UiO : Department of Chemistry
University of Oslo

Guldberg Waage lecture 2018

Hydrogen

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Thanks to students and colleagues through a long career with protons and hydrogen, at UiO but also at CoorsTek Membrane Sciences AS, SINTEF, NTNU…

Department of Chemistry
University of Oslo

Centre for Materials Science
and Nanotechnology (SMN)

FERMiO
Oslo Innovation Centre

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GEOLOGISK
MUSEUM

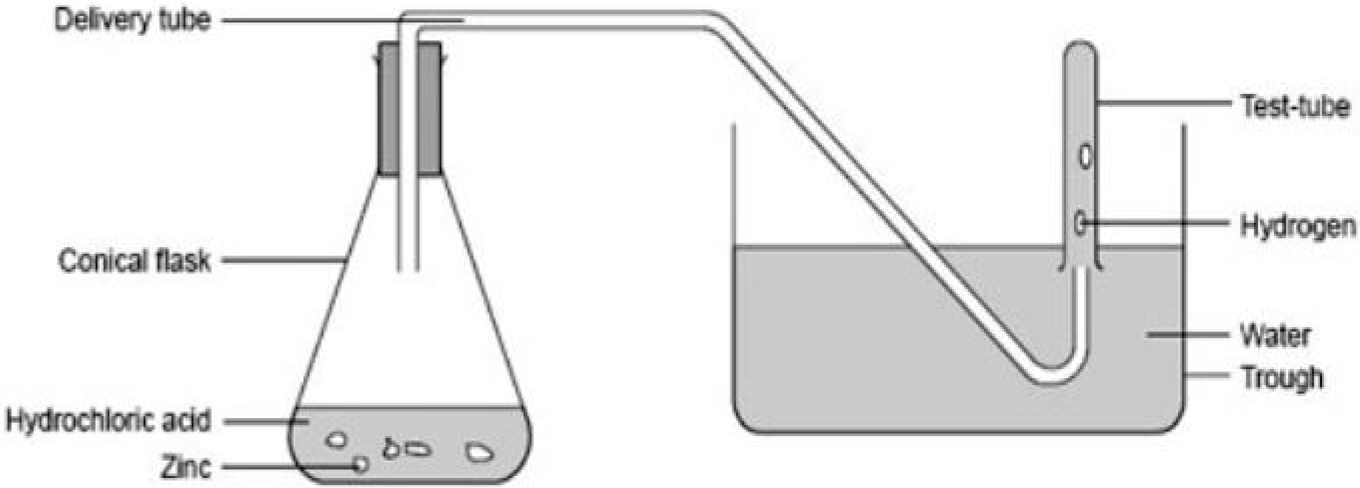
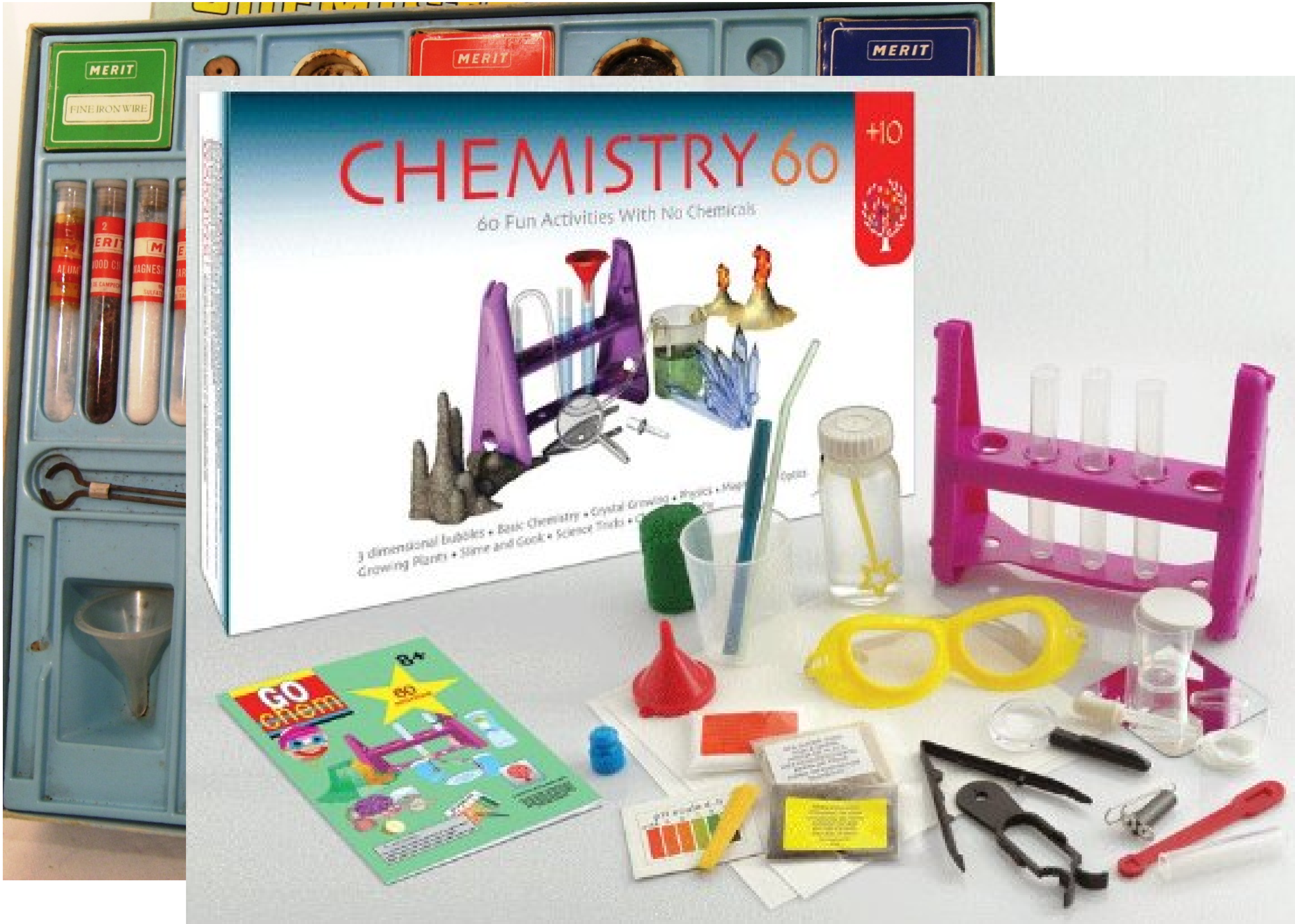

Delivery tube
Conical flask
Hydrochloric acid
Zinc
Test-tube
Hydrogen
Water
Trough

Fig.1


MERIT
FINE IRON WIRE
MERIT
MERIT
CHEMISTRY 60
+10
60 Fun Activities With No Chemicals
3 dimensional bubbles • Basic Chemistry • Crystal Growing • Physics
Growing Plants • Slime and Gook • Science Tools
GO chem
8+

Many more small steps along the way…

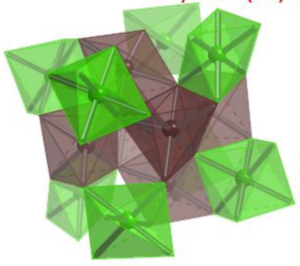
- Nerliens Kemisk-Tekniske shop window display in Oslo
- Buying chemicals at Nerliens for my lab in the basement
- Seeing the need for a textbook in chemistry
  …written by myself 14 years old
- Making unexpectedly large amounts of chlorine gas one day in the basement
- Making hydrogen
  …and checking if it is sufficiently free from air to not explode
- Extracting alcaloids from birch
- Driving my chemistry teacher crazy
  …$CuSO_4(aq) + 2KI(aq) = CuI(s) + KI_3(aq)$
- UiO studies and career…

Xuemei Cui

Master project:

New inert anodes for Al electrolysis

- Elkem
- Y_2O_3 should be stable enough
  Megon AS



- Can we dope Y_2O_3 to become an electronic conductor?
- No. Y_2O_3 doesn't want that, at all. Too big band gap!
- It likes protons H^+. From $H_2O(g)$. Even at 1000°C.
  PhD: Protons in Y_2O_3 and other oxides

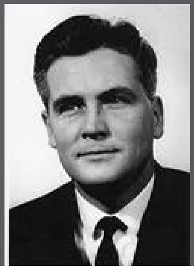
Per Kofstad (1929-97)

Univ. Oslo

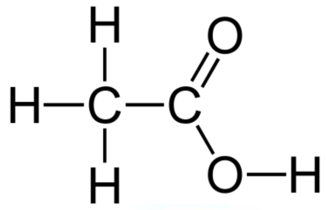
Physical/inorganic chemistry

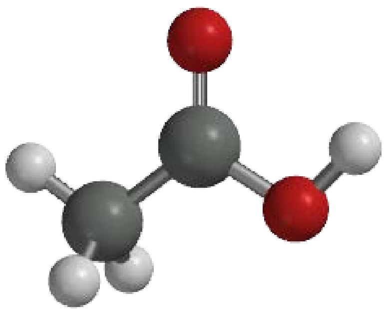
Solid-state electrochemistry; reactivity, defects, transport

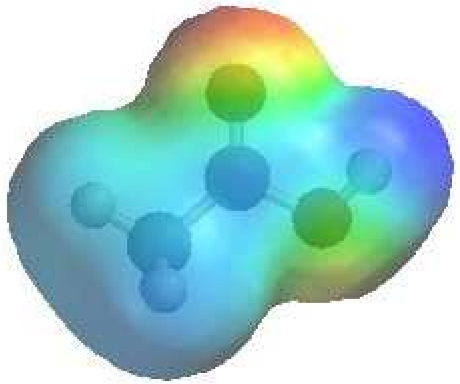
PhD UC@Berkeley 1953



Hydrogen is an extraordinary element







H^+

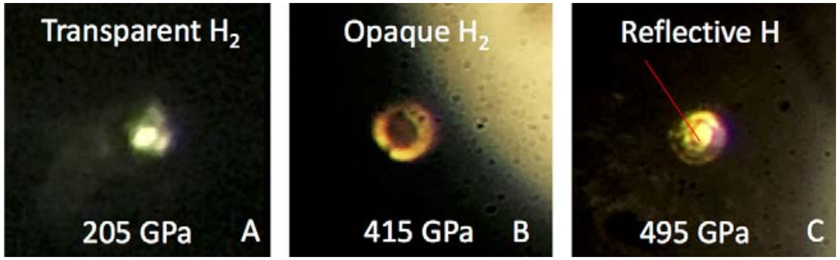
- 10^{-5} Å – always embedded in other nuclei's electron clouds

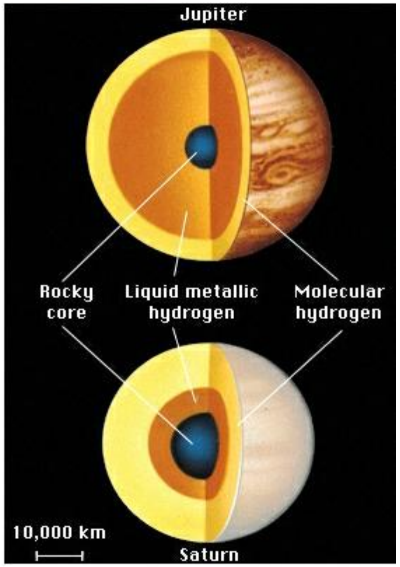
O_2H^+

H_3^+

OH^*

H



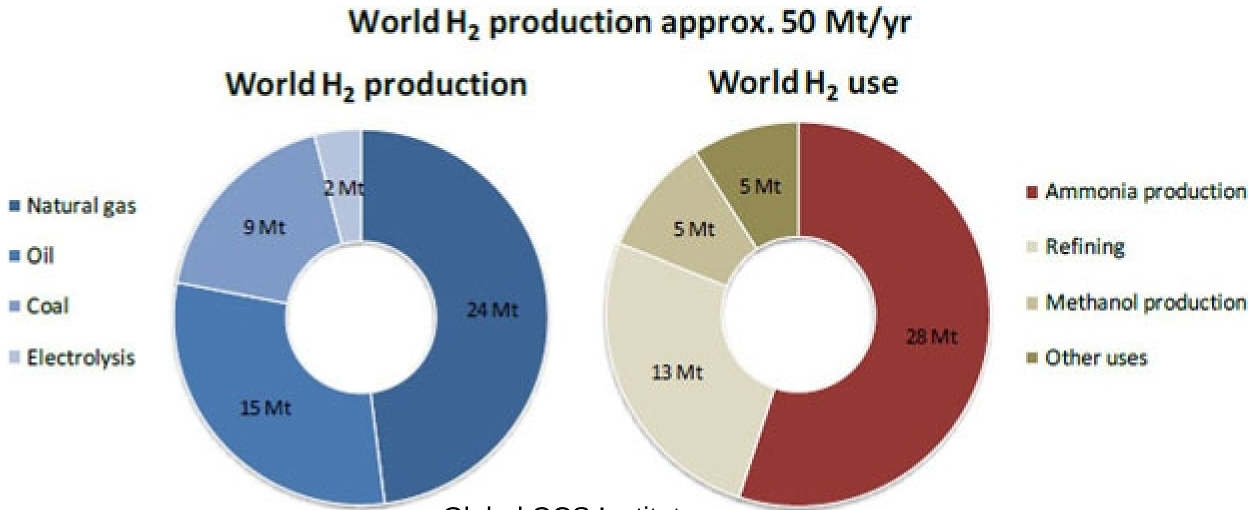


H_2

- Ortho, para
- Gas, liquid, solid, metallic, superconducting

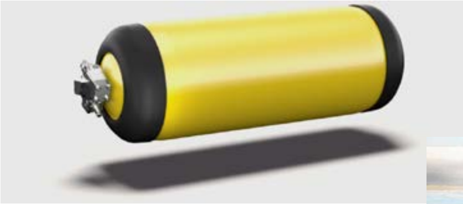
H^-

Hydrogen, H_2



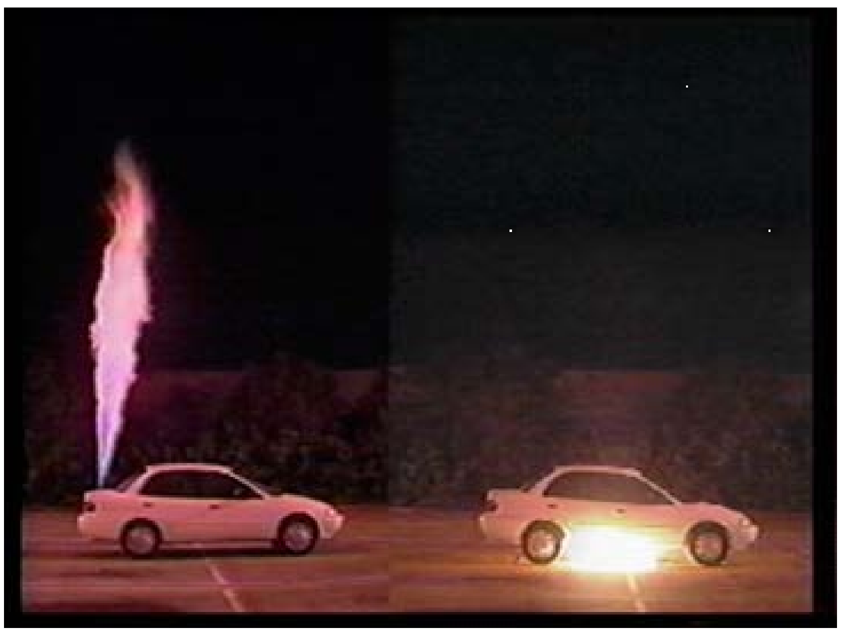
Global CCS Institute

- $100 billion industry
- 50 million metric tons per year
  - From natural gas reforming, oil, and coal gasification
  - Electrolysis (4% only – 8 GW)



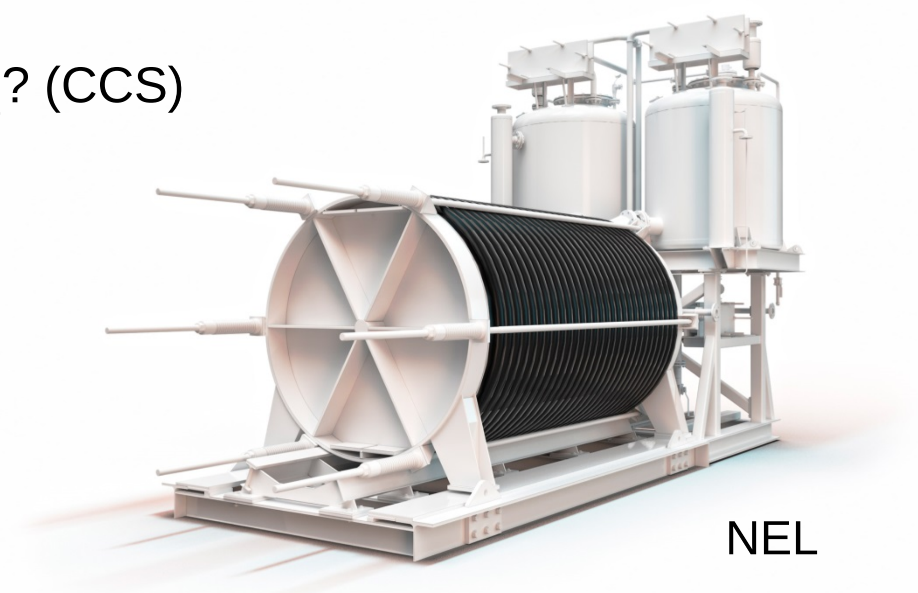
- Main use
  - Ammonia, refineries, methanol
- Handling H_2 is standard and safe technology
- Future new uses comprise:
  - Transportation
  - Energy carrier
  - Stationary intermittent storage of renewable energy.

