UNIVERSITY OF
CAMBRIDGE

Ionic conductors

Lecture 9

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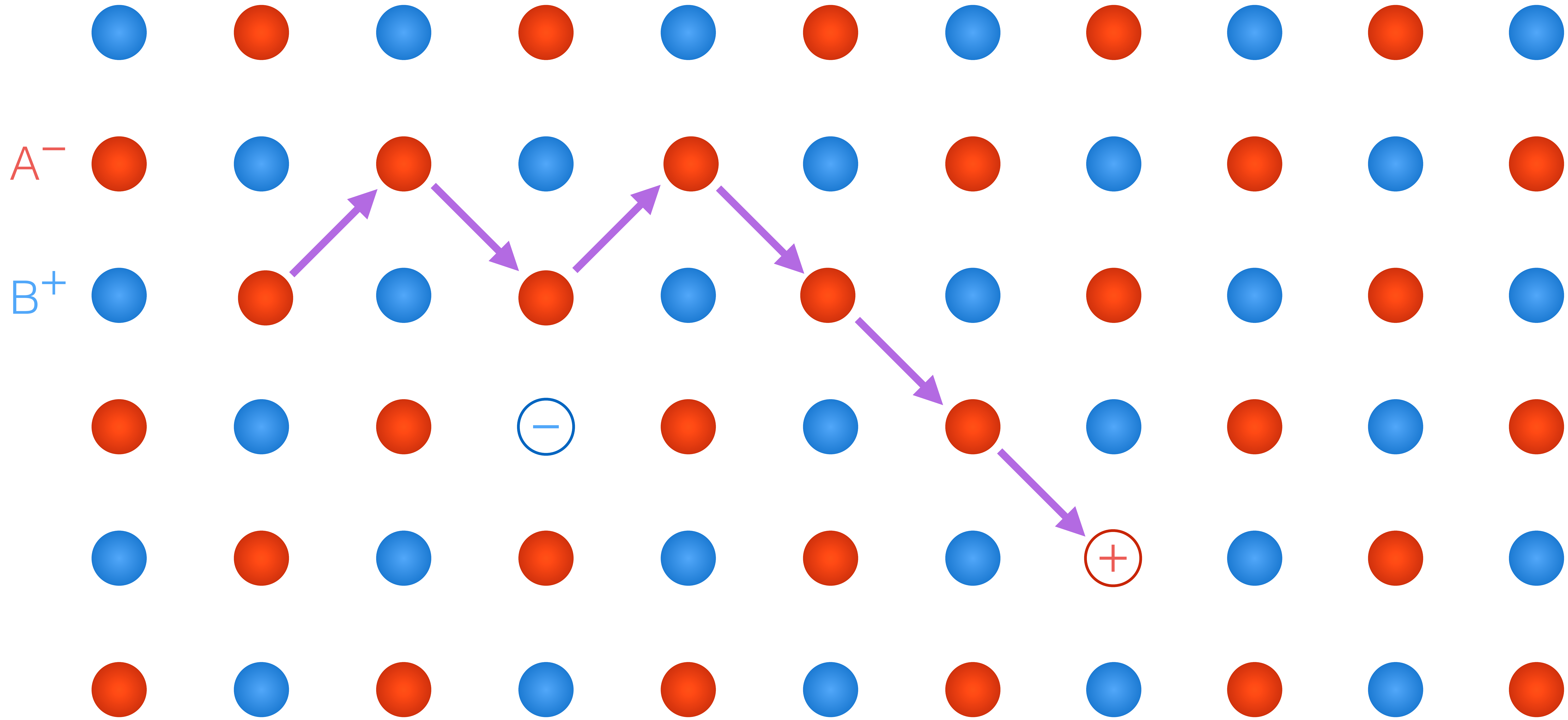
Course B: Materials for Devices

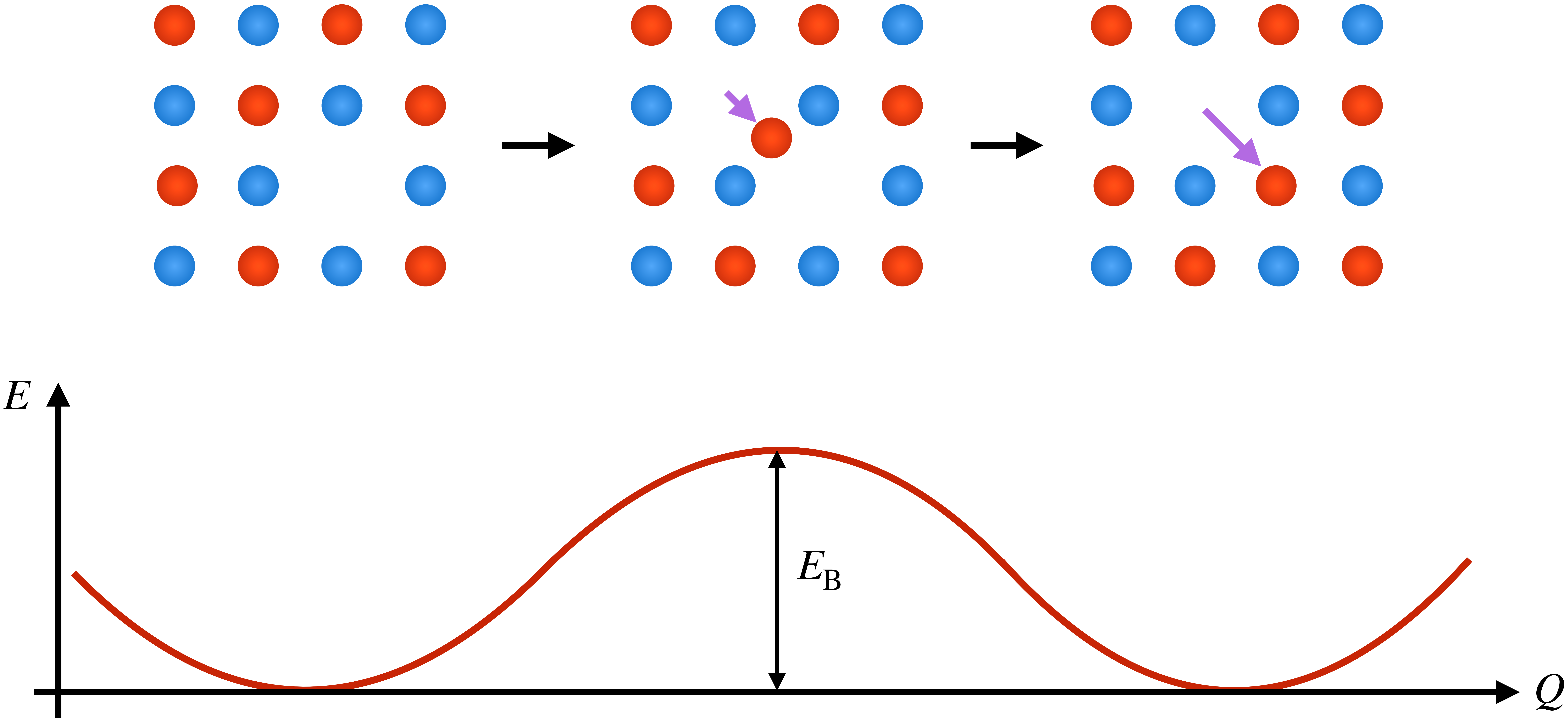
Professor M does Science

http://www.tcm.phy.cam.ac.uk/~bm418/

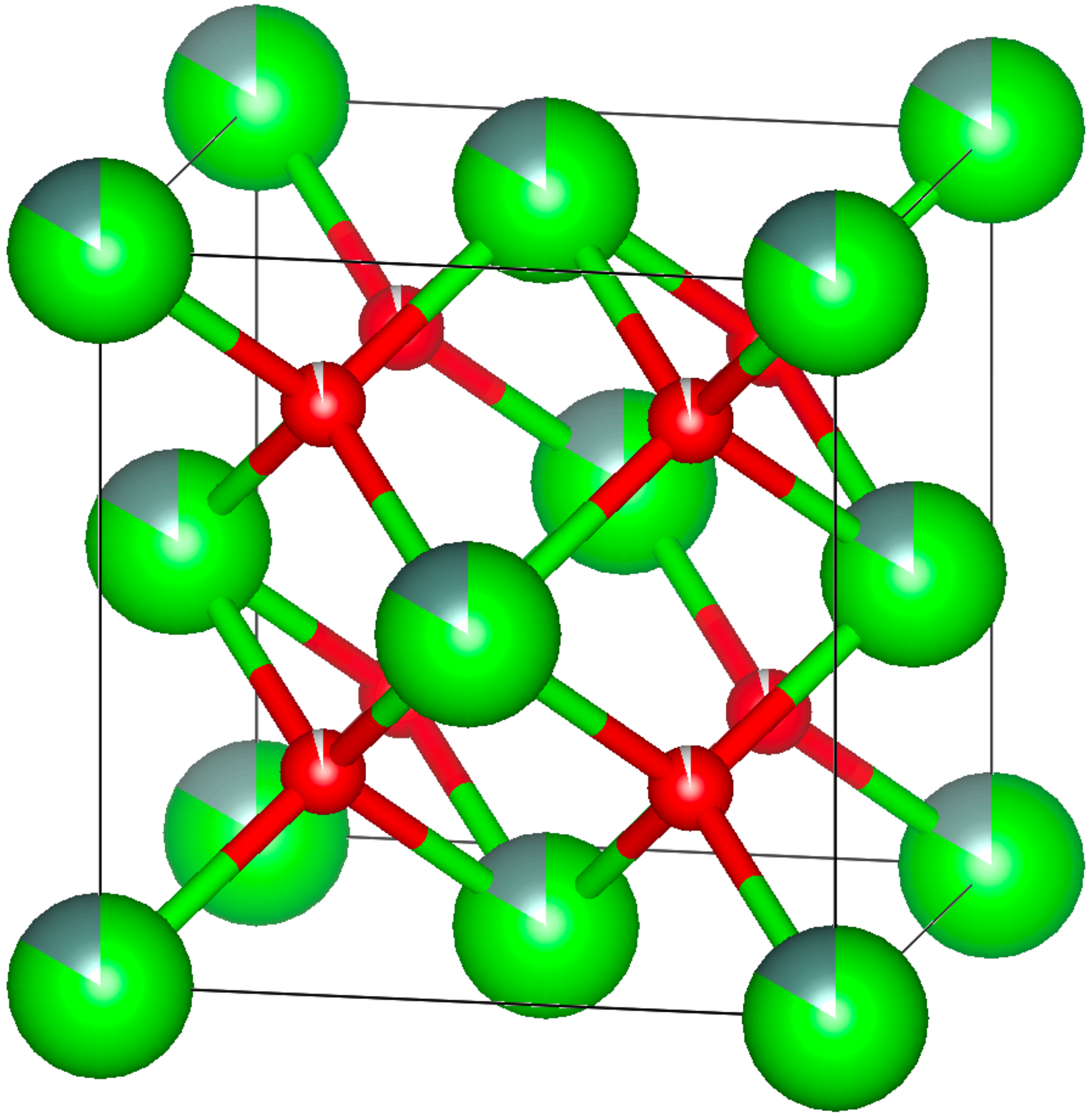
Ionic motion in crystals



Site jump

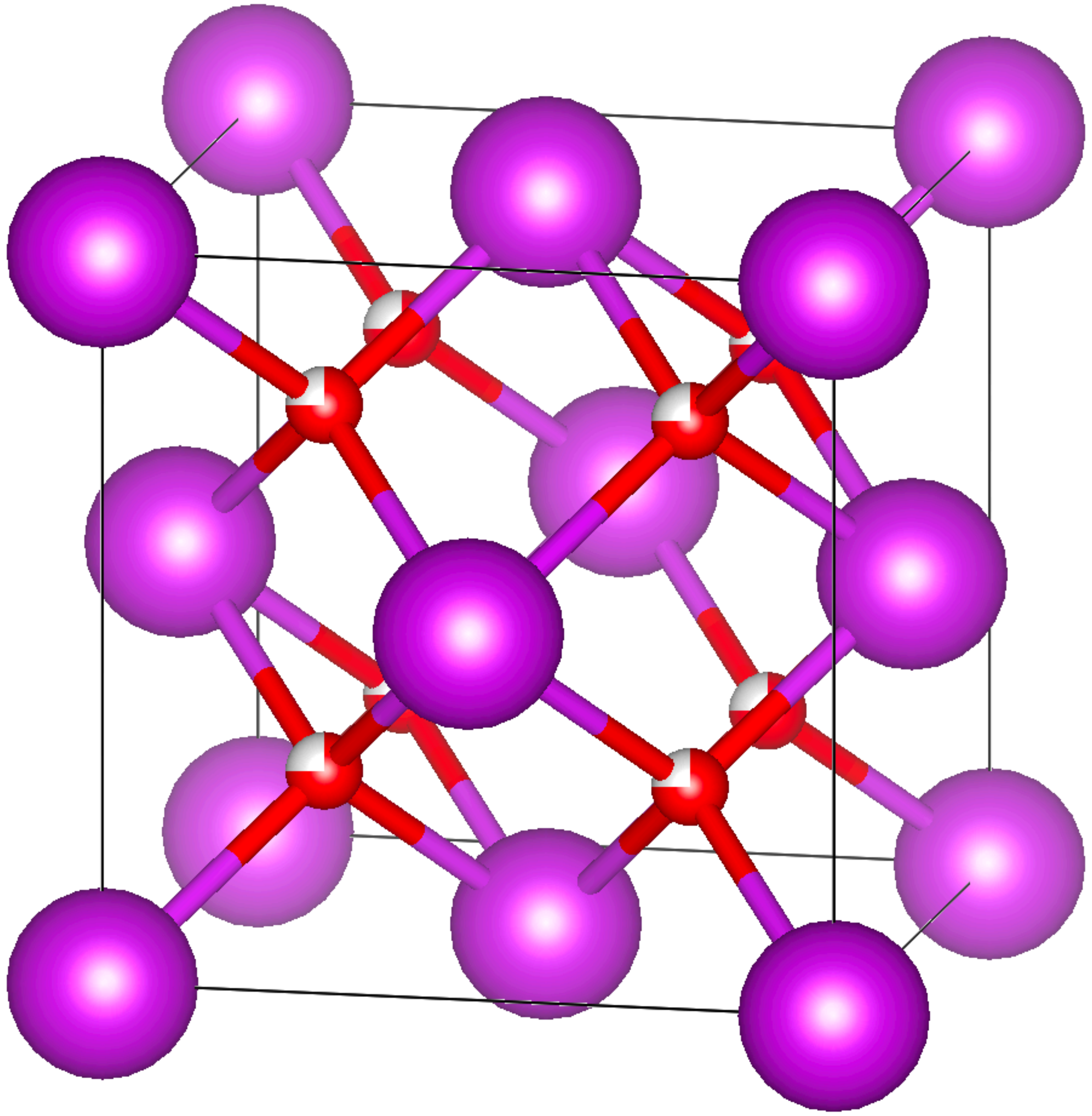


Yttria-stabilised zirconia (YSZ)



