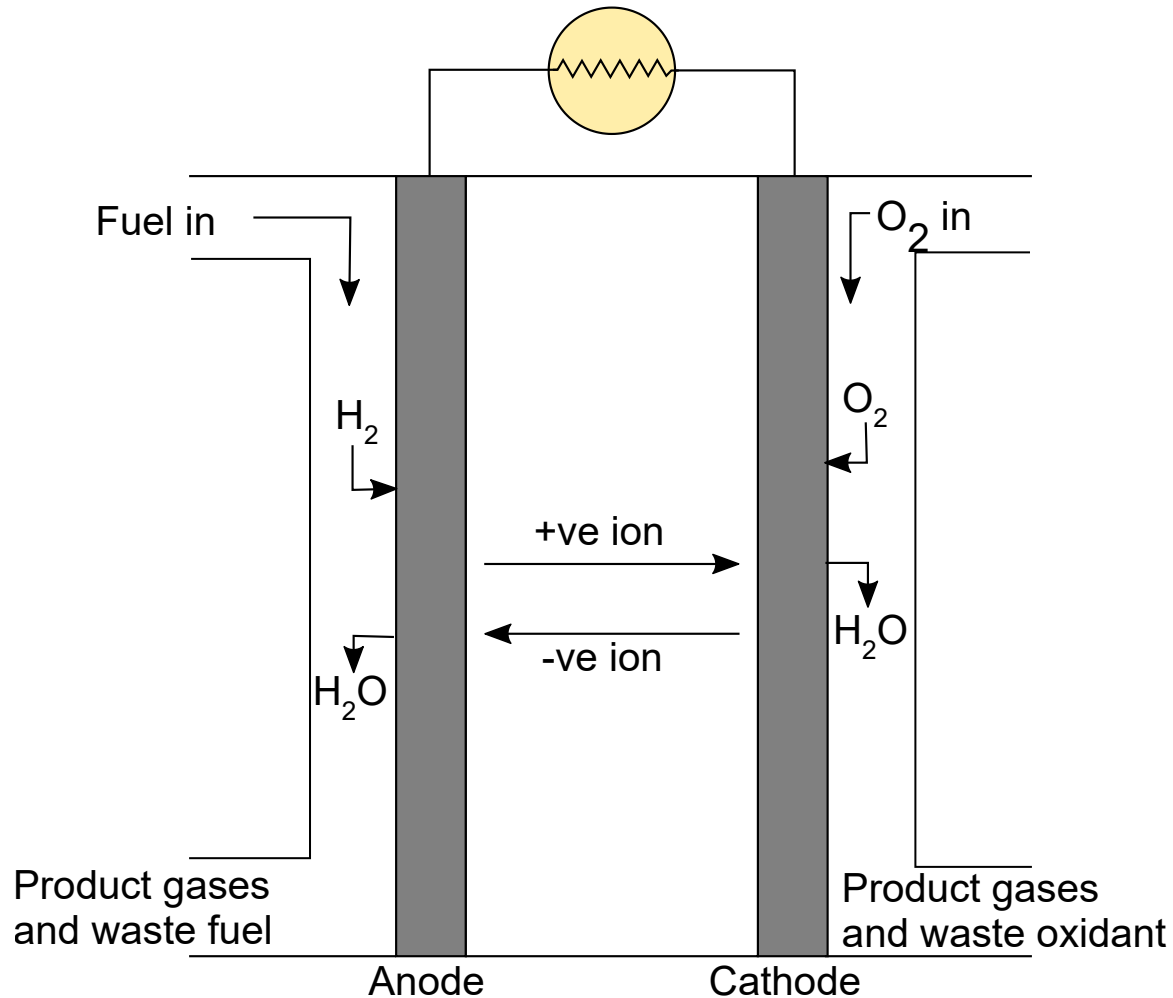# Fuel Cells

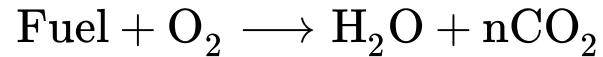# Fuel Cells

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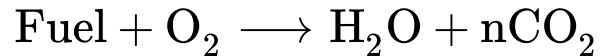
Fuel cell history

Fuel cell fundamentals

$$\text{Fuel} + \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{nCO}_2$$

- Fuel cells a divided into *low-temperature (LT)* (< 200 °C) and *high-temperature (HT)* (> 450 °C).

- H_2 is the preferred fuel

    - Particularly for LT devices.
    - Doesn't produce CO_2

Fuel cell fundamentals

$$\text{Fuel} + \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{nCO}_2$$

- Fuel cells a divided into *low-temperature (LT)* (< 200 °C) and *high-temperature (HT)* (> 450 °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) can also be used, particularly for HT devices

  - *e.g.* for CH_4, steam reforming $\left(\text{CH}_4 + \text{H}_2\text{O} \xrightarrow{>700^\circ C} \text{CO} + 3\,\text{H}_2\right)$ 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 $2\,\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O}$ $(\Delta H = -571.6\ \mathrm{kJ\ mol^{-1}})$:

Cathode: $\quad 4\,\mathrm{H^+} + \mathrm{O_2} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} \qquad \mathrm{E} = +1.229\ \mathrm{V}$