H_2 safety



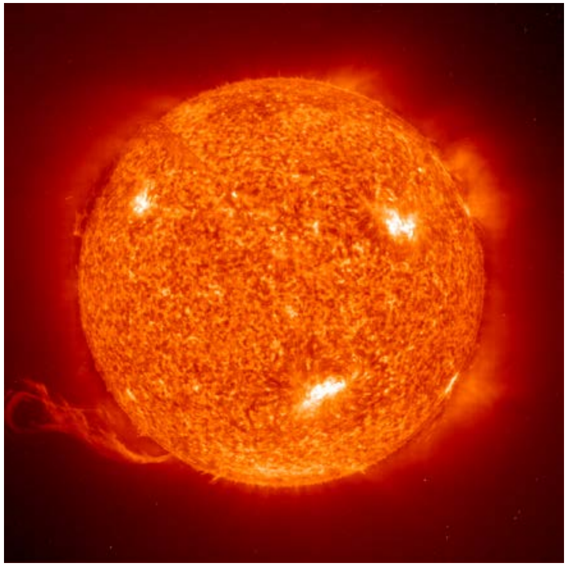
Hydrogen production chemistry

- Electrolysis $2H_2O = 2H_2 + O_2$
  - Source of electricity? Renewable or fossil?
- Gasification & shift $C + 2H_2O = 2H_2 + CO_2$
- Reforming & shift $CH_4 + 2H_2O = 4H_2 + CO_2$
  - Can we capture and store the CO_2? (CCS)
- Back to renewables
  - Electrolysis
  - Direct solar
    - Thermochemical looping
    - Photoelectrochemical water splitting
    - Bio

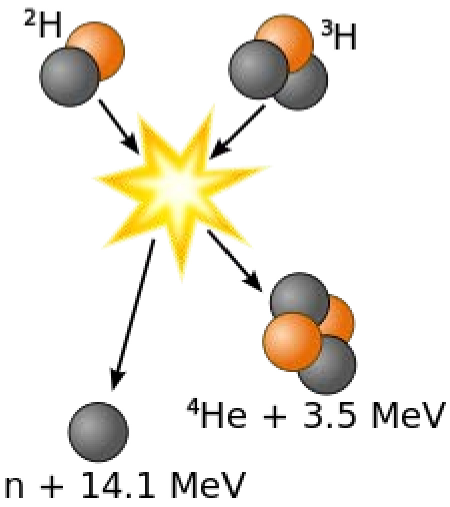


NEL

Nuclear H



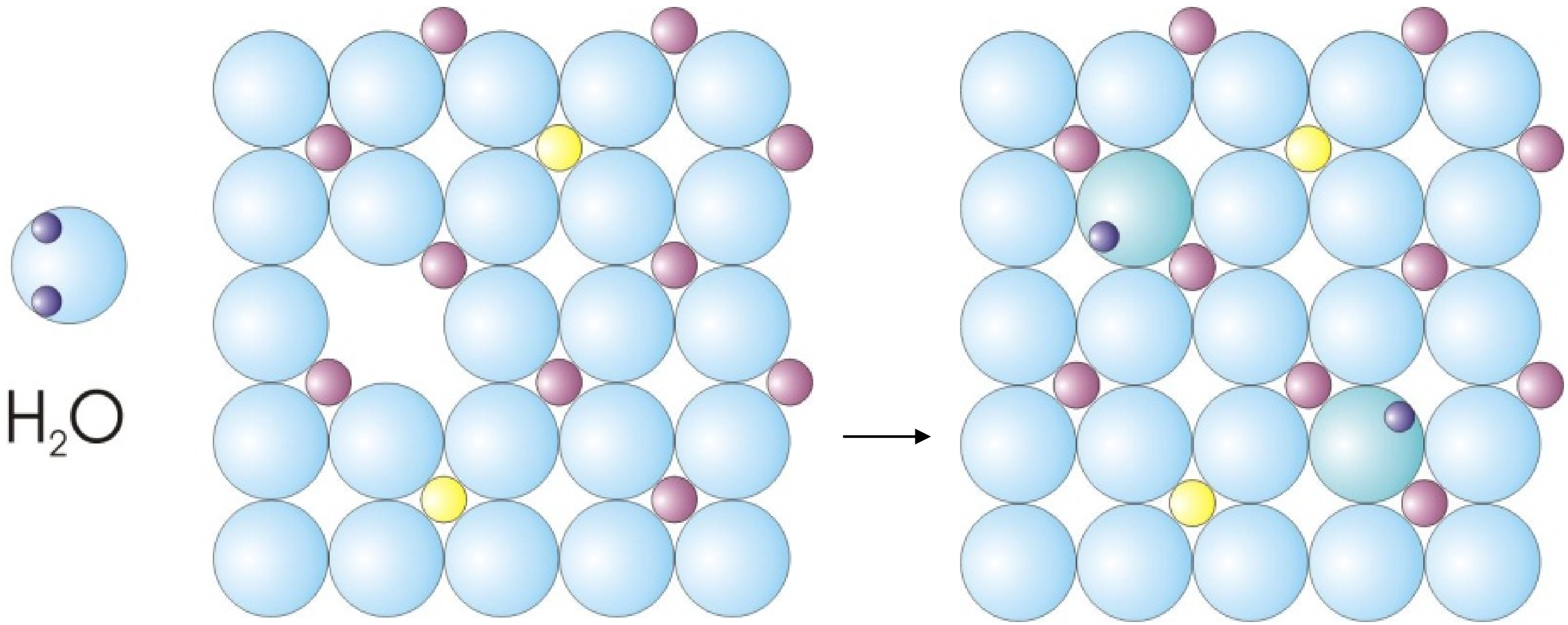
- Fusion
  - $4H^+ = He^{2+} + 2e^+ + \ldots$
  - LiD



$$^6\mathrm{Li} + \mathrm{n} \rightarrow {}^4\mathrm{He} + {}^3\mathrm{T}$$

Back to my Y_2O_3

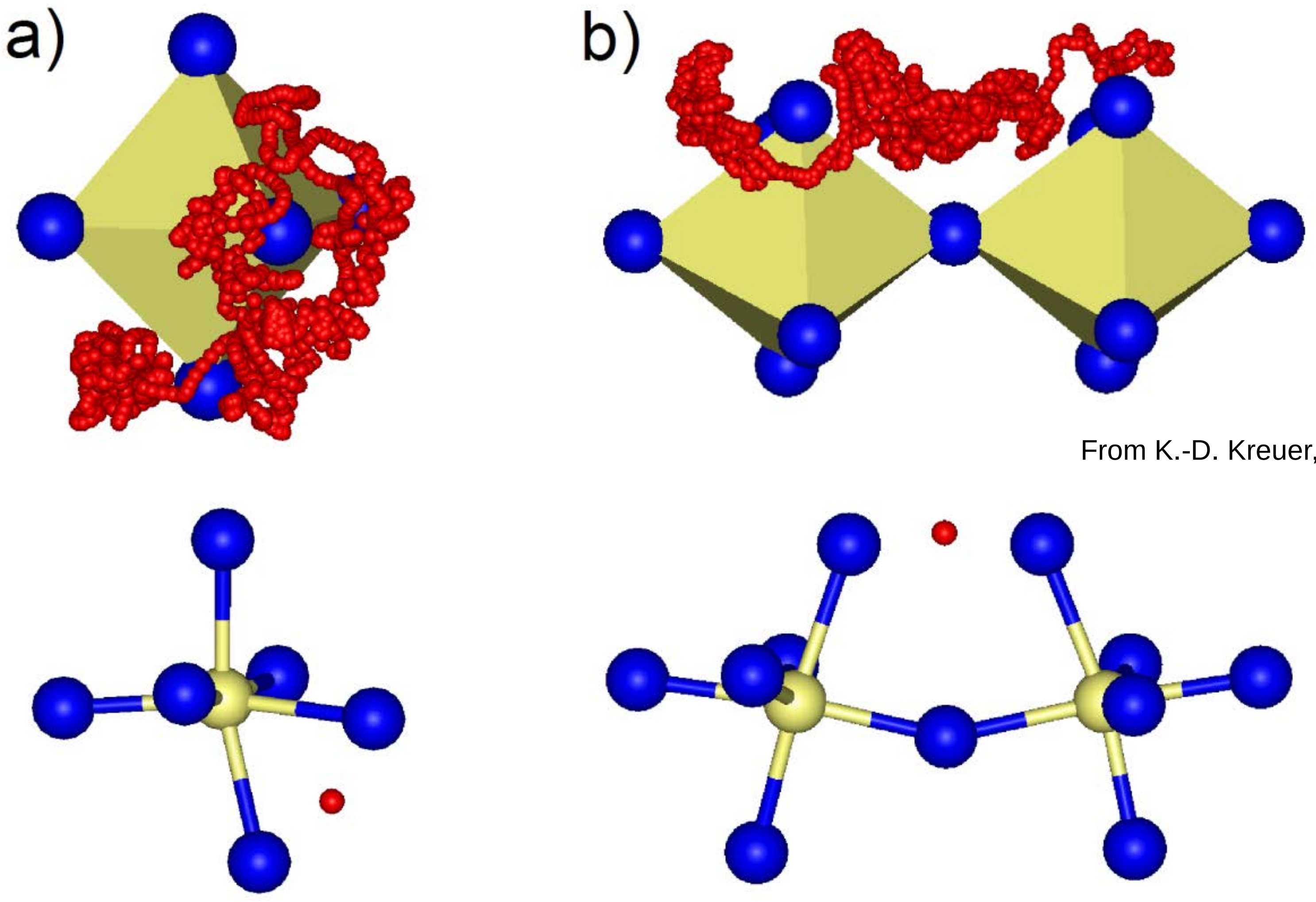
Proton conducting oxides by hydration of oxygen vacancies



$$H_2O(g) + v_O + O_O^{2-} = 2OH_O^-$$

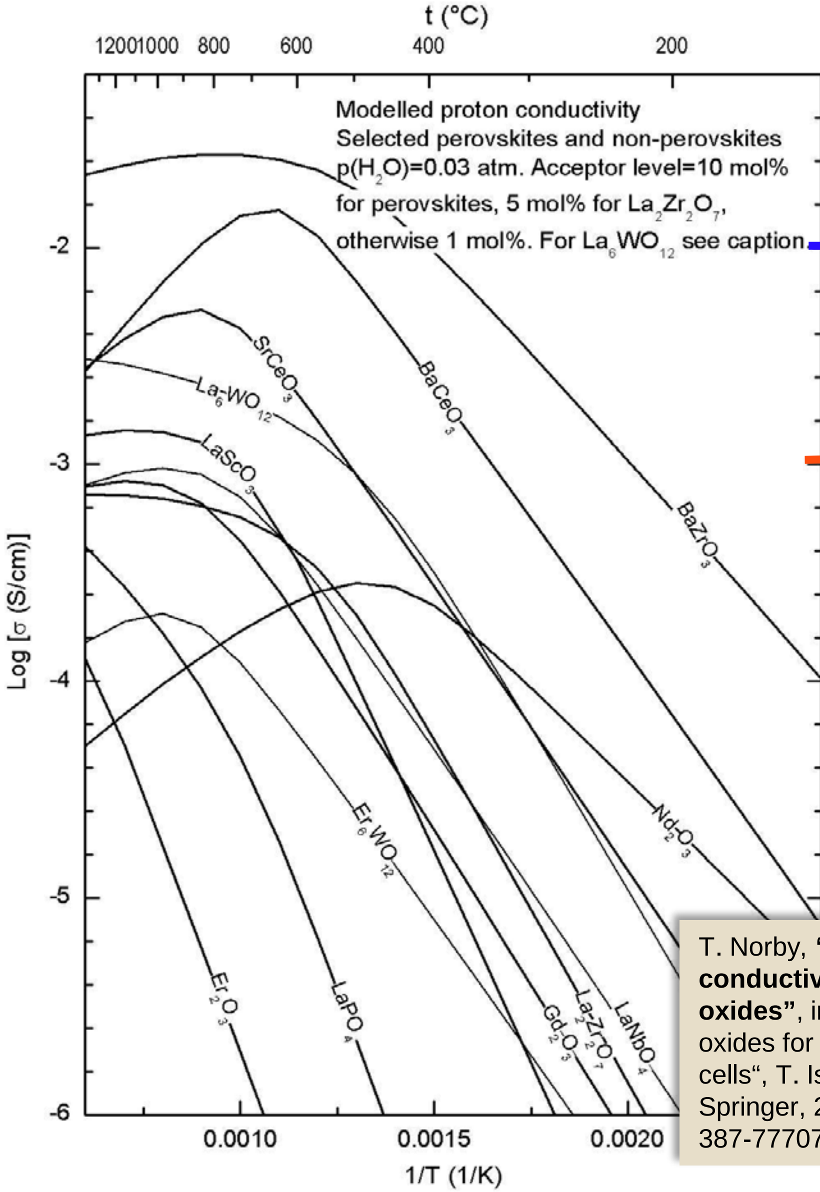
$$H_2O(g) + v_O^{\bullet\bullet} + O_O^x = 2OH_O^\bullet$$