- Yttria-stabilised zirconia
- Oxygen vacancies mediate ionic conduction

δ-Bi_2O_3

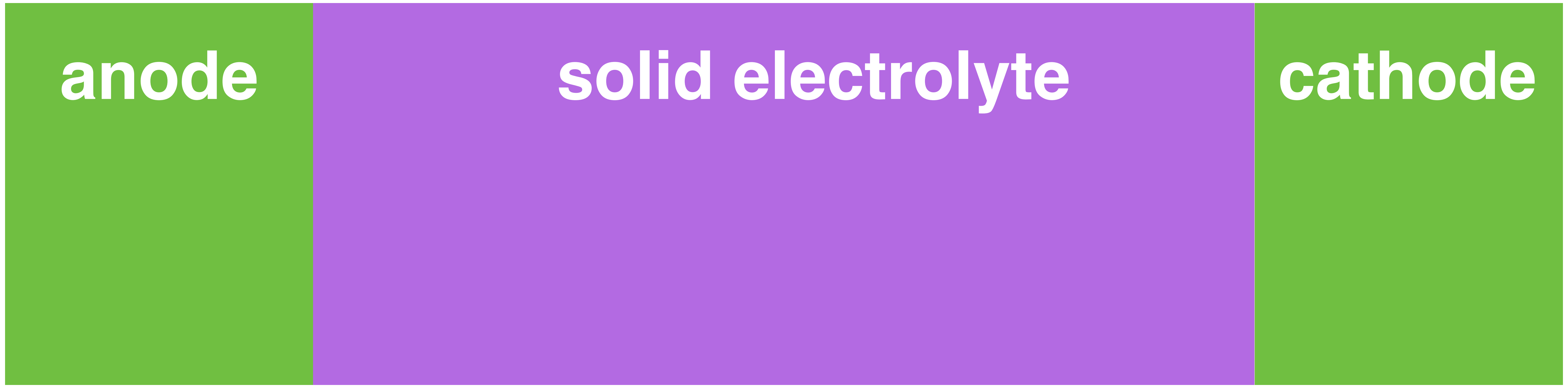


- δ-Bi_2O_3
- Average of 6/8 oxygens per cell
- Oxygen vacancies mediate ionic conduction

Oxygen sensors

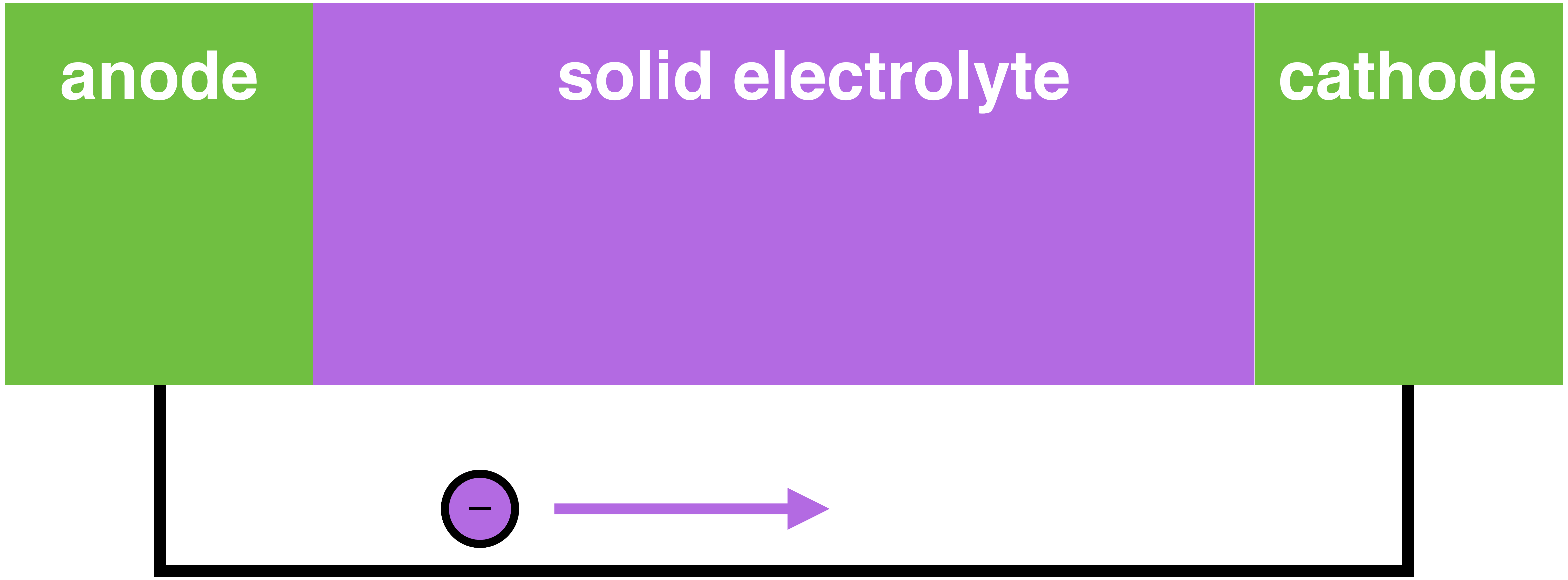
Credit: George McCaa, U.S. Bureau of Mines

Oxygen concentration cell

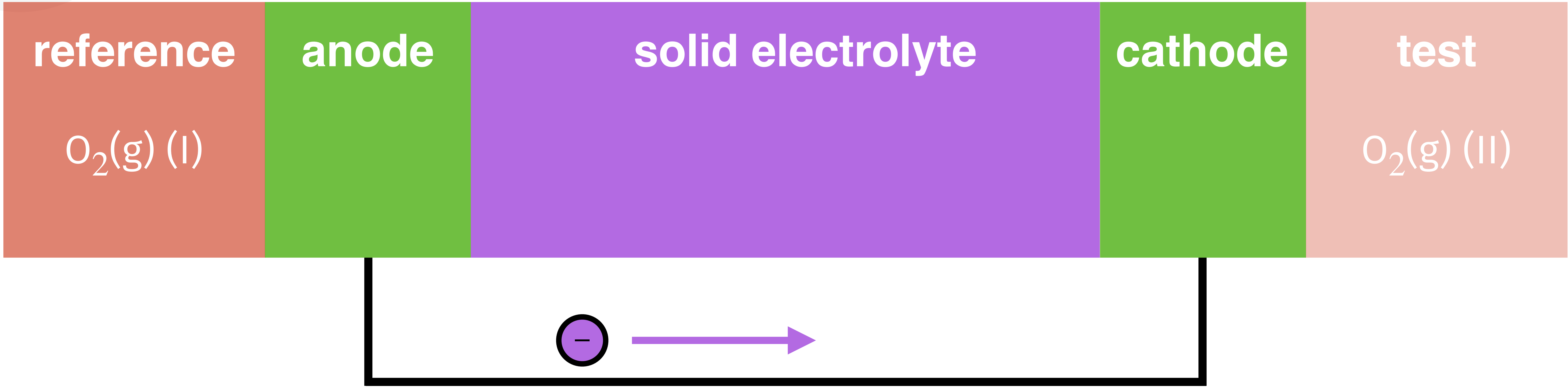


- Electrolyte: conducting through ionic motion but not through electron motion (e.g. YSZ)
- Anode: electrical conductor through which current enters the device (e.g. Pt)
- Cathode: electrical conductor through which current leaves the device (e.g. Pt)

Oxygen concentration cell

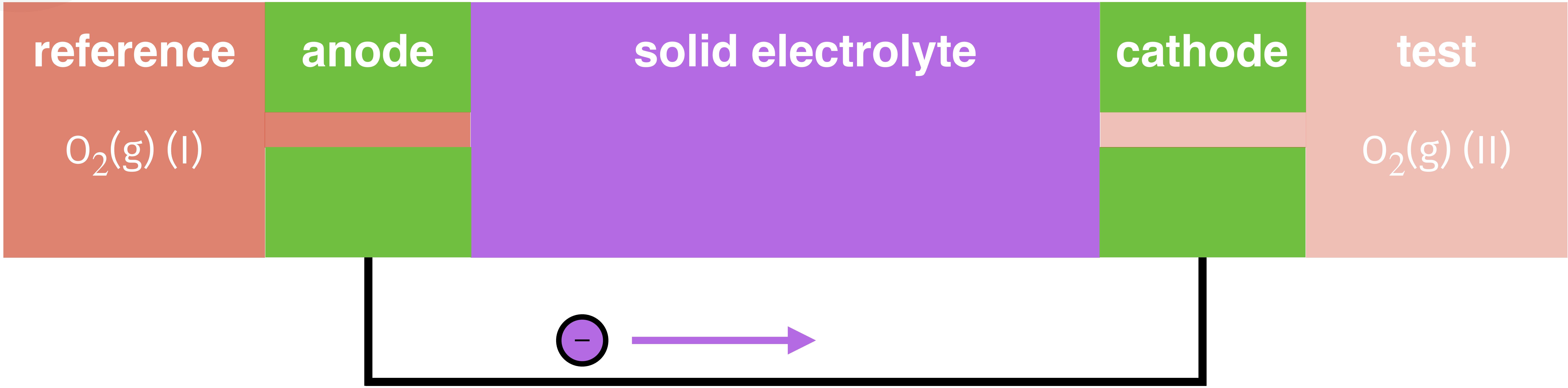


Oxygen concentration cell



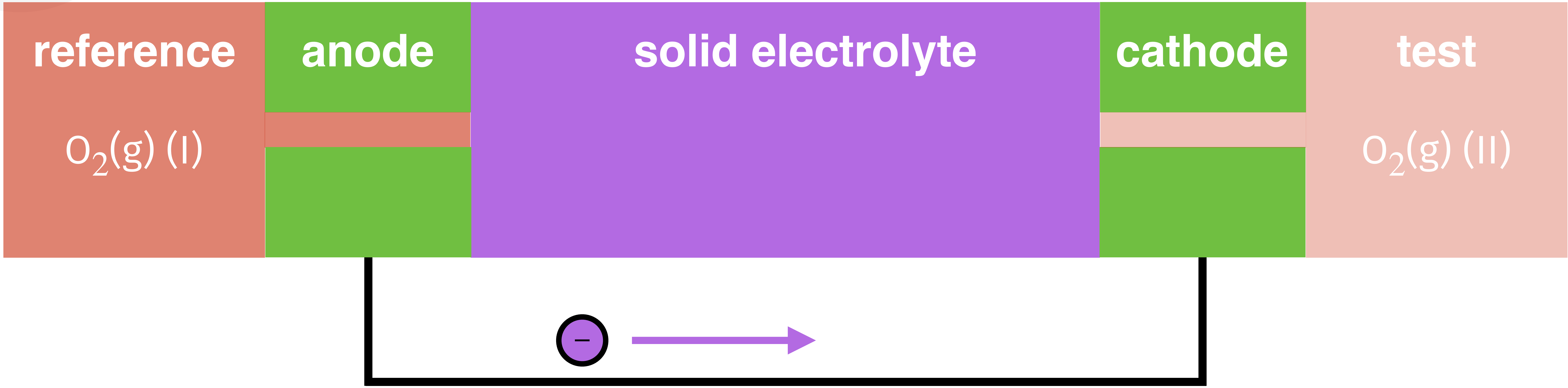
- Reference sample: known partial pressure of oxygen
- Test sample: unknown partial pressure of oxygen

Oxygen concentration cell



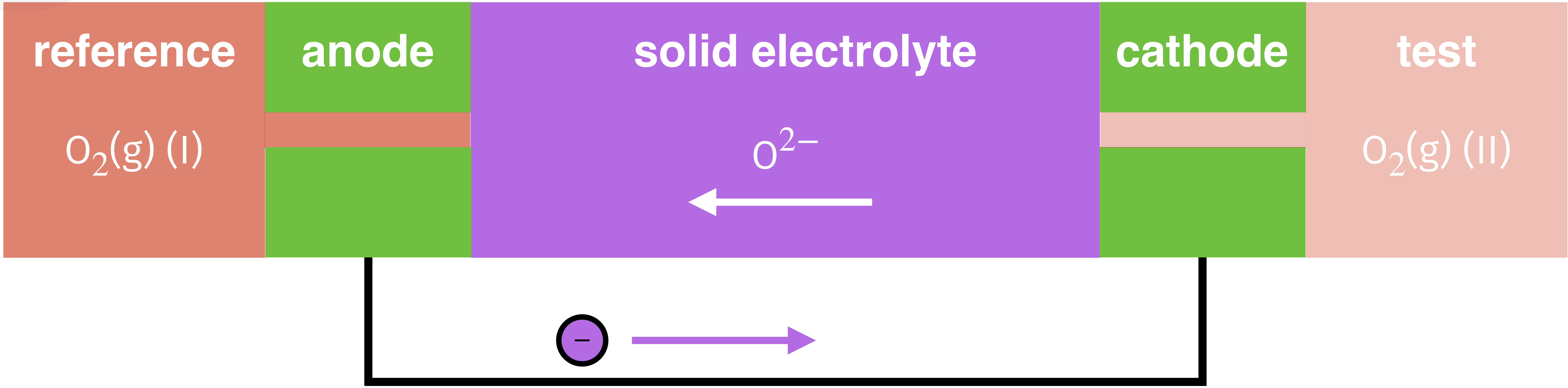
- Pt electrodes are porous to let gas through

