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# High Temperature Steam and CO<sub>2</sub> Electrolysis with Proton Conducting Ceramics

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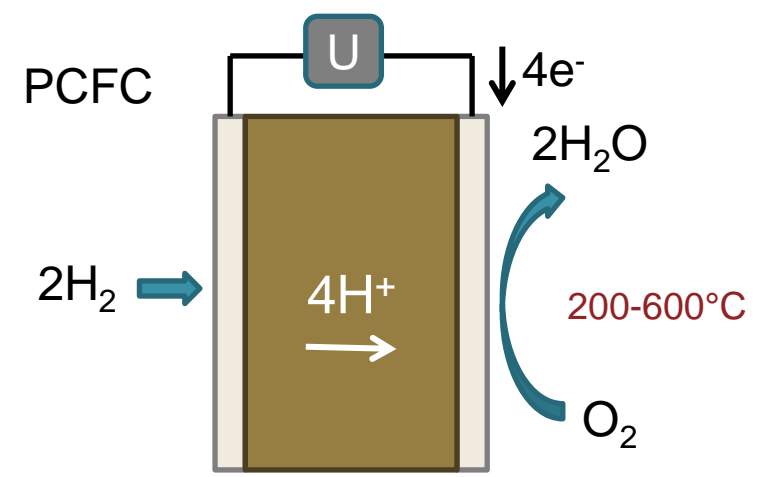
Centre for Materials Science and Nanotechnology (SMN)

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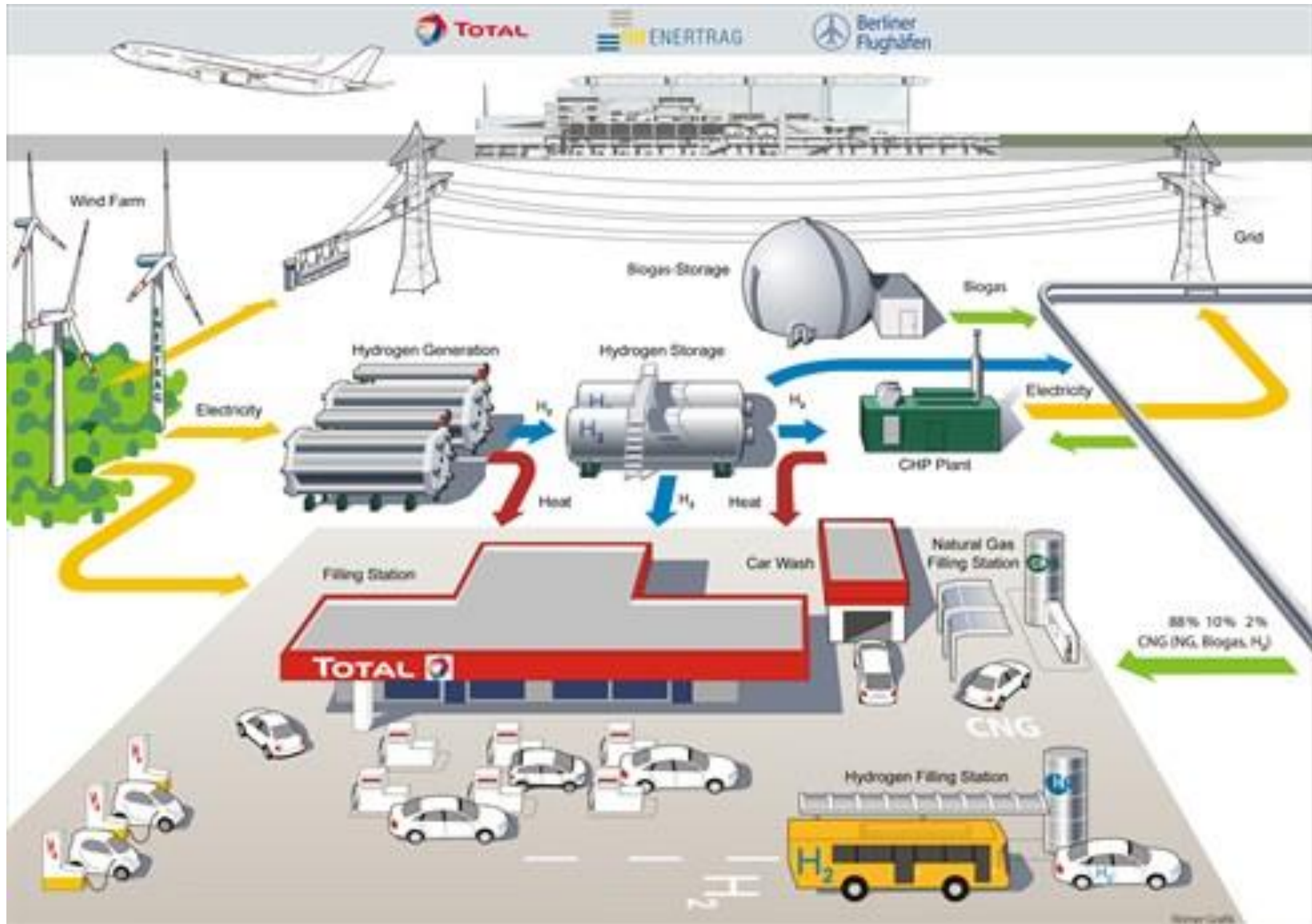