Protons transport: rotation and hydrogen bond jumps



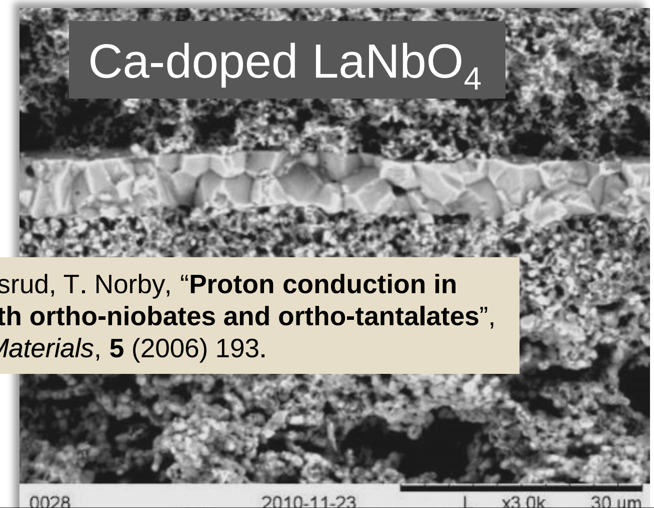
From K.-D. Kreuer, 2008

Proton conductivity in acceptor-doped oxides

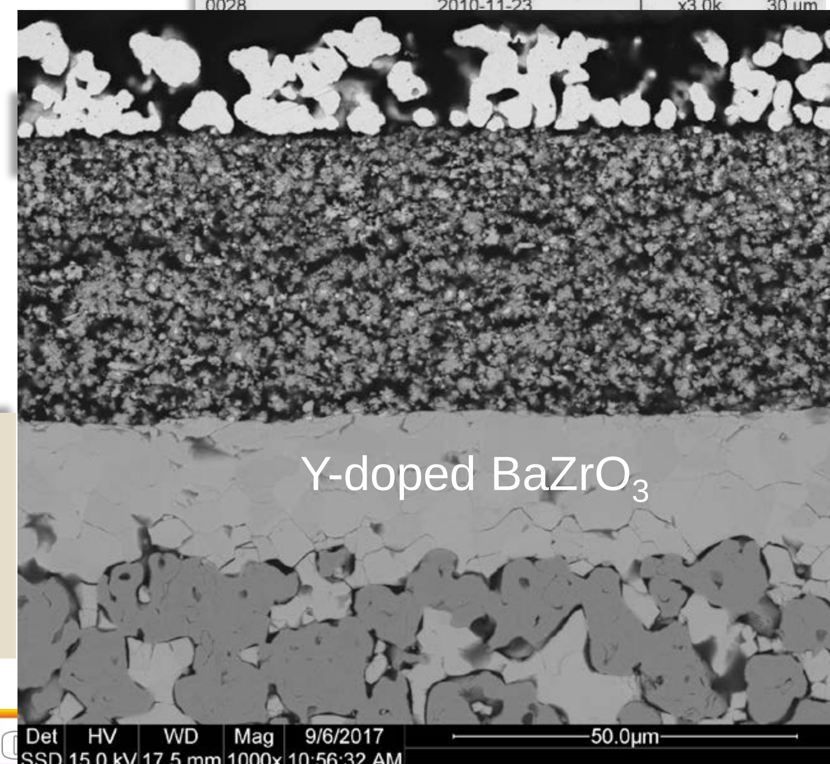


0.1 Ωcm^2
10 µm

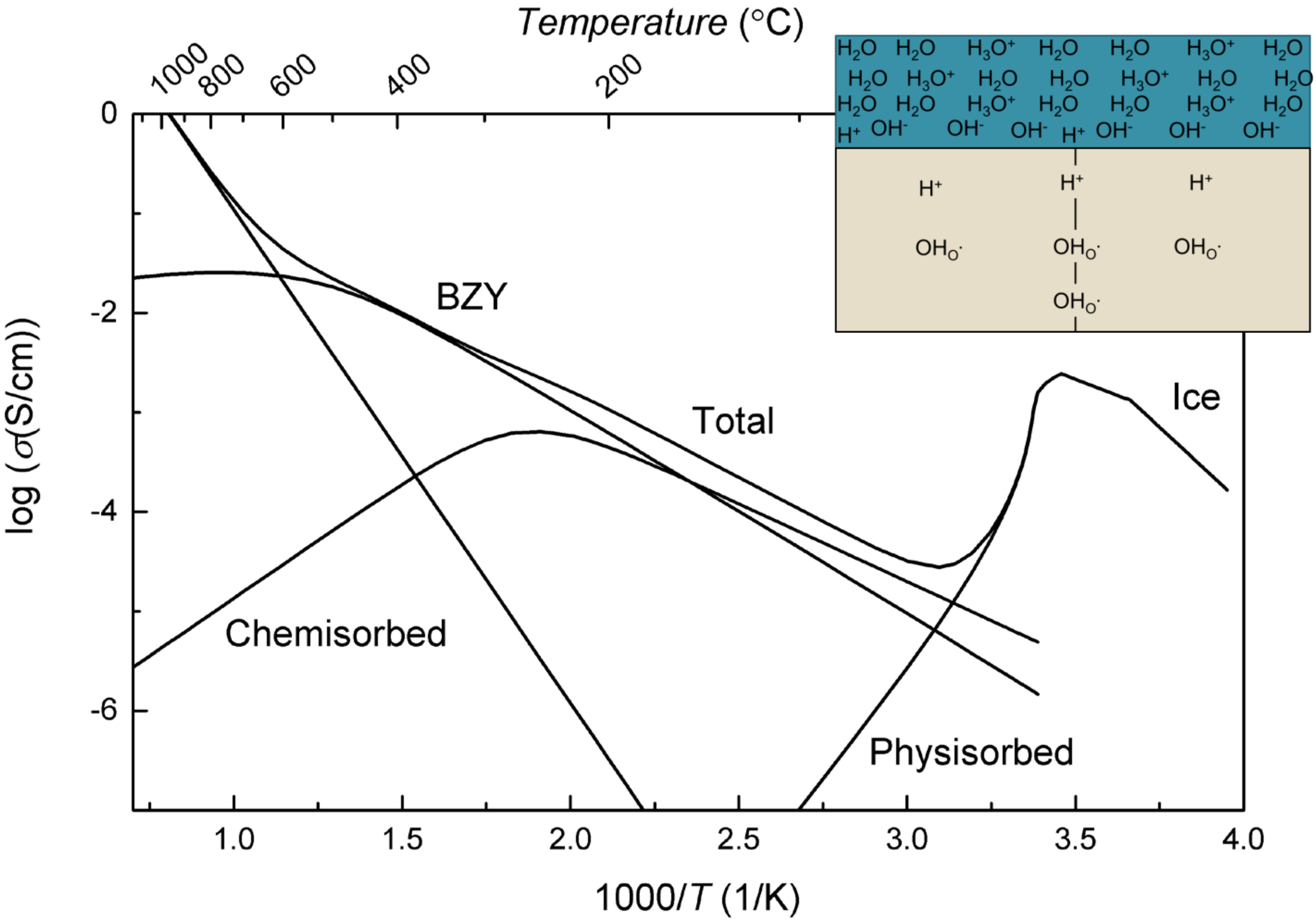
0.1 Ωcm^2
1 µm



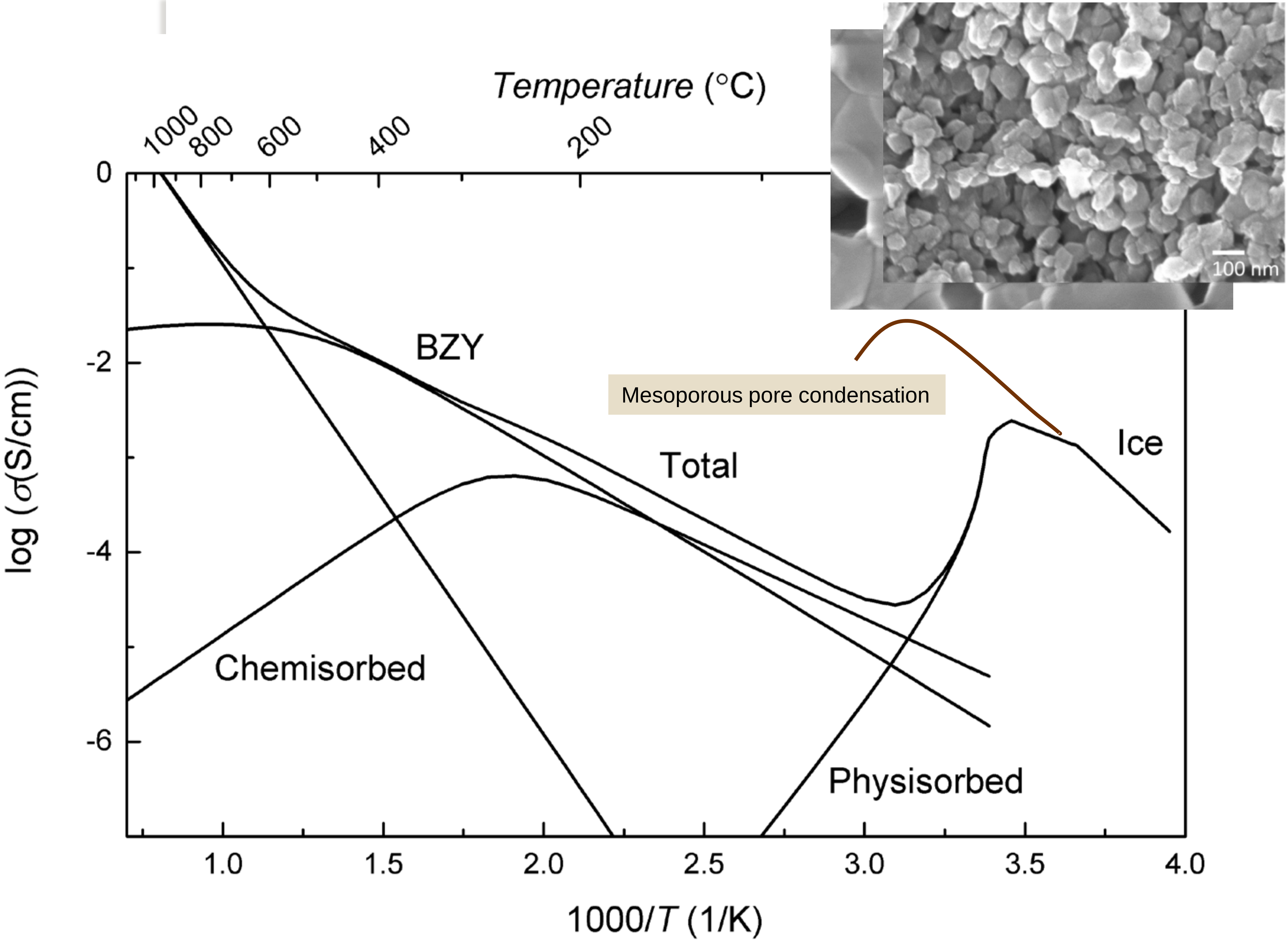
R. Haugsrud, T. Norby, "**Proton conduction in rare earth ortho-niobates and ortho-tantalates**", *Nature Materials*, **5** (2006) 193.



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.



Temperature (°C)
1000
800
600
400
200
0
-2
-4
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
H2O H2O H3O+ H2O H2O H3O+ H2O
H2O H3O+ H2O H2O H3O+ H2O H2O
H2O H2O H3O+ H2O H2O H3O+ H2O
H+ OH- OH- OH- H+ OH- OH- OH-
H+ H+ H+
OHO· OHO· OHO·
OHO·



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1000
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0
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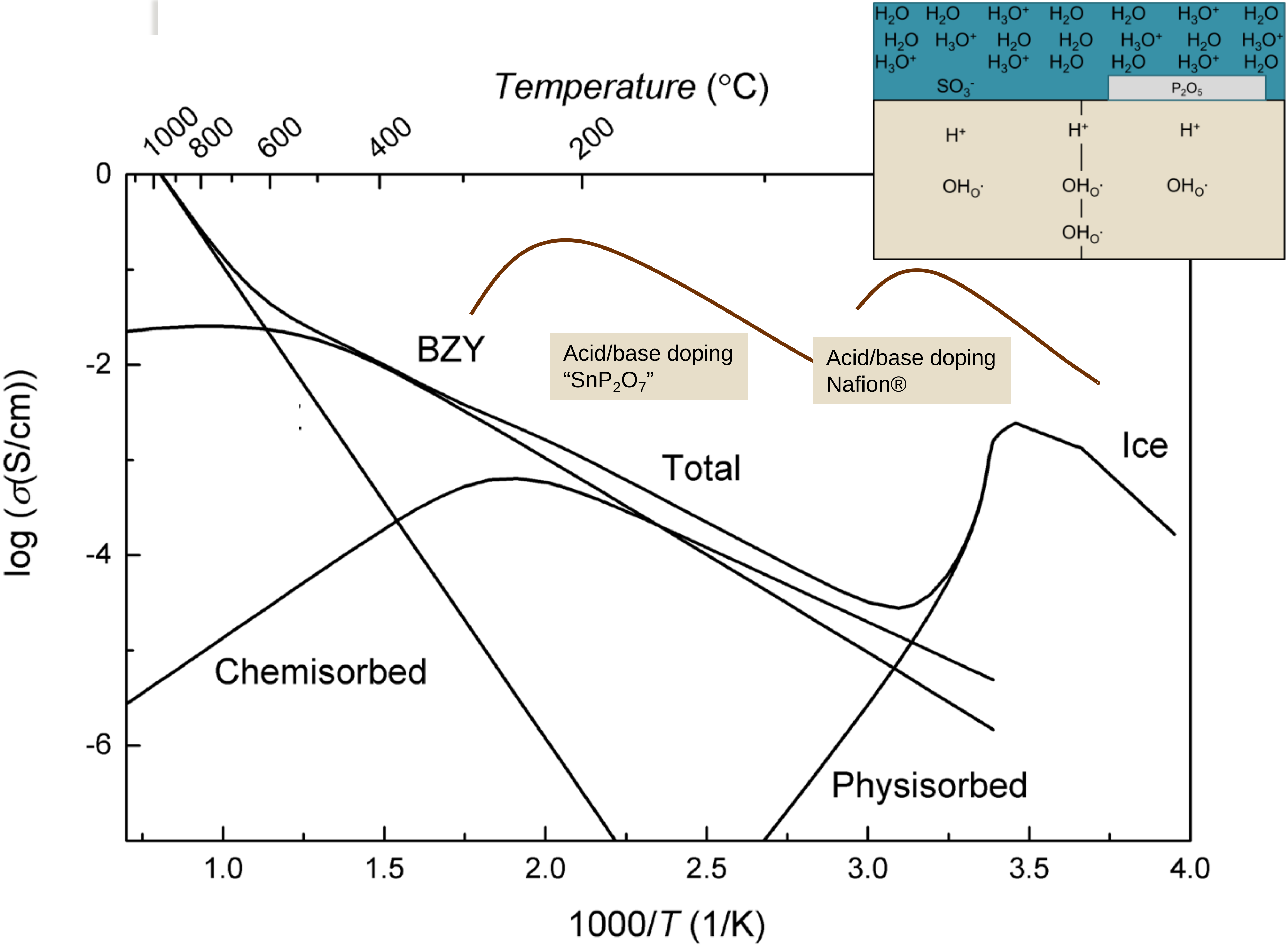
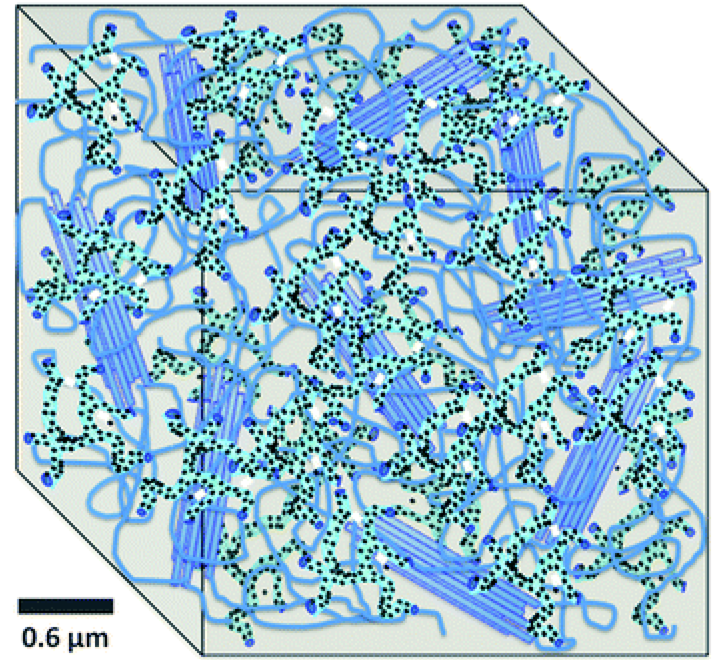
-6
log (σ(S/cm))
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
Mesoporous pore condensation
100 nm



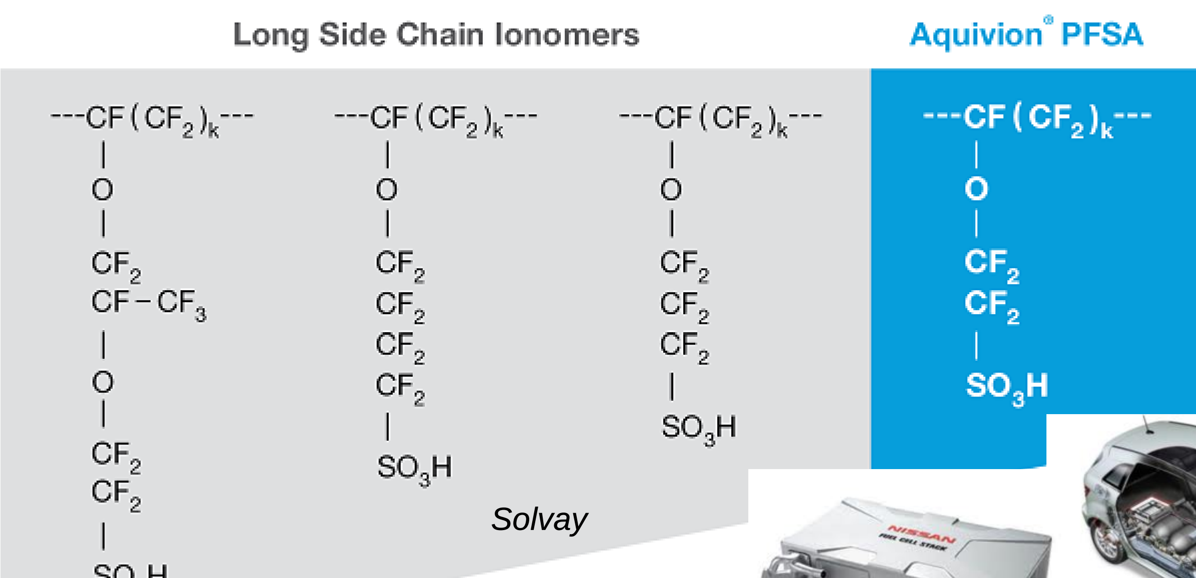
Temperature (°C)
1000
800
600
400
200
log (σ(S/cm))
0
-2
-4
-6
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1000/T (1/K)
BZY
Total
Chemisorbed
Physisorbed
Ice
Acid/base doping "SnP2O7"
Acid/base doping Nafion®
H2O H2O H3O+ H2O H2O H3O+ H2O
H2O H3O+ H2O H2O H3O+ H2O H3O+
H3O+ H3O+ H2O H2O H3O+ H2O
SO3-
P2O5
H+
H+
H+
OHO·
OHO·
OHO·
OHO·

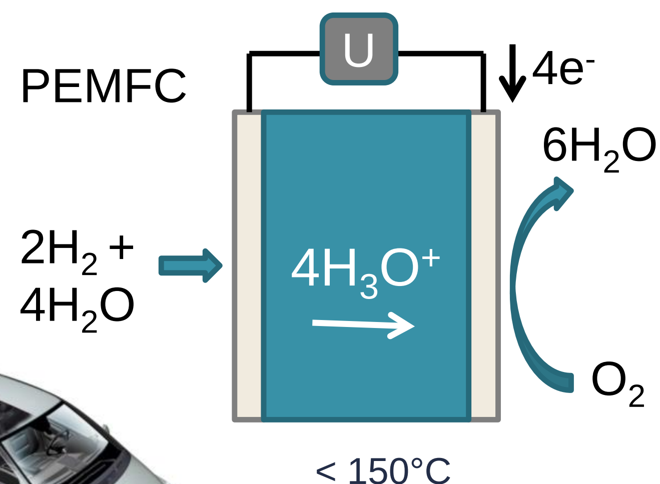
Polymer protonic electrolytes

- Swell to make aqueous channels
- Proton Exchange Membranes (PEM)
  - e.g. Nafion® and Aquivion®
  - Hydrated H_3O^+
- Anion exchange membranes
  - Hydrated OH^-

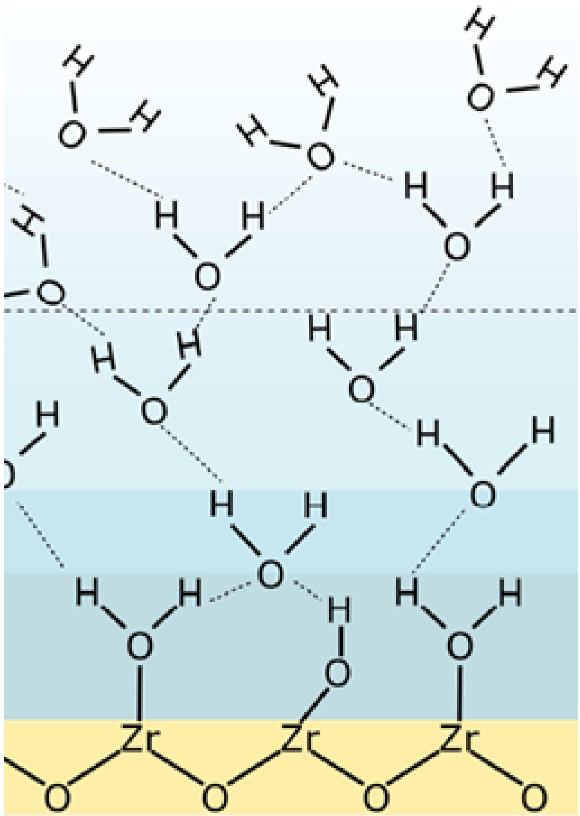


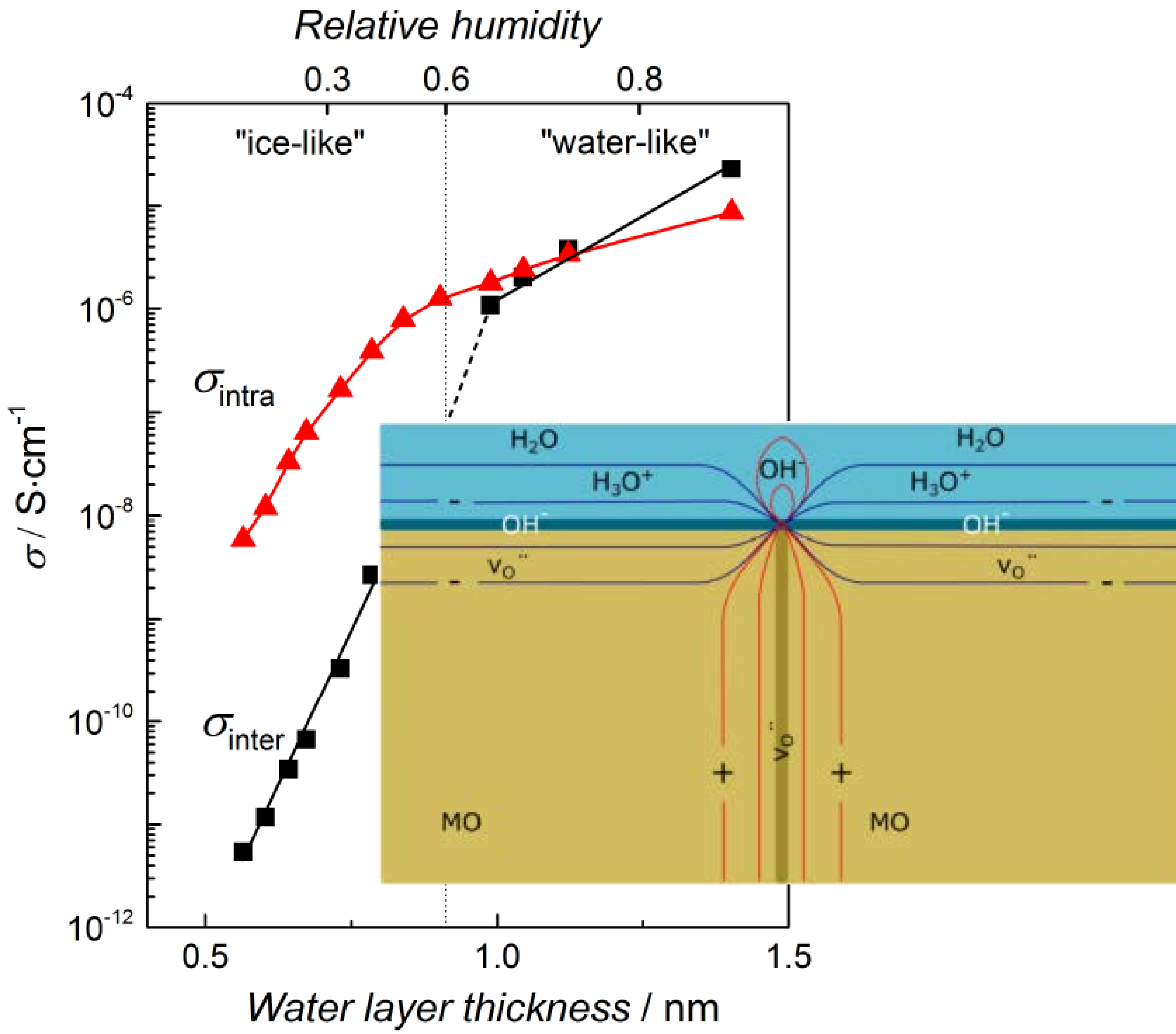
Elliott, Wu, Paddison, Moore, *Soft Matter*, 2011,7, 6820-6827