Oxygen concentration cell



Pt(s) | O_2(g) (I) | YSZ | O_2(g) (II) | Pt(s)

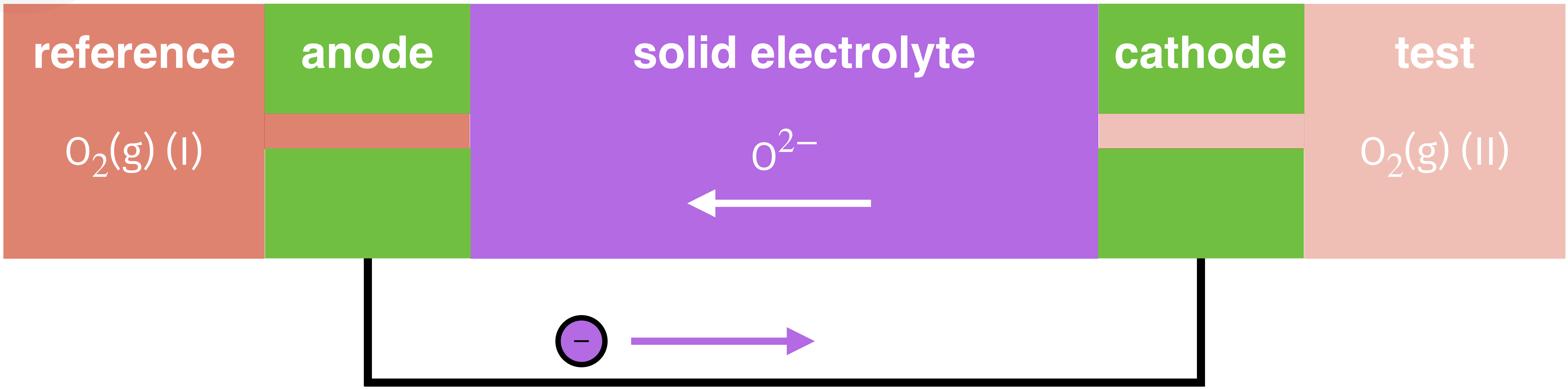
Oxygen concentration cell



Pt(s) | O_2(g) (I) | YSZ | O_2(g) (II) | Pt(s)

pO_2(g) (I) < pO_2(g) (II):

Oxygen concentration cell



reference

$O_2(g)$ (I)

anode

solid electrolyte

O^{2-}

cathode

test

$O_2(g)$ (II)

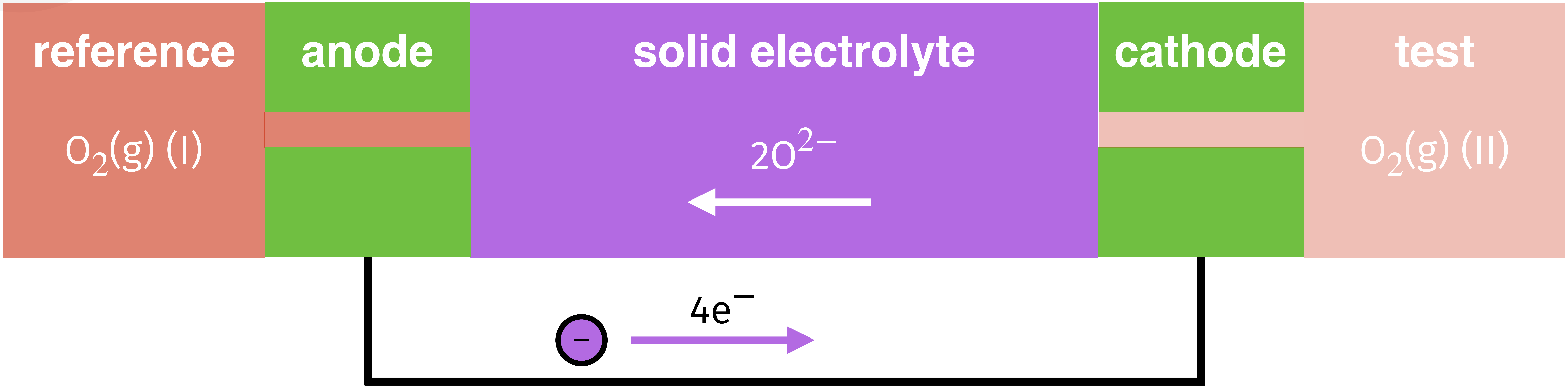
$-$

Pt(s) | $O_2(g)$ (I) | YSZ | $O_2(g)$ (II) | Pt(s)

$pO_2(g)$ (I) < $pO_2(g)$ (II):

- RHS: $O_2(g)\ (II) + 4e^- \longrightarrow 2O^{2-}$ reduction (cathode)
- LHS: $2O^{2-} \longrightarrow O_2(g)\ (I) + 4e^-$ oxidation (anode)

Oxygen concentration cell

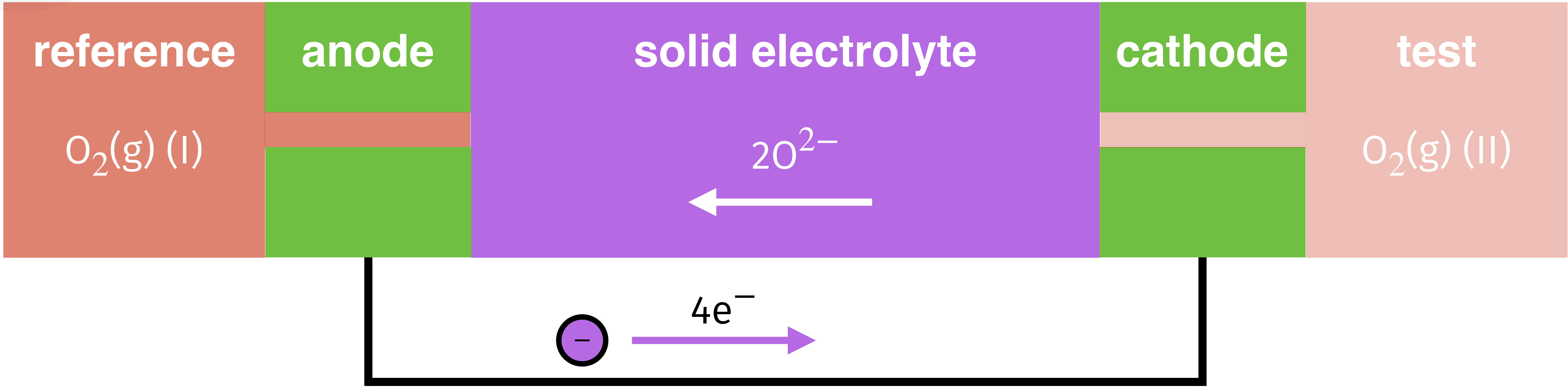


Pt(s) | $O_2(g)$ (I) | YSZ | $O_2(g)$ (II) | Pt(s)

$pO_2(g)$ (I) < $pO_2(g)$ (II):

- RHS: $O_2(g) \text{ (II)} + 4e^- \longrightarrow 2O^{2-}$ reduction (cathode)
- LHS: $2O^{2-} \longrightarrow O_2(g) \text{ (I)} + 4e^-$ oxidation (anode)

Oxygen concentration cell



$$\boxed{E = -\frac{RT}{4F}\ln\left(\frac{pO_2(I)}{pO_2(II)}\right)}$$

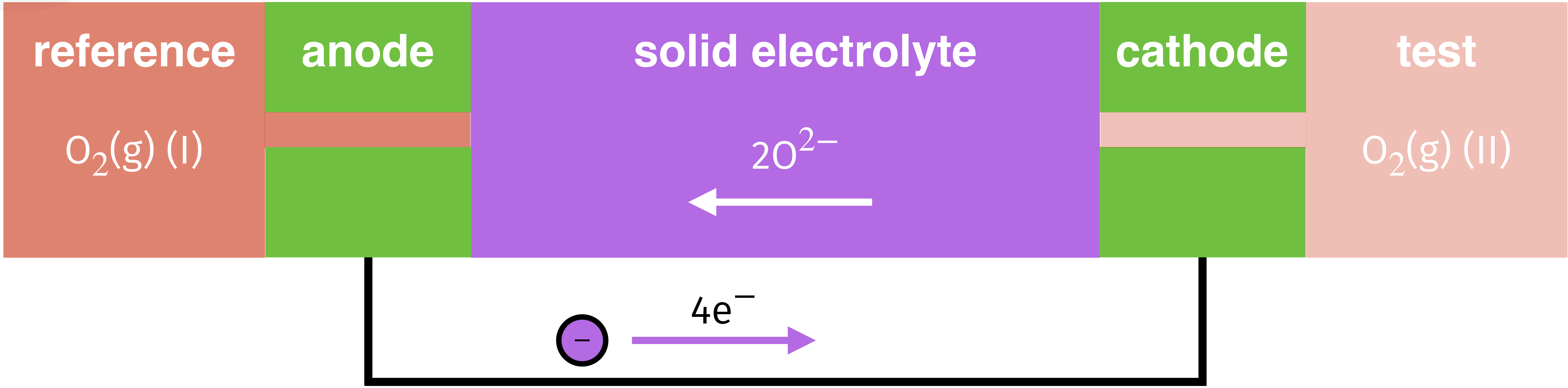
E : electrochemical cell potential [V]

R : gas constant [$8.314\,\mathrm{J\,K^{-1}mol^{-1}}$]

T : temperature [K]

F : Faraday constant [$9.649 \times 10^4\,\mathrm{C\,mol^{-1}}$]

Oxygen concentration cell



$$\boxed{E = -\frac{RT}{4F}\ln\left(\frac{pO_2(I)}{pO_2(II)}\right)}$$

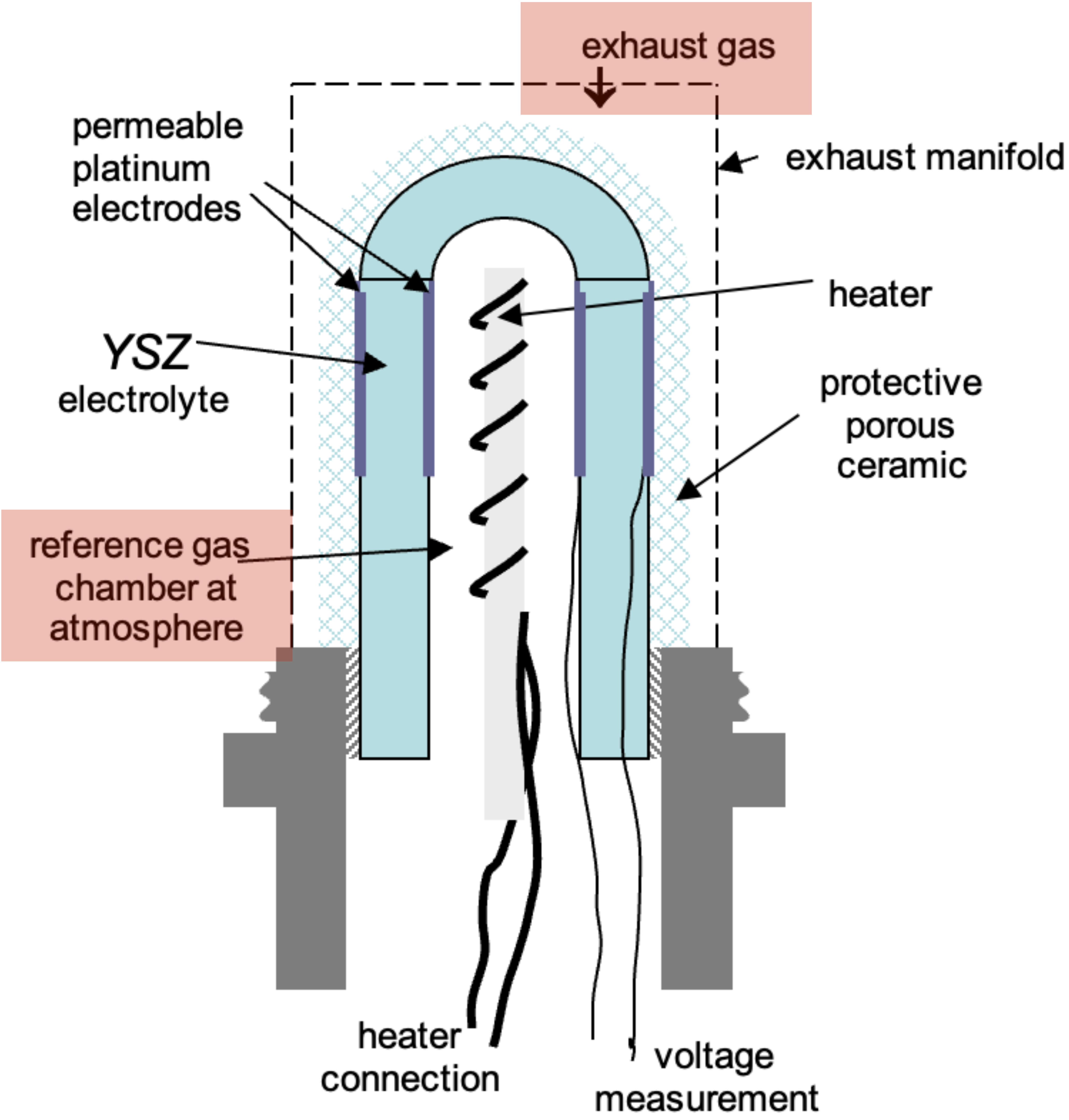
- If $pO_2(I) < pO_2(II)$: $E > 0$ O^{2-}: (II)→(I)
- If $pO_2(I) > pO_2(II)$: $E < 0$ O^{2-}: (I)→(II)