Anode: $\qquad\quad 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longleftarrow 2\,\mathrm{H_2} \qquad\quad E = 0.00\ \mathrm{V}$
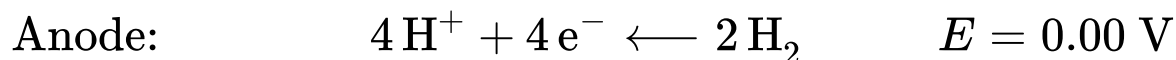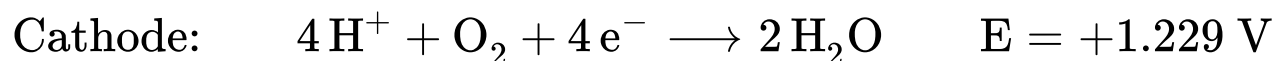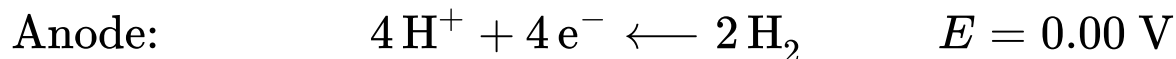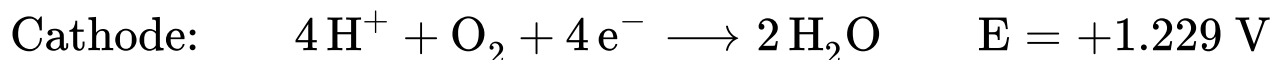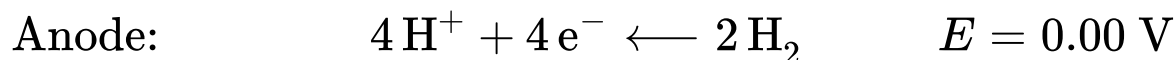
Fuel cell efficiency

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 $2\,\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O}$ $(\Delta H = -571.6\ \mathrm{kJ\ mol^{-1}})$:

$$\begin{aligned}
\text{Cathode:} \quad & 4\,\mathrm{H^+} + \mathrm{O_2} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} \qquad E = +1.229\ \mathrm{V} \\
\text{Anode:} \quad & 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longleftarrow 2\,\mathrm{H_2} \qquad E = 0.00\ \mathrm{V}
\end{aligned}$$

$$\begin{aligned}
\Delta G &= -nFE \\
&= -4 \times F \times 1.229 \\
&= -474.3\ \mathrm{kJ\ mol^{-1}} \qquad (\text{per mole } \mathrm{O_2})
\end{aligned}$$

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 $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ $(\Delta H = -571.6\ \text{kJ mol}^{-1})$:

$$\begin{array}{llll}
\text{Cathode:} & 4\,H^+ + O_2 + 4\,e^- \longrightarrow 2\,H_2O & & E = +1.229\ \text{V} \\
\text{Anode:} & 4\,H^+ + 4\,e^- \longleftarrow 2\,H_2 & & E = 0.00\ \text{V}
\end{array}$$

$$\begin{aligned}
\Delta G &= -nFE \\
&= -4 \times F \times 1.229 \\
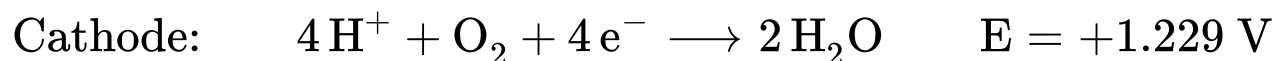&= -474.3\ \text{kJ mol}^{-1} \qquad (\text{per mole } O_2)
\end{aligned}$$

Efficiency = η = -474.3 / 571.6 = **83%**

Efficiency with temperature

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

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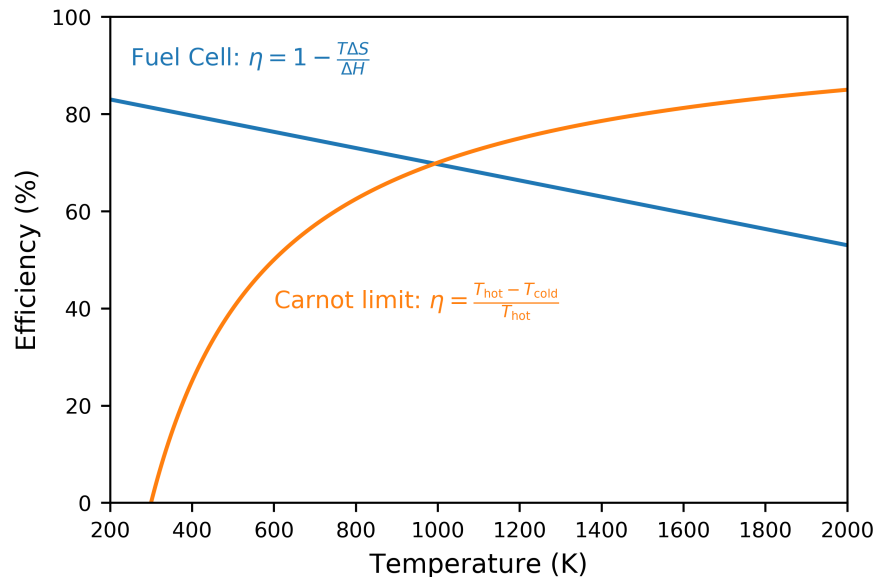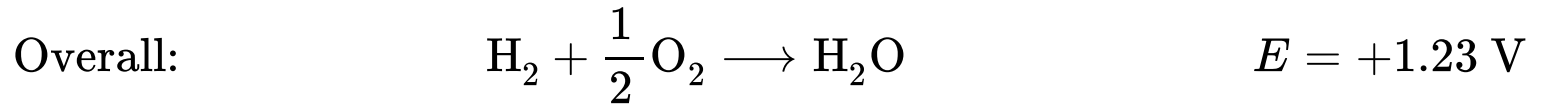
$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}$$

