UiO : Department of Chemistry
University of Oslo

16th Asian SSI, 19th National SSI, 5th Asian SOFC
Shanghai, August, 2018

Proton ceramic cells for fuel cells, electrolyzers, and natural gas conversion

Truls Norby

This work has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreements No ***779486/GAMER*** *and* ***621244/ELECTRA****. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.*

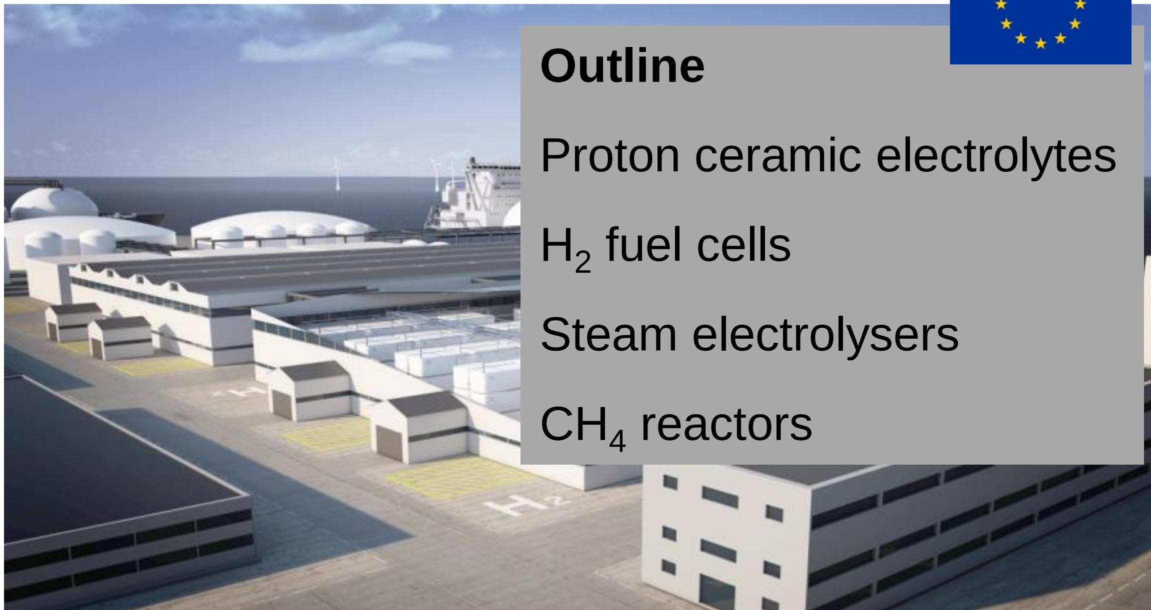
Thanks to colleagues at CoorsTek MS AS, SINTEF, ITQ Valencia, CRI, Abengoa Hidrogeno, and UiO

Department of Chemistry
University of Oslo

Centre for Materials Science
and Nanotechnology (SMN)