Oxygen sensor

- Measure oxygen levels in air for safety
- Lambda sensor used in vehicle exhaust system

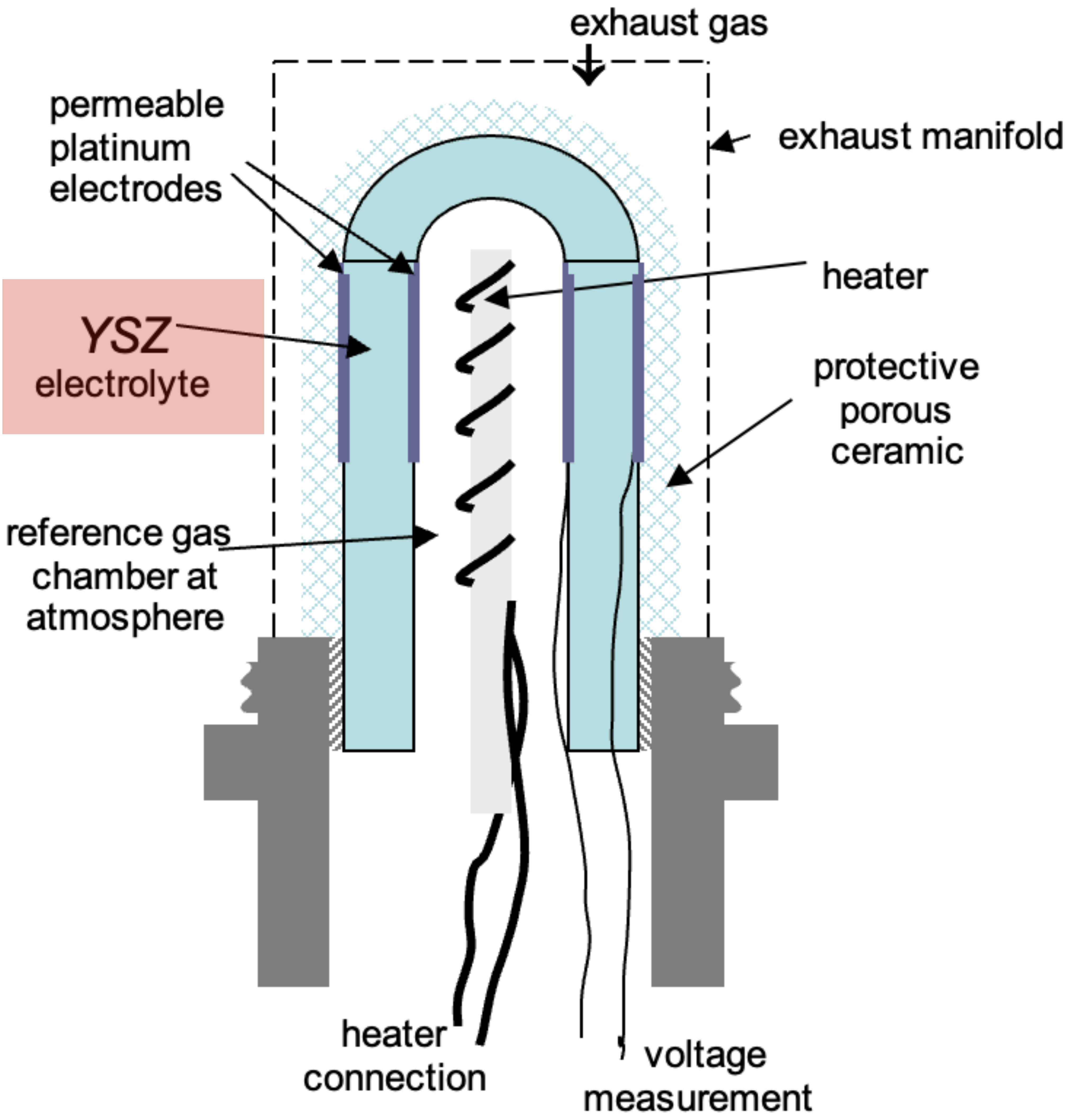
Credit: George McCaa, U.S. Bureau of Mines

Oxygen sensor: lambda sensor



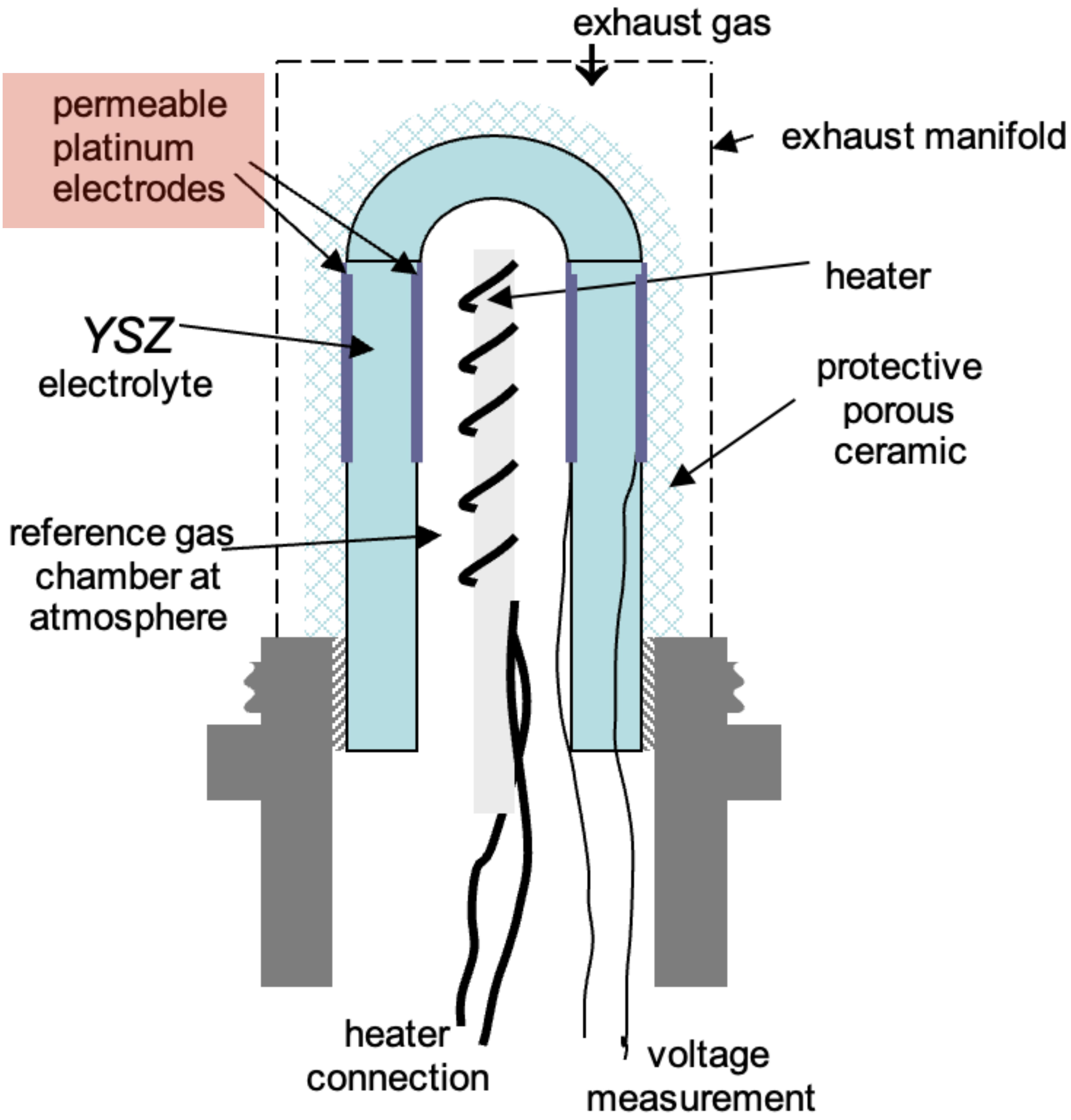
- Reference gas and exhaust (test) gas

Oxygen sensor: lambda sensor



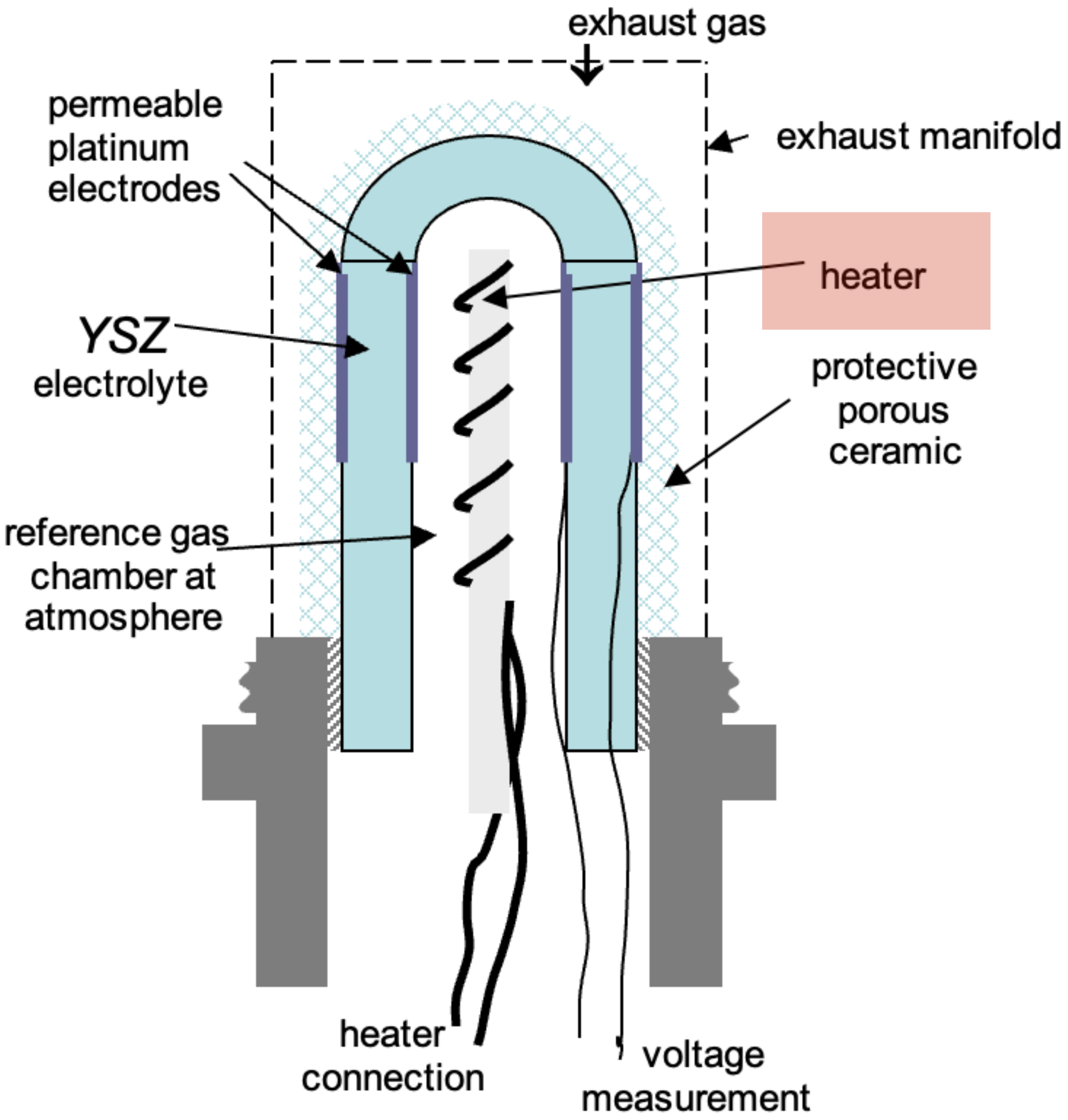
- Reference gas and exhaust (test) gas
- YSZ electrolyte in the middle