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# H<sub>2</sub> for grid and transport





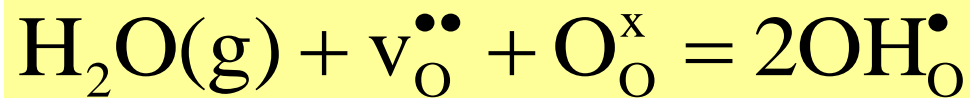
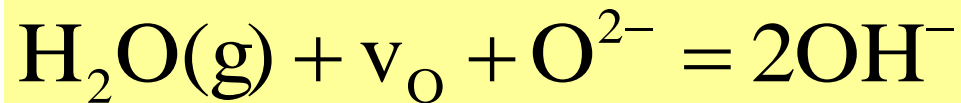
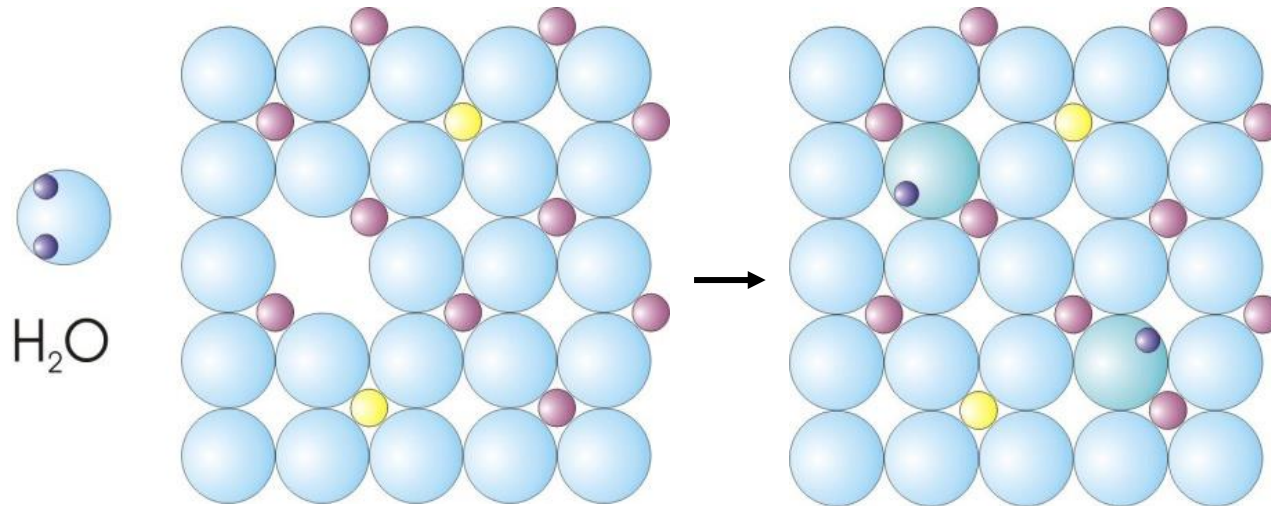
# Hydrogen H<sub>2</sub>

