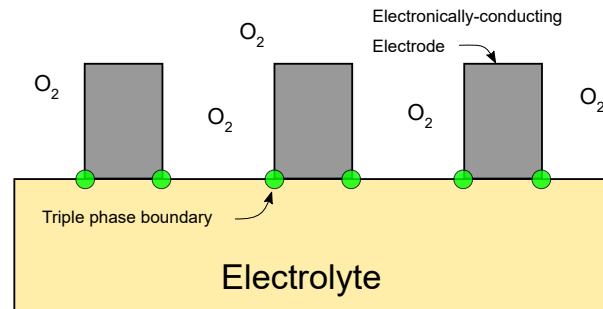
As well as: Chemical stability, similar thermal expansion, cost, ...

# Improving electrodes

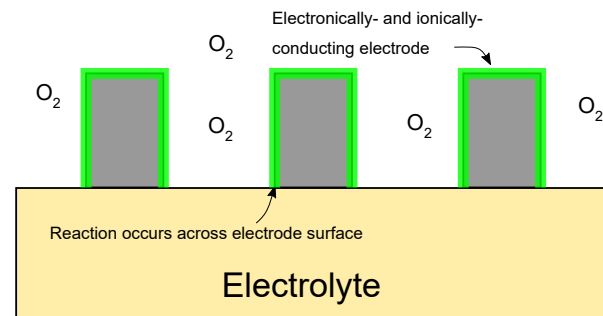
Ideally want a perfect mixed electronic/ionic conductor, with high chemical stability, high catalytic activity etc...

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



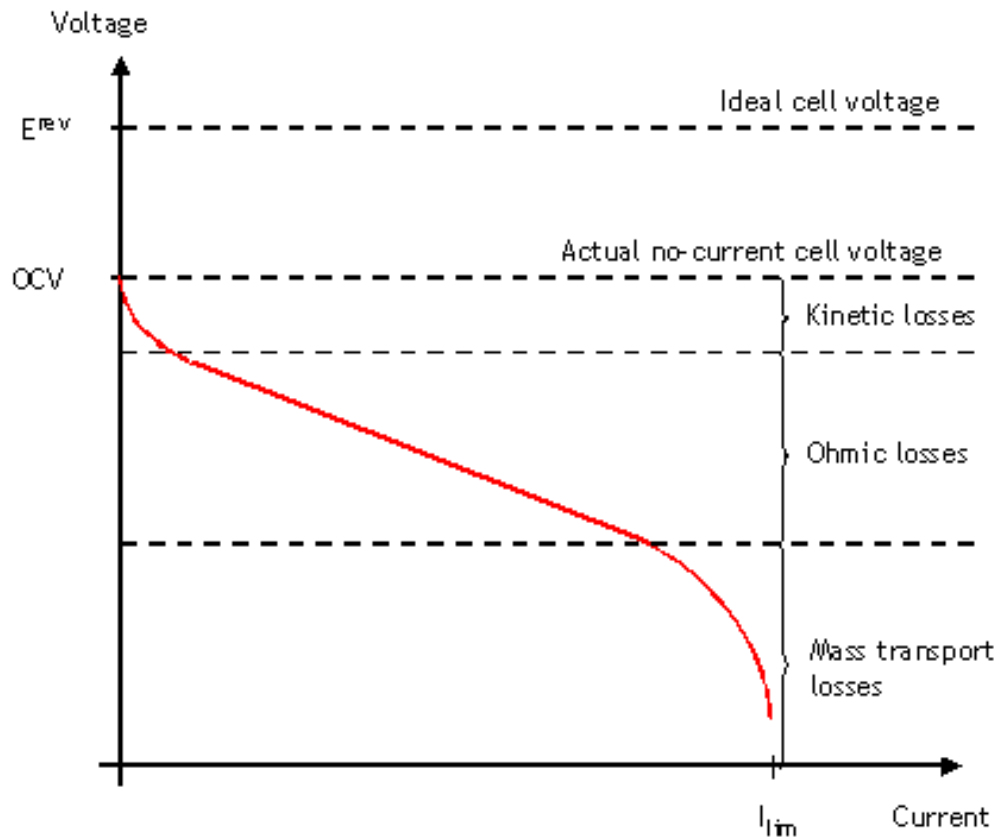
## Mixed conductor



# 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:

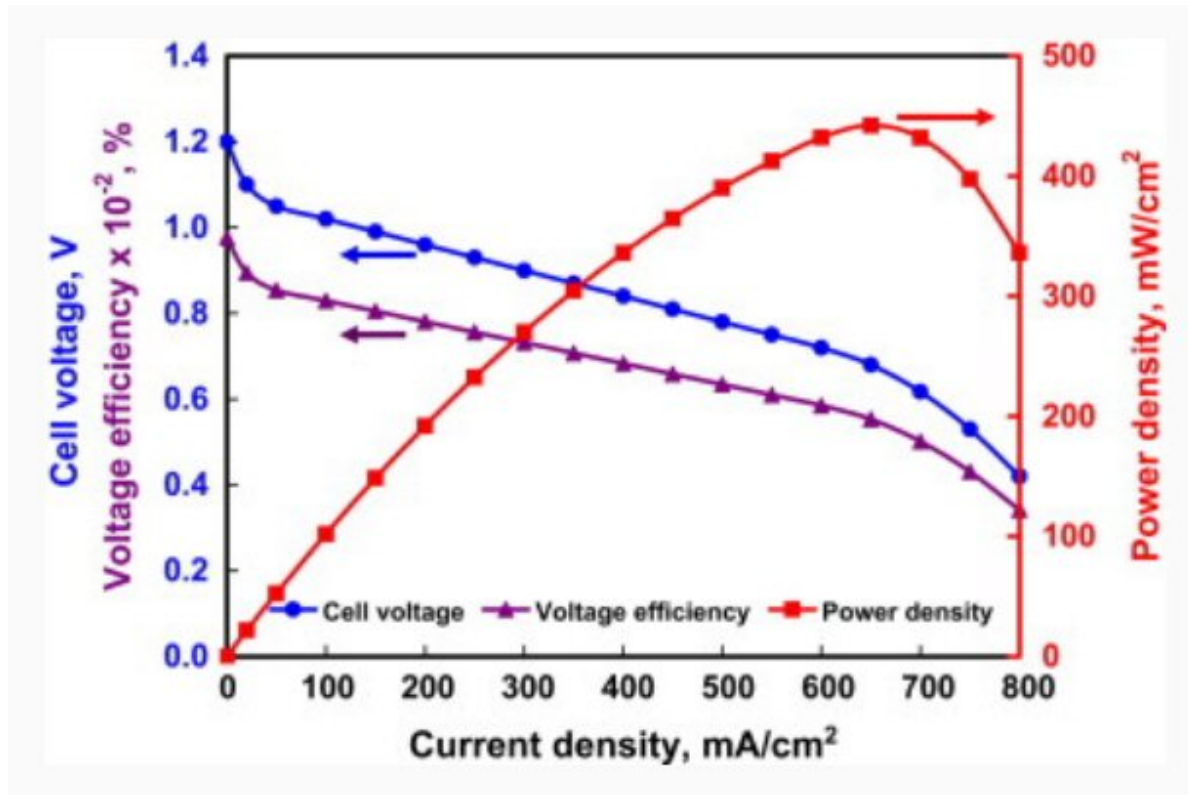


# Practical efficiency

- 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
  - O<sub>2</sub> 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 O<sub>2</sub> 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