Oxygen sensor: lambda sensor



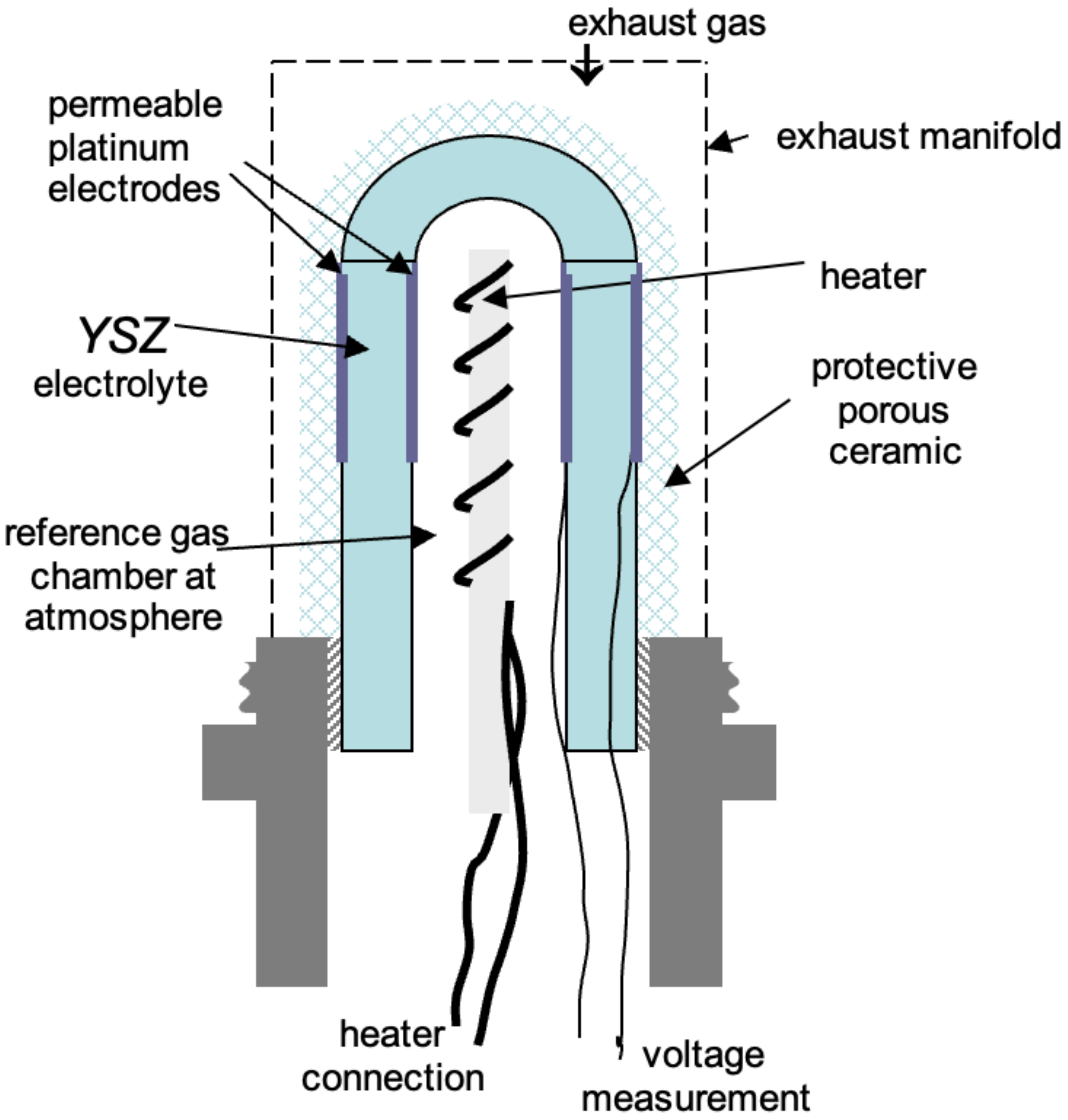
- Reference gas and exhaust (test) gas
- YSZ electrolyte in the middle
- Permeable Pt electrodes

Oxygen sensor: lambda sensor



- Reference gas and exhaust (test) gas
- YSZ electrolyte in the middle
- Permeable Pt electrodes
- Heater to promote ionic conductivity in YSZ

Oxygen sensor: lambda sensor

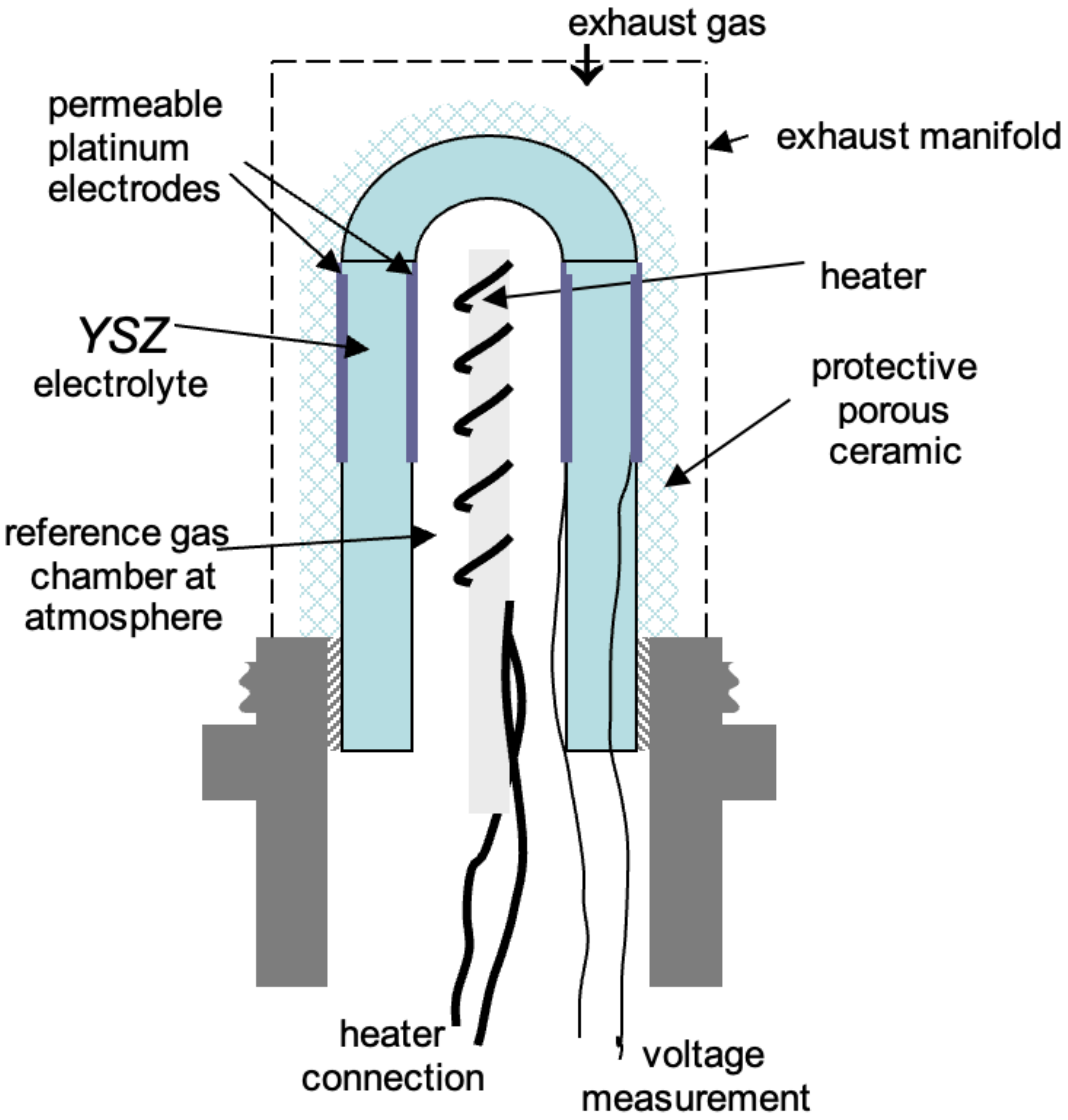


- Measures difference between exhaust and atmosphere oxygen partial pressures
- Linked to fuel injection system to control air/fuel ratio
- Aim to achieve complete stoichiometric conversion of fuel to minimise emissions:

$$C_8H_{18} + \frac{25}{2} O_2 \longrightarrow 8CO_2 + 9H_2O$$

- Non-stoichiometric conversion leads to CO, NO_x, …

Oxygen sensor: lambda sensor



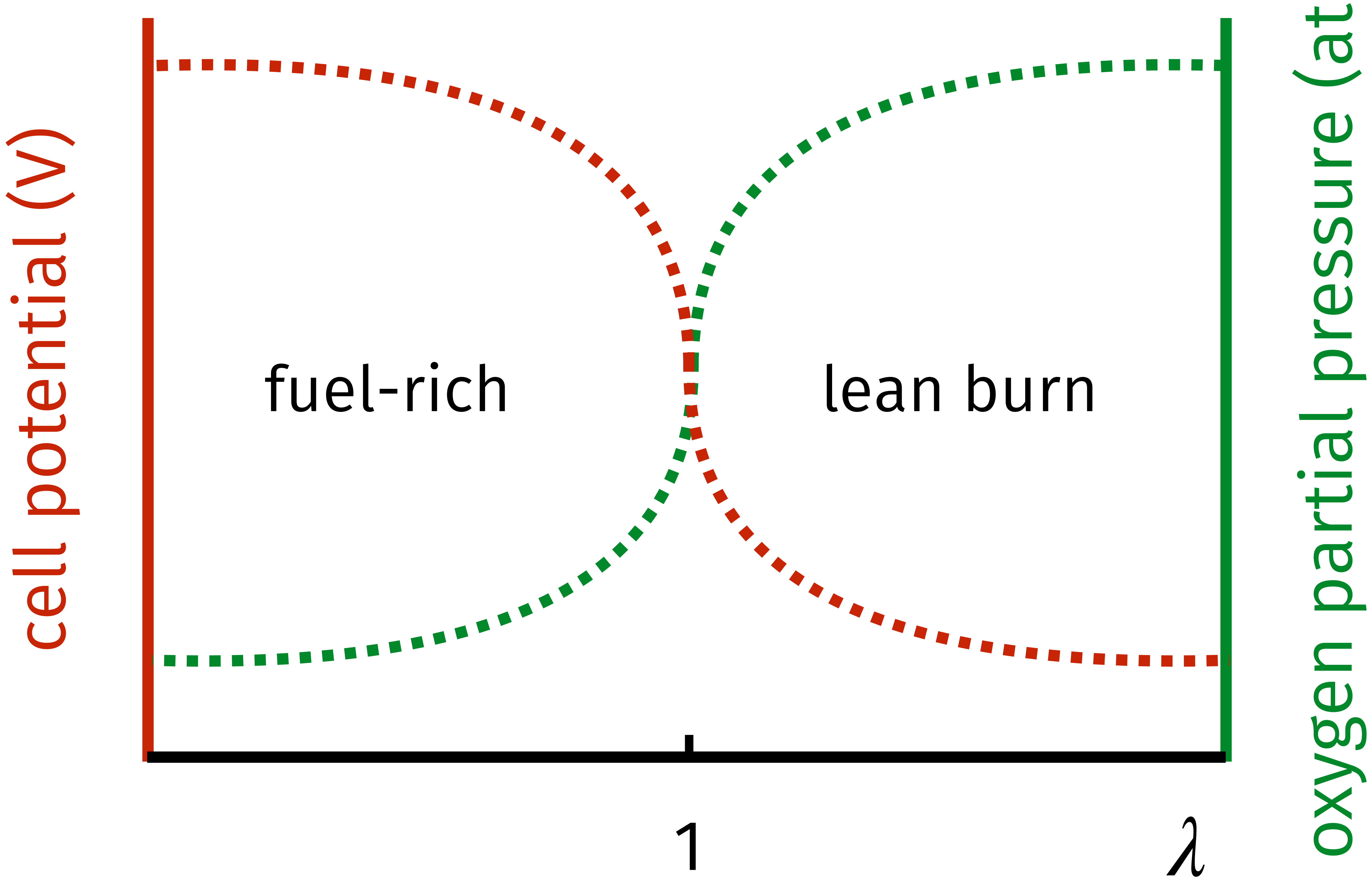
$$C_8H_{18} + \frac{25}{2} O_2 \longrightarrow 8CO_2 + 9H_2O$$

- From relative molecular masses (remembering air is about $4N_2{:}O_2$), we get stoichiometric combustion when air-to-fuel ratio by weight is 14.6:

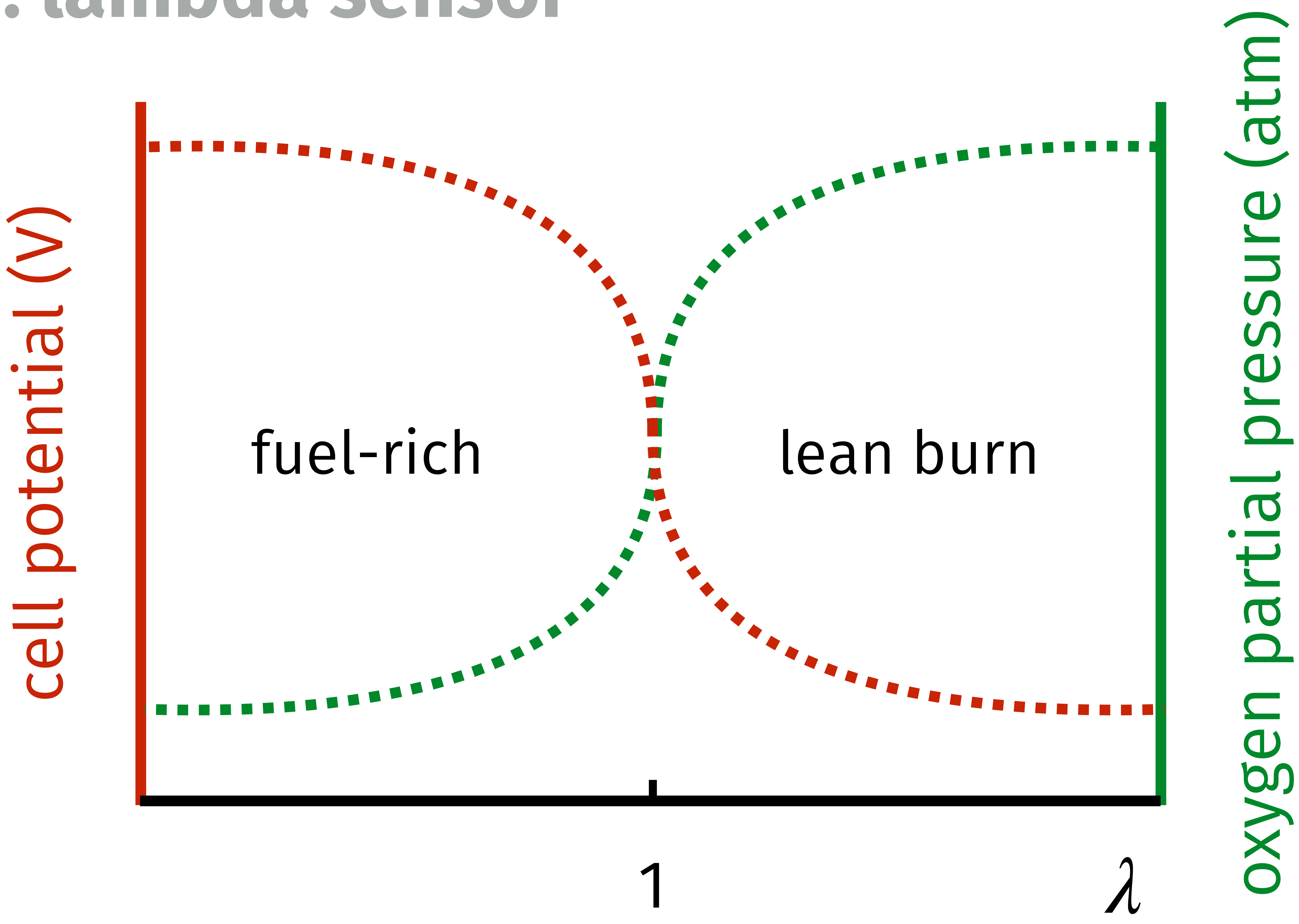
$$\boxed{\lambda = \frac{\text{measured ratio}}{14.6}}$$