- Energy carrier
- Made from hydrogen rich compound + energy:
  - Reforming+shift from fossil ☹ or bio ☺. They have both H and energy.
    - $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$        $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$
  - Electrolysis (water/steam + electrical energy)
    - $2\text{H}_2\text{O}(\text{g}) = 2\text{H}_2 + \text{O}_2$
- $\text{H}_2\text{O}(\text{l}) = \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$        $\Delta H^0 = +286 \text{ kJ/mol}$      $\Delta G^0 = +237 \text{ kJ/mol}$
- $\text{H}_2\text{O}(\text{g}) = \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$        $\Delta H^0 = +242 \text{ kJ/mol}$      $\Delta G^0 = +229 \text{ kJ/mol}$
- Beneficial to use steam if heat generation (loss) is moderate
- Steam: Industry. Geothermal, solar, nuclear power.
- Electricity: Peak renewable



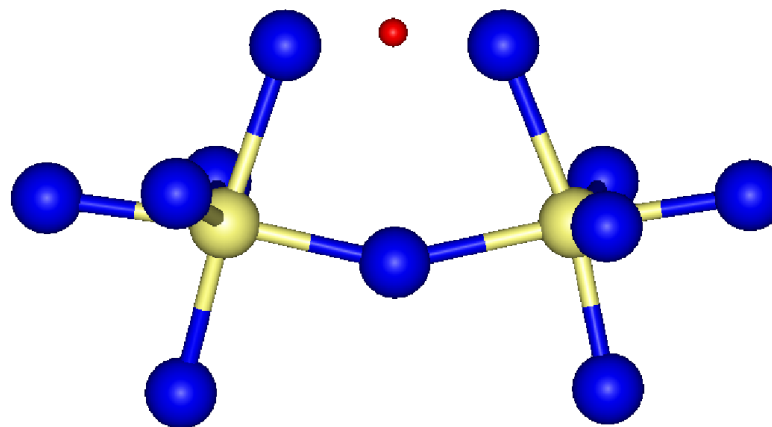
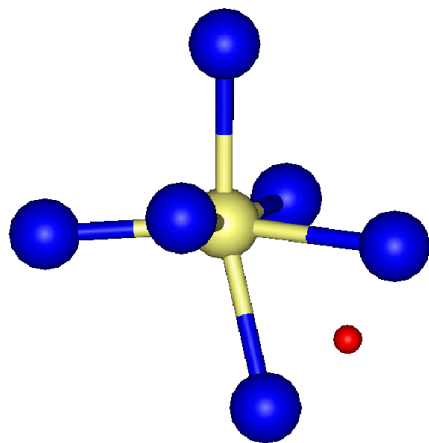
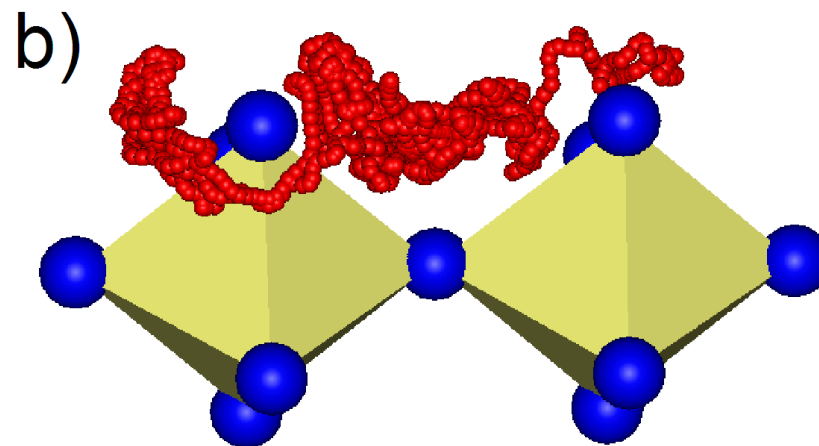
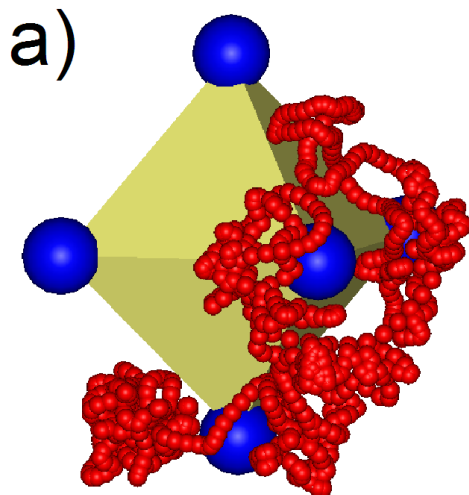
## Acceptor doped oxides:

- Oxide ion conduction by oxygen vacancies
- Hydration at low  $T$  and high  $p_{\text{H}_2\text{O}}$  gives proton conduction



# Proton migration by rotation and jumps

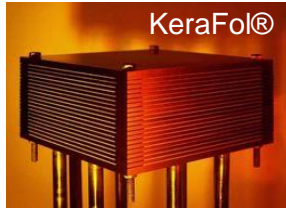
a) Intra- and b) inter-octahedral proton diffusion paths in a perovskite, by MD:



From K.-D. Kreuer, 2008

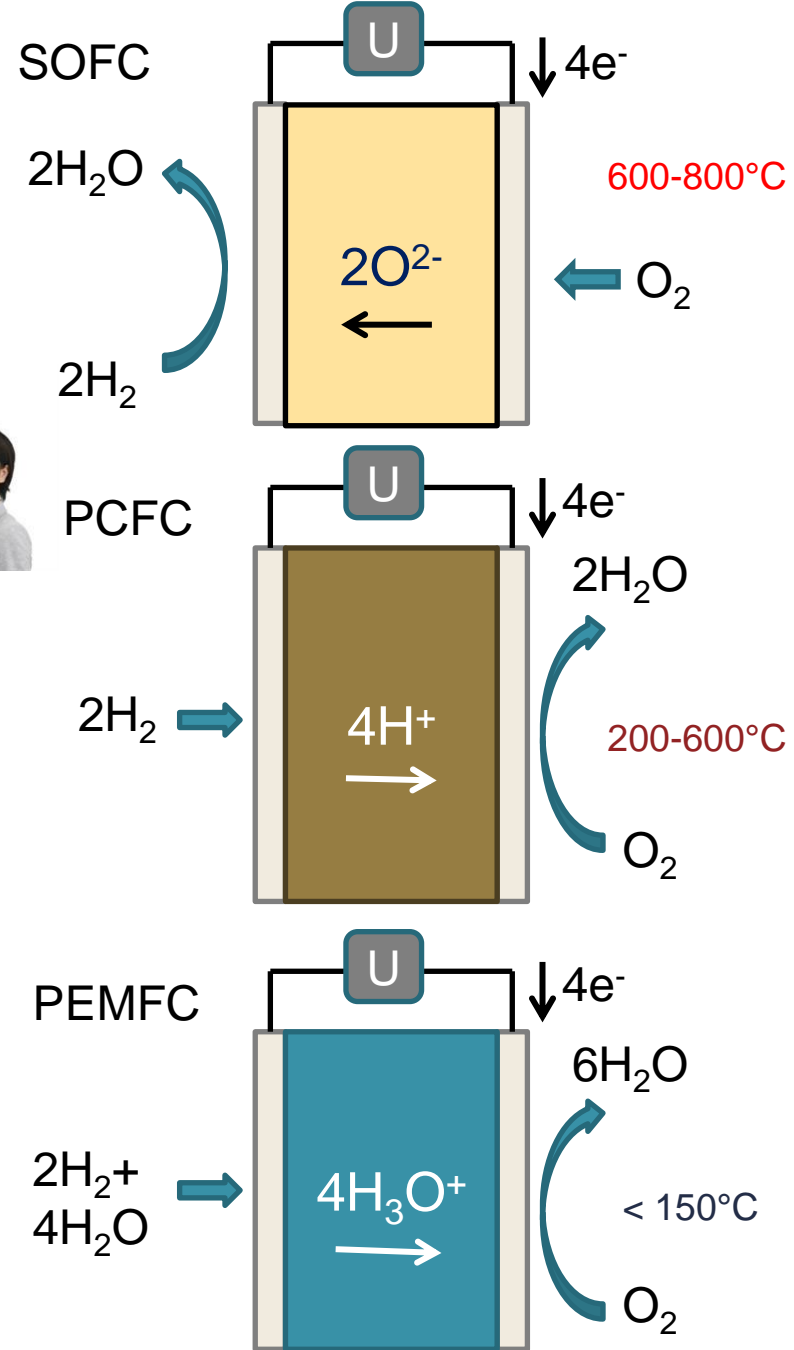
# Solid-state fuel cells

- Examples with  $H_2$  as fuel
- SOFC: High T, low fuel utilisation, anode oxidation