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:
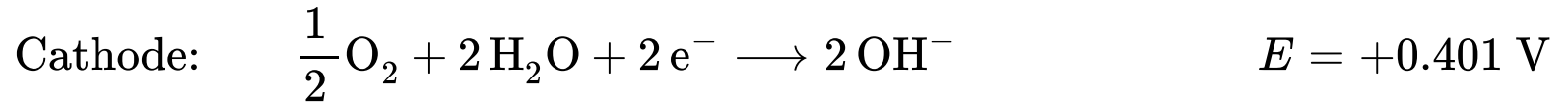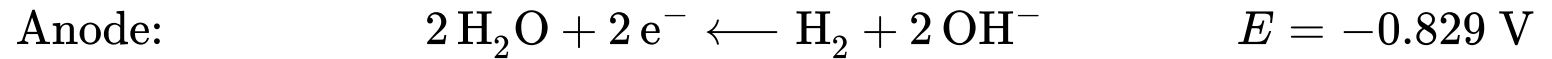
$$\eta = \frac{T_{\mathrm{hot}} - T_{\mathrm{cold}}}{T_{\mathrm{hot}}}$$

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	
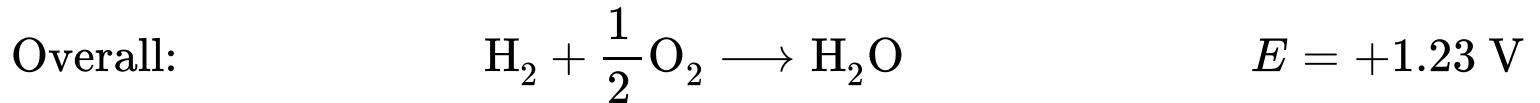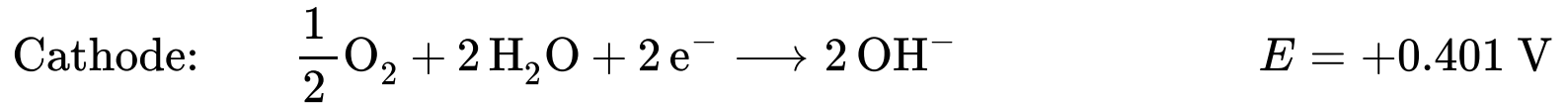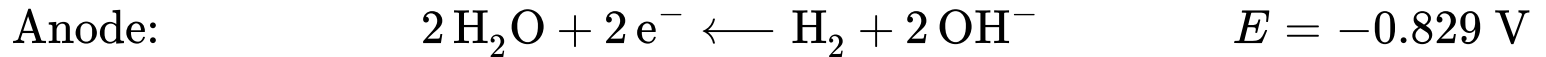
L. Carrette, *Fuel Cells*, 2001, 5.

Alkaline Fuel cell (AFC)

Anode: $\qquad 2\,H_2O + 2\,e^- \longleftarrow H_2 + 2\,OH^- \qquad E = -0.829\ \text{V}$

Cathode: $\quad \dfrac{1}{2}O_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,OH^- \qquad E = +0.401\ \text{V}$

Overall: $\qquad H_2 + \dfrac{1}{2}O_2 \longrightarrow H_2O \qquad E = +1.23\ \text{V}$

Alkaline Fuel cell (AFC)

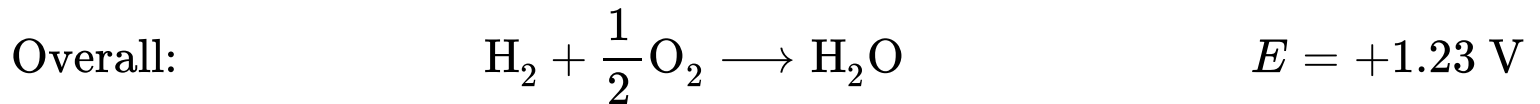|		
Anode:	$2\,H_2O + 2\,e^- \longleftarrow H_2 + 2\,OH^-$	$E = -0.829\text{ V}$
Cathode:	$\frac{1}{2}O_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,OH^-$	$E = +0.401\text{ V}$
Overall:	$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$	$E = +1.23\text{ V}$

- 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 ✔

Alkaline Fuel cell (AFC)

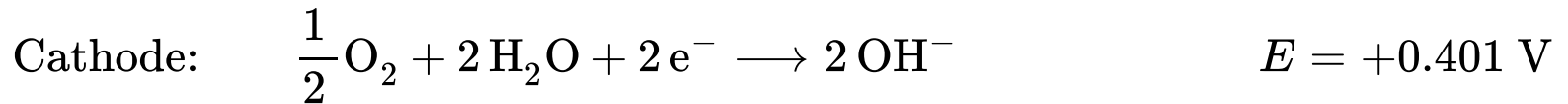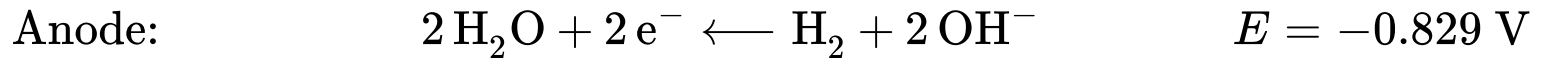|		
Anode:	$2\,H_2O + 2\,e^- \longleftarrow H_2 + 2\,OH^-$	$E = -0.829\text{ V}$
Cathode:	$\frac{1}{2}O_2 + 2\,H_2O + 2\,e^- \longrightarrow 2\,OH^-$	$E = +0.401\text{ V}$
Overall:	$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$	$E = +1.23\text{ V}$