FERMiO
Oslo Science Park

truls.norby@kjemi.uio.no



Outline

Proton ceramic electrolytes

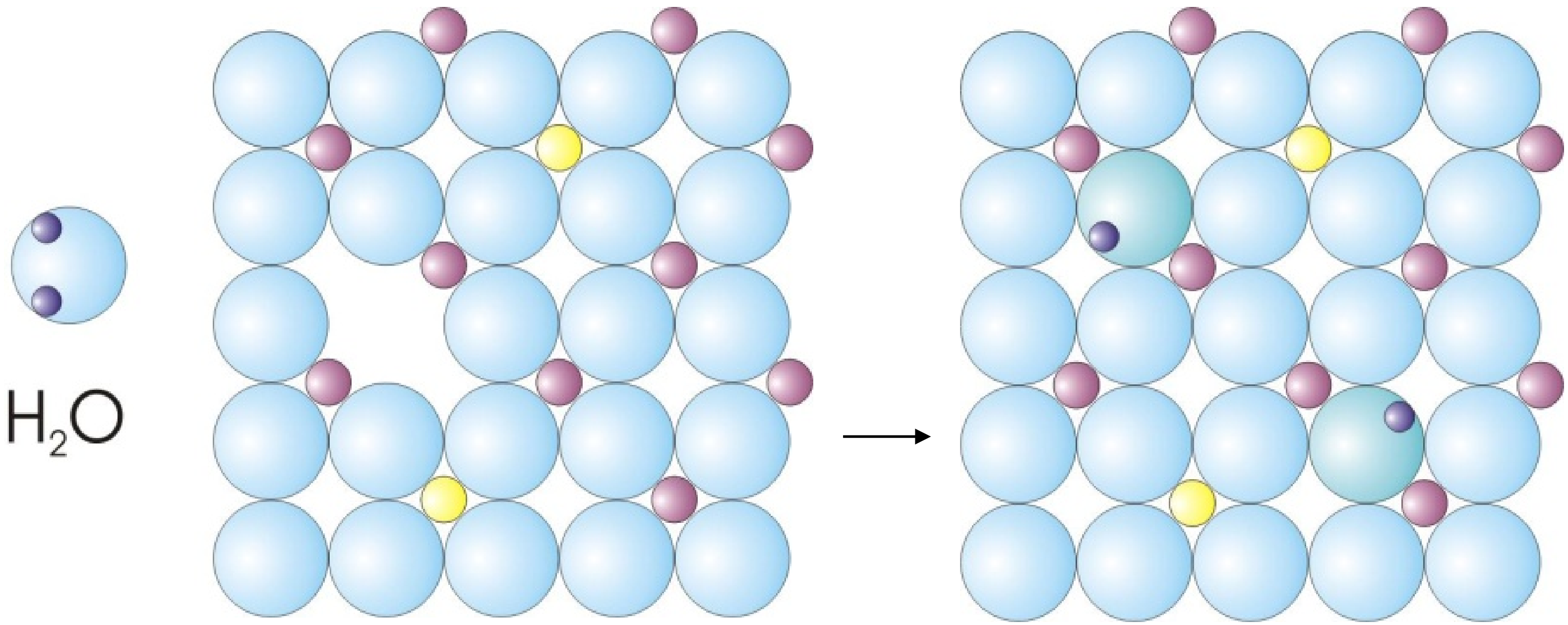
H_2 fuel cells

Steam electrolysers

CH_4 reactors

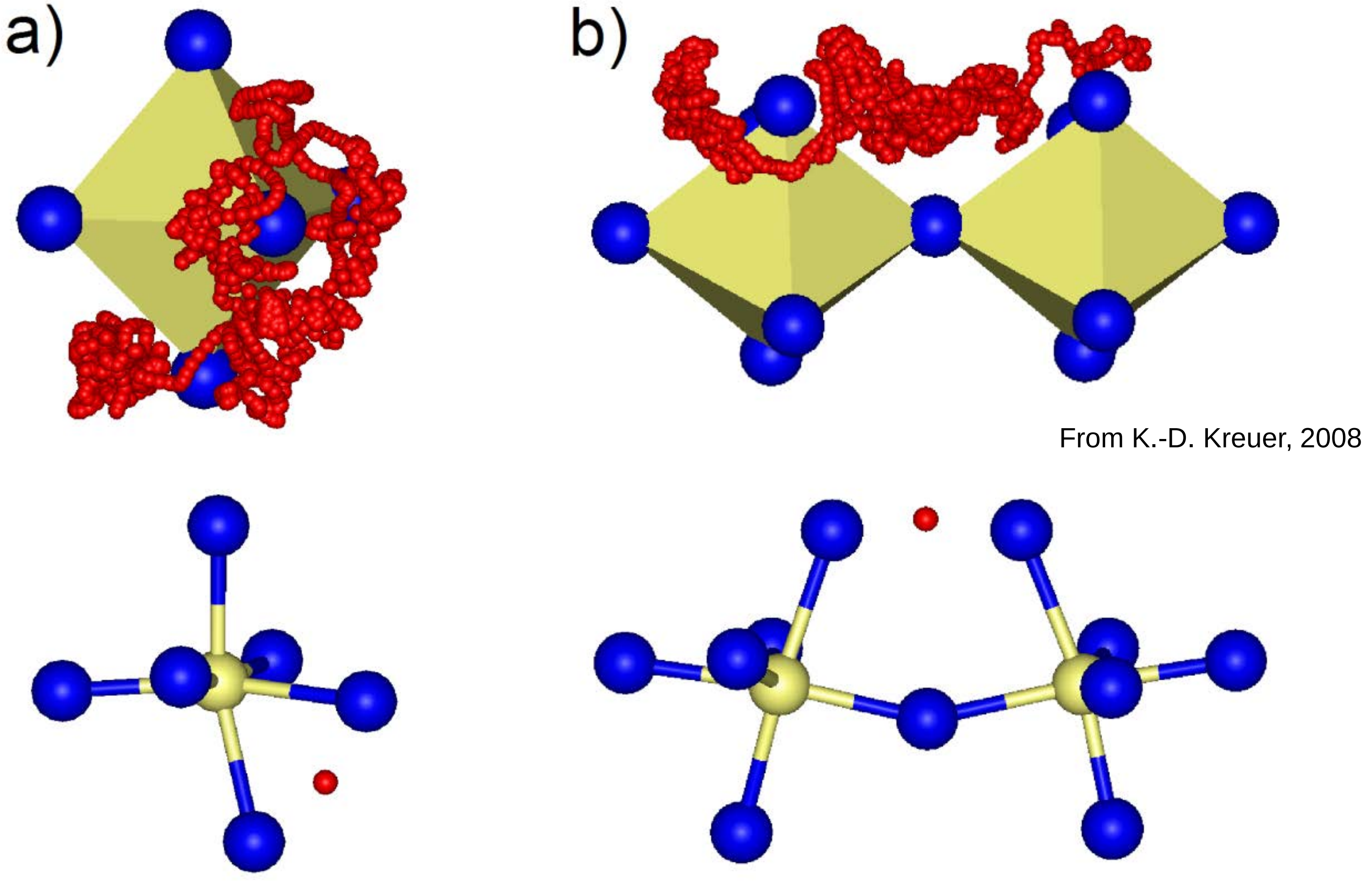
Proton ceramic electrolyte

Proton conducting oxides by hydration of oxygen vacancies



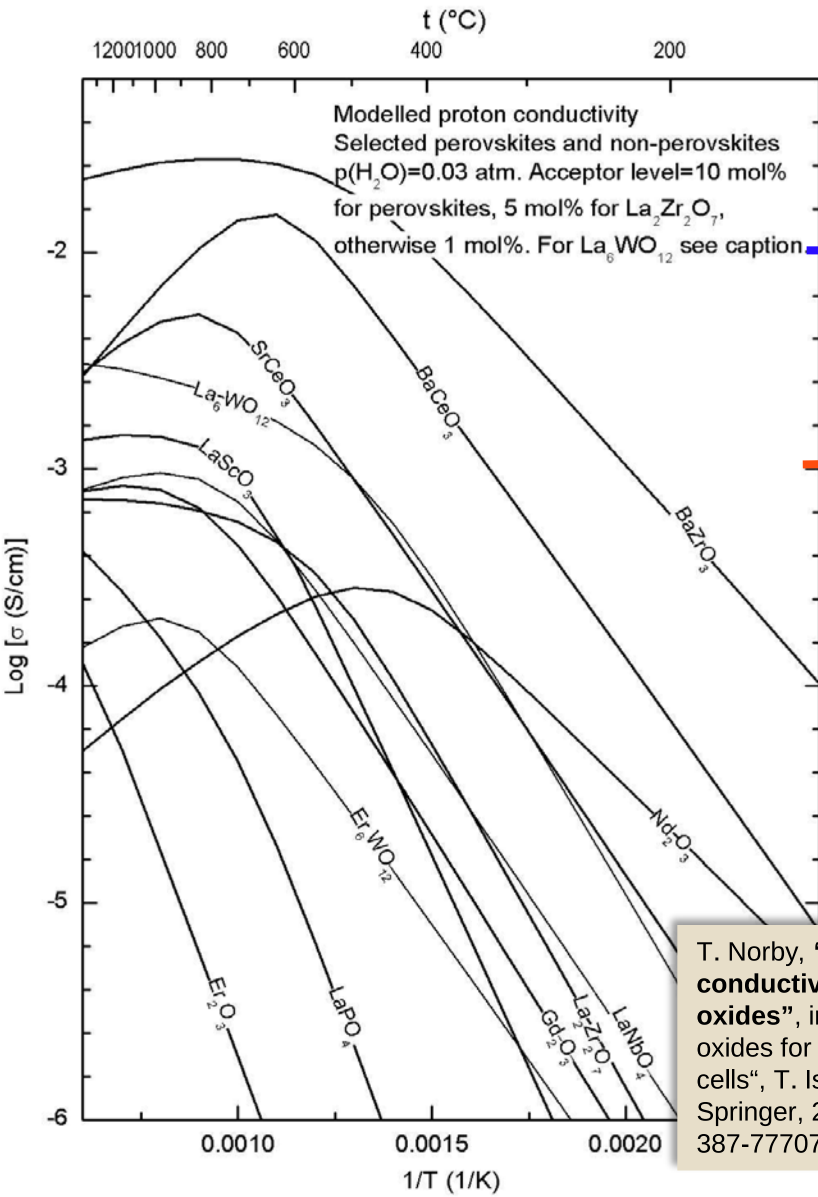
$$H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^{\bullet}$$

Protons transport: rotation and hydrogen bond jumps



From K.-D. Kreuer, 2008

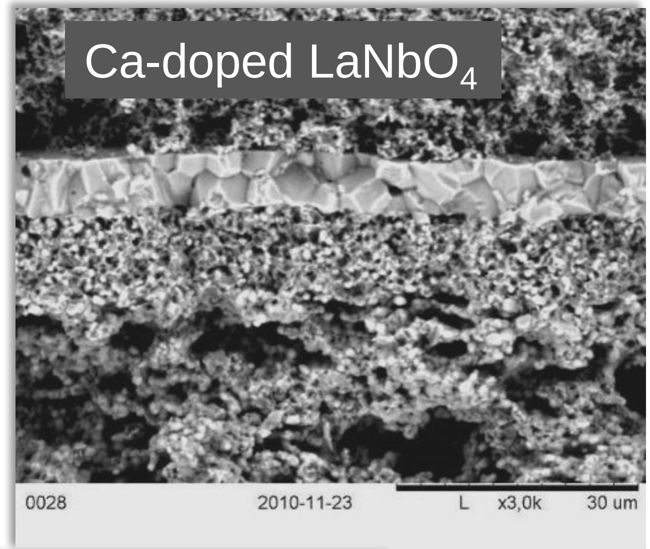
Proton conductivity in acceptor-doped oxides



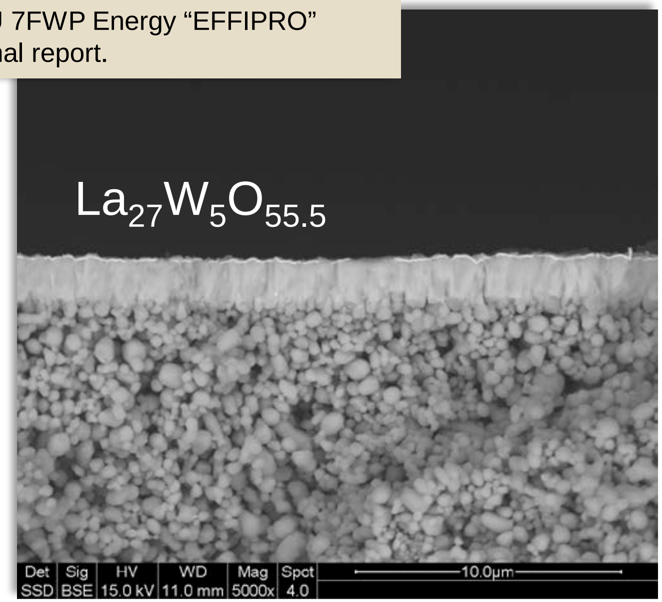
0.1 Ωcm^2
10 μm

0.1 Ωcm^2
1 μm

T. Norby, **"Proton conductivity in perovskite oxides"**, in "Perovskite oxides for solid oxide fuel cells", T. Ishihara, ed., Springer, 2009, ISBN 978-0-387-77707-8.

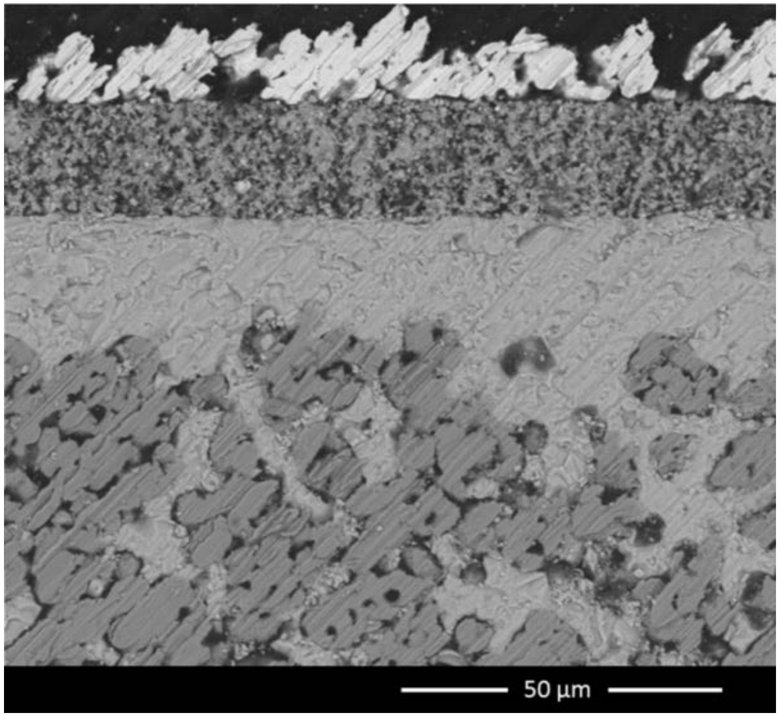


EU 7FWP Energy "EFFIPRO"
Final report.



$BaZrO_3$ vs ZrO_2

- One more cation
  - Higher reactivity with electrodes, interconnects, seals
- Basic
  - Reactivity with CO_2
  - Higher p-type electronic conductivity
- Dehydration
  - Maximum in proton conductivity
  - Oxide ion conductivity («co-ionic»)
  - Chemical expansion
- High sintering temperature
  - Add Ce and sintering aids. SSRS.
  - Evaporation of Ba
- Interfaces highly charged
  - Resistive grain boundaries
  - Space charge related electrode impedances?
- No good mixed protonic electronic mixed conductors (MPECs)?