Surface protonics



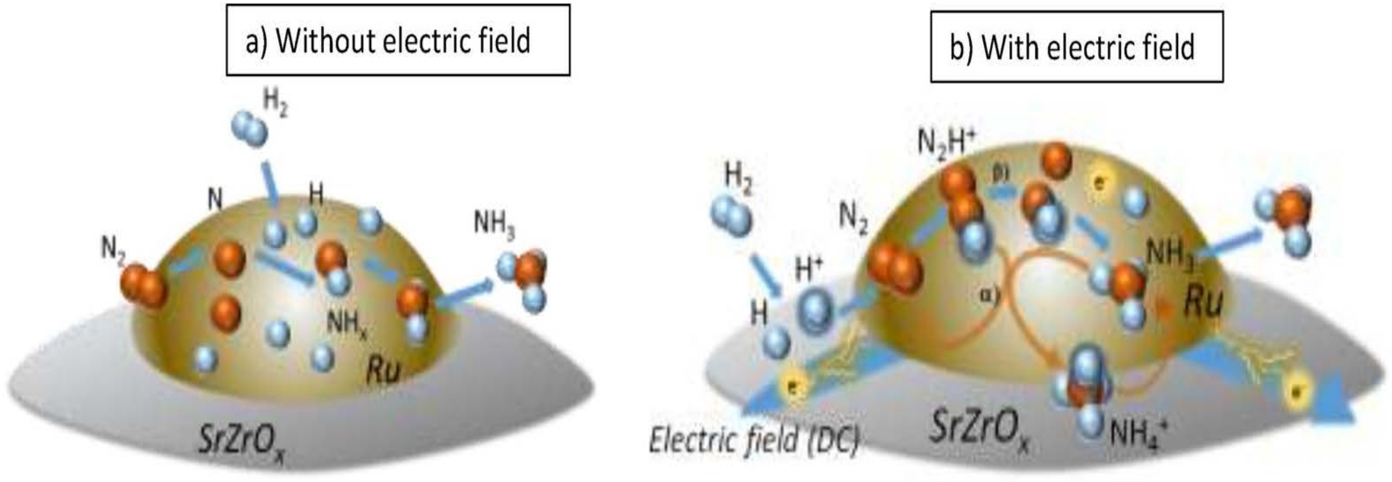


S.Ø. Stub, E. Vøllestad, T. Norby, **"Protonic surface conduction controlled by space charge of intersecting grain boundaries in porous ceramics"**, *J. Mater. Chem. A*, [6] (2018) 8265-8270.

Surface protonics:
Heterogeneous catalysis enhanced by electric field

- $N_2 + 3H_2 = 2NH_3$

and other industrially important exothermic reactions

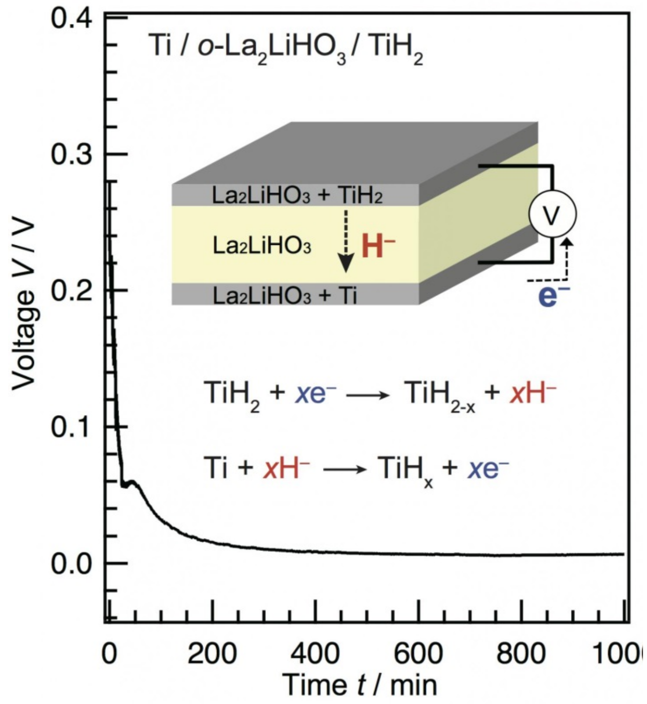


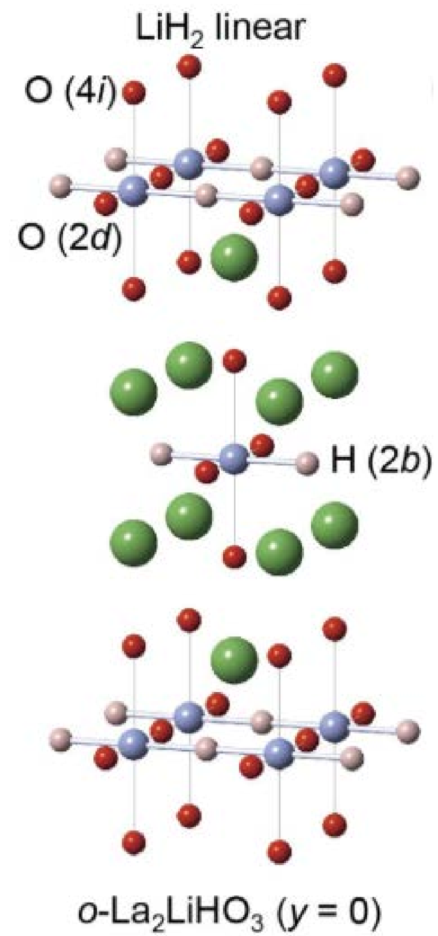
Ref: K. Murakami, et al. Catalysis Today 303 (2018) 271–275

K. Murakami, Y. Kamite, R. Manabe, A. Gondo, Y. Hisai, R. Sakai, T. Yabe, S. Ogo, T. Norby, Y. Sekine, **"Surface Protonics Promotes Catalytic Ammonia Synthesis: Faster Reaction at Lower Temperature",** submitted.

Hydride ions; H^-

- H storage materials
- Metal hydride batteries
- $2La + 3/2\ H_2 = 2LaH_3$
- $2La + 2H_2O = 2LaHO + H_2$
- $BaTiO_{3-x}H_x$
- La_2LiHO_3





G. Kobayashi, *et al.*, *Science* , 351, 6279 (2016) 1314

X Liu, TS Bjørheim, R Haugsrud, **Formation and migration of hydride ions in $BaTiO_{3-x}H_x$ oxyhydride**, *J. Mater. Chem. A*, **5** (3) (2017) 1050.

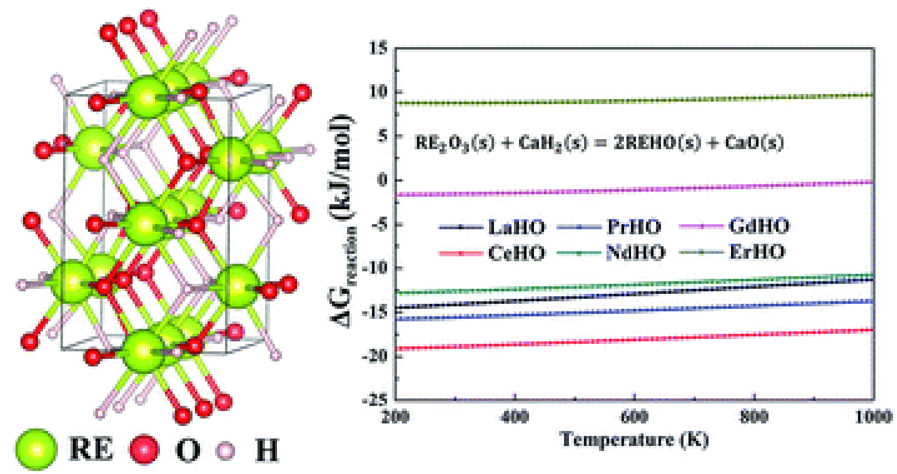
Ø.S. Fjellvåg, J. Armstrong, P. Vajeeston, A.O. Sjåstad, **New Insights into Hydride Bonding, Dynamics, and Migration in La_2LiHO_3 Oxyhydride.** *Journal of Physical Chemistry Letters*. (2018) 353- 358.

Computational solid-state electrochemistry

- DFT / *ab initio / first principles* calculations
- Quantum mechanical electrons – classic nuclei; Protons borderline

- Molecular dynamics (MD) and Nudged Elastic Band (NEB) for diffusion and kinetics

- Crystalline (periodic) lattices
- Interfaces (slabs)
- Clusters
- Defects

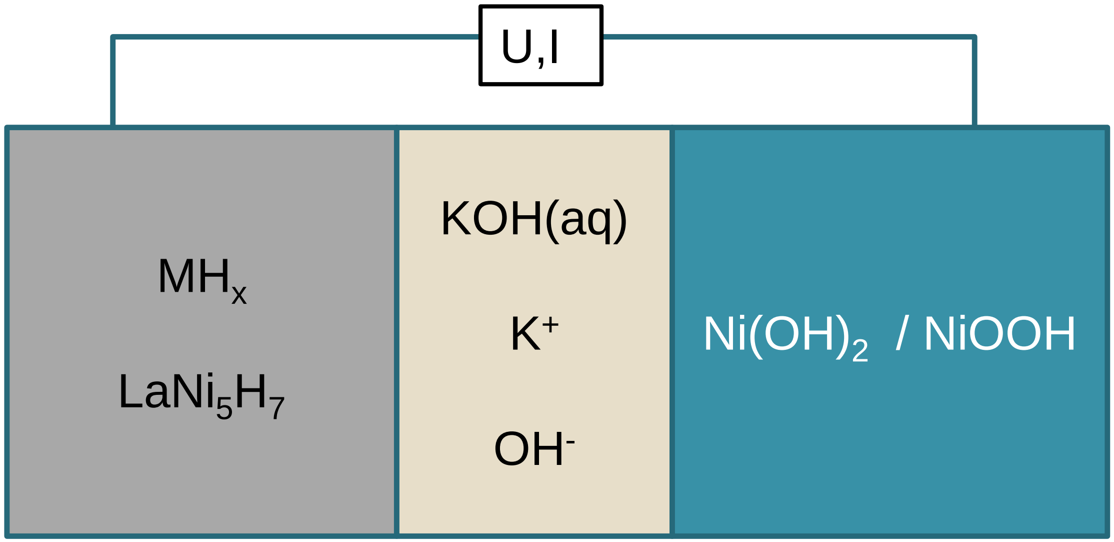


Liu, Bjørheim, Haugsrud, **Thermochemical properties of rare-earth oxyhydrides from first principles phonon calculations,** *RSC Adv.*, **6** (2016) 9822.

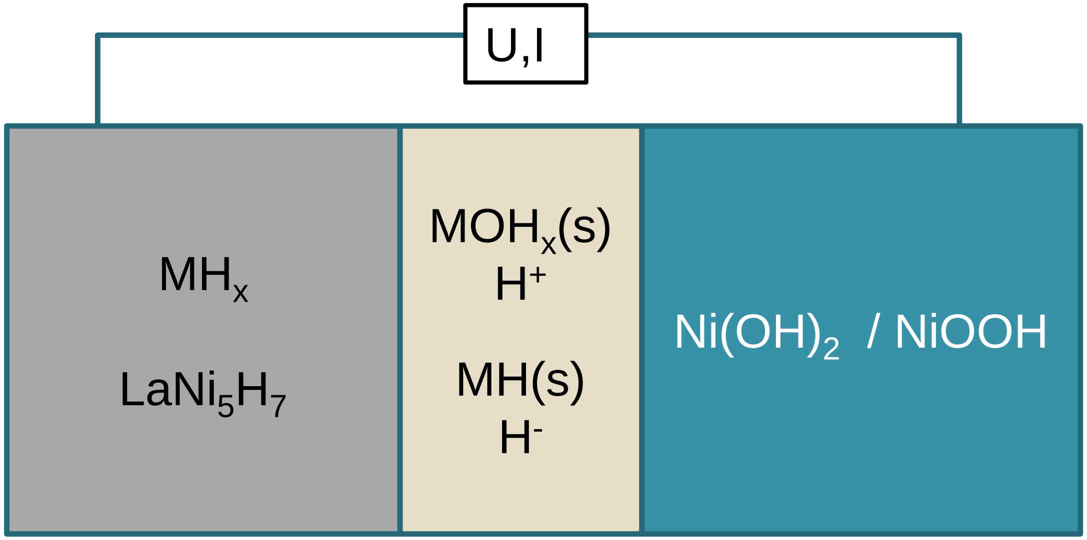
- Energies and entropies (phonon modes)

The proton MH battery

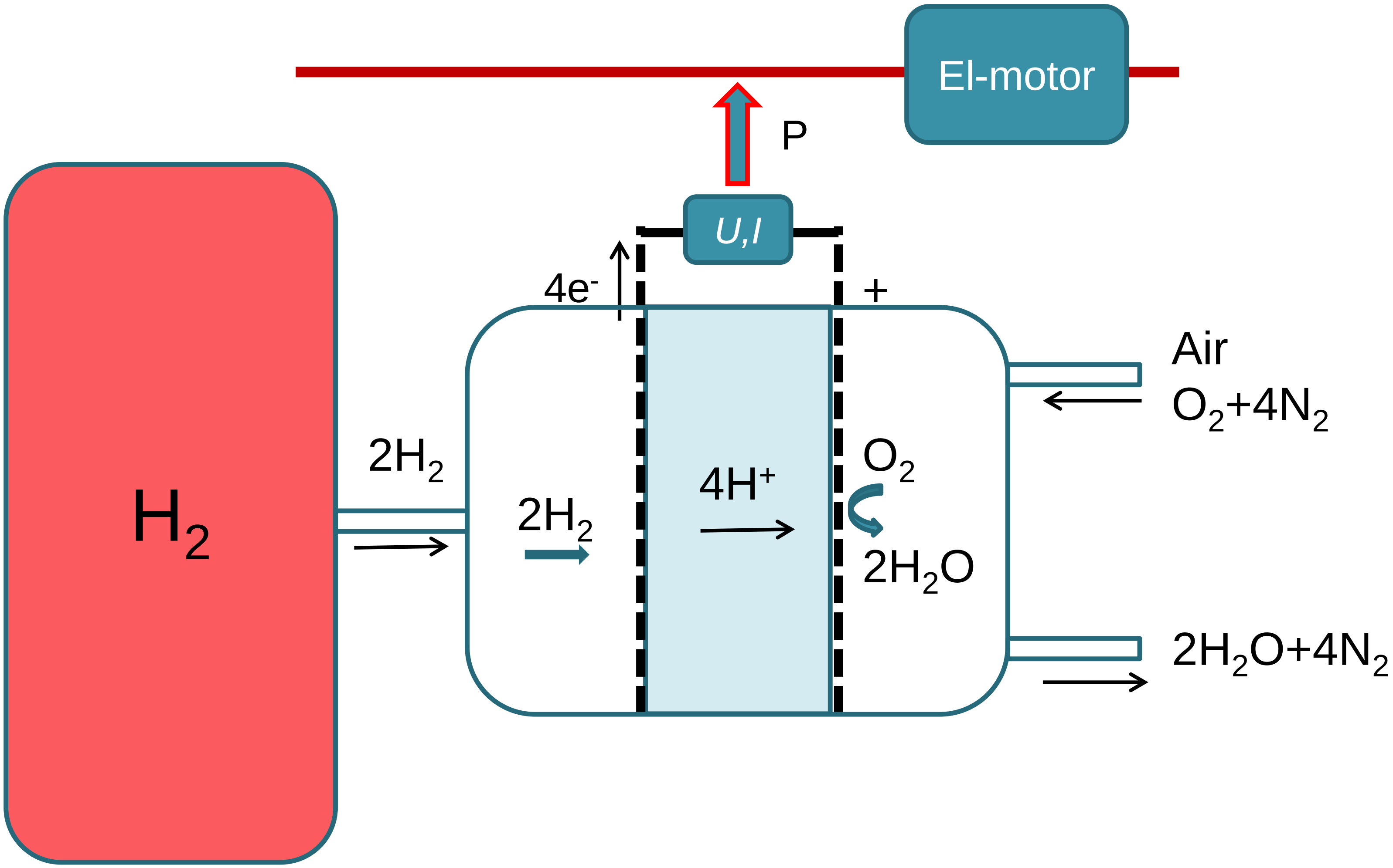
- Alkaline KOH electrolyte



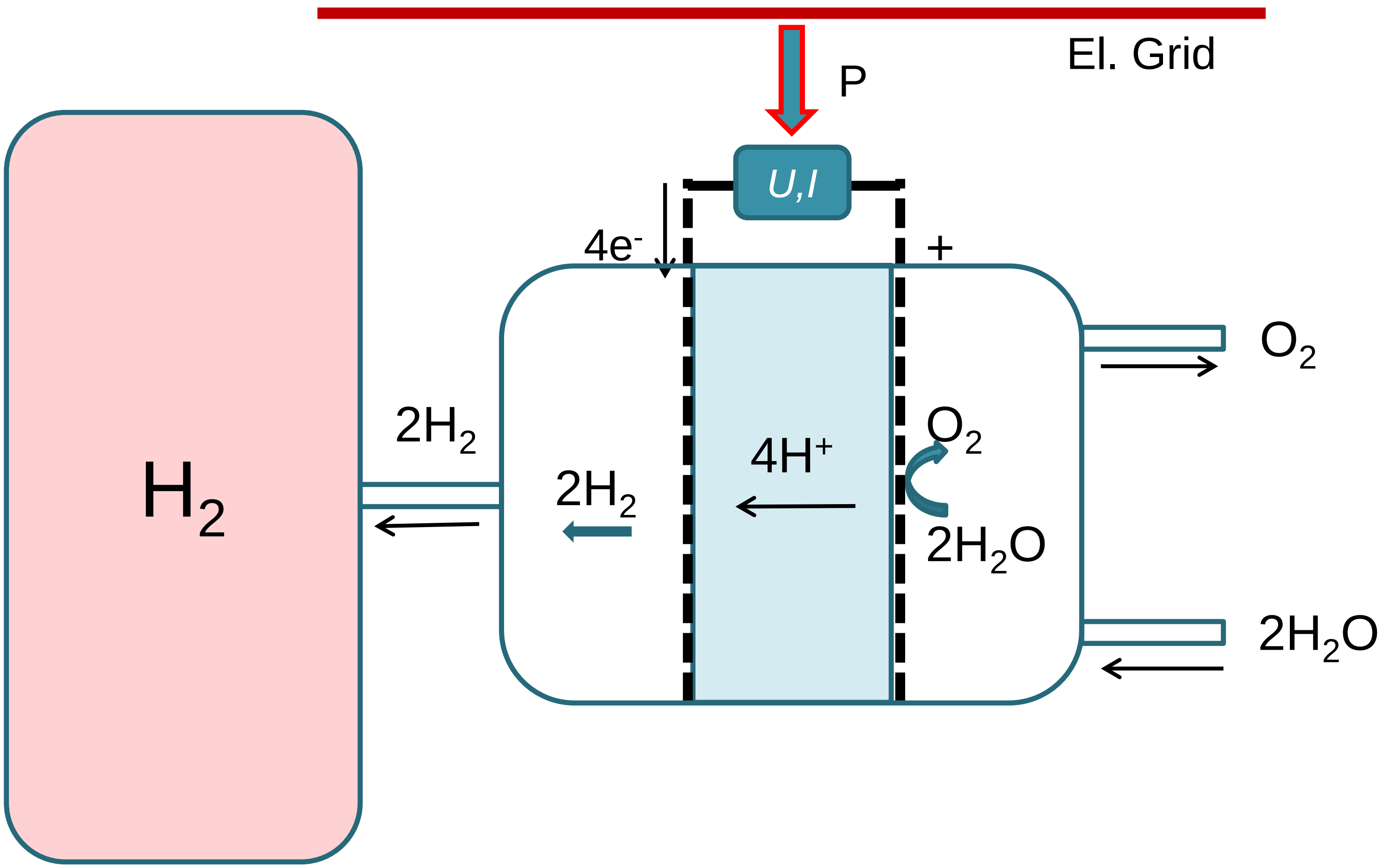
- Rocking chair proton or hydride ceramic electrolyte