- 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_2 poisoning: ✘
  - $2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$
  - K_2CO_3 goes on to block electrode
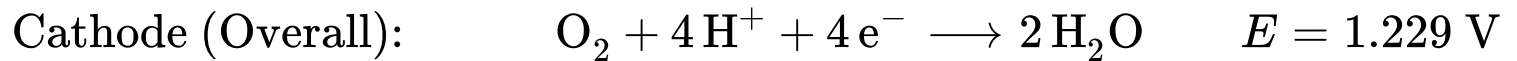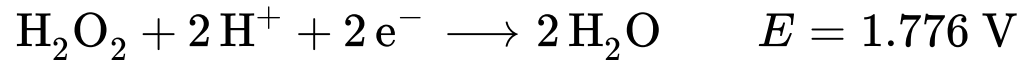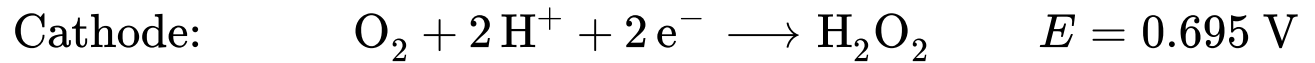
- Requires pure H_2 and O_2 ✘

Proton exchange membrane fuel cell (PEMFC)

- First developed for the Gemini space vehicle
- Based around an acidic proton-conducting polymer

  - *e.g.* Nafion
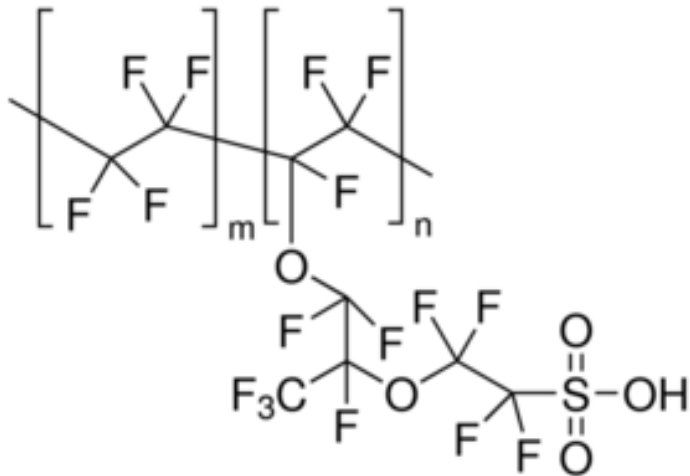
- Use H_2 as fuel, but can work with MeOH (less efficiently)

PEMFC + H$_2$

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

PEMFC + H$_2$

Anode:	$2\,H^+ + 2\,e^- \longleftarrow H_2$	$E = 0\;V$
Cathode:	$O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O_2$	$E = 0.695\;V$
	$H_2O_2 + 2\,H^+ + 2\,e^- \longrightarrow 2\,H_2O$	$E = 1.776\;V$
Cathode (Overall):	$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$	$E = 1.229\;V$
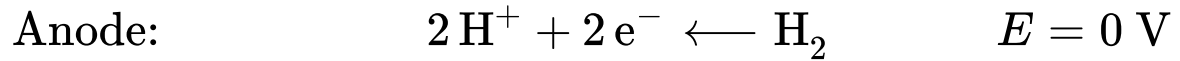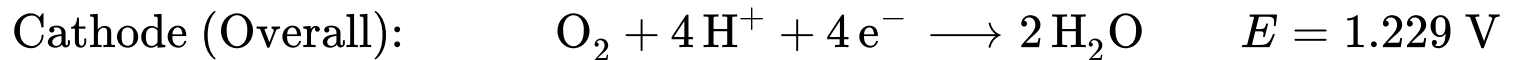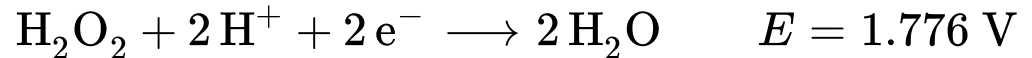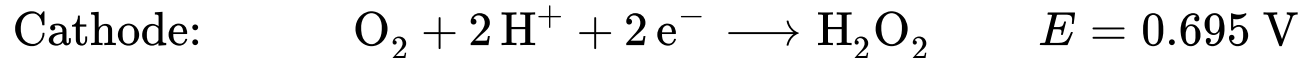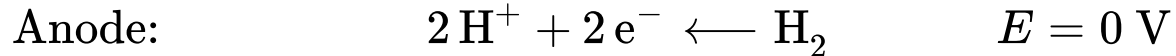
- PEMFCs give good Low-temperature (< 100 °C) operation ✔
  - Quick to start/stop
  - Suitable for portable applications

- In acidic conditions, H$_2$O$_2$ forms ✗

  - Corrodes carbon-containing electrodes
  - Lowers cell voltage
  - Requires Pt or Pd catalysts to promote H$_2$O$_2$ decomposition

    - ~0.5 mg cm^{-3}
    - Expensive
    - Poor tolerance to CO or NH$_3$

- 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

$$\text{Anode:} \qquad CO_2 + 6\,H^+ + 6\,e^- \longleftarrow CH_3OH + H_2O \qquad E = 0.046 \text{ V}$$

$$\text{Cathode:} \qquad \frac{3}{2}O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O \qquad E = 1.229 \text{ V}$$

$$\text{Overall:} \qquad CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2\,H_2O \qquad E = 1.183 \text{ V}$$

PEMFC + Methanol

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

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

$$\text{Anode:} \qquad CO_2 + 6\,H^+ + 6\,e^- \longleftarrow CH_3OH + H_2O \qquad E = 0.046\ \text{V}$$

$$\text{Cathode:} \qquad \frac{3}{2}O_2 + 6\,H^+ + 6\,e^- \longrightarrow 3\,H_2O \qquad E = 1.229\ \text{V}$$