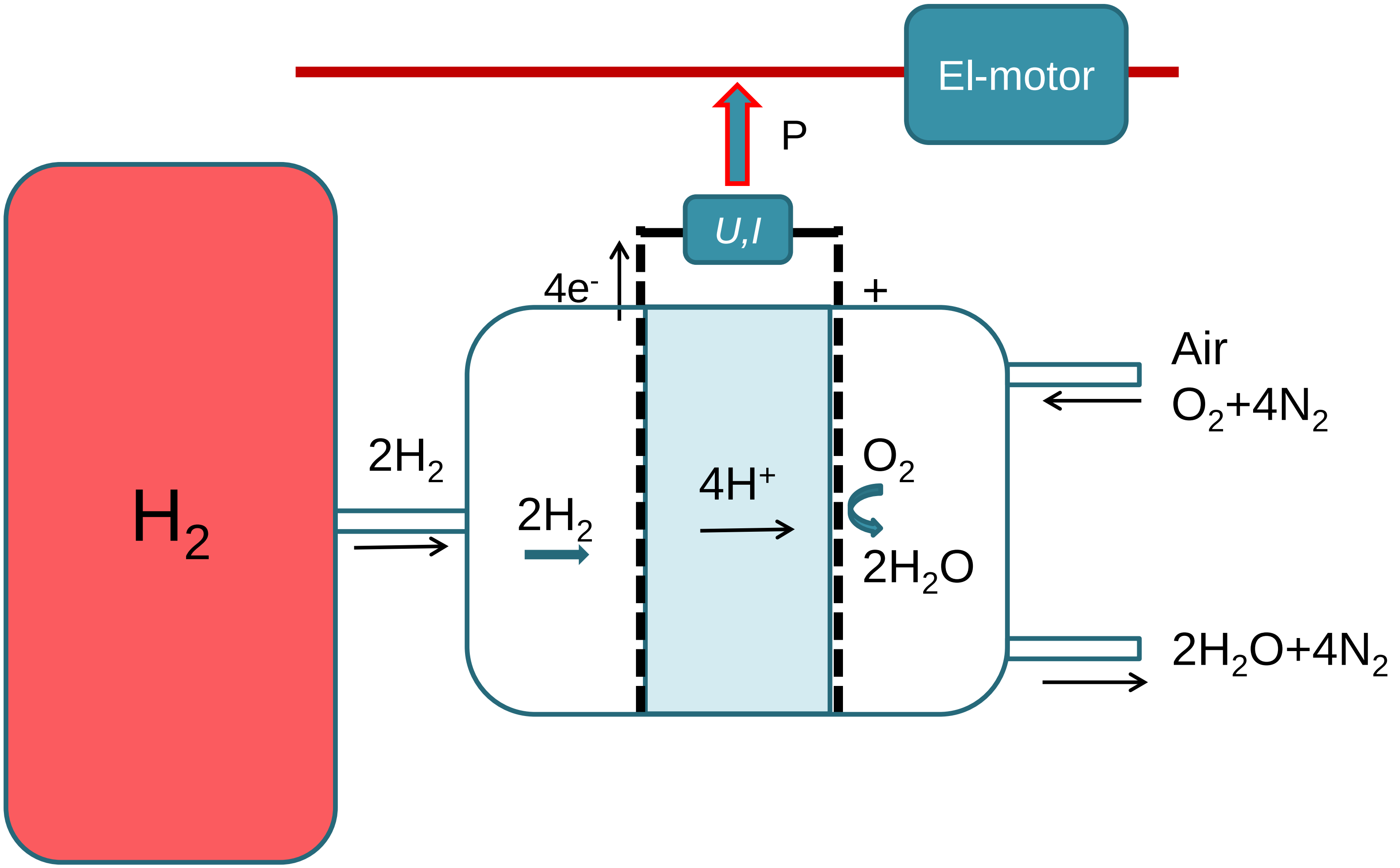


Proton ceramic fuel cells (PCFCs)

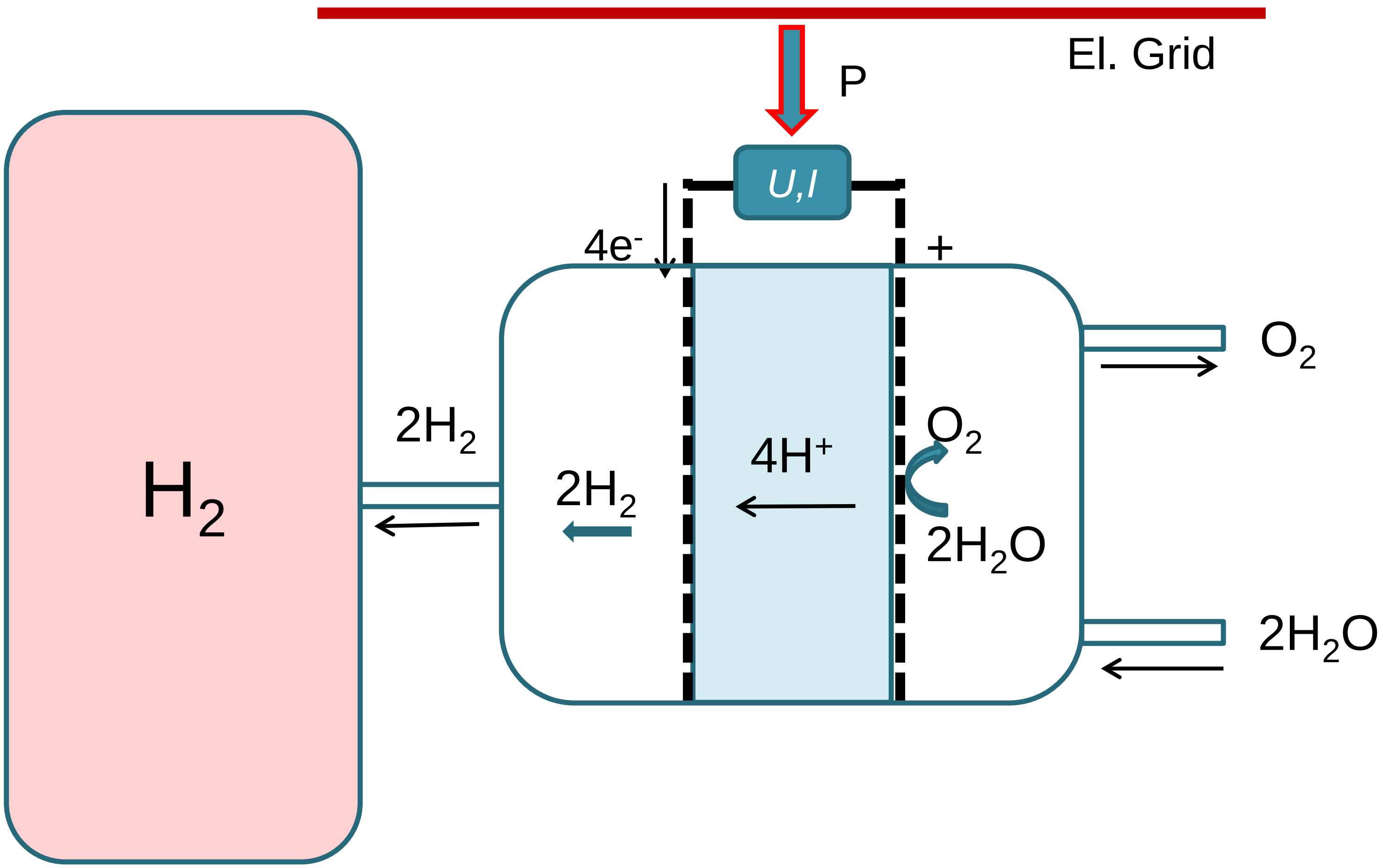
and

Proton ceramic electrolysers (PCEs)