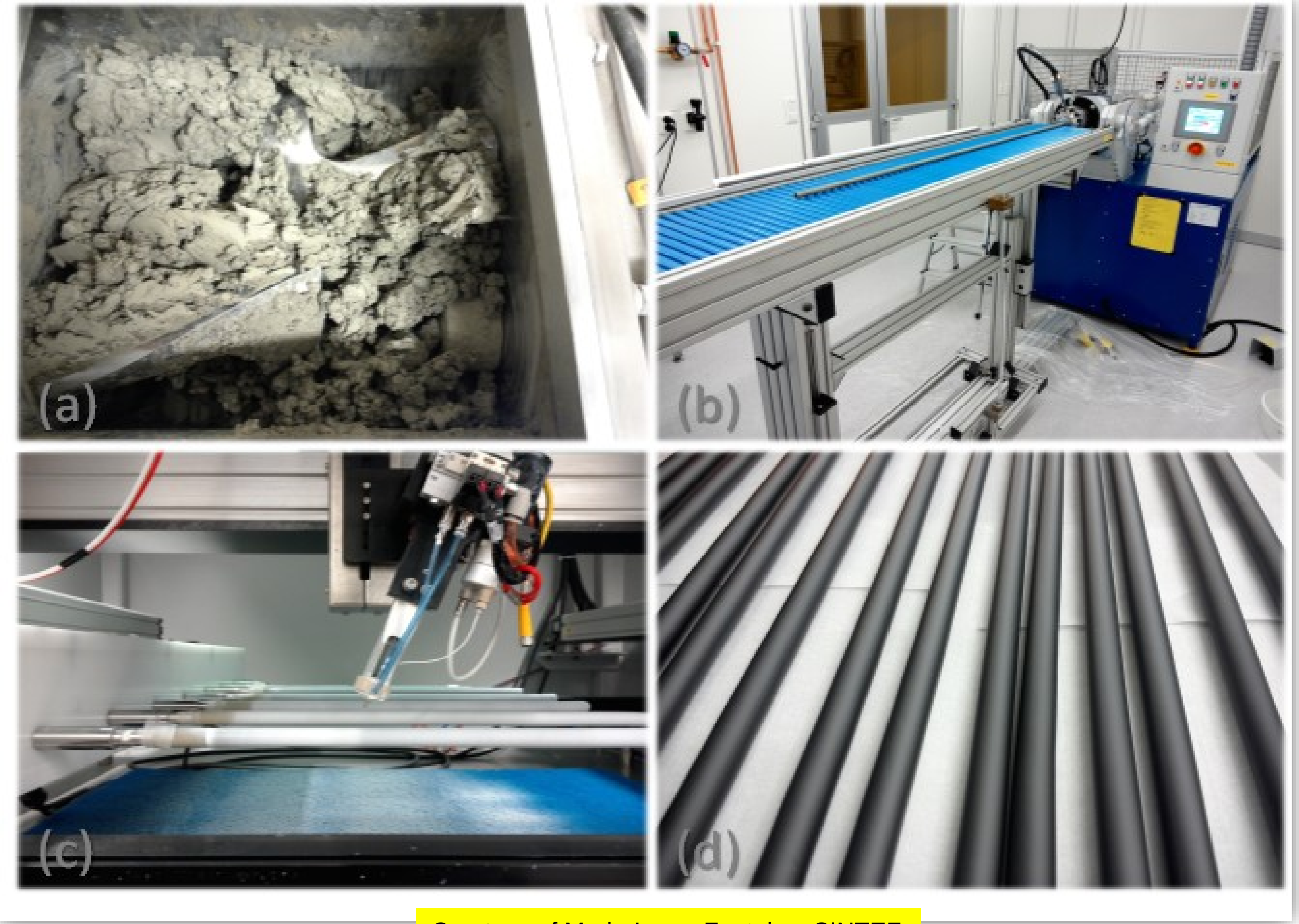
Fuel cell



Electrolyser and electrochemical compressor



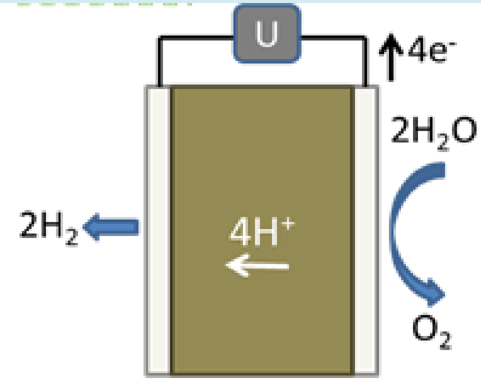
ELECTRA and GAMER EU projects: Production of tubes



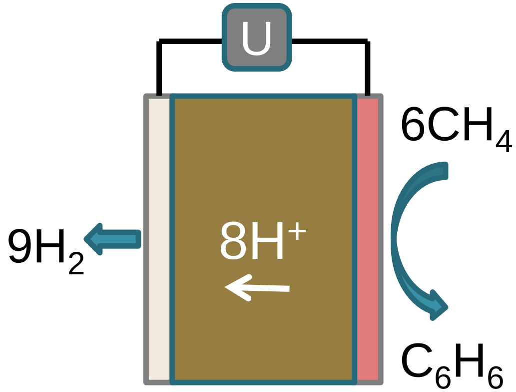
Courtesy of Marie-Laure Fontaine, SINTEF

3 technologies for proton ceramics and H_2

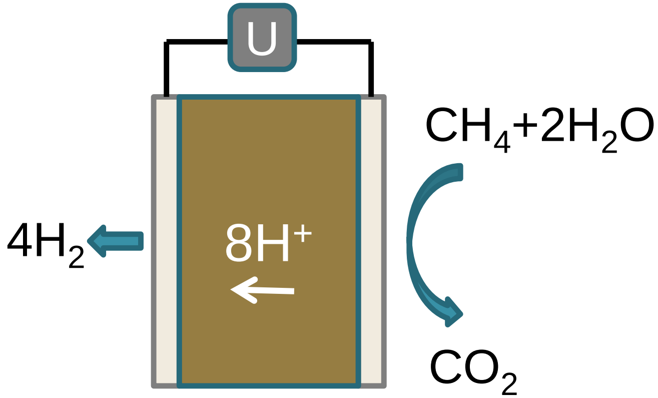
- Steam electrolysis and electrochemical compressor
  - $2H_2O = O_2 + 2H_2$



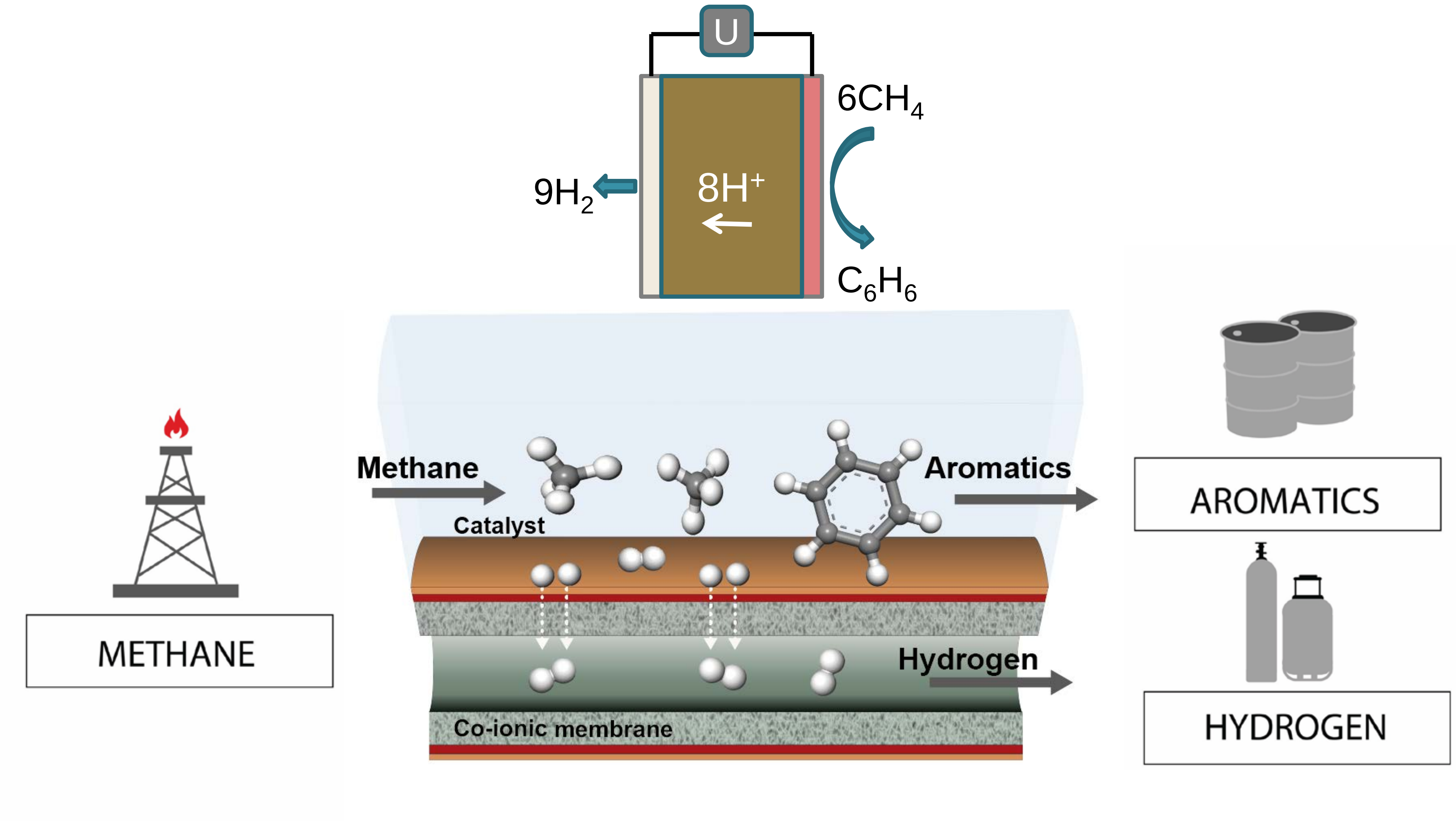
- Methane dehydroaromatization (MDA); GTL
  - $6CH_4 = C_6H_6 + 9H_2$



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

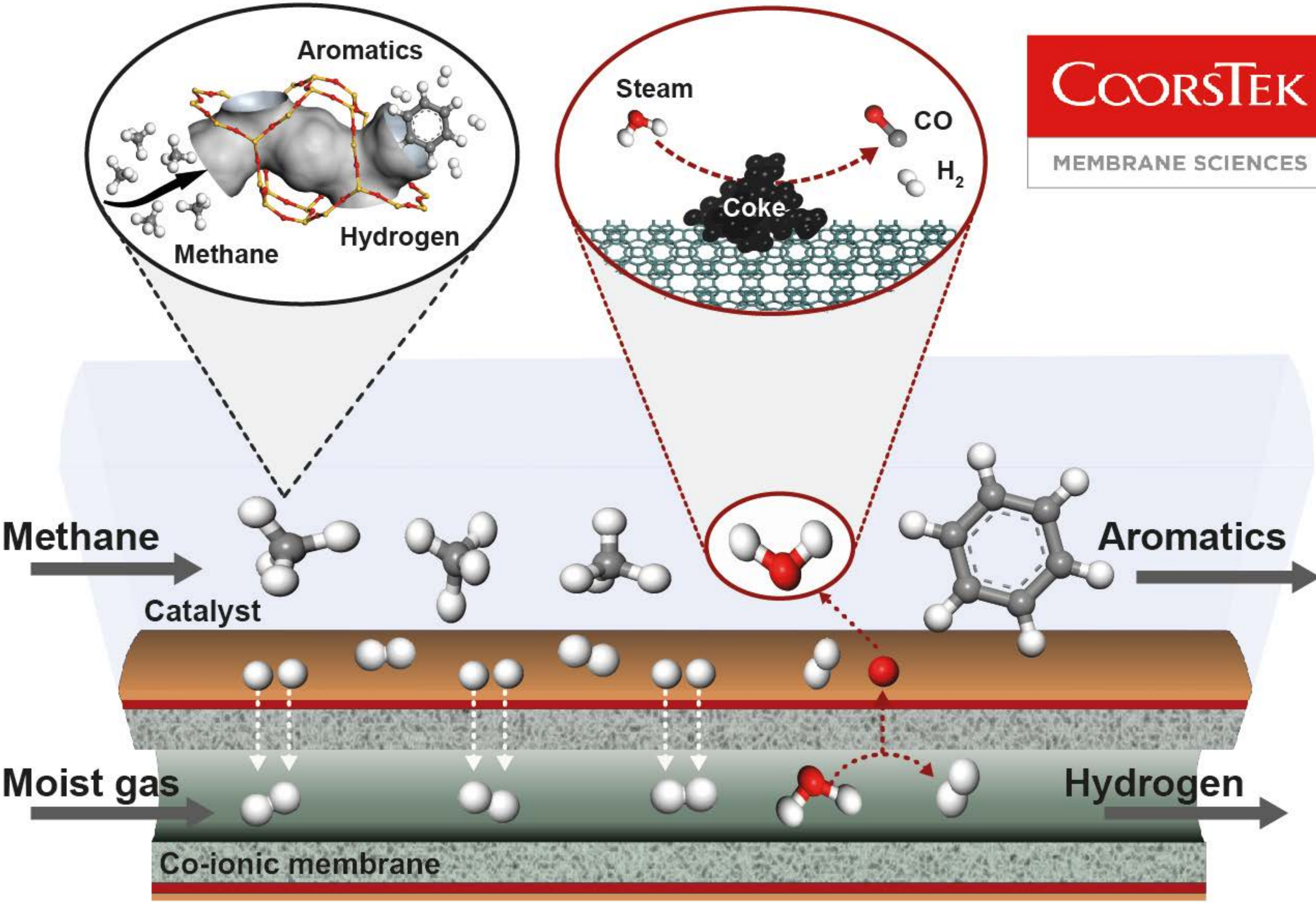


Catalytic dehydroaromatisation of natural gas using proton and co-ionic ceramics



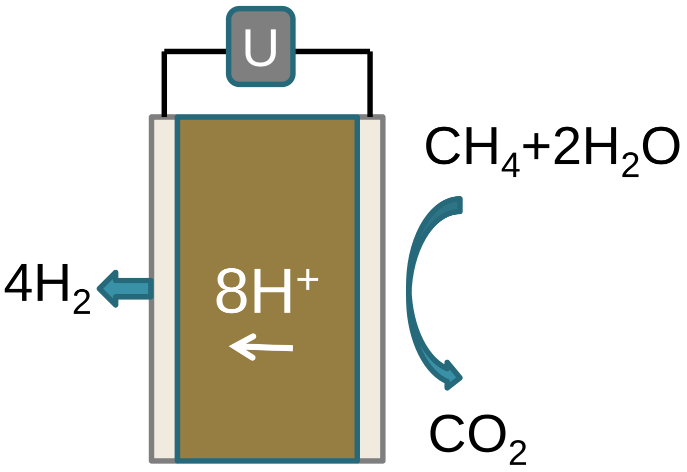
S.H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P.K. Vestre, W.G. Coors, A. Martínez, T. Norby, J.M. Serra, C. Kjølseth, **"Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor"**, *Science*, **353** [6299] (2016) 563-566.

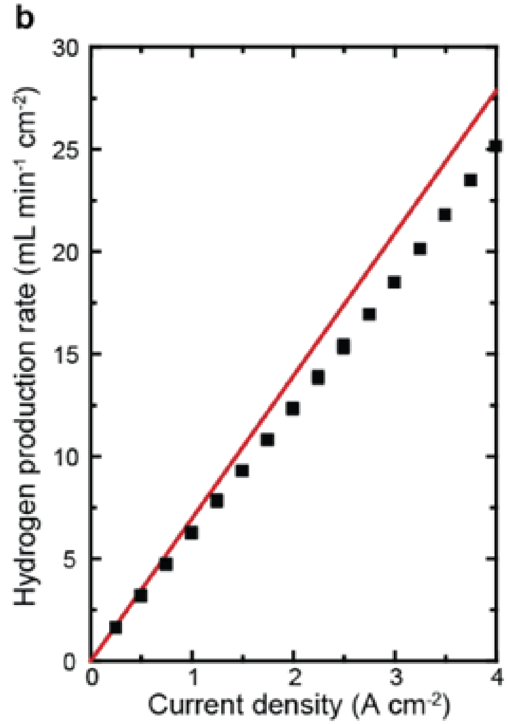
Catalytic dehydroaromatisation of natural gas using proton and co-ionic ceramics

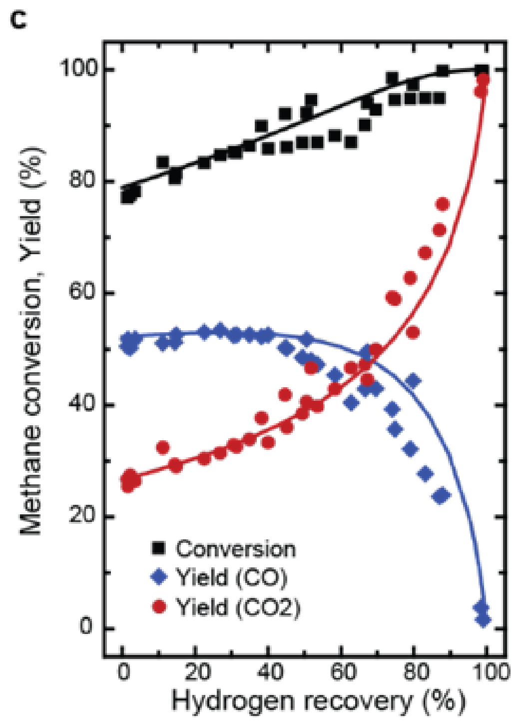


S.H. Morejudo, R. Zanón, S. Escolástico, I. Yuste-Tirados, H. Malerød-Fjeld, P.K. Vestre, W.G. Coors, A. Martínez, T. Norby, J.M. Serra, C. Kjølseth, **"Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor"**, *Science*, **353** [6299] (2016) 563-566.