- Aim for $\lambda = 1$

Oxygen sensor: lambda sensor



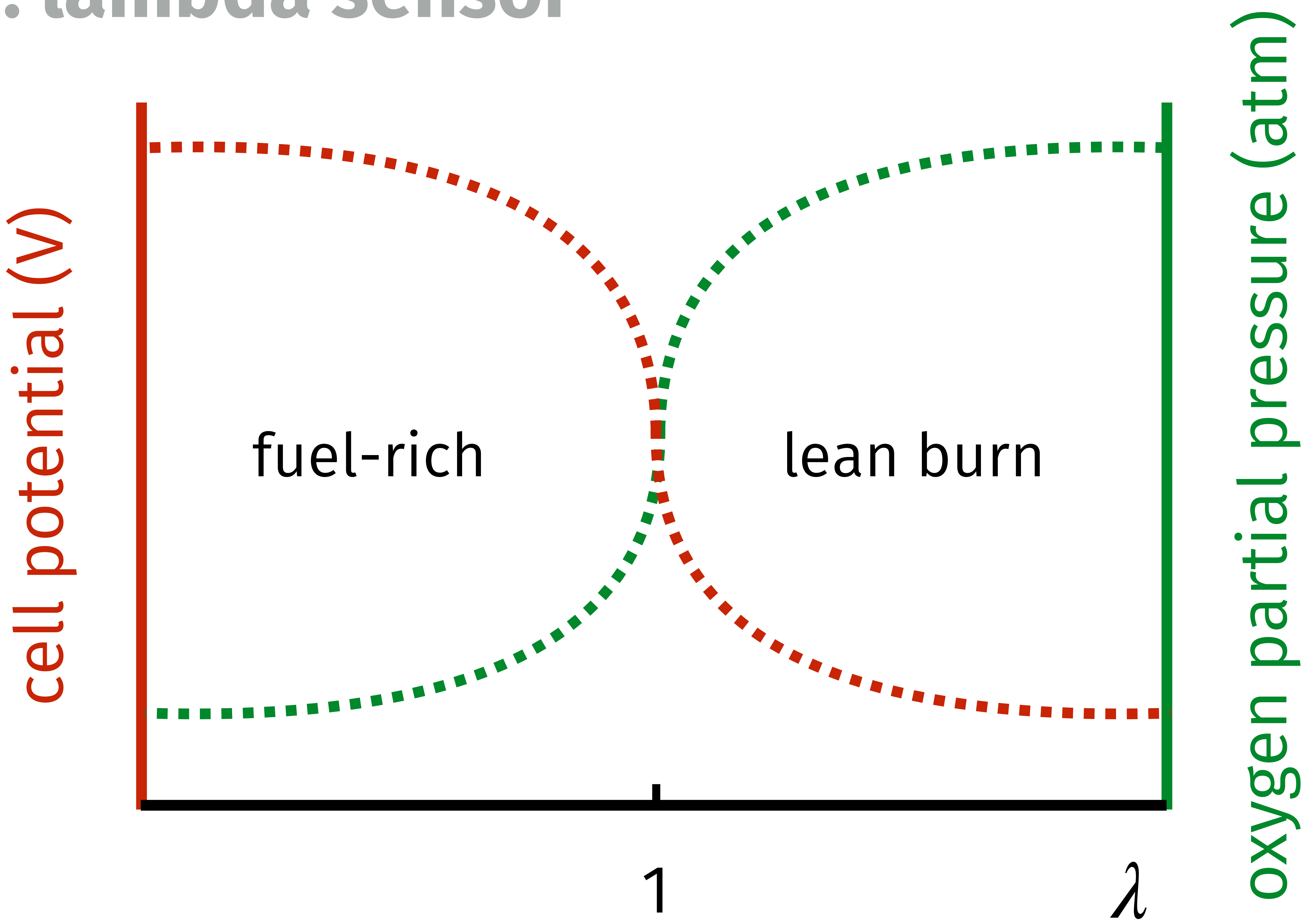
Oxygen sensor: lambda sensor



Fuel rich (burn all oxygen):

- Low oxygen pressure in exhaust
- High cell potential

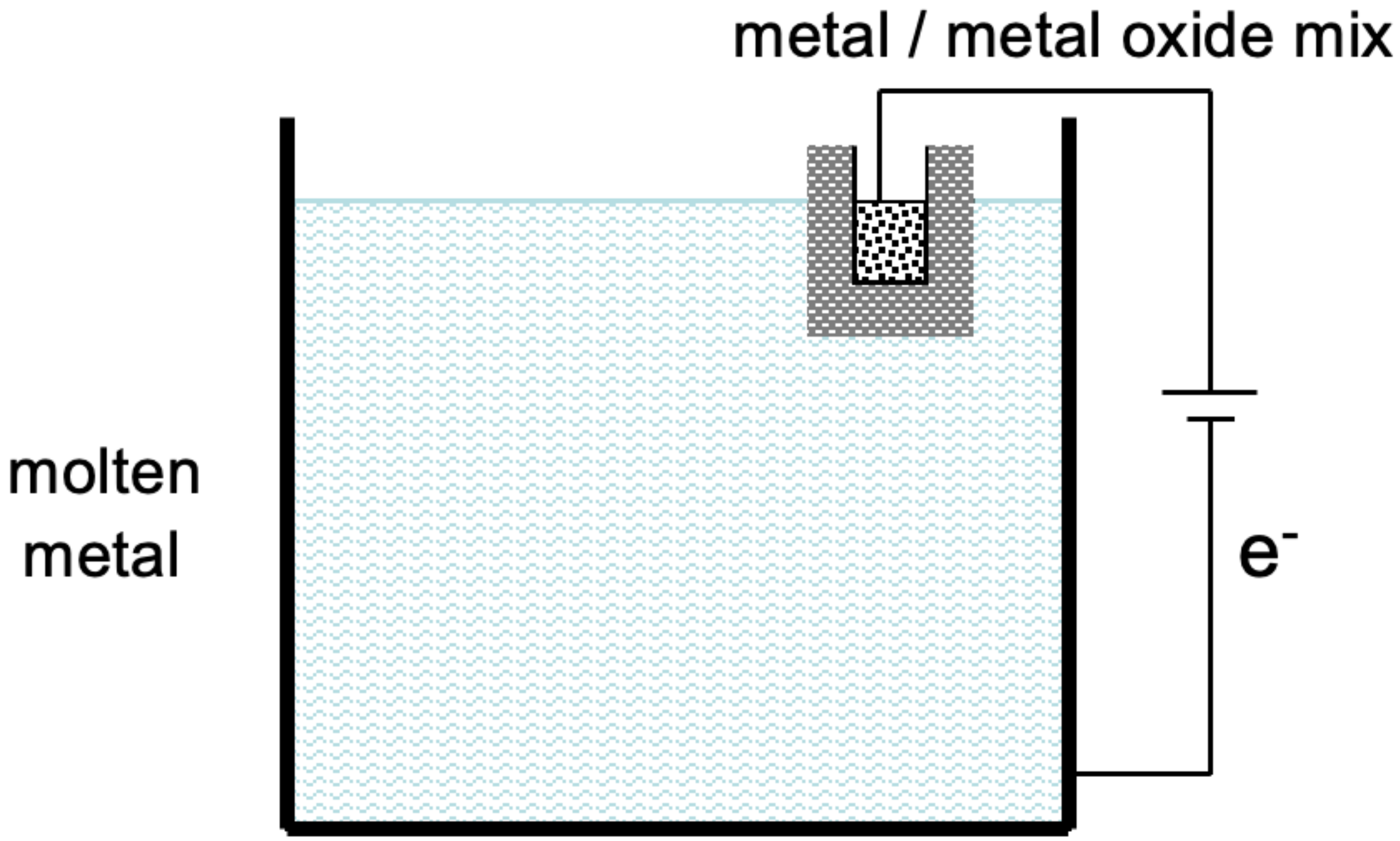
Oxygen sensor: lambda sensor



Lean burn (too little fuel):

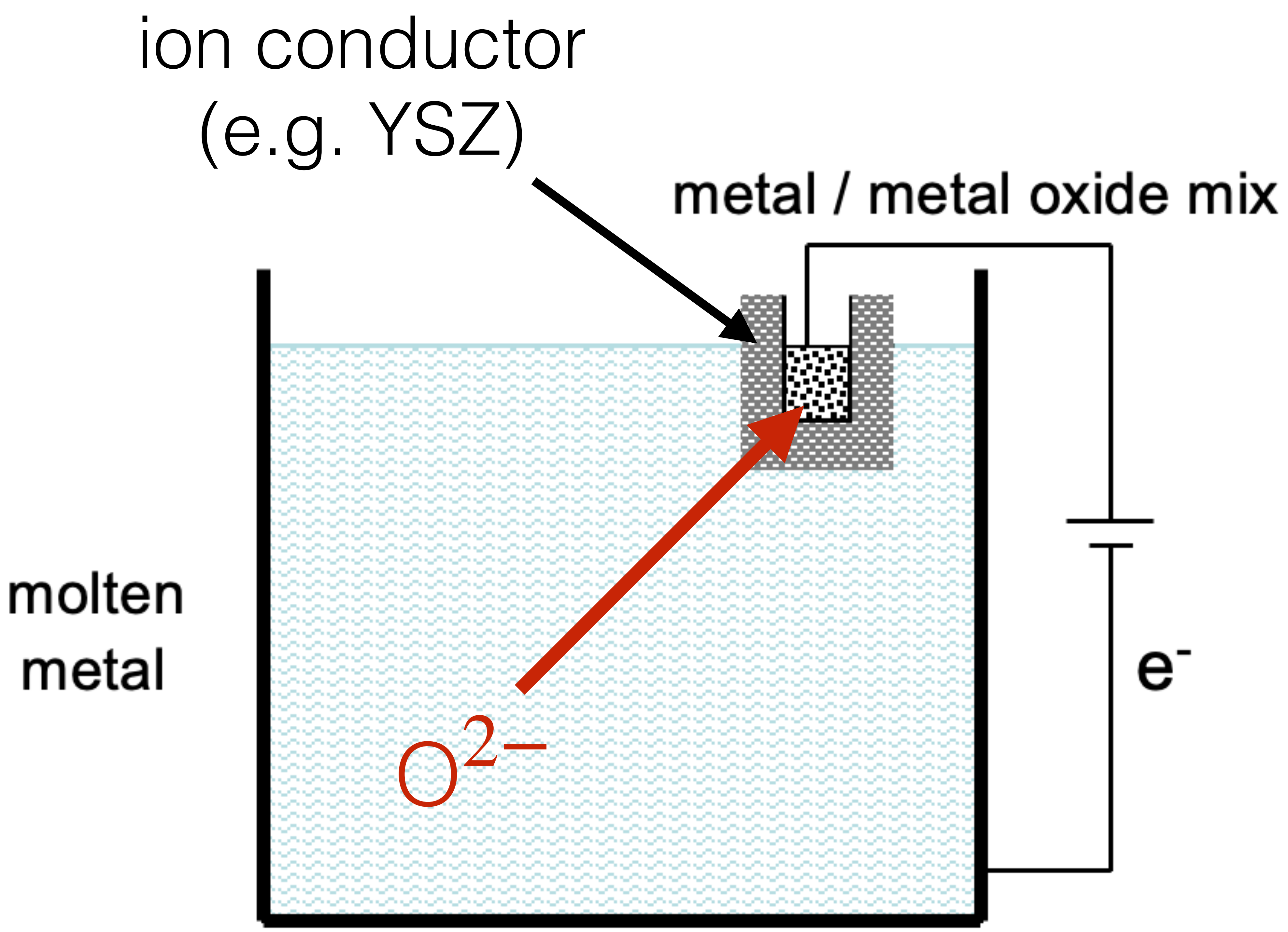
- High oxygen pressure in exhaust
- Low cell potential

Oxygen pump



- Aim to purify molten metal
- Apply external potential to drive oxygen ions from the molten metal to the metal oxide mixture
- Driving ions from region of low concentration to region of high concentration

Oxygen pump



- Aim to purify molten metal
- Apply external potential to drive oxygen ions from the molten metal to the metal oxide mixture
- Driving ions from region of low concentration to region of high concentration

Fuel cell

- Gas-fired power station:

chemical energy	→	**thermal energy**	→	**mechanical energy**	→	**electrical energy**
burn fuel (react CH_4 with O_2)		gas steam		spin turbine		electricity generator

Fuel cell

- Gas-fired power station:

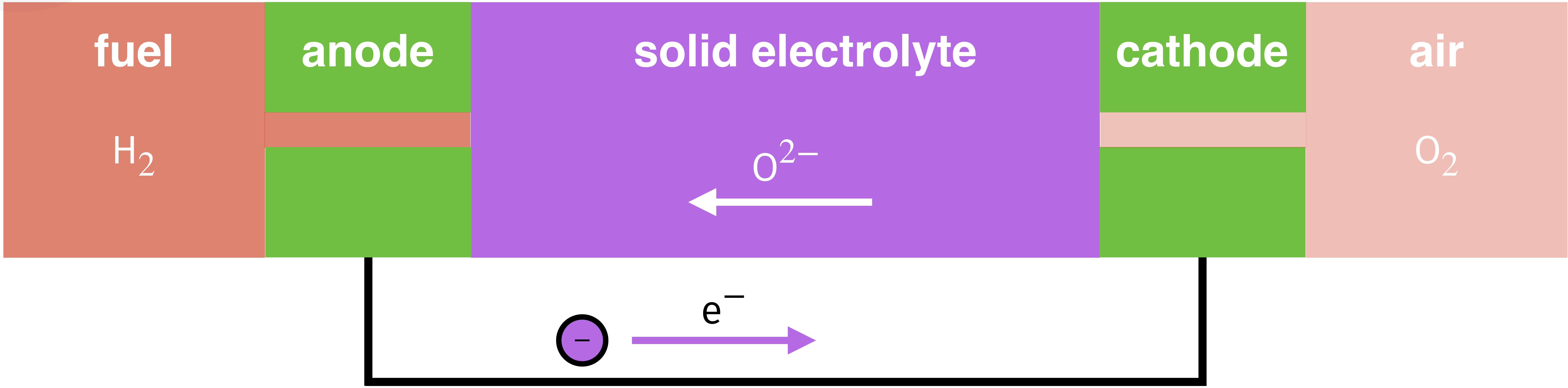
chemical energy → **thermal energy** → **mechanical energy** → **electrical energy**

chemical energy	**thermal energy**	**mechanical energy**	**electrical energy**
burn fuel (react CH_4 with O_2)	gas steam	spin turbine	electricity generator

- Fuel cell:

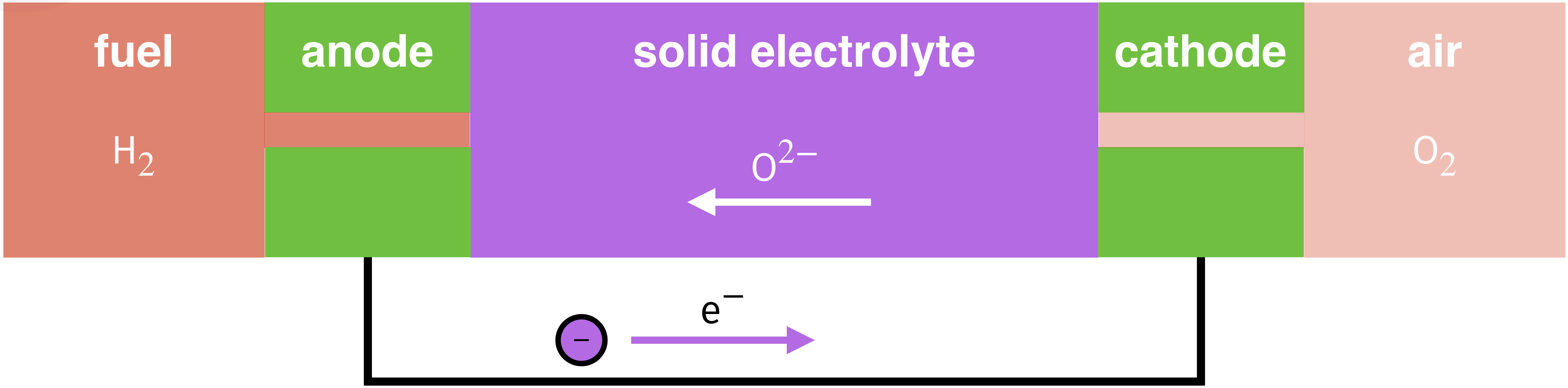
chemical energy → **electrical energy**

Fuel cell



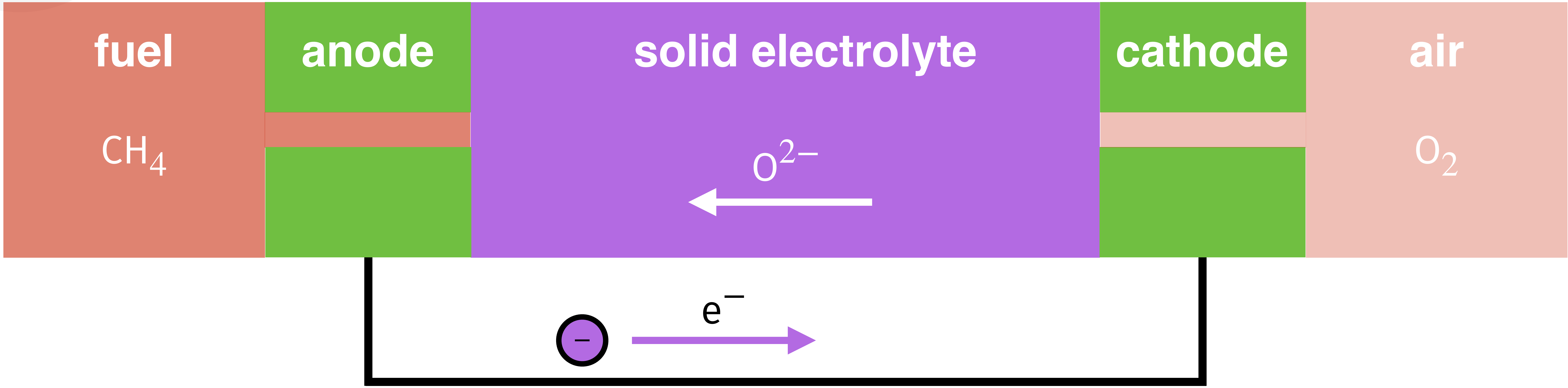
- Electrolyte: conducting through ionic motion but not through electron motion (e.g. YSZ)
- Anode: porous electrical conductor
- Cathode: porous conducting material resistant to oxidation

Fuel cell



- RHS: $O_2 + 4e^- \longrightarrow 2O^{2-}$ reduction (cathode)
- LHS: $2H_2 + 2O^{2-} \longrightarrow 2H_2O + 4e^-$ oxidation (anode)

Fuel cell



- RHS: $2O_2 + 8e^- \longrightarrow 4O^{2-}$ reduction (cathode)
- LHS: $CH_4 + 4O^{2-} \longrightarrow CO_2 + 2H_2O + 8e^-$ oxidation (anode)

Fuel cell

H_2 fuel

anode | H_2(g) | YSZ | O_2(g) | cathode

- Overall cell reactions:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

- Half cell reactions:

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

$$2H_2 + 2O^{2-} \longrightarrow 2H_2O + 4e^-$$

CH_4 fuel

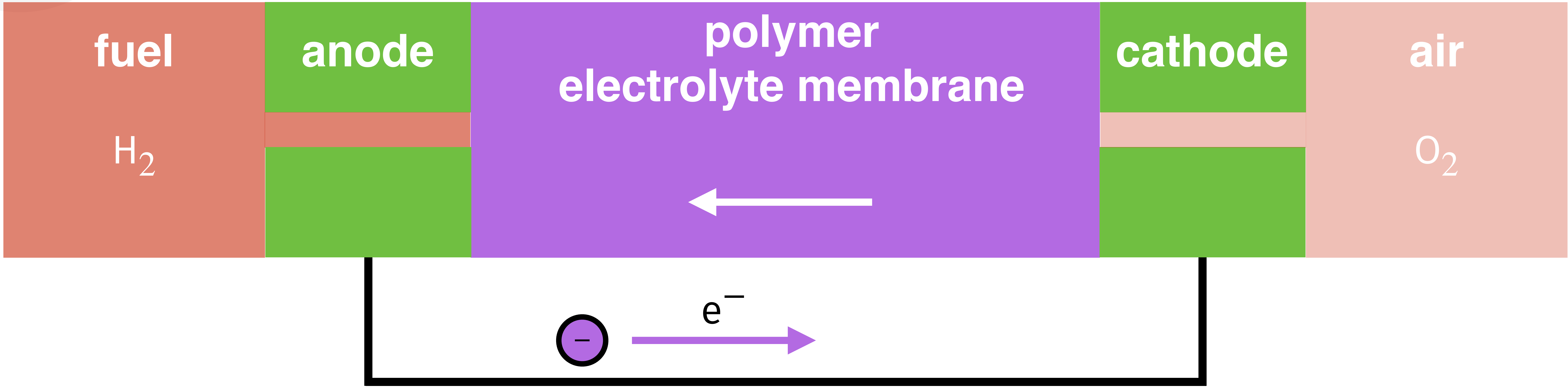
anode | CH_4(g) | YSZ | O_2(g) | cathode

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

$$2O_2 + 8e^- \longrightarrow 4O^{2-}$$

$$CH_4 + 4O^{2-} \longrightarrow CO_2 + 2H_2O + 8e^-$$

Fuel cell



fuel

H_2

anode

polymer electrolyte membrane

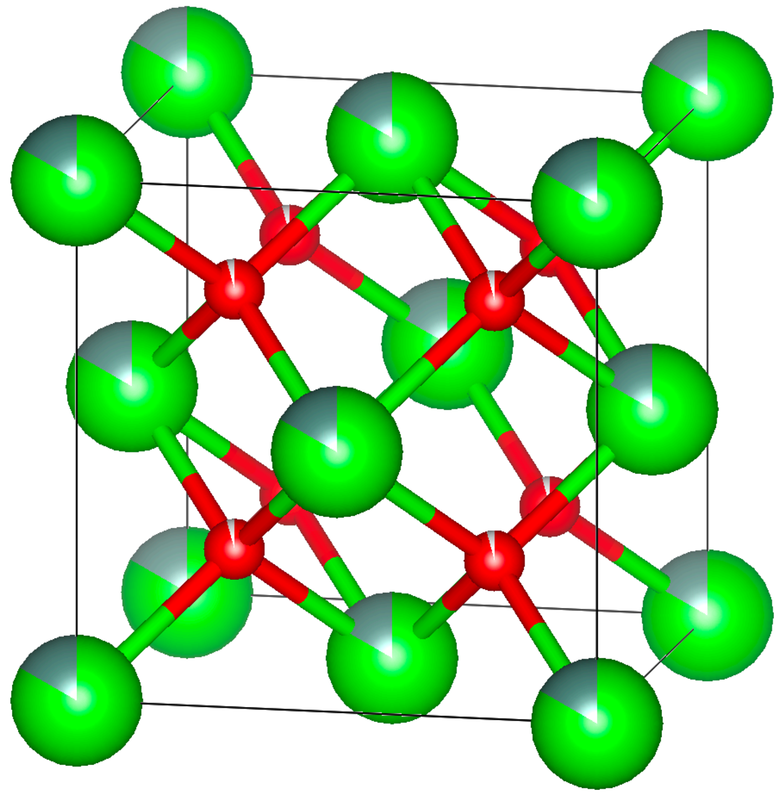
cathode

air

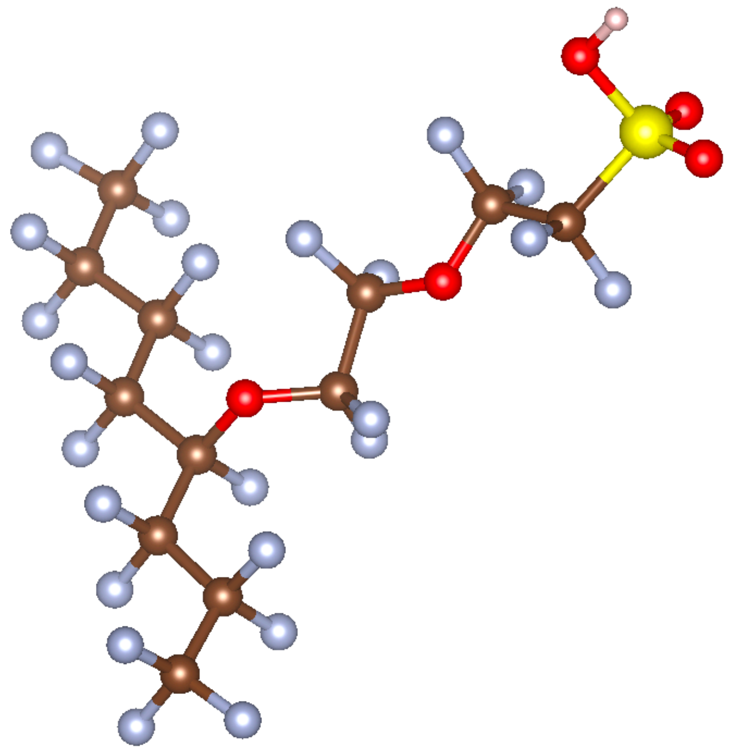
O_2

e^-

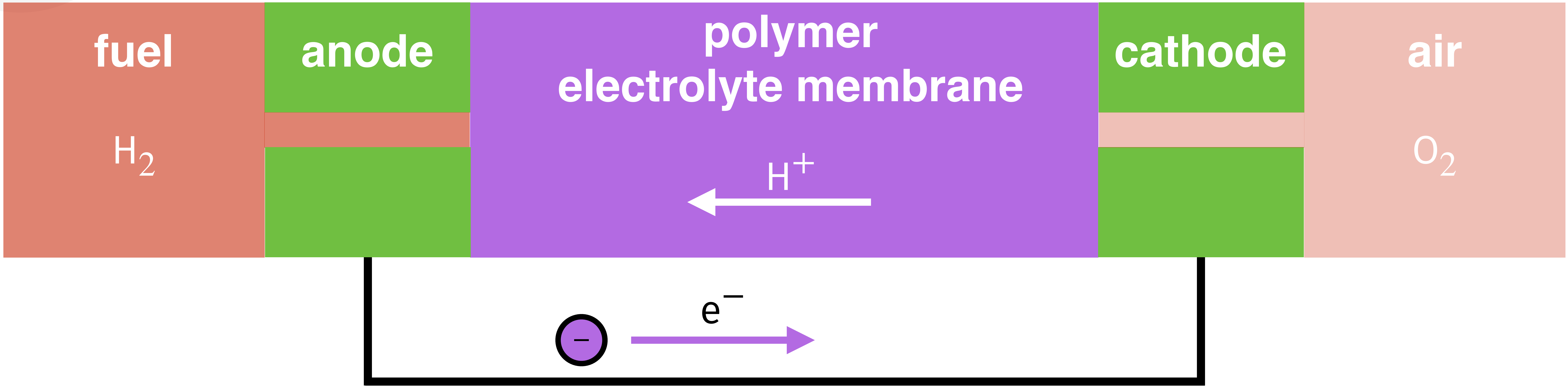
yttria-stabilised zirconia electrolyte



polymer electrolyte membrane



Fuel cell



- Polymer electrolyte membrane:
  - Thin and flexible polymer membranes (see Lecture 10)
  - Operate at about 80 °C (cf. YSZ operates at 600-1,000 °C)
  - Conduct protons H^+