Fuel cell

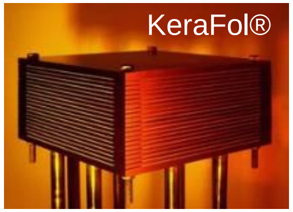


Electrolyser and electrochemical compressor

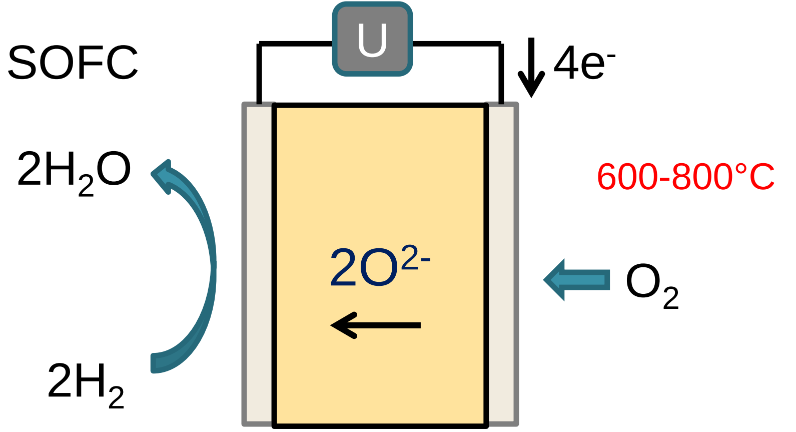


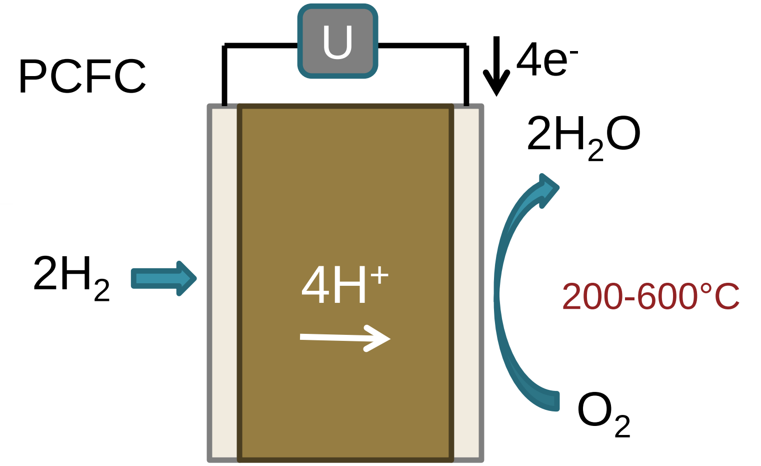
Solid-state fuel cells

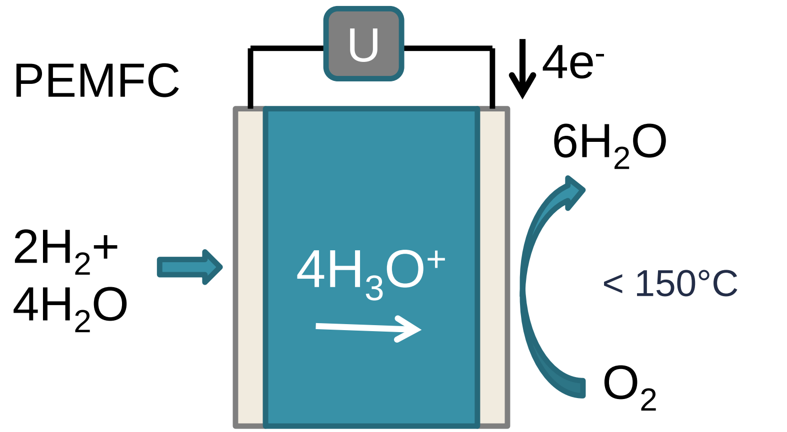
- Examples with H_2 as fuel
- SOFC: High T, low fuel utilisation, anode oxidation



- PCFC: Intermediate T, high fuel utilisation, no anode oxidation
- PEMFC: Low T, water management, cooling challenges







Some recent progress in PCFCs

- O'Hayre's group: Facile production and high performance
  - Solid State Reactive Co-Sintering
  - «Triple Conducting Oxide (TCO)» cathode

C. Duan *et al.*, *Science (2015)* 349, 6254, 1321-1326

- Haile's group: High performance PCFC cathode
  - New perovskite formulation for enhanced MIEC (MPEC)
  - Improved deposition and microstructure

C. Choi *et al.*, *Nature Energy* (2018). DOI: 10.1038/s41560-017-0085-9

- Merkle/Maier: Better cathodes - new understanding
  - Model for interaction between holes h^+ and protons H^+
  - Zn^{2+} substitution on perovskite B site

R. Zohourian *et al.*, *Adv. Funct. Mater.* **2018**, 1801241

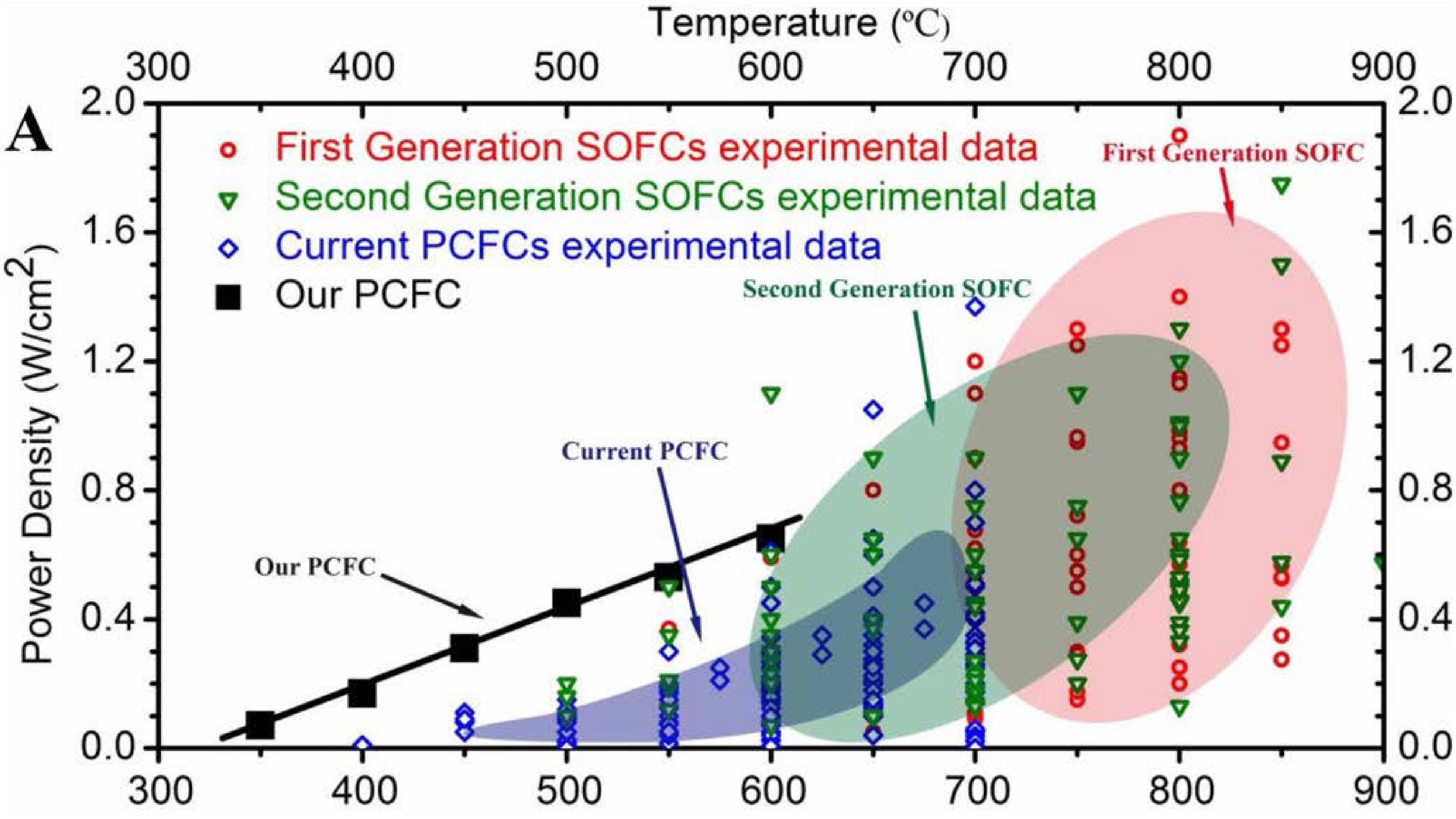
- O'Hayre's group: PCFCs for hydrocarbon fuels
  - Good stable performance
  - Little coking on Ni-based anodes

