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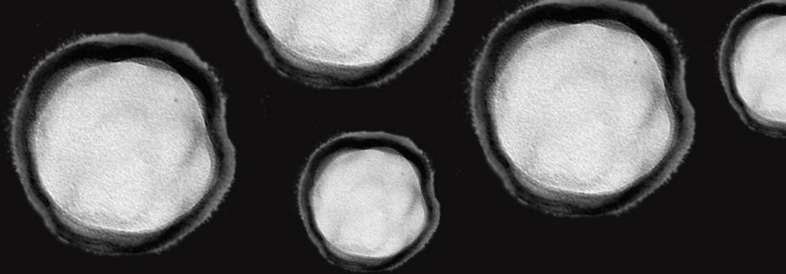
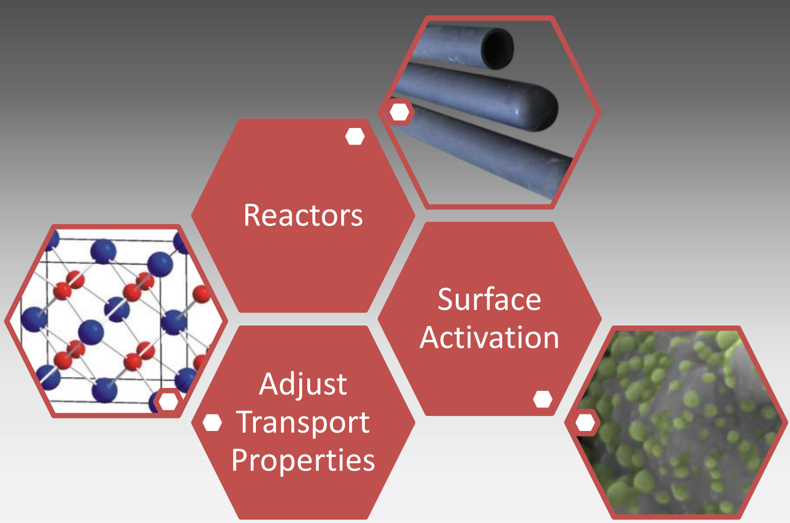


Advanced proton-transport materials for application in membranes and fuel cells



EXCELENCIA SEVERO OCHOA

Jose M. Serra

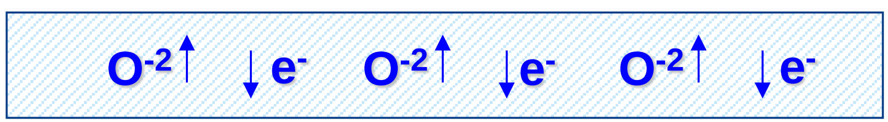
CSIC
Consejo Superior de Investigaciones Científicas

Universitat Politècnica de València

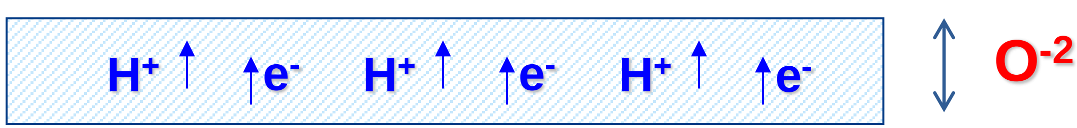
Ion-Conducting Materials?
Ion-Transport Membranes?

- Ion Conducting Oxides are (crystalline) mixed oxides than can transport oxide-ions or protons through their lattice
- Ion conduction is typically activated in 400-1000°C
- Ideally, we can distinguish between:

→ Oxygen Ion Conductors: Pure Ionic / Mixed Ionic-Electronic (OTM)