$$\text{Overall:} \qquad CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2\,H_2O \qquad E = 1.183\ \text{V}$$
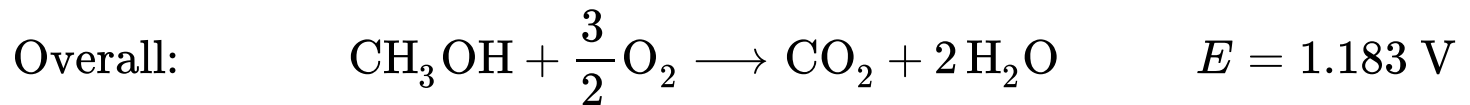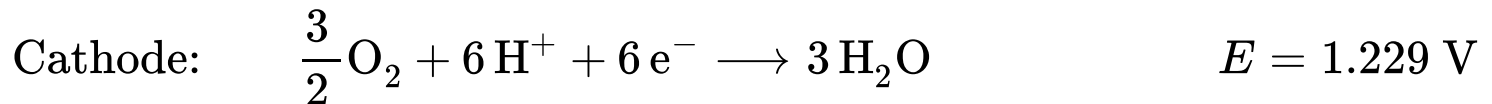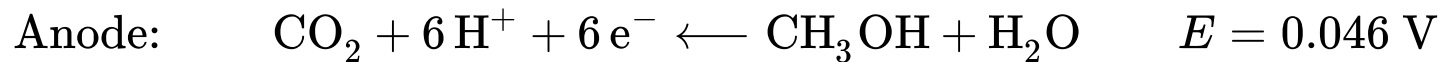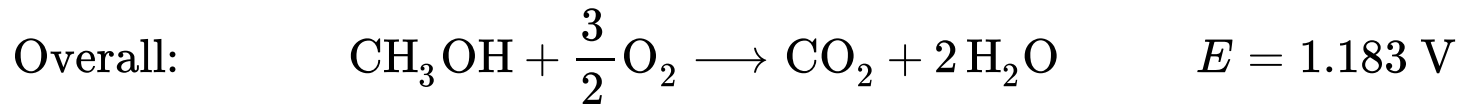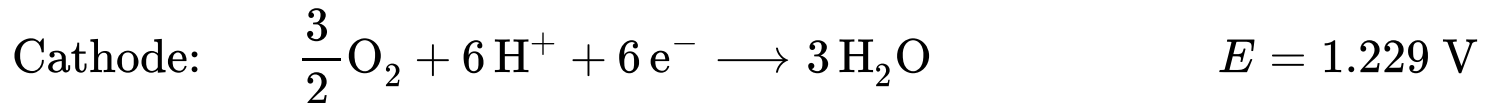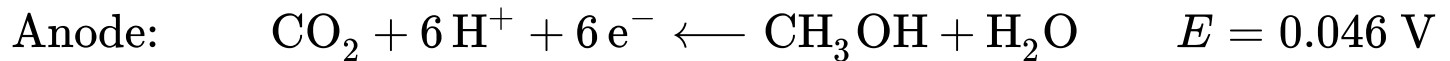
Problems:

- MeOH is fairly soluble in membrane, crossing from anode to cathode ✗
  - Reduces cell voltage to ~0.5 V
- CO is formed in a side-reaction, blocking reaction sites ✗
  - Improved by adding more Pt catalyst (~3 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
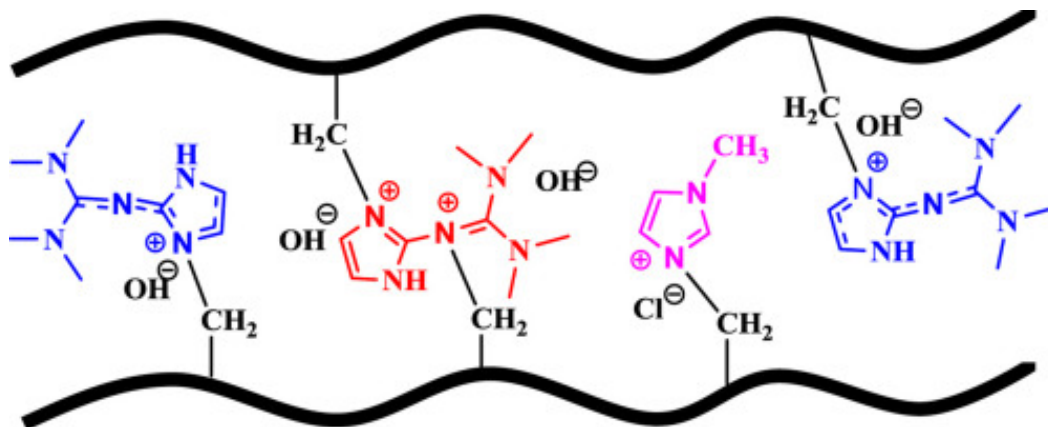
Unfortunately, current OH⁻ conducting polymers currently have low ionic conductivity at practical temperatures!

Phosphoric Acid (PAFC)

Operates at 200 °C
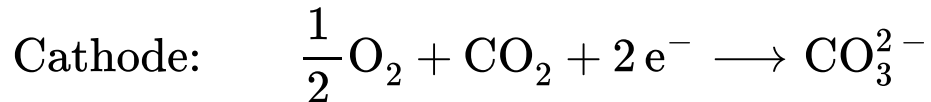
- High temperature acid prevents build up of H_2O_2 ✓

- 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 H_2:

$$CH_4 + 2\,H_2O \longrightarrow \quad CO_2 + 4\,H_2 \quad \text{or} \quad CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

followed by: $\qquad CO + H_2O \rightleftharpoons CO_2 + H_2$

Anode: $\qquad CO_2 + H_2O + 2\,e^- \longleftarrow H_2 + CO_3^{2-}$

Cathode: $\qquad \dfrac{1}{2}O_2 + CO_2 + 2\,e^- \longrightarrow CO_3^{2-}$

Molten Carbonate (MCFC)

- Optimum temperature 560 °C
- Range of fuel choices

  - High temperature allows steam reforming (water-gas shift reaction) to generate H_2:

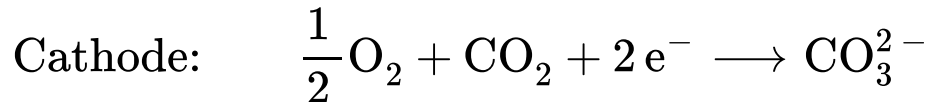$$CH_4 + 2\,H_2O \longrightarrow \quad CO_2 + 4\,H_2 \quad \text{or} \quad CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

followed by: $\quad CO + H_2O \rightleftharpoons CO_2 + H_2$

$$\text{Anode:} \quad CO_2 + H_2O + 2\,e^- \longleftarrow H_2 + CO_3^{2-}$$
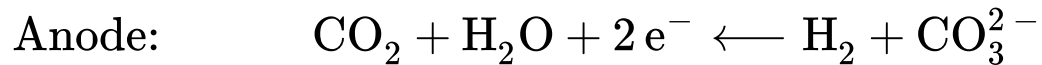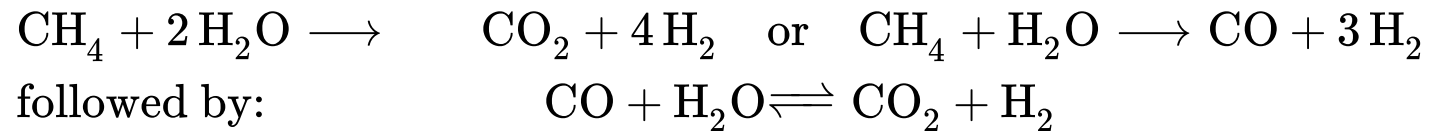
$$\text{Cathode:} \quad \frac{1}{2}O_2 + CO_2 + 2\,e^- \longrightarrow CO_3^{2-}$$
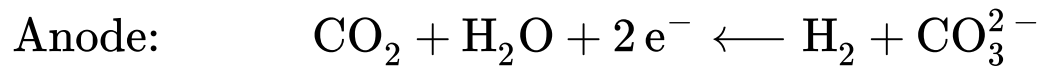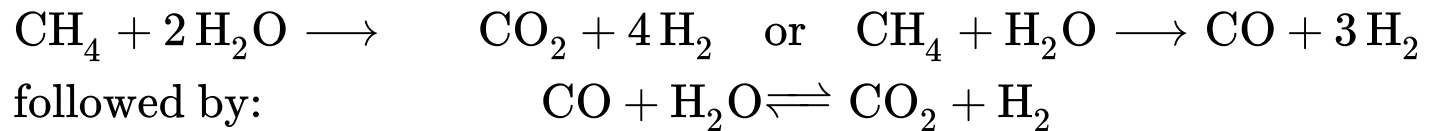
- Cathode - porous NiO
- Anode - porous Ni
- No need for expensive catalyst materials
- Molten alkali-metal carbonates are highly corrosive

  - 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

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-}:

$$\text{Anode (depending on fuel):} \quad \begin{cases} 2\,H_2O + 4\,e^- & \longleftarrow 2\,H_2 + 2\,O^{2-} \\ 2\,CO_2 + 4\,e^- & \longleftarrow 2\,CO + 2\,O^{2-} \\ H_2O + \frac{1}{2}\,CO_2 + 4\,e^- & \longleftarrow \frac{1}{2}\,CH_4 + 2\,O^{2-} \end{cases}$$

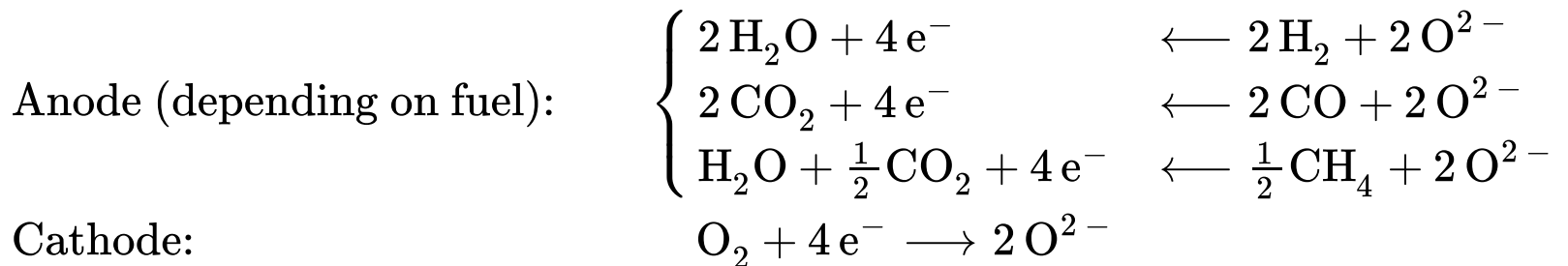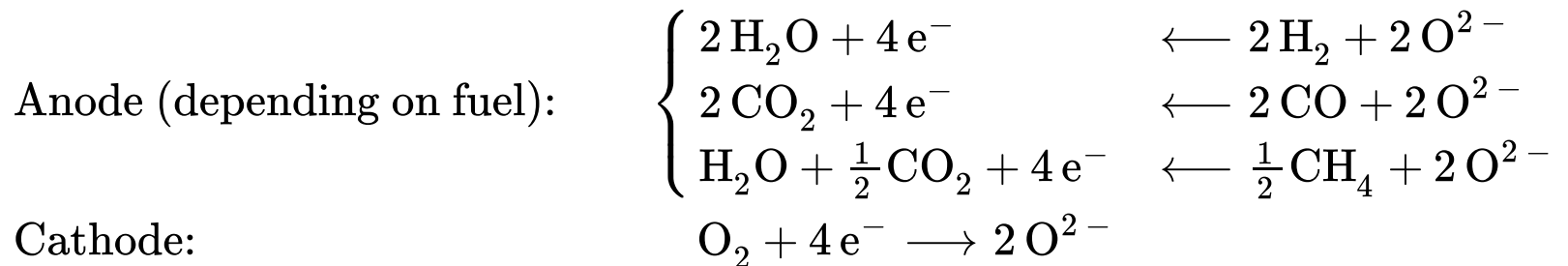$$\text{Cathode:} \quad O_2 + 4\,e^- \longrightarrow 2\,O^{2-}$$