C. Duan *et al.*, *Nature* **557** (2018) 217–222

C. Duan *et al.*, *Science (2015)* 349, 6254, 1321-1326

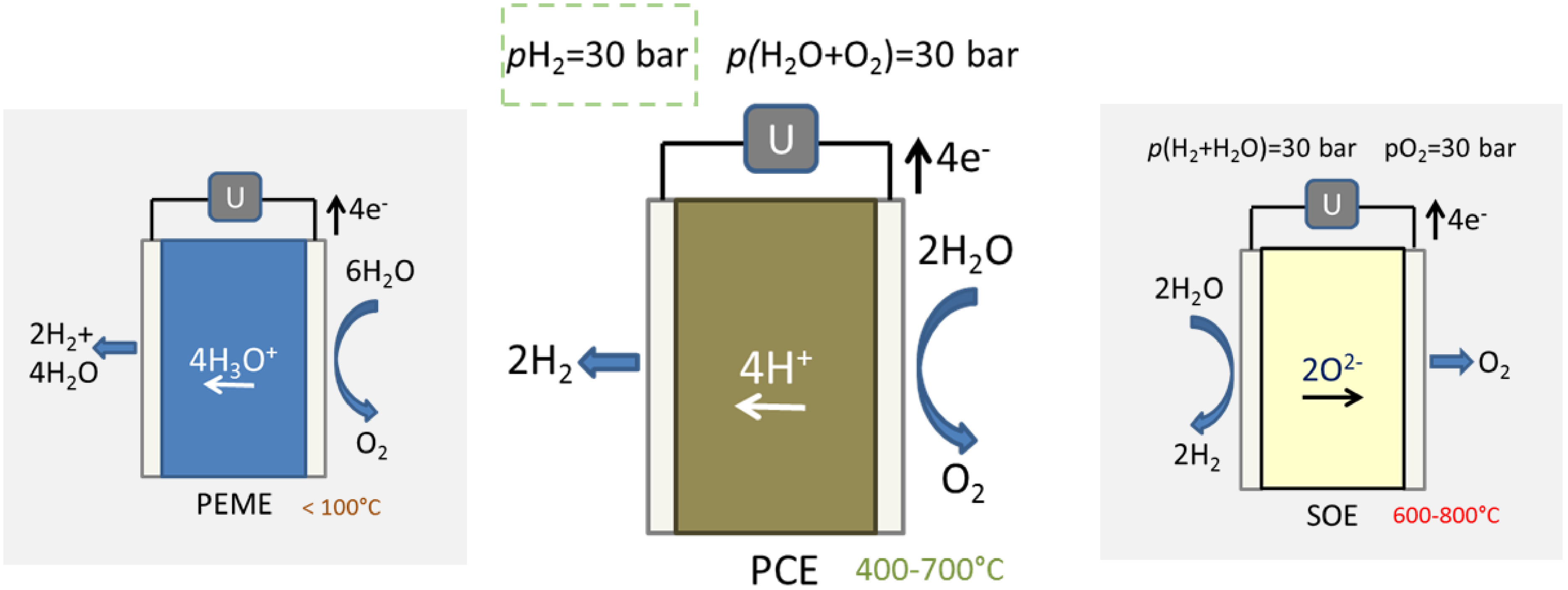
PCFC

C. Duan *et al.*, *Science (2015)* 349, 6254, 1321-1326



Proton ceramic electrolyzers

Advantages of PCEs



UiO : Department of Chemistry
University of Oslo

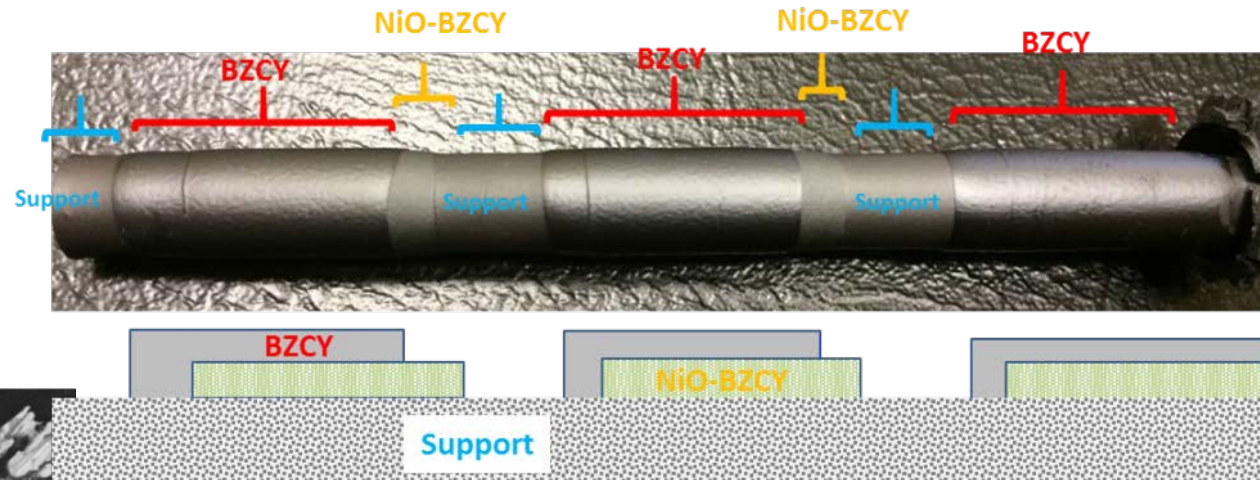
FERMiO

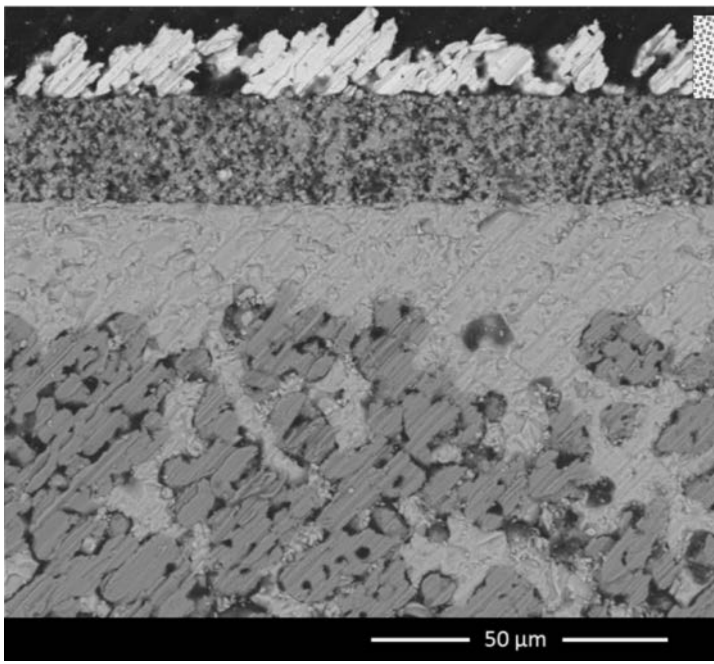
SMN SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

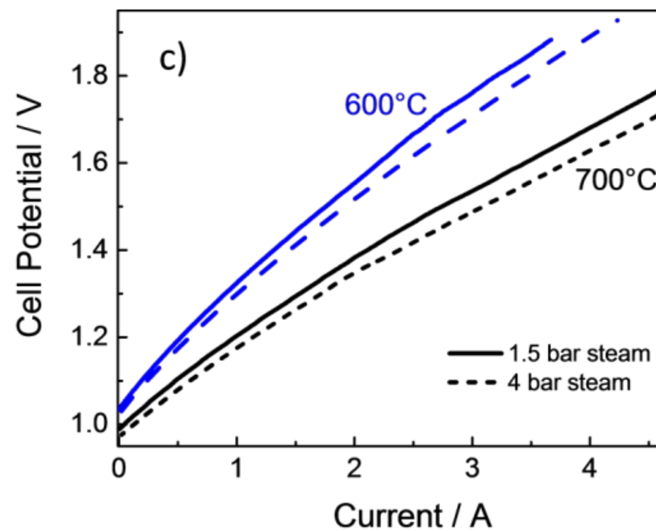
High temperature electrolyser with novel proton ceramic tubular modules (2014-2017)

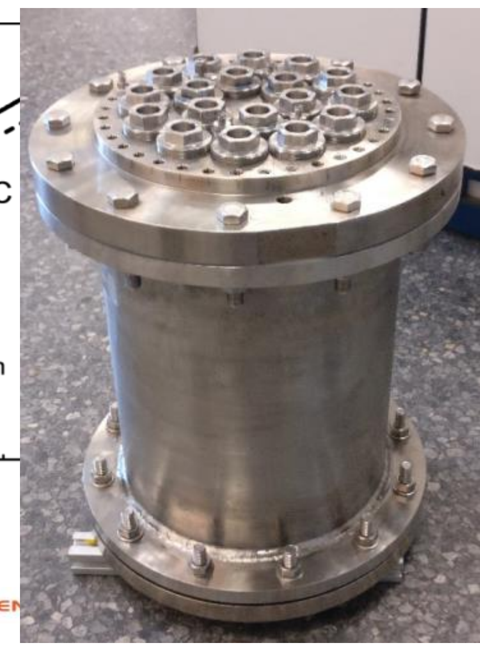
Electra

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING





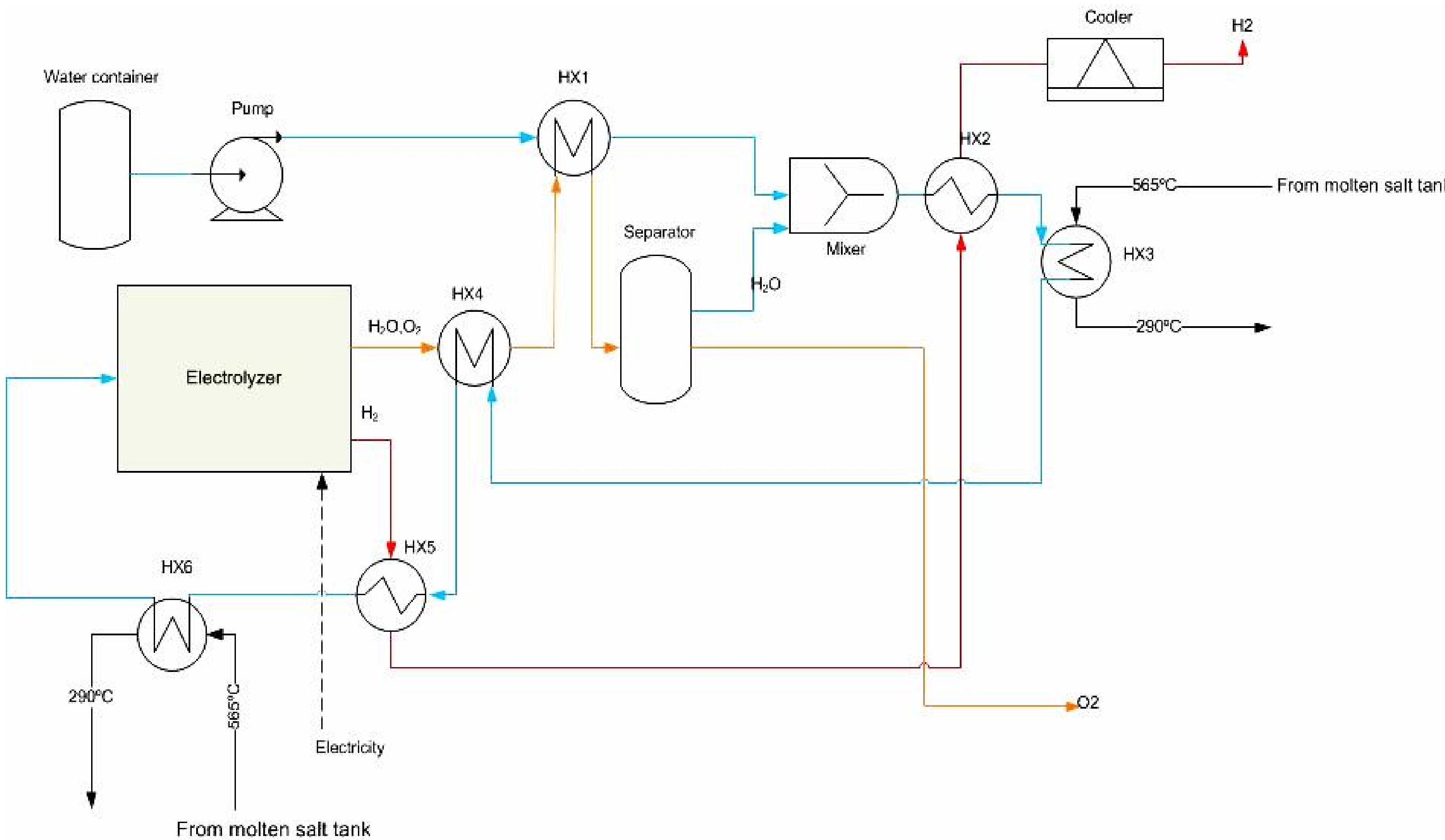




CSIC SINTEF COORSTEK MEMBRANE SCIENCES Marion Technologie ABEN

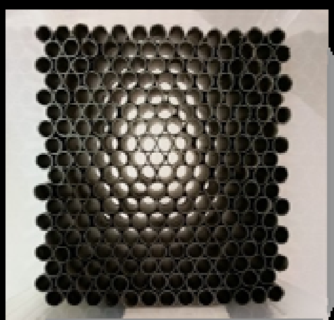
UiO : Department of Chemistry University of Oslo FERMIO SMN