Fuel cell

YSZ electrolyte

anode | H_2(g) | YSZ | O_2(g) | cathode

polymer electrolyte membrane

anode | H_2(g) | PEM | O_2(g) | cathode

- Overall cell reactions:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

- Half cell reactions:

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

$$2H_2 + 2O^{2-} \longrightarrow 2H_2O + 4e^-$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

$$2H_2 \longrightarrow 4H^+ + 4e^-$$

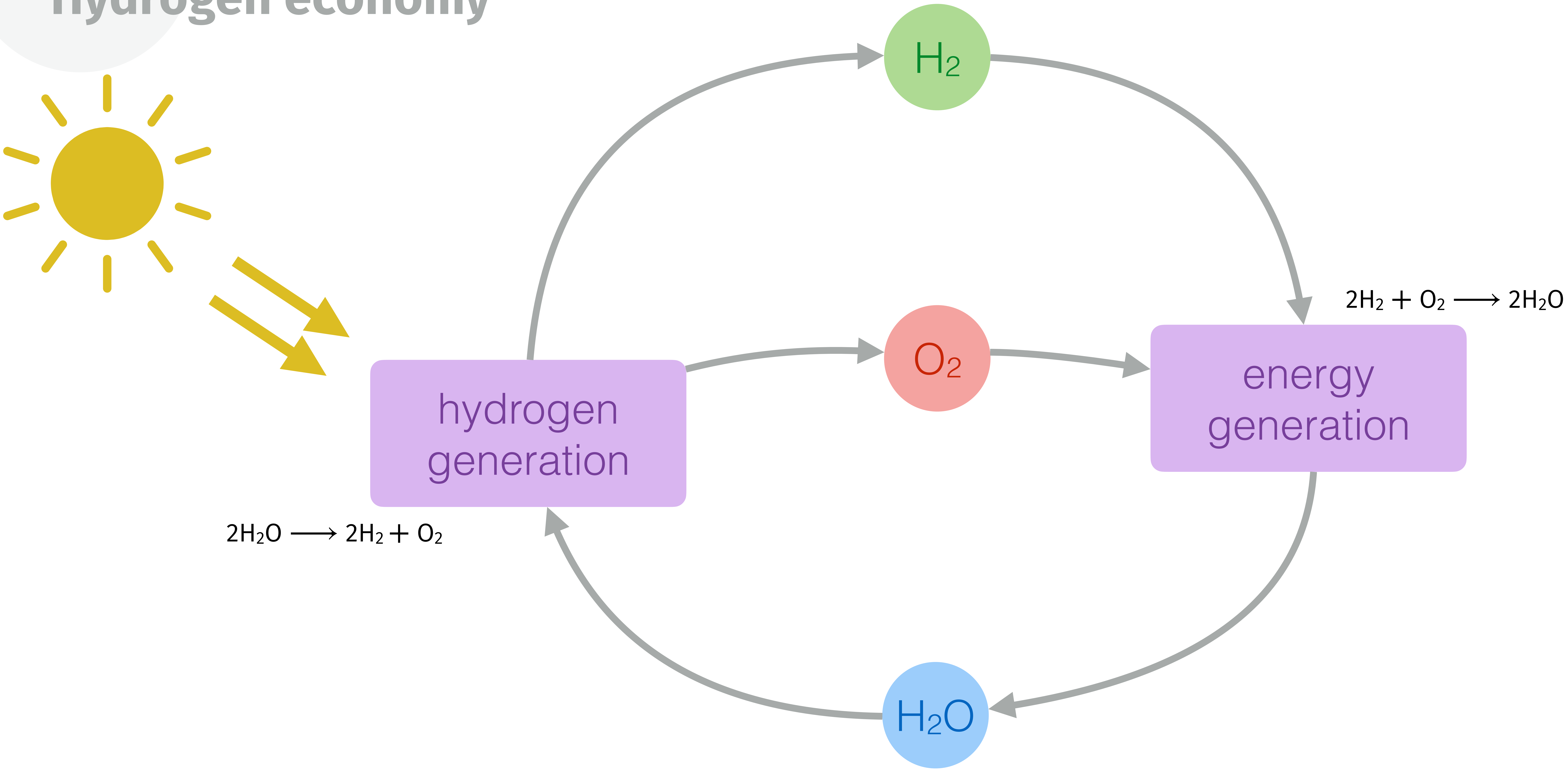
Fuel cells

- **Advantages:**
  - Direct conversion: about twice as efficient as internal combustion engine
  - No polluting emissions if fuel is H_2
  - No noise (no mechanical parts)

- **Disadvantages:**
  - Hydrogen storage is energy intensive (compress or liquify gas)
  - Hydrogen is extremely flammable

- **Material challenges:**
  - Matched or low thermal expansion coefficient (high operating temperature)
  - Chemically resistant (harsh oxidation and reduction chemical environments)

Hydrogen economy



H_2

$2H_2 + O_2 \longrightarrow 2H_2O$

O_2

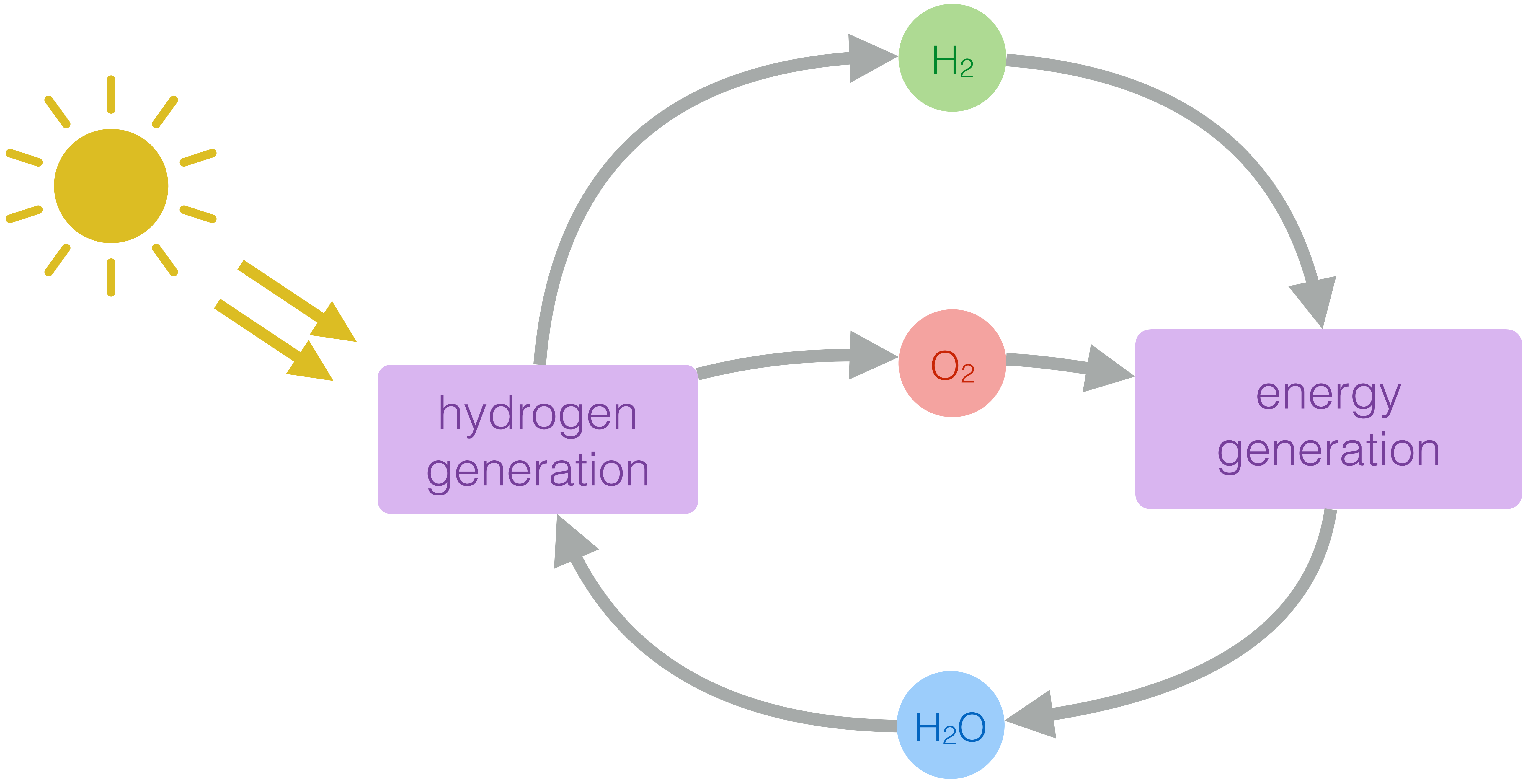
hydrogen generation

energy generation

$2H_2O \longrightarrow 2H_2 + O_2$

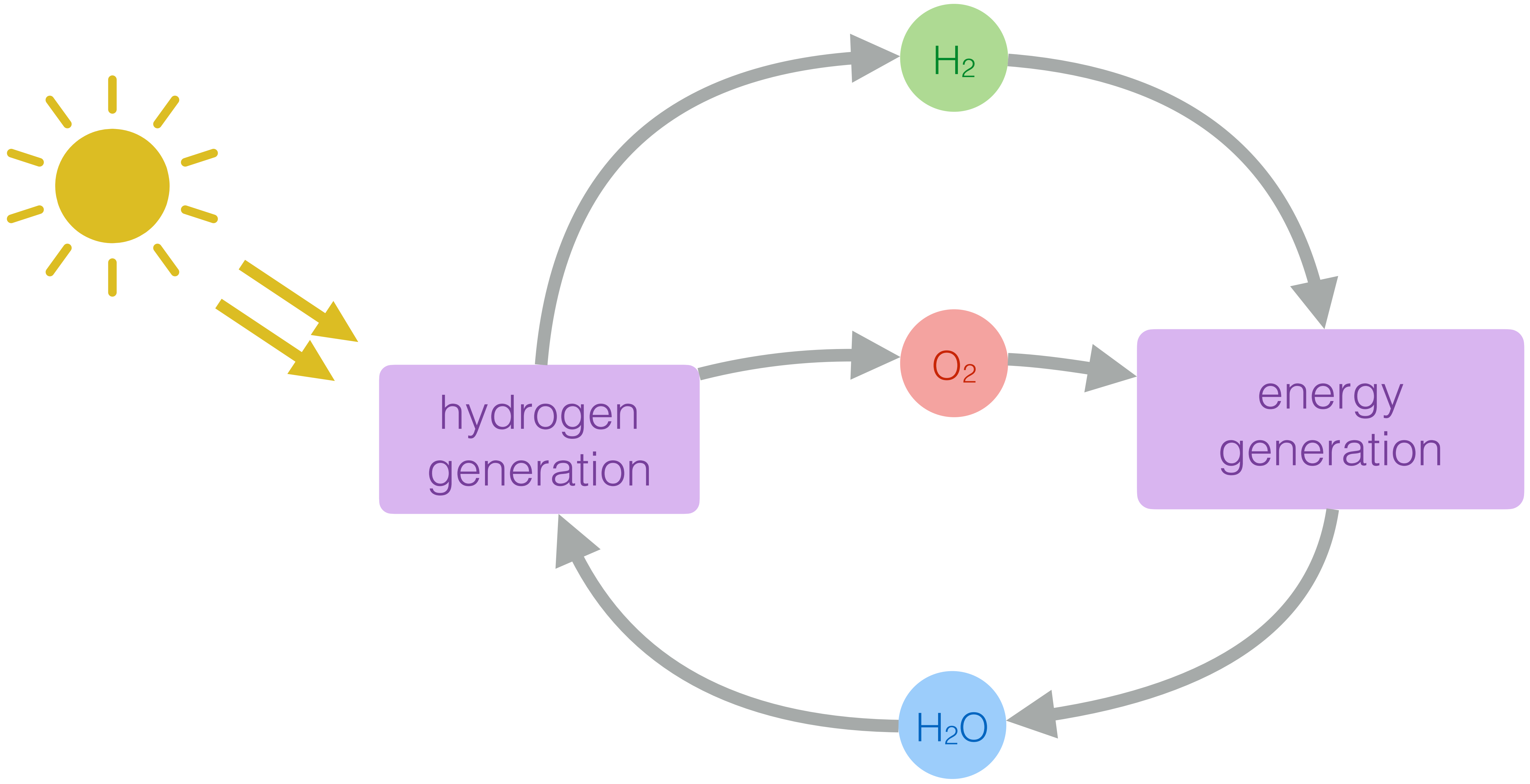
H_2O

Hydrogen economy: challenges



- **Hydrogen generation:**
  - Splitting water requires energy (electrolysis of water)
  - For this to be sustainable, the energy source would ideally be solar energy
  - Unsolved problem

Hydrogen economy: challenges



- **Hydrogen storage:**
  - Compressed or liquified gas — very energy intensive
  - Hydrogen is highly flammable
  - Possible solution: using porous materials (e.g. metal-organic frameworks)