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

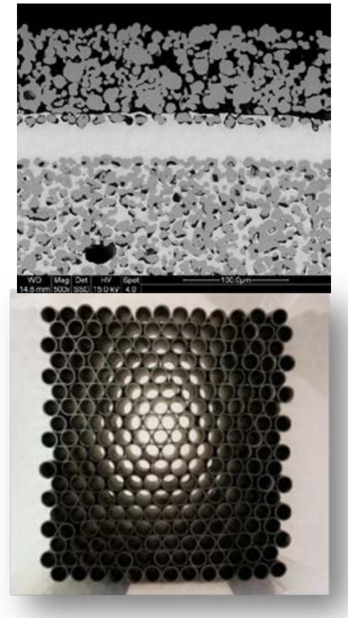




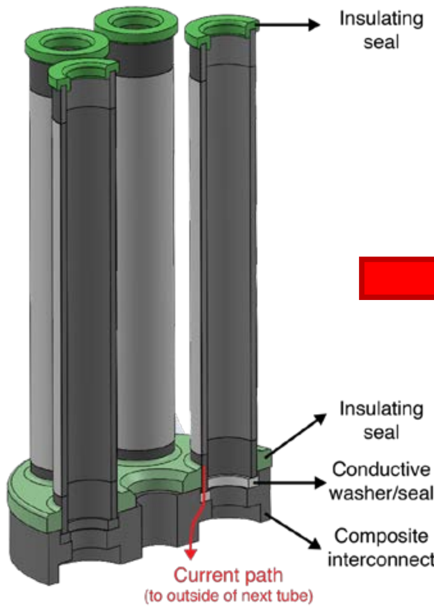


H. Malerød-Fjeld, D. Clark, I. Yuste-Tirados, R. Zanón, D. Catalán-Martinez, D. Beeaff, S.H. Morejudo, P.K. Vestre, T. Norby, R. Haugsrud, J.M. Serra, C. Kjølseth, **“Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss”**, *Nature Energy*, **2** [12] (2017)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

Fabrication – modularity – scaling up

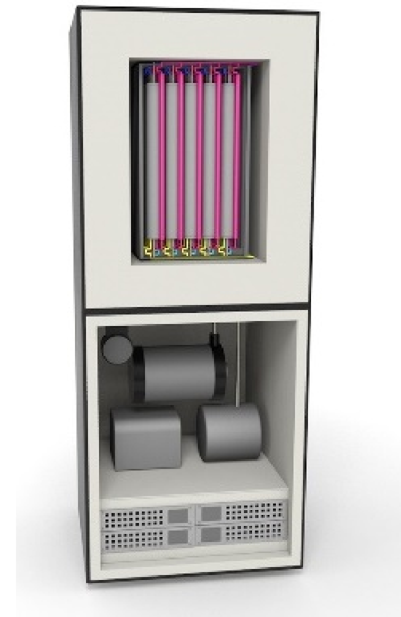


Tubular cells (electrodes, electrolyte, current collectors)



Key enabling technologies for SEU assembly (seal, manifolds, interconnects)

Cell integration in SEU (pressurized vessels, gas and electrical connections)



SEU integration in hot box with required ancillary equipment

H2 for medium and large cars

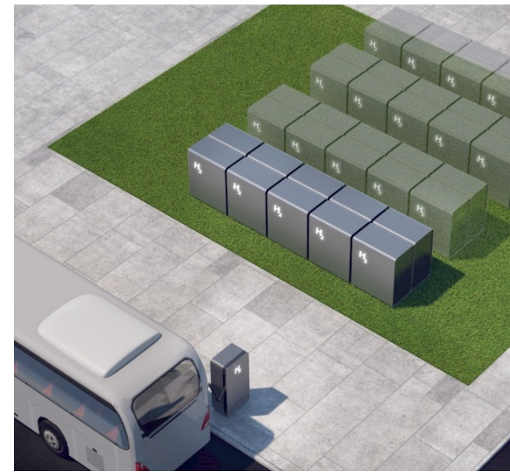
Customer-focused H_2 infrastructure to drive FCEV sales

Hydrogen at Home

Owners can fill H_2 at home (like a BEV) and heat water

Autonomous Fuel 'n Park

Business fleets can self-organize with robotic fueler



Modular Scalability

Bus/truck companies can expand by adding modules

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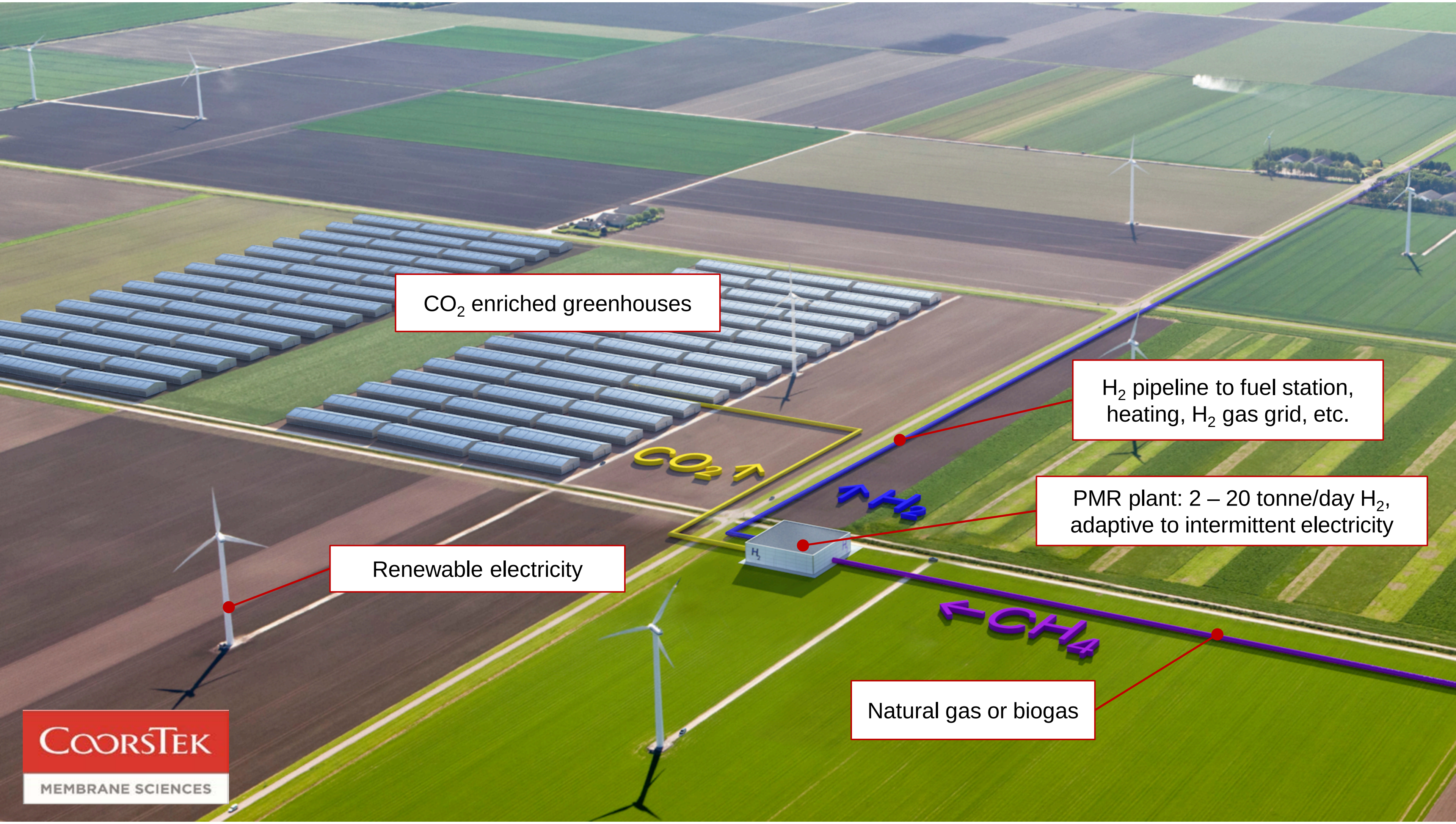
Blended hydrogen heating



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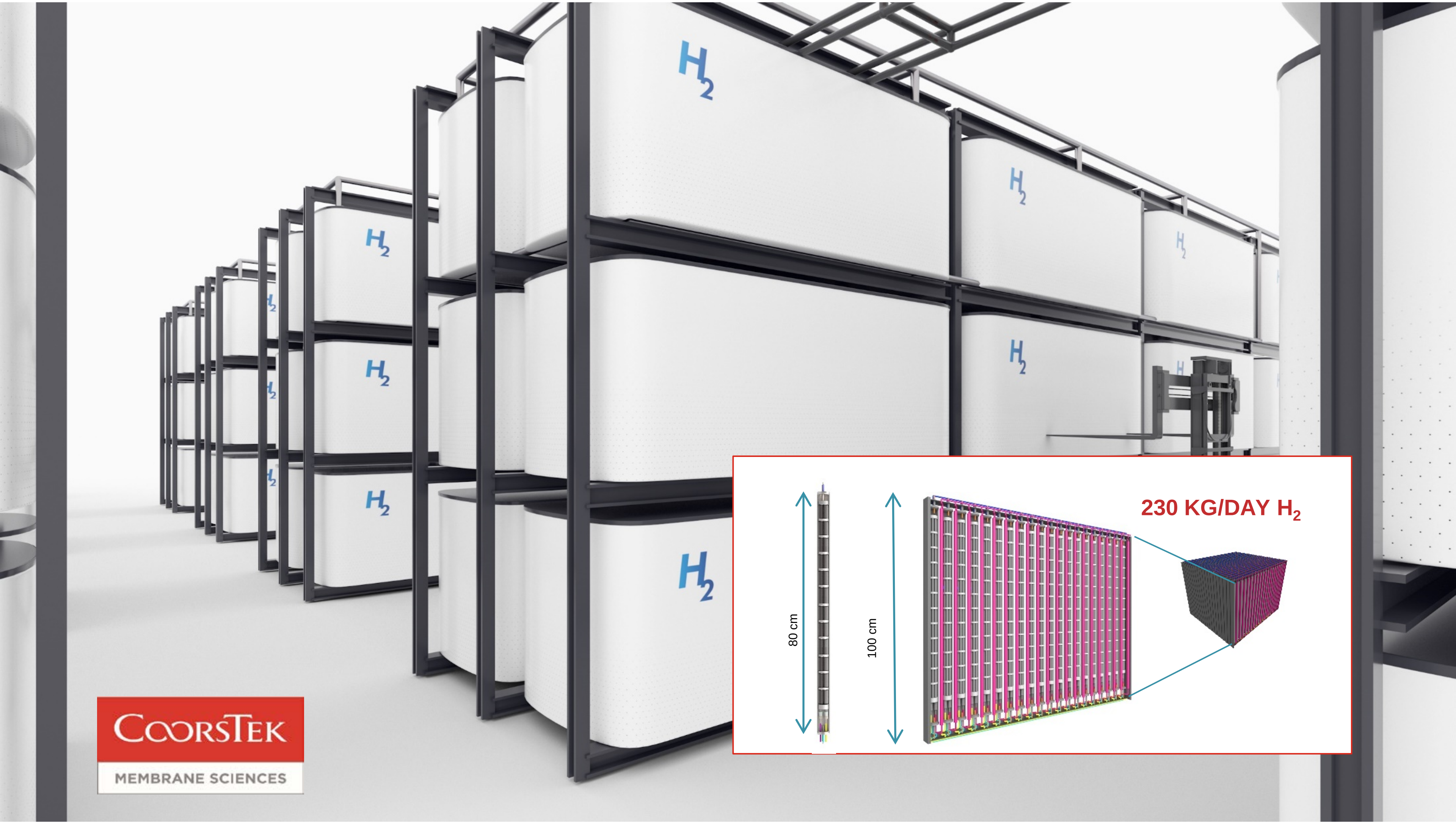
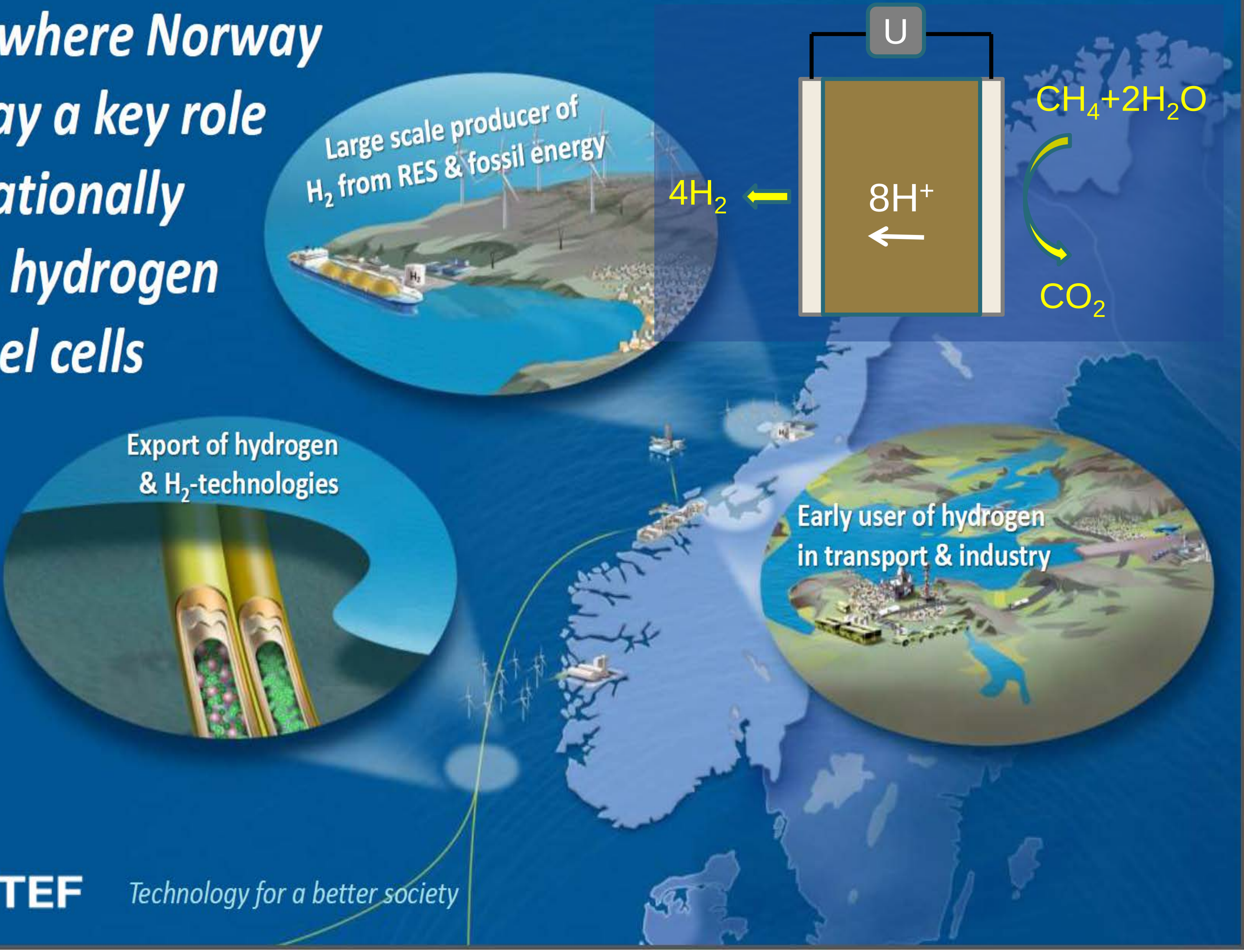
Industrial Hydrogen



Areas where Norway can play a key role internationally within hydrogen and fuel cells



Conclusions ☺

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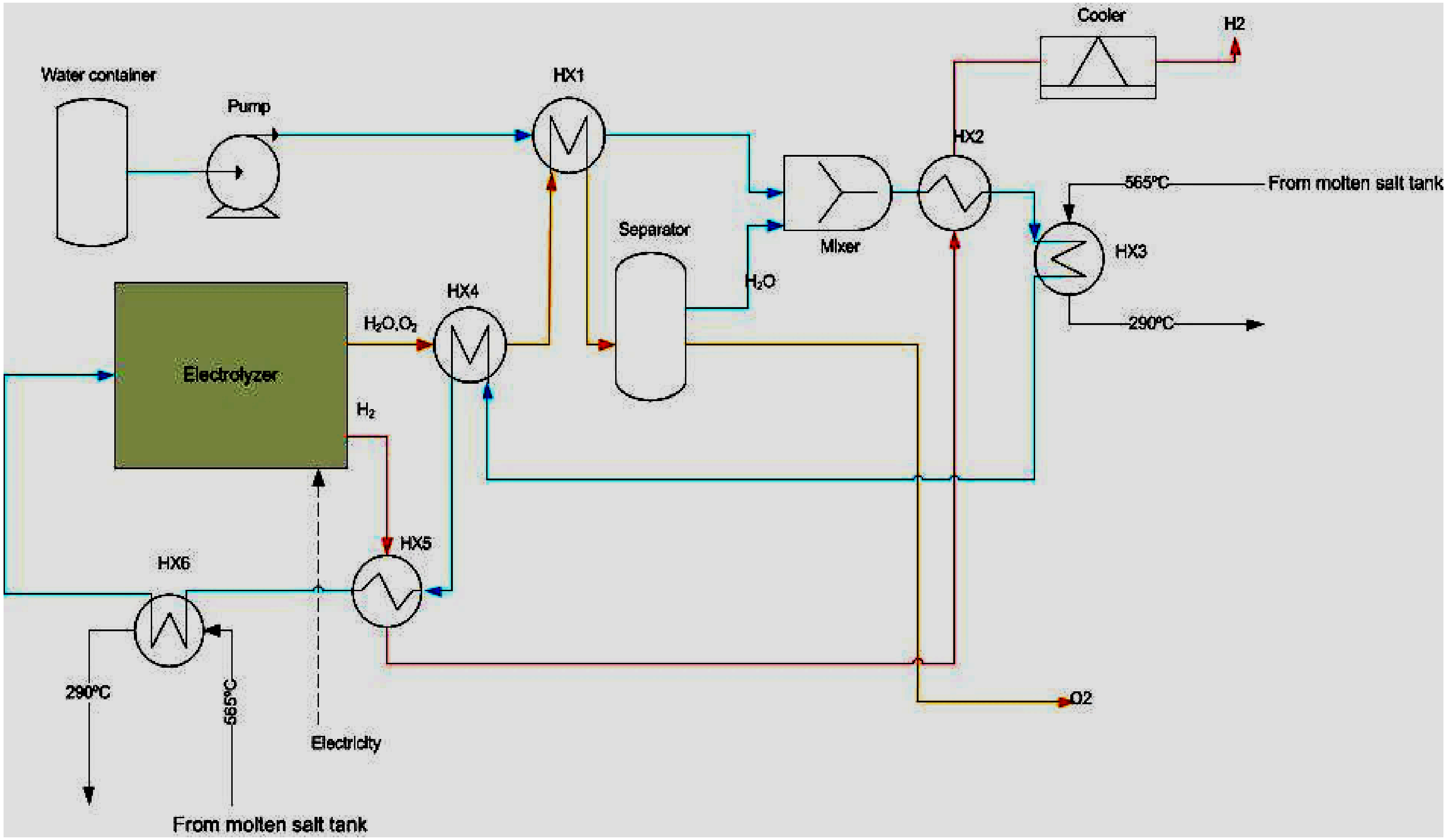
Acknowledgements