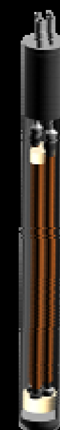
Steam electrolysis coupled with thermal energy sources: Example of solar-thermal molten salt plant



GAMER

Game changer in high temperature steam electrolysers with novel tubular cells and stacks geometry for pressurized hydrogen production



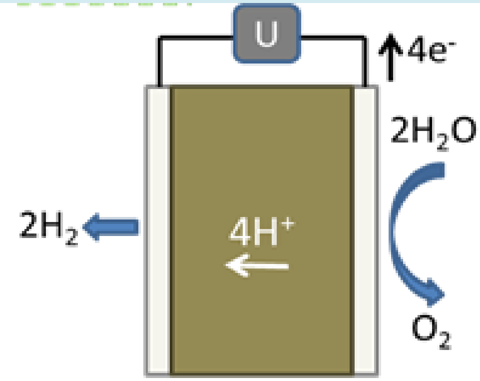


Tubular cells (electrodes, electrolyte, current collectors)	Key enabling technologies for SEU assembly (seal, manifolds, interconnects)	Cells integration in SEU (pressurized vessels, gas and electrical connectors)	SEUs integration in hot box with required ancillary equipments

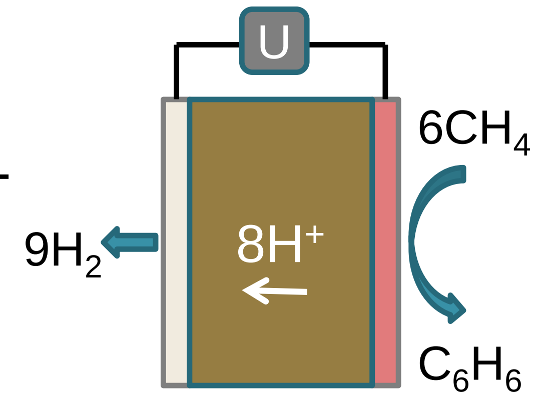
Proton ceramic electrochemical reactors (PCERs) for natural gas

3 technologies for proton ceramics and H_2

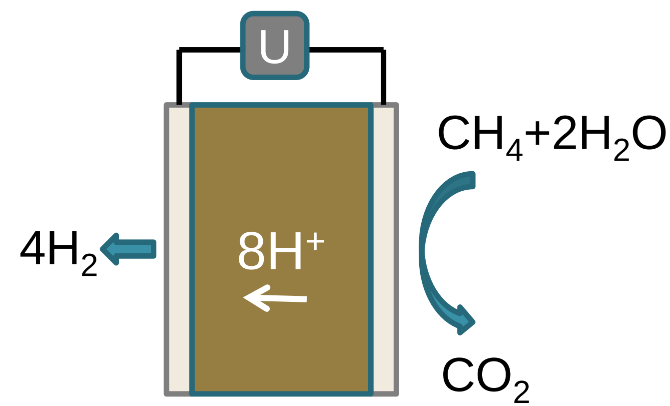
- Steam electrolysis and electrochemical compressor
  - $2H_2O = O_2 + 2H_2$



- Methane dehydroaromatization (MDA); GTL
  - $6CH_4 = C_6H_6 + 9H_2$

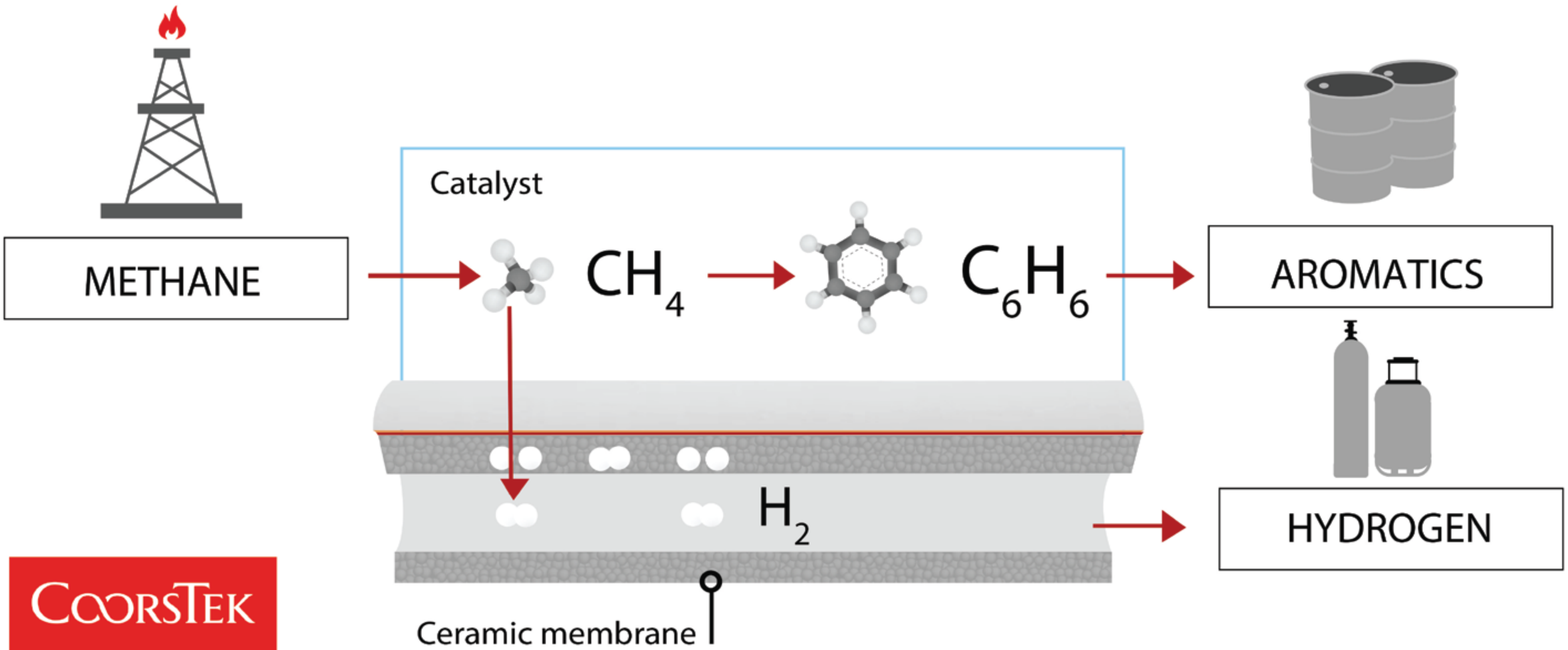


- Methane steam reforming shift electrochemical compressor
  - $CH_4 + 2H_2O = CO_2 + 4H_2$



Catalytic dehydroaromatisation of natural gas (GTL) using proton and co-ionic ceramics