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-}:

Anode (depending on fuel):
$$\begin{cases} 2\,H_2O + 4\,e^- & \longleftarrow 2\,H_2 + 2\,O^{2-} \\ 2\,CO_2 + 4\,e^- & \longleftarrow 2\,CO + 2\,O^{2-} \\ H_2O + \frac{1}{2}CO_2 + 4\,e^- & \longleftarrow \frac{1}{2}CH_4 + 2\,O^{2-} \end{cases}$$

Cathode:
$$O_2 + 4\,e^- \longrightarrow 2\,O^{2-}$$

- 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

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

Electrolyte

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

Cathode

- High electronic conductivity
- High catalytic activity for O_2 reduction
- High ionic conductivity
- Stable in HT oxidising conditions

Requirements for SOFC materials

Anode

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

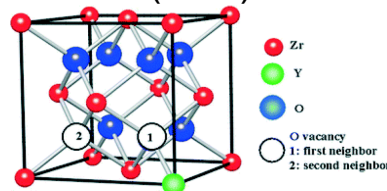Typically a cermet (*i.e.* mixture) of Ni and electrolyte

- 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.

- $Gd_{0.1}Ce_{0.9}O_{1.95}$ (CGO)
- $Y_{0.15}Zr_{0.85}O_{1.925}$ (YSZ)

Zr
Y
O
O vacancy
1: first neighbor
2: second neighbor

Cathode

- High electronic conductivity
- High catalytic activity for O_2 reduction
- High ionic conductivity
- Stable in HT oxidising conditions

- $La_{1-x}Sr_xCoO_{3-y}$: a good mixed conductor, but with high thermal expansion
- La_2NiO_{4+x}: an intersitial oxide ion conductor

Requirements for SOFC materials

Anode

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

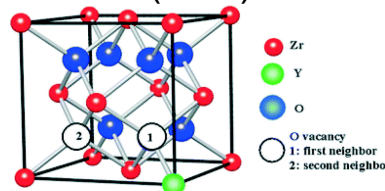Typically a cermet (*i.e.* mixture) of Ni and electrolyte

- 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.

- $Gd_{0.1}Ce_{0.9}O_{1.95}$ (CGO)
- $Y_{0.15}Zr_{0.85}O_{1.925}$ (YSZ)

Zr
Y
O
O vacancy
1: first neighbor
2: second neighbor

Cathode

- High electronic conductivity
- High catalytic activity for O_2 reduction
- High ionic conductivity
- Stable in HT oxidising conditions

- $La_{1-x}Sr_xCoO_{3-y}$: a good mixed conductor, but with high thermal expansion
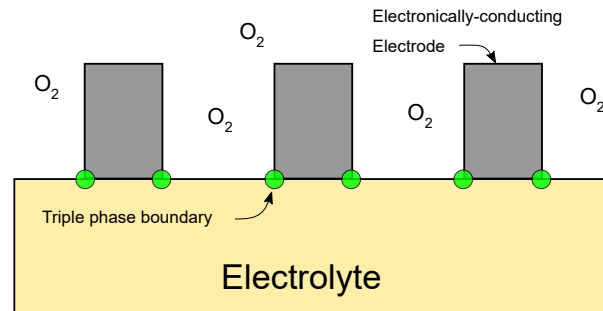- La_2NiO_{4+x}: an intersitial oxide ion conductor

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**
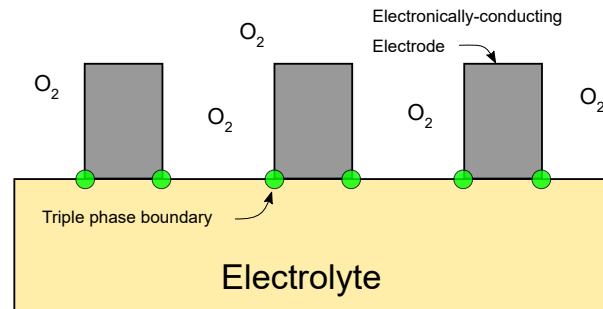
Electronic Conductor
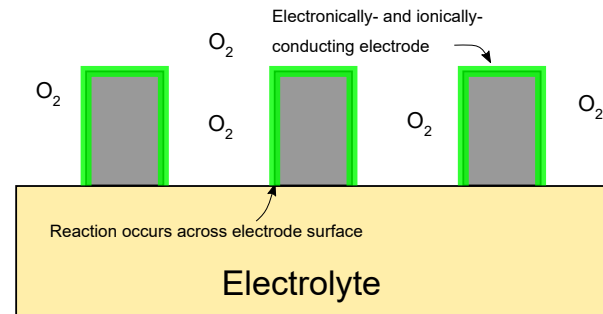
Improving electrodes