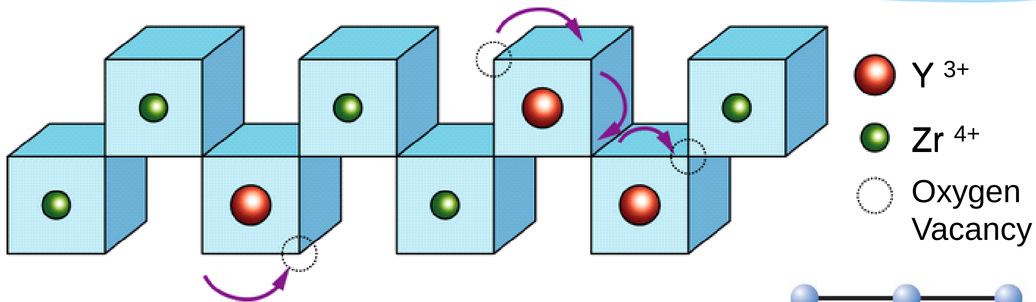


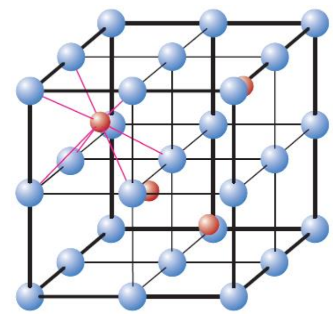
→ Proton Conductors: Pure Protonic/ Mixed Protonic-Electronic (HTM)



Oxide-Ion Conduction

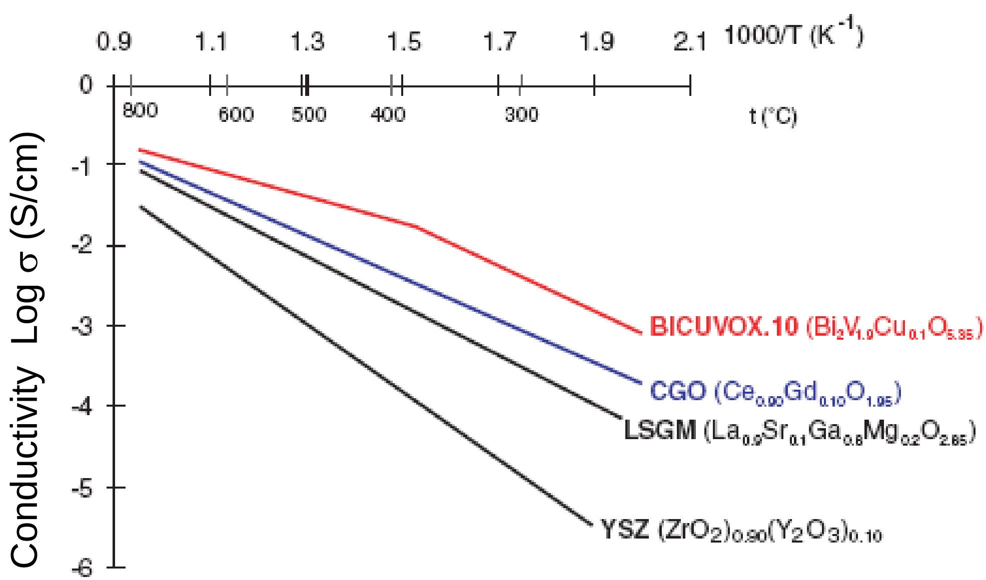
Oxygen Diffusion
in Fluorite Sturcture
through oxygen Vacancies