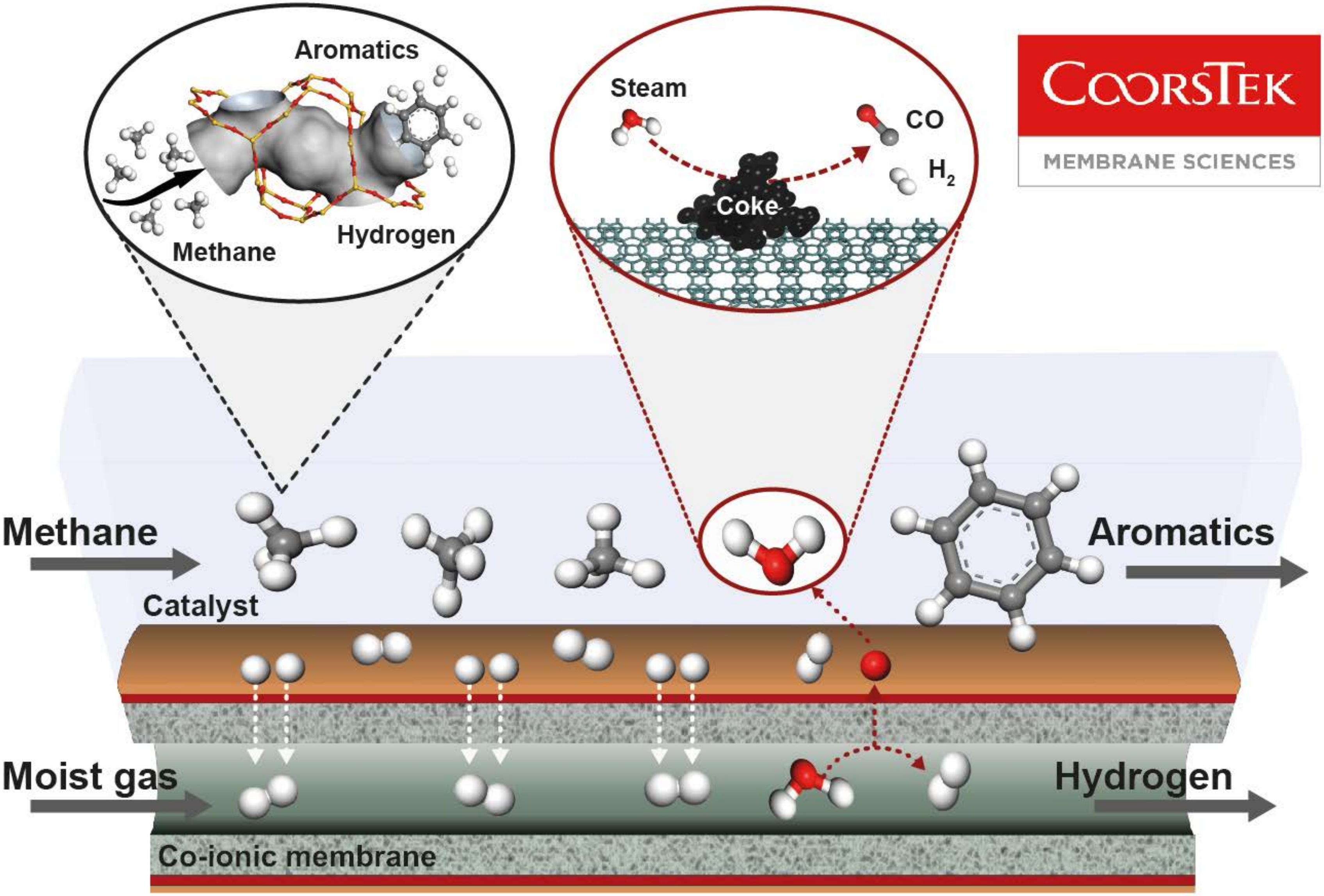
Catalytic dehydroaromatisation of natural gas using proton and co-ionic ceramics



CoorsTek MEMBRANE SCIENCES

S.H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P.K. Vestre, W.G. Coors, A. Martínez, T. Norby, J.M. Serra, C. Kjølseth, **"Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor"**, *Science*, **353** [6299] (2016) 563-566.

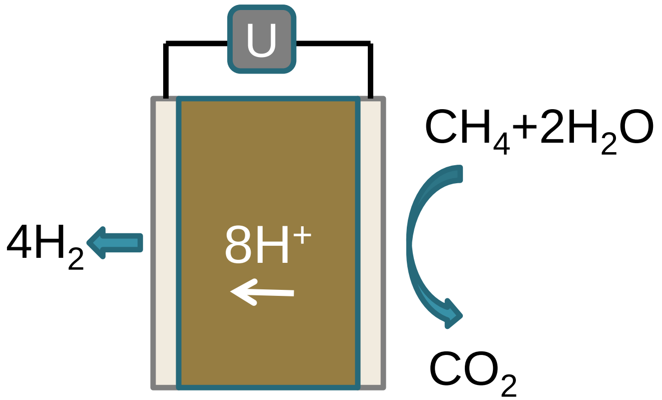
Catalytic dehydroaromatisation of natural gas using proton and co-ionic ceramics

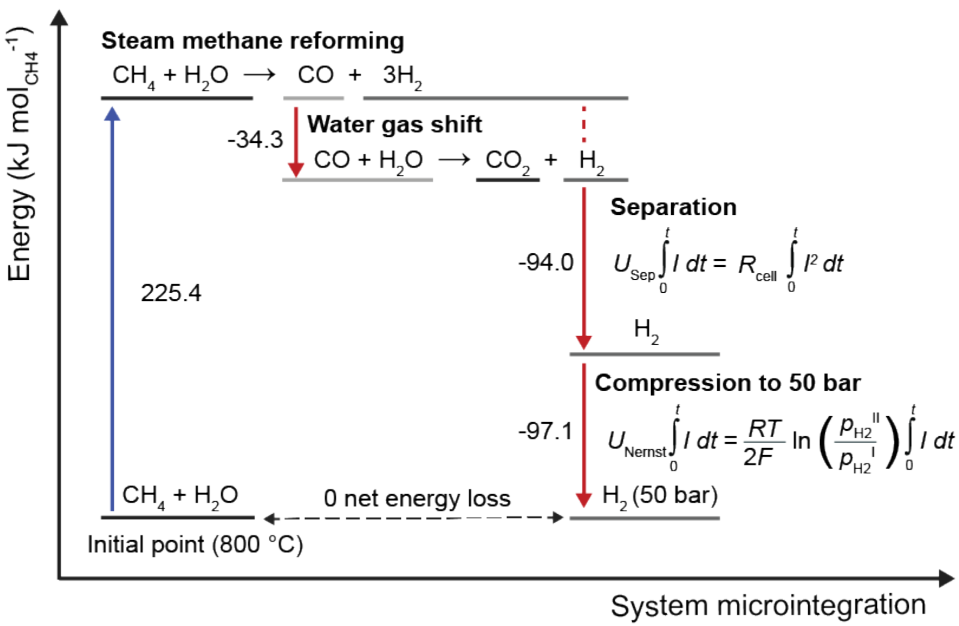


S.H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P.K. Vestre, W.G. Coors, A. Martínez, T. Norby, J.M. Serra, C. Kjølseth, **"Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor"**, *Science*, **353** [6299] (2016) 563-566.

Methane steam reformer shift electrochemical compressor

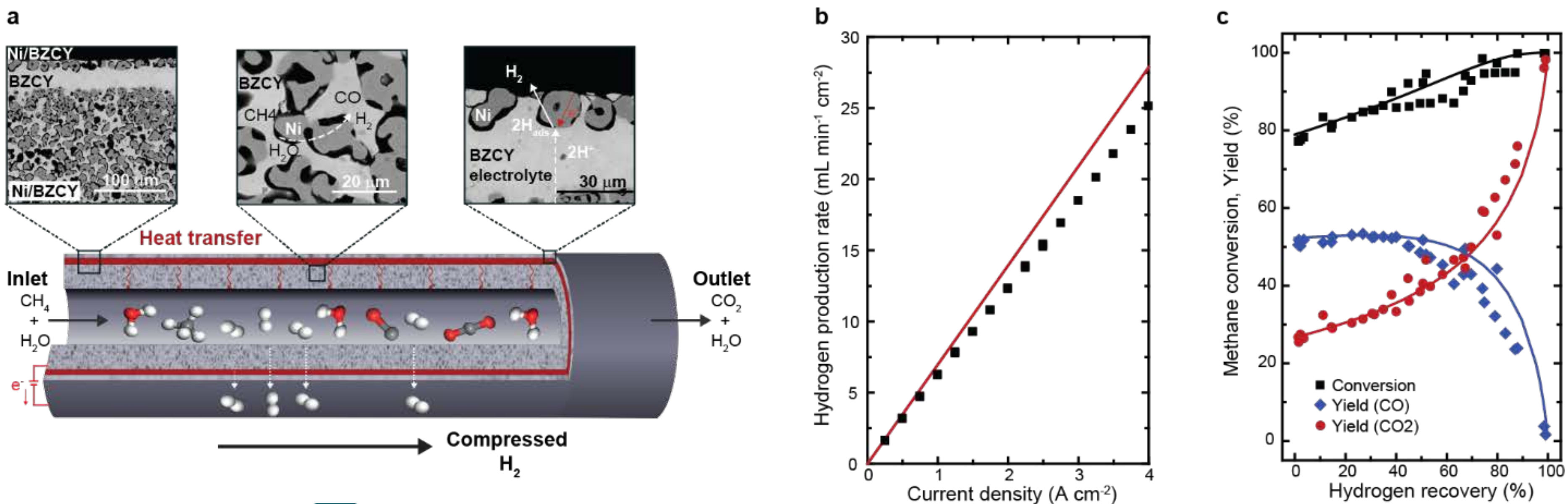
Steam reforming and electrochemical exctraction and compression of H_2 with thermal microintegration

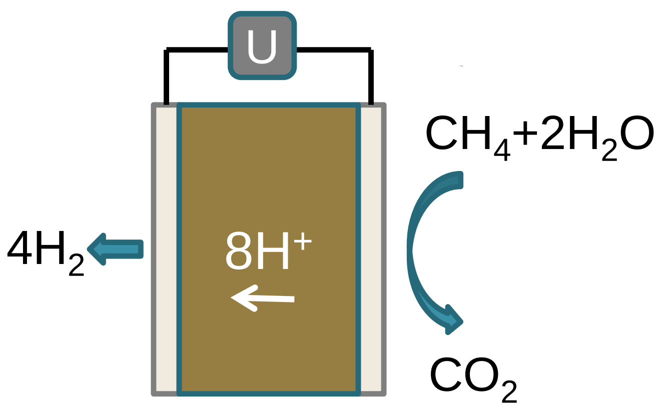




H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martinez, D. Beeaff, S.H. Morejudo, P.K. Vestre, T. Norby, R. Haugsrud, J.M. Serra, C. Kjølseth, **"Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss"**, *Nature Energy*, **2** [12] (2017) 923.