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

Electronically-conducting Electrode

O_2

O_2

O_2

O_2

O_2

O_2

Triple phase boundary

Electrolyte

Mixed conductor

Electronically- and ionically-conducting electrode

O_2

O_2

O_2

O_2
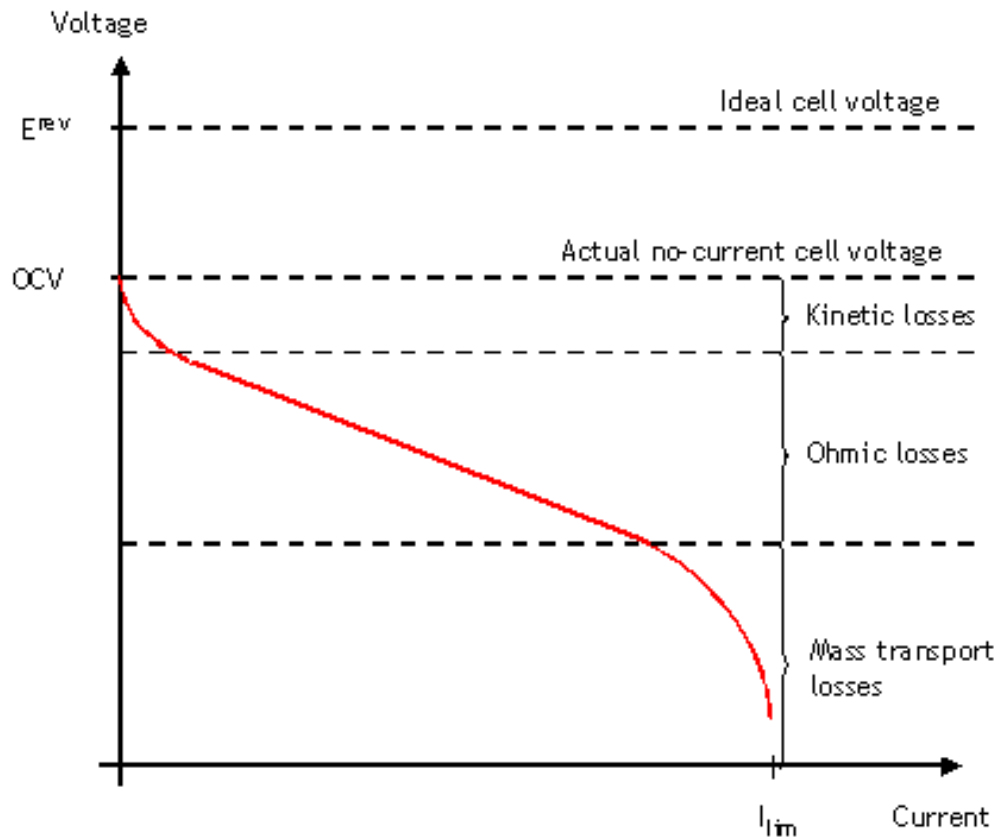
O_2

O_2

Reaction occurs across electrode surface

Electrolyte

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

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_2 reduction is kinetically slow
    - Improved by higher temperatures or presence of catalysts

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_2 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

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_2 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_2 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 ↓ as current ↑, power (= IV) will show a peak:
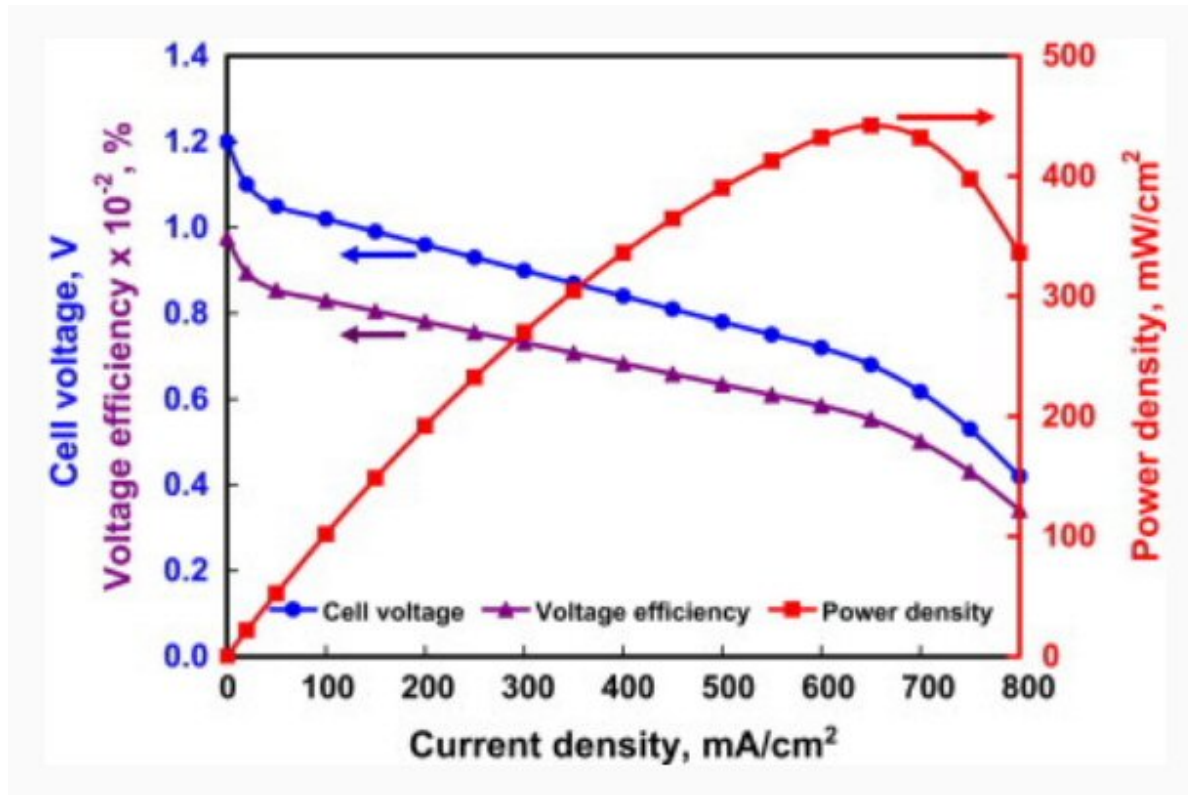
Typically, these peak powers are lower than batteries