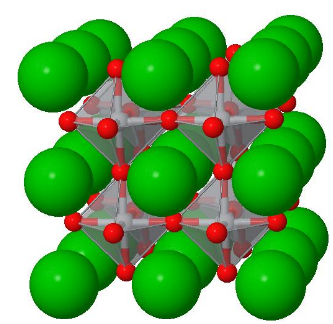




Fluorite $MO_{2-\delta}$

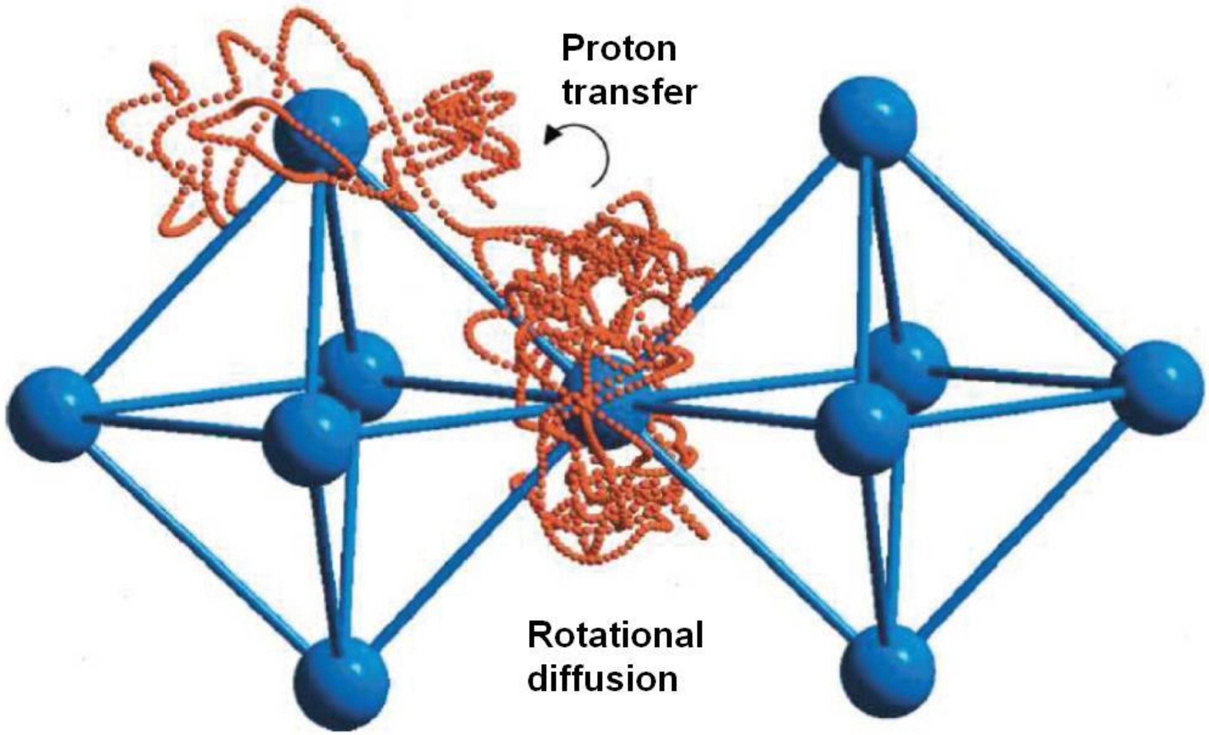
State-of-the-Art Oxygen-Ion Electrolytes

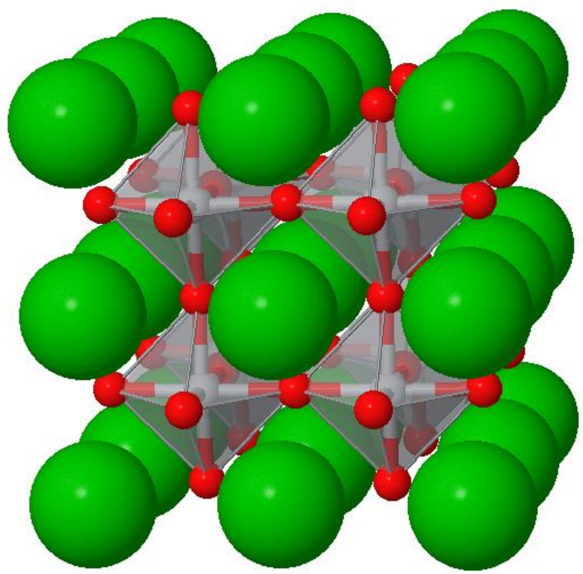




Perovskite $ABO_{3-\delta}$

Proton Conductors: Incorporation in the structure





W. Munch, G. Seifert, K. D. Kreuer, J. Maier, Solid State Ionics, **86**, 647 (1996)

Oxide Proton Conductors

Cubic Perovskites