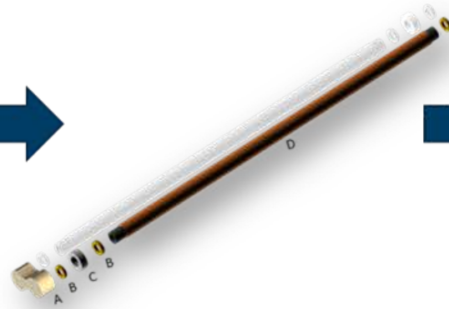
Steam reforming and electrochemical exctraction and compression of H_2 with thermal microintegration





H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martinez, D. Beeaff, S.H. Morejudo, P.K. Vestre, T. Norby, R. Haugsrud, J.M. Serra, C. Kjølseth, **"Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss"**, *Nature Energy*, **2** [12] (2017) 923..

Fabrication – modularity - scaling up



Tubular cells (electrodes, electrolyte, current collectors)	Key enabling technologies for SEU assembly (seal, manifolds, interconnects)	Cells integration in SEU (pressurized vessels, gas and electrical connectors)	SEUs integration in hot box with required ancillary equipments

CoorsTek
MEMBRANE SCIENCES

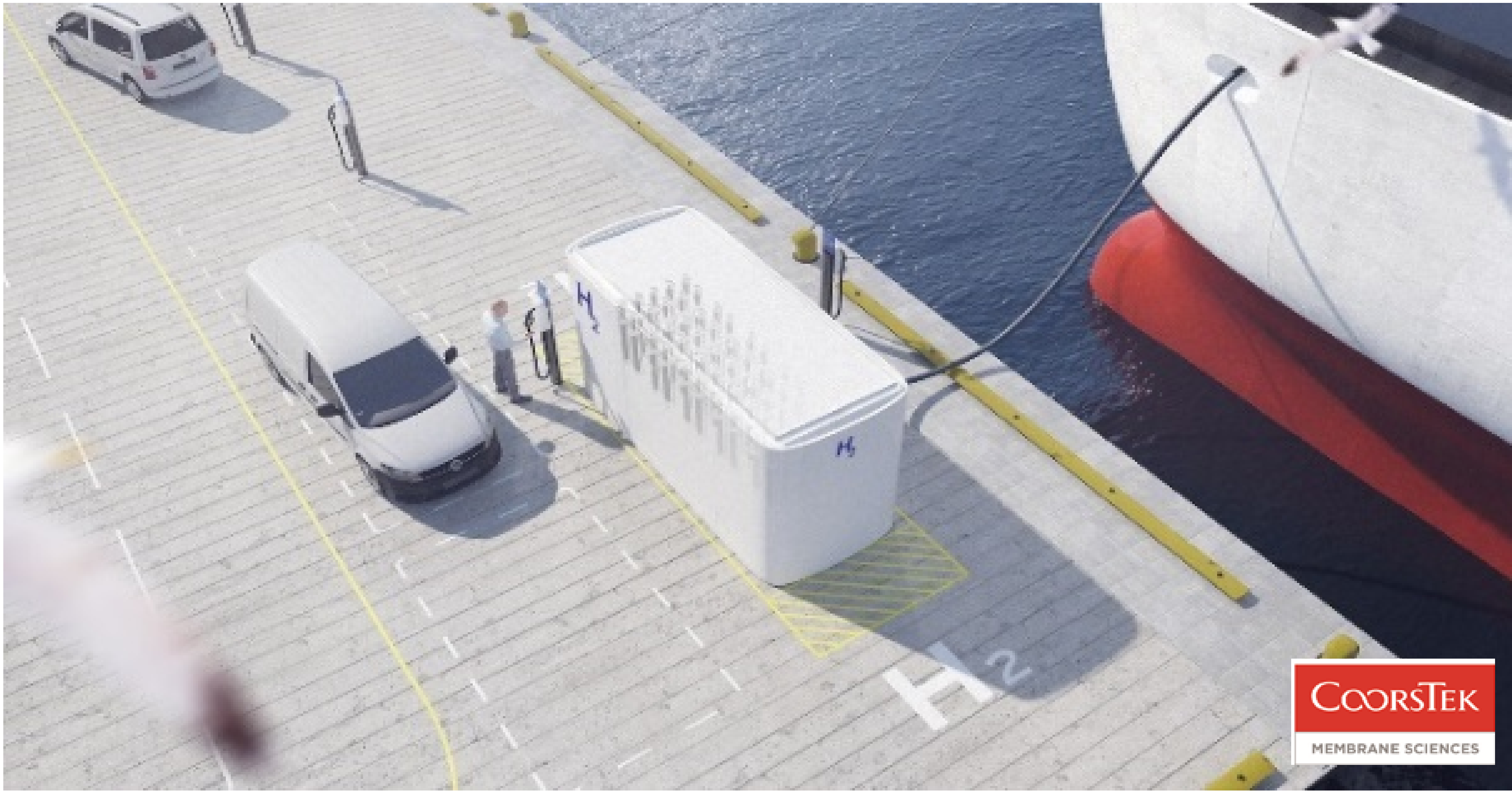
Small scale – one SEU

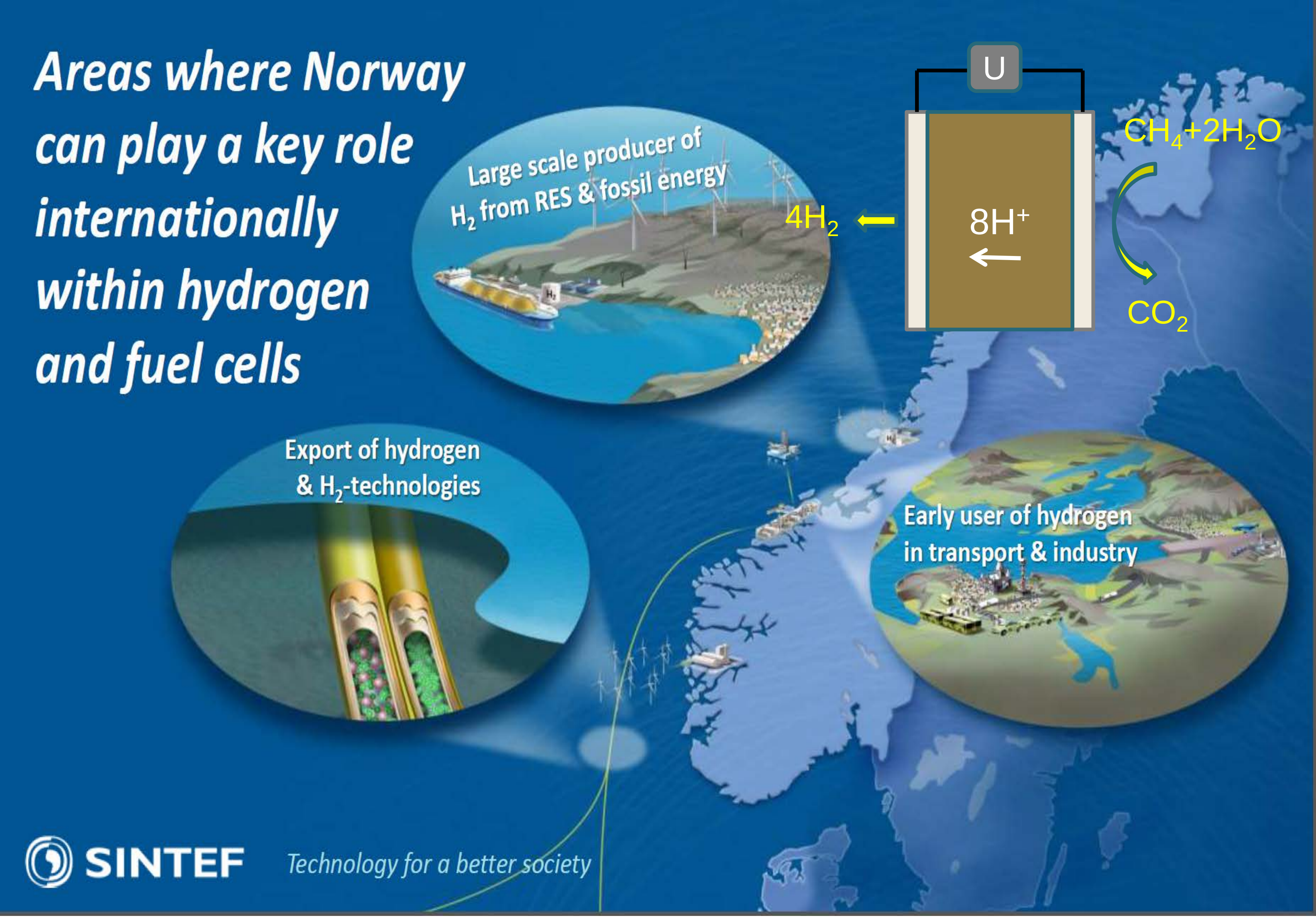
UiO : Department of Chemistry
University of Oslo

FERMiO

SMN
SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

Larger scale:
Vehicle fleets. Trucks. Trains. Marine. Industry.
One or more «boxes»




Areas where Norway can play a key role internationally within hydrogen and fuel cells
Large scale producer of H_2 from RES & fossil energy
U
CH_4+2H_2O
$4H_2$
$8H^+$
CO_2
Export of hydrogen & H_2-technologies
Early user of hydrogen in transport & industry
SINTEF
Technology for a better society

Large scale

Conclusion ☺