- *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.*

- *This work has received funding from the Research Council of Norway (RCN) through the NaProCs (216039), FOXCET (228355), ROMA (219194), CIEPRO (256264), AH2A (268010) projects.*

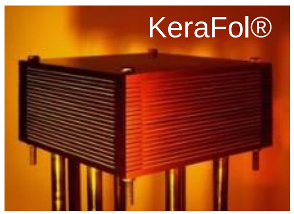
Backup slides

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

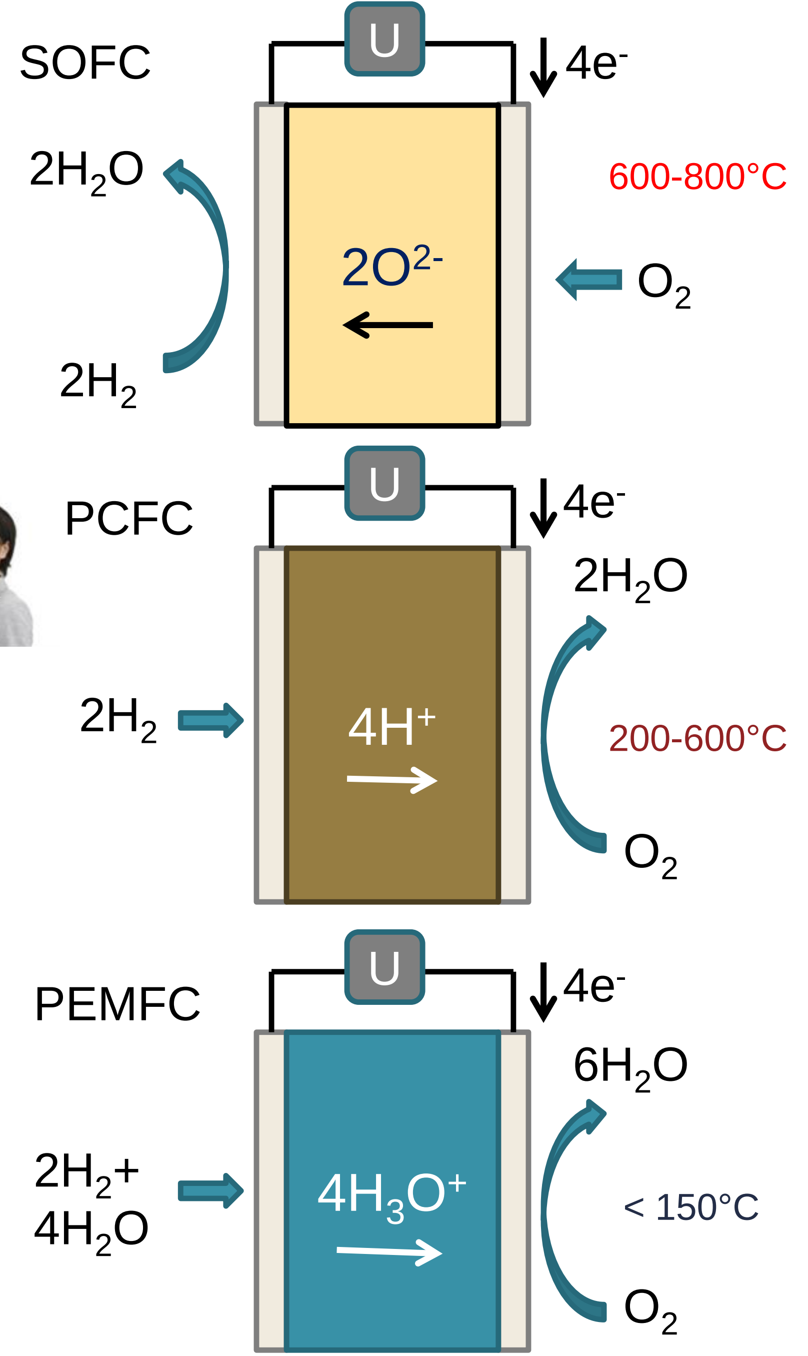


Solid-state fuel cells

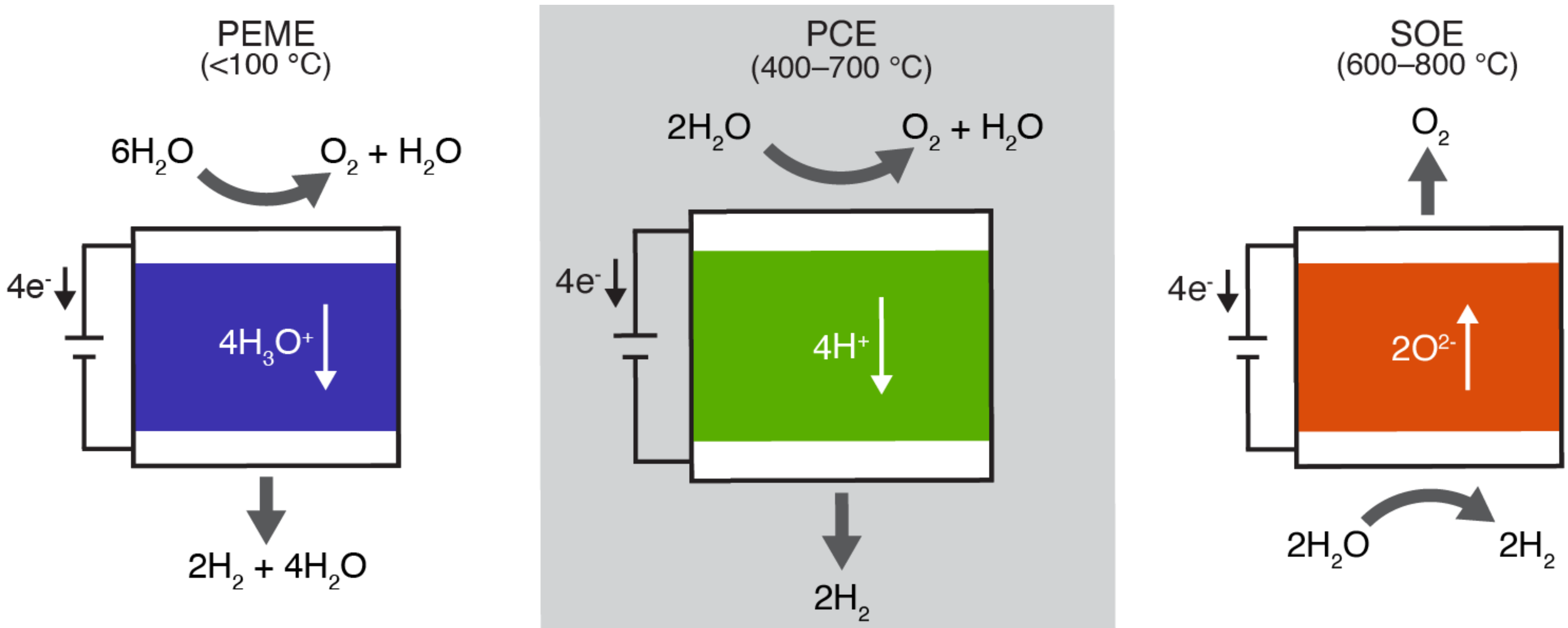
- Examples with H_2 as fuel
- SOFC: High T, low fuel utilisation, anode oxidation



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

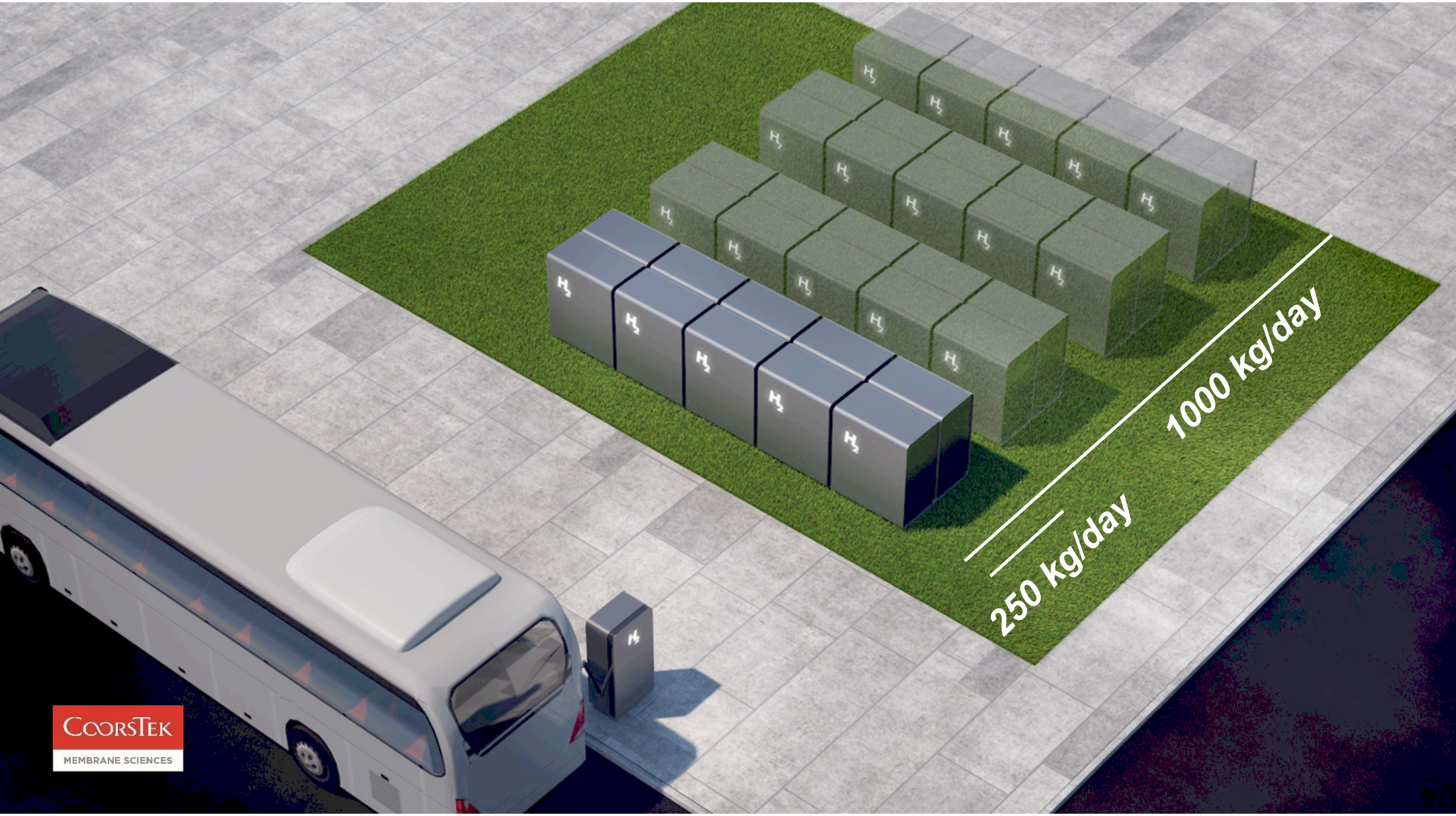


Comparative advantages of PCEs

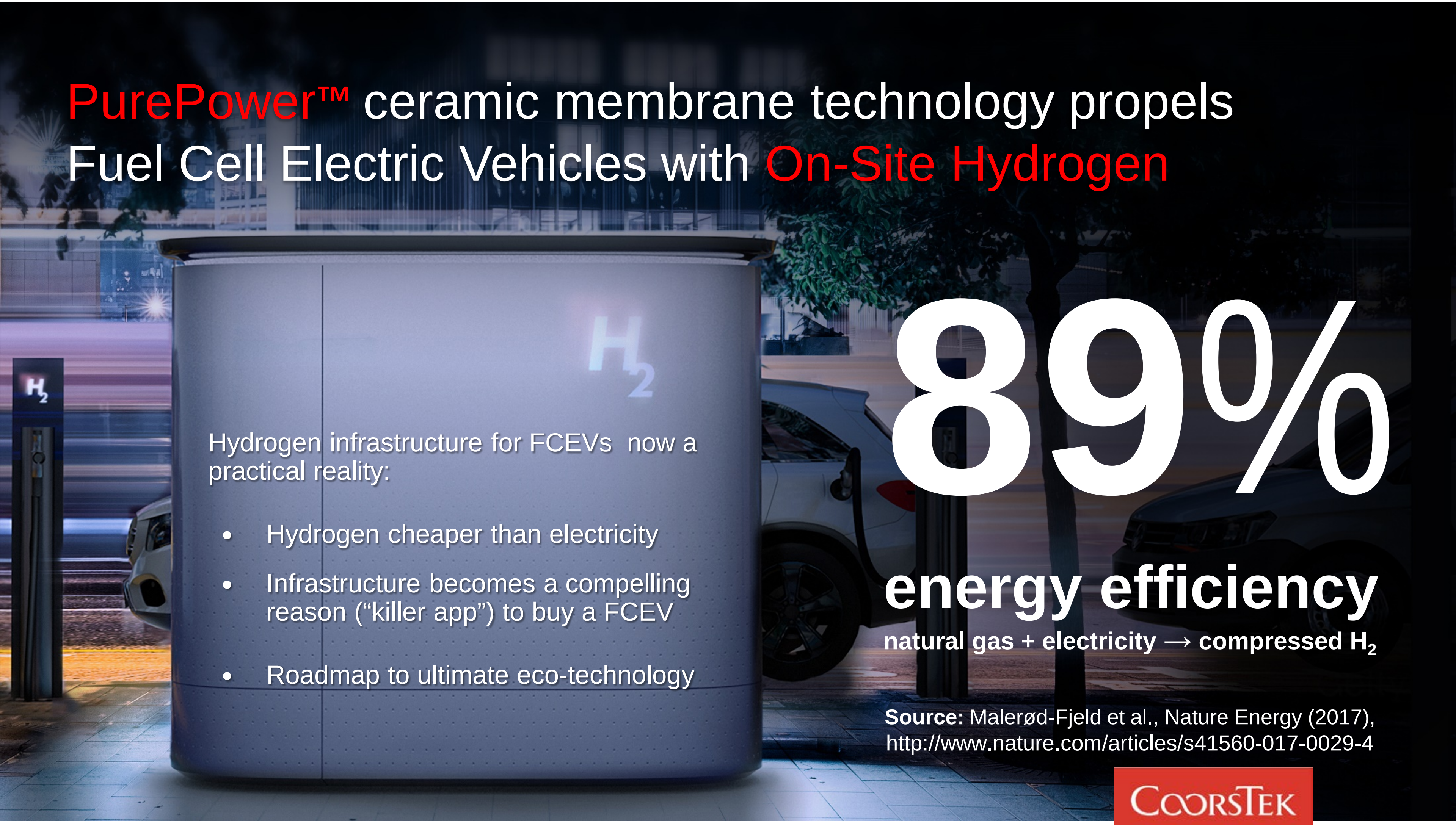


Industrial Hydrogen

2) City Buses



1) Medium and large cars



PurePower™ ceramic membrane technology propels Fuel Cell Electric Vehicles with On-Site Hydrogen

Hydrogen infrastructure for FCEVs now a practical reality:

- Hydrogen cheaper than electricity
- Infrastructure becomes a compelling reason ("killer app") to buy a FCEV
- Roadmap to ultimate eco-technology

89%

energy efficiency

natural gas + electricity → compressed H_2

Source: Malerød-Fjeld et al., Nature Energy (2017), http://www.nature.com/articles/s41560-017-0029-4

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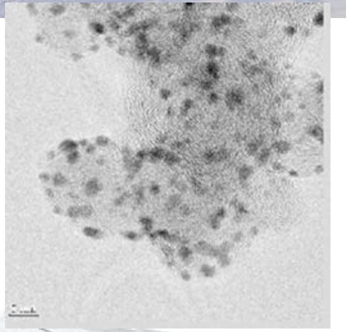
Typical hydrogen car 2014

- Hyundai iX35 H2-FCEV (or HFCV)
- First commercial tHFCV



- Zero emission

- 100 kW electric motor
- 100 kW fuel cell + 24 kW Li polymer battery
- Top speed : 160 km/h. 0-100 km/h: 12.5 s

- Two H_2 tanks: Ca. 6 kg H_2 @ 700 bar
- Consumption: Ca. 1 kg H_2/100 km (NEDC): Range: 600 km