- PCFC: Intermediate T, high fuel utilisation
- no anode oxidation

- PEMFC: Low T, water management, cooling challenges



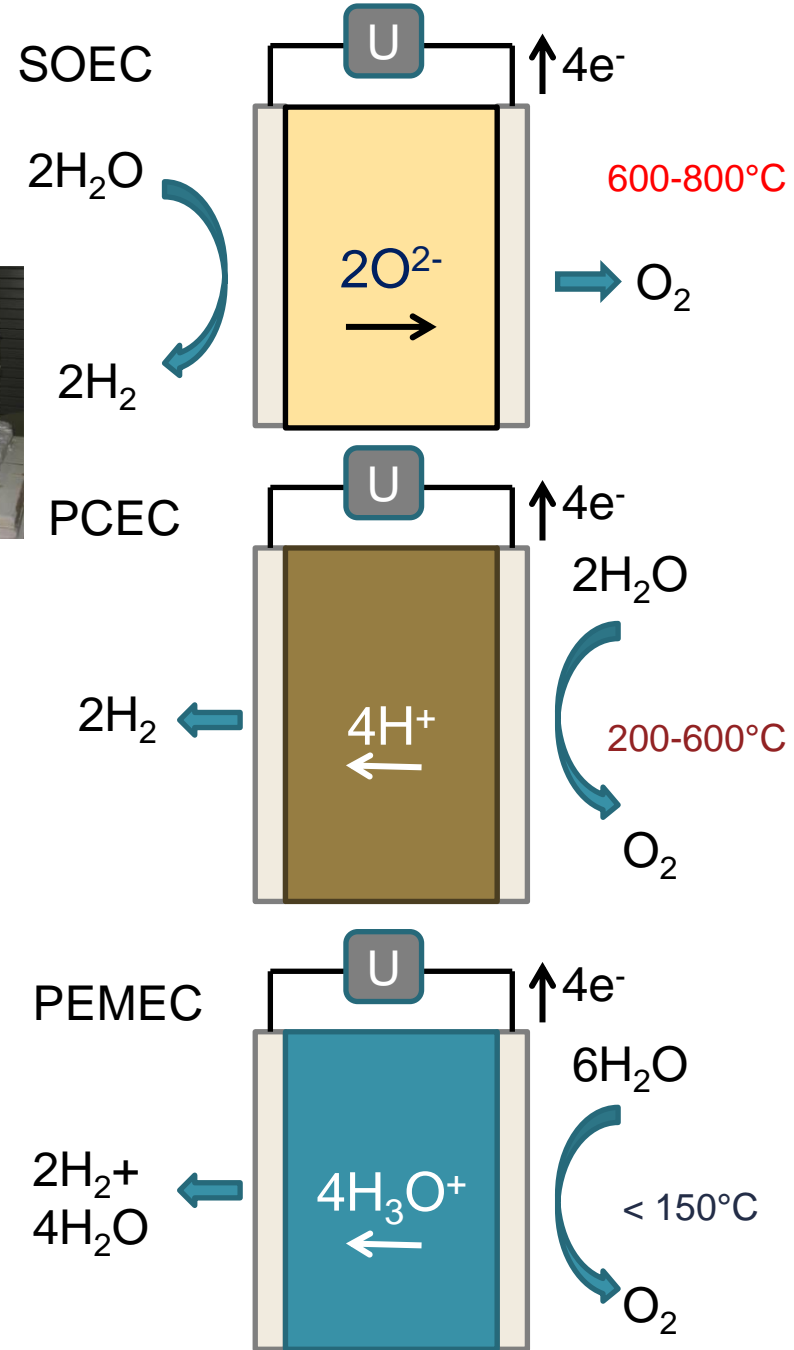
# Solid-state electrolyser cells

- SOEC: Utilises steam&heat
- Produces wet  $H_2$



- PCEC: Utilises steam&heat
- Produces dry  $H_2$  directly
  - Metallic  $H_2$  electrode and support not exposed to oxidising conditions
  - Also standalone  $H_2$  compression

- PEMEC: Uses liquid water
- Produces wet  $H_2$



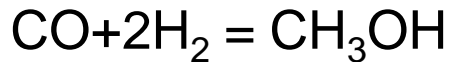


# Co-electrolysis; From CO<sub>2</sub> and renewable electricity to liquid fuels

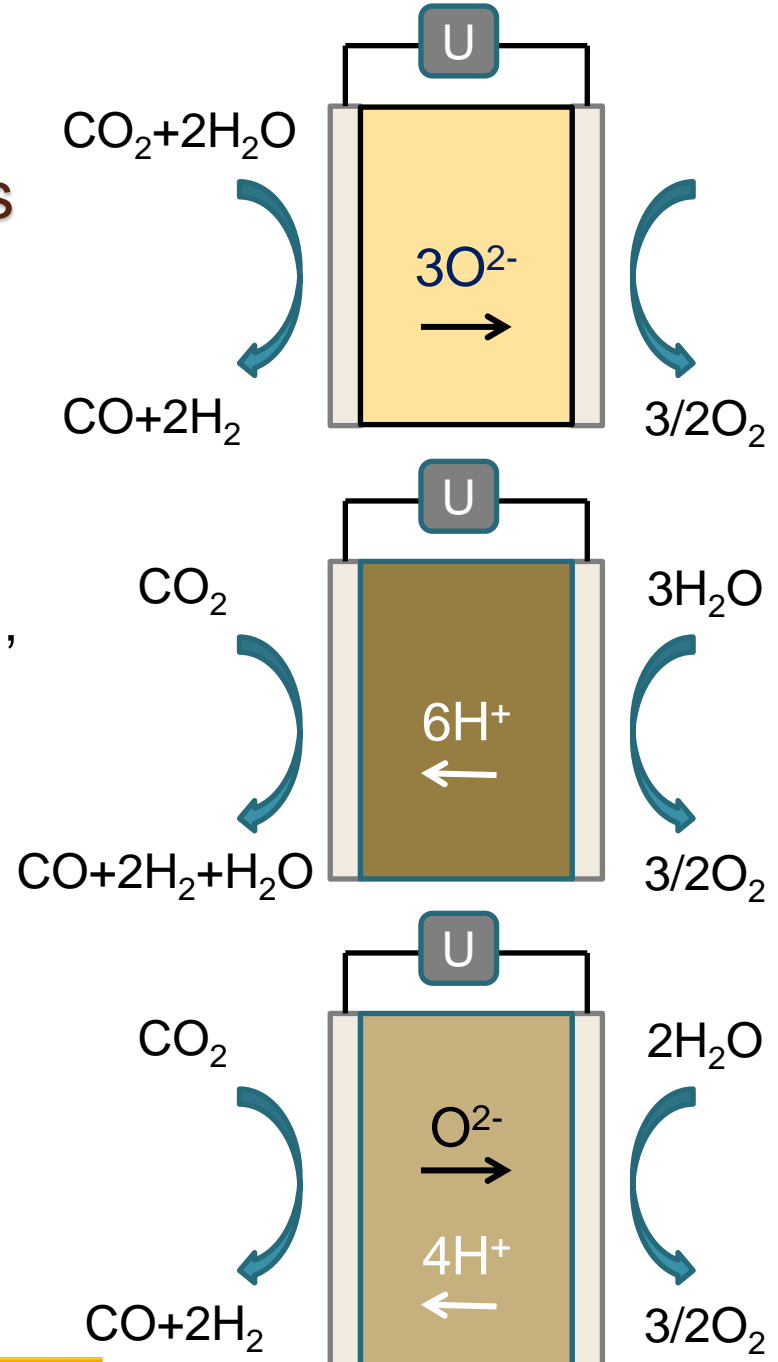
- *Co-electrolysis* of CO<sub>2</sub> and steam to syngas:



for further production of liquid fuels, e.g.,

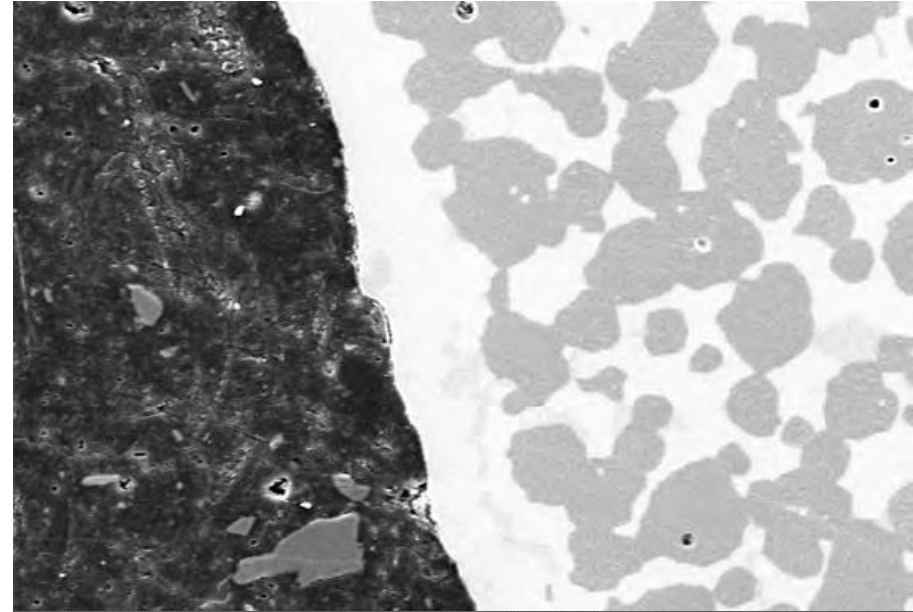


- Pure H<sup>+</sup> conductor less suitable here
- H<sup>+</sup> + O<sup>2-</sup> *co-ionic* conductivity is OK and gives new operational possibilities



# Anode-supported Y-doped Ba(Zr,Ce)O<sub>3</sub> (BZCY):

- CoorsTek/Protia:
- Reaction sintering:  
 $\text{BaCO}_3/\text{BaSO}_4 + \text{ZrO}_2 + \text{CeO}_2 + \text{Y}_2\text{O}_3 (+\text{NiO})$
- Slip-cast/extrude BZCY-NiO composite
- Spray/dip/spin on BZCY electrolyte precursor
- Co-sinter
- Reduce NiO to Ni in H<sub>2</sub>
  - Sufficient porosity for PCFC, PCEC with H<sub>2</sub>
- 10 mmØ, 1 mm wall, 20 µm BZCY, 30 cm
- Bubble-free at 2 bar overpr. in isopropanol
- Development of O<sub>2</sub> side electrodes



# UiO + SINTEF projects on PCECs

- METALLICA

- RCN EnergiX
- Proton Ceramic Electrolyser Cells (PCECs) on metallic supports
- BZY electrolyte, alloy supported H<sub>2</sub>-side electrodes (cathode), PLD...
- Project leader: Marit Stange (SINTEF)

-  *Electra*

- EU FCH JU
- Tubular segmented cermet-supported PCECs
- 7 partners (3 NO, 1 FR, 2 ES, 1 IC)
- Project coordinator: Truls Norby (UiO)

- Fundamental supporting projects; FOXCET, ...



# Conclusions; PCECs

- Production of H<sub>2</sub> from renewables
- Grid balance and transport
- Utilise steam in SOECs and PCECs
- PCECs produce dry H<sub>2</sub> directly
- PCECs can do electrochemical compression of H<sub>2</sub> directly
- Co-electrolysis of CO<sub>2</sub> by co-ionic electrolytes
- Perovskite proton conducting ceramics, BZCY
- Challenges: Moderate proton conductivities, chemical expansion, sintering
- Develop oxygen-side electrodes