- Full tank in 3 minutes

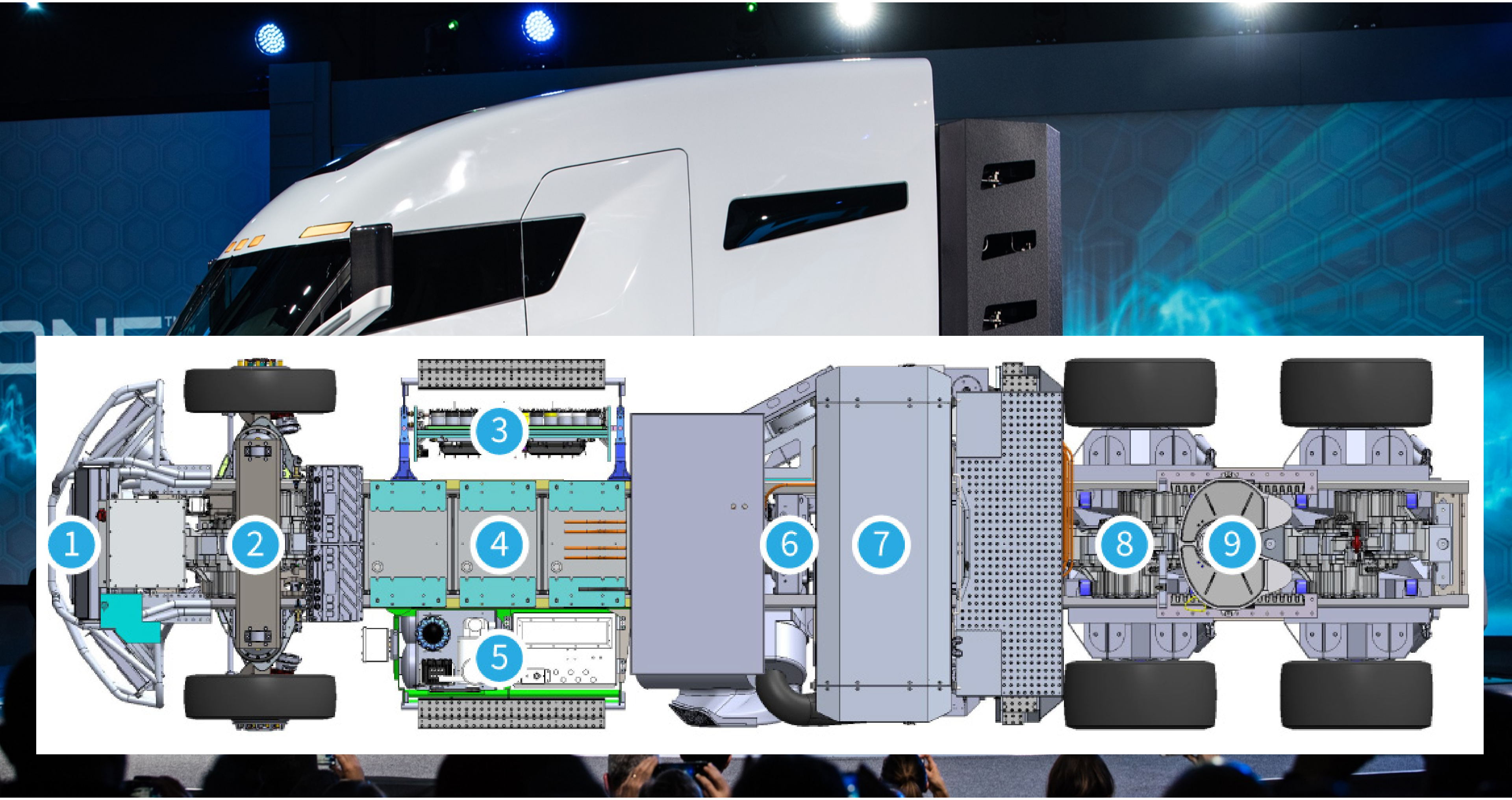
Range: Energy density (MJ/kg)

• Wood	16		
• Coal	30		
• Gasoline	47		x 20%: 10
• Hydrogen	142	With tank: 7	x 50%: 3.5
• Lithium ion battery	1		x 60%: 0.6

HFCV buses

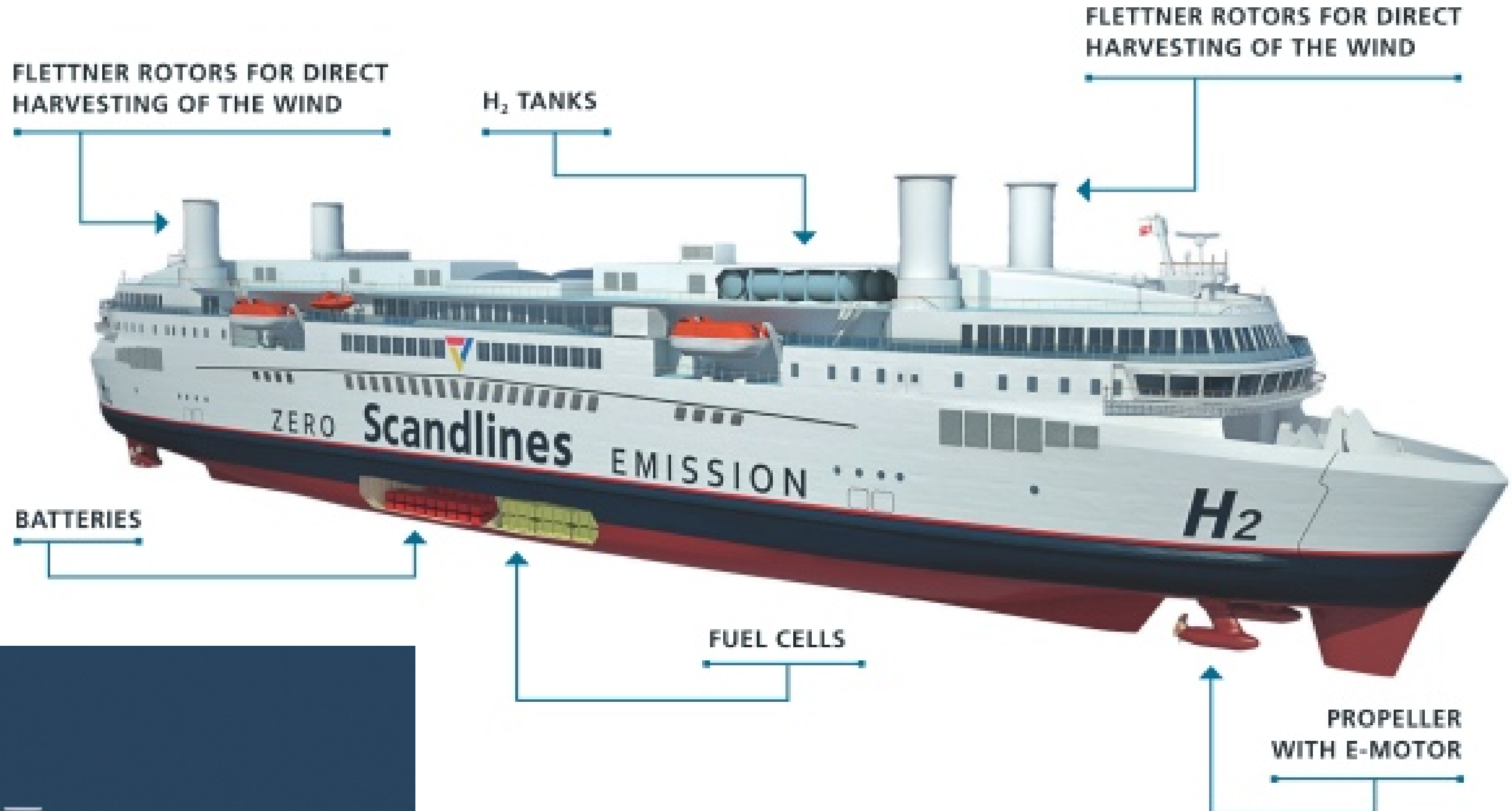

NIKOLA

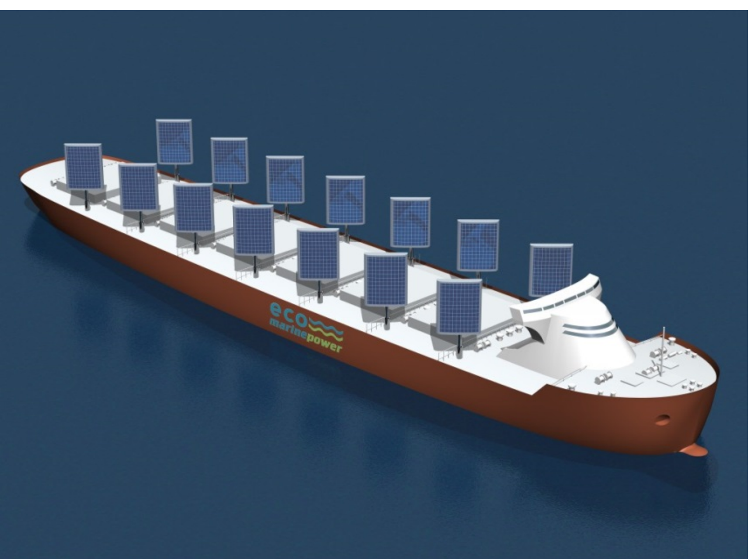
Hydrogen fuel cell heavy trucks



Hydrail - Hydrogen on track

Green ships: Fill H_2 from land
Make hydrogen onboard from sun and wind?





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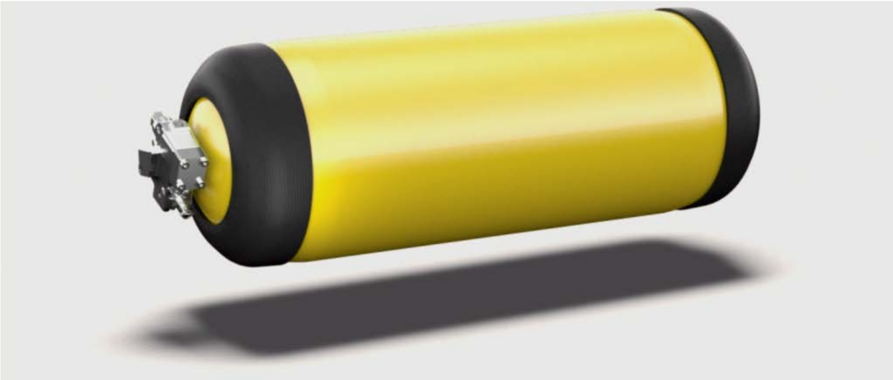
How do we store hydrogen?

- As gas at 700 bar
  - 3 x a regular gas cylinder!

- Tanks lined with carbon fiber
  - Bullet proof
  - Collision proof
  - …



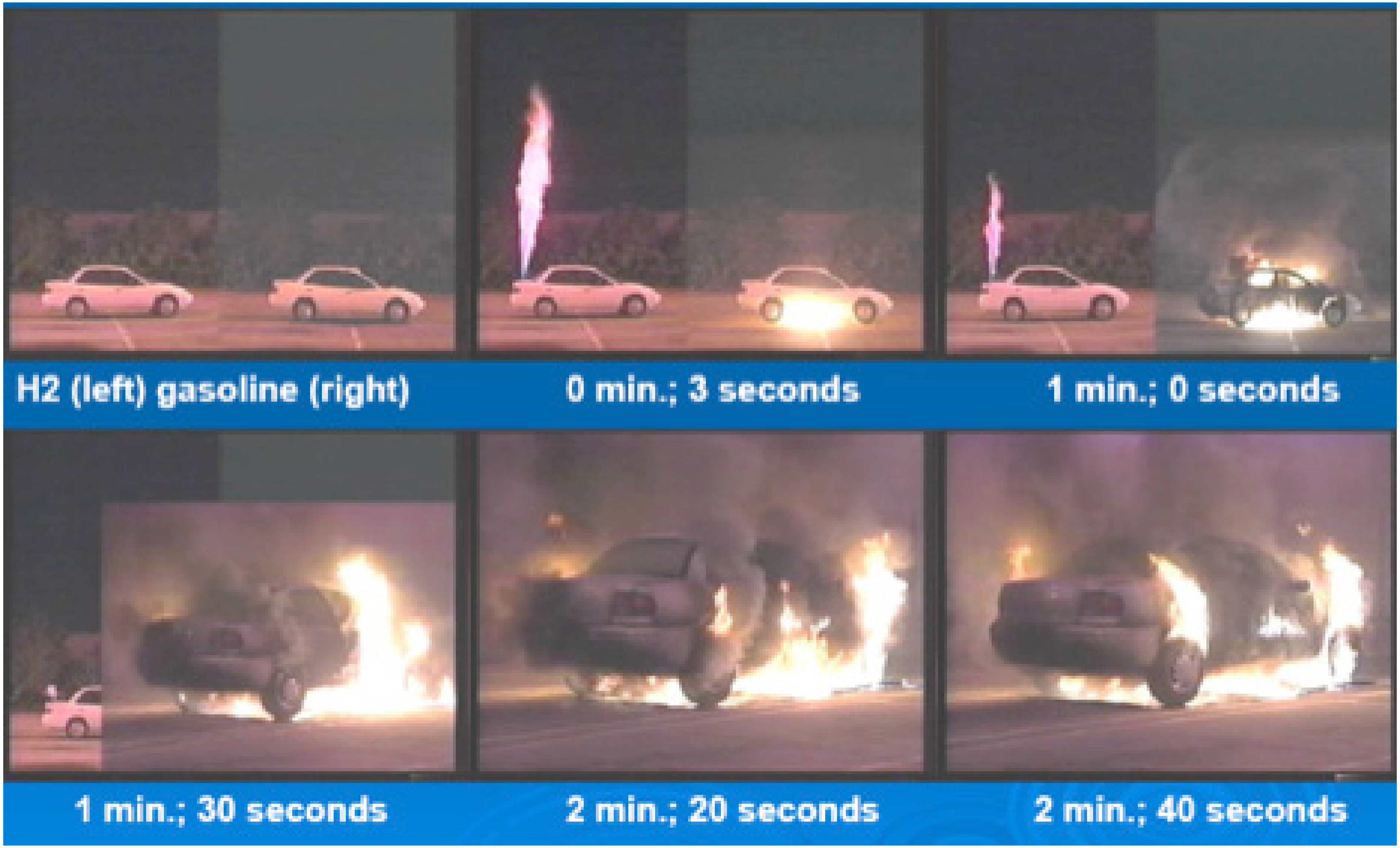
Hydrogen infrastructure and filling stations

- Hydrogen is made at the station or comes in pipelines or on tanks
  - Norwegian industry: Hexagon

- Hydrogen made by
  - Electrolysis
    - In Norway near 100% renewable
    - Norwegian industry: NEL
  - Gasification of biomass
  - Reforming of natural gas

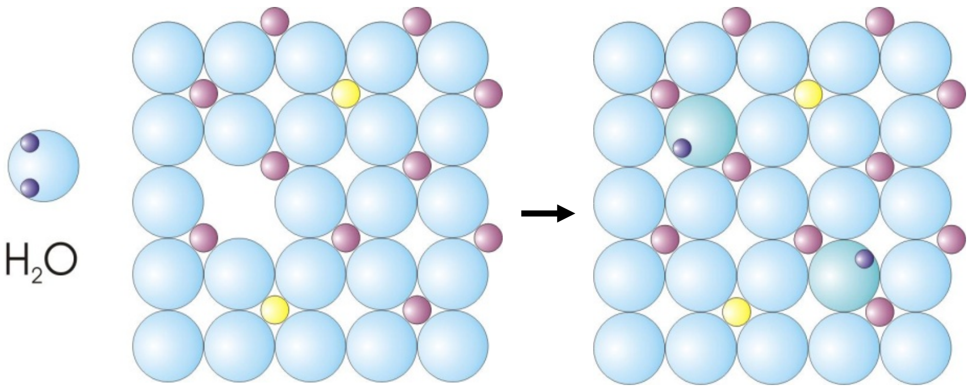
- High demands for purity
- Fills a car in 3 minutes via 1000 bar cooled H_2
- Price…
- Growing hub of stations in/around Oslo (HYOP; Uno-X)

H_2 safety

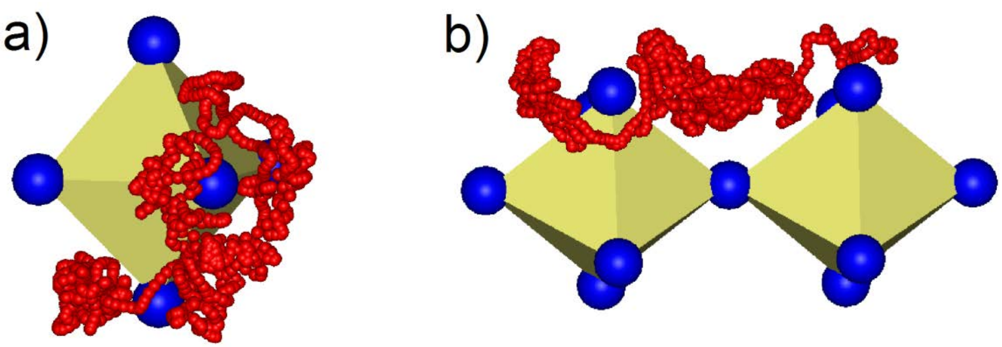


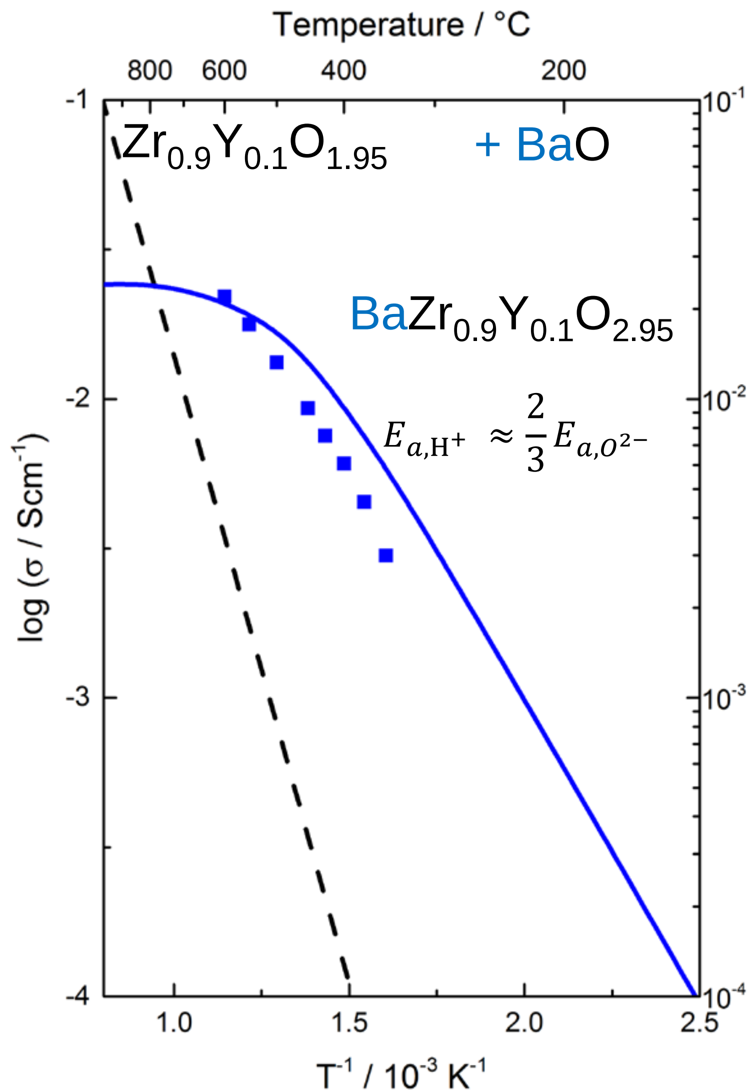
Swain 2001

Proton conducting oxides; proton ceramics



$$H_2O(g) + v_O + O_O^{2-} = 2OH_O^{-}$$





From Kreuer, .K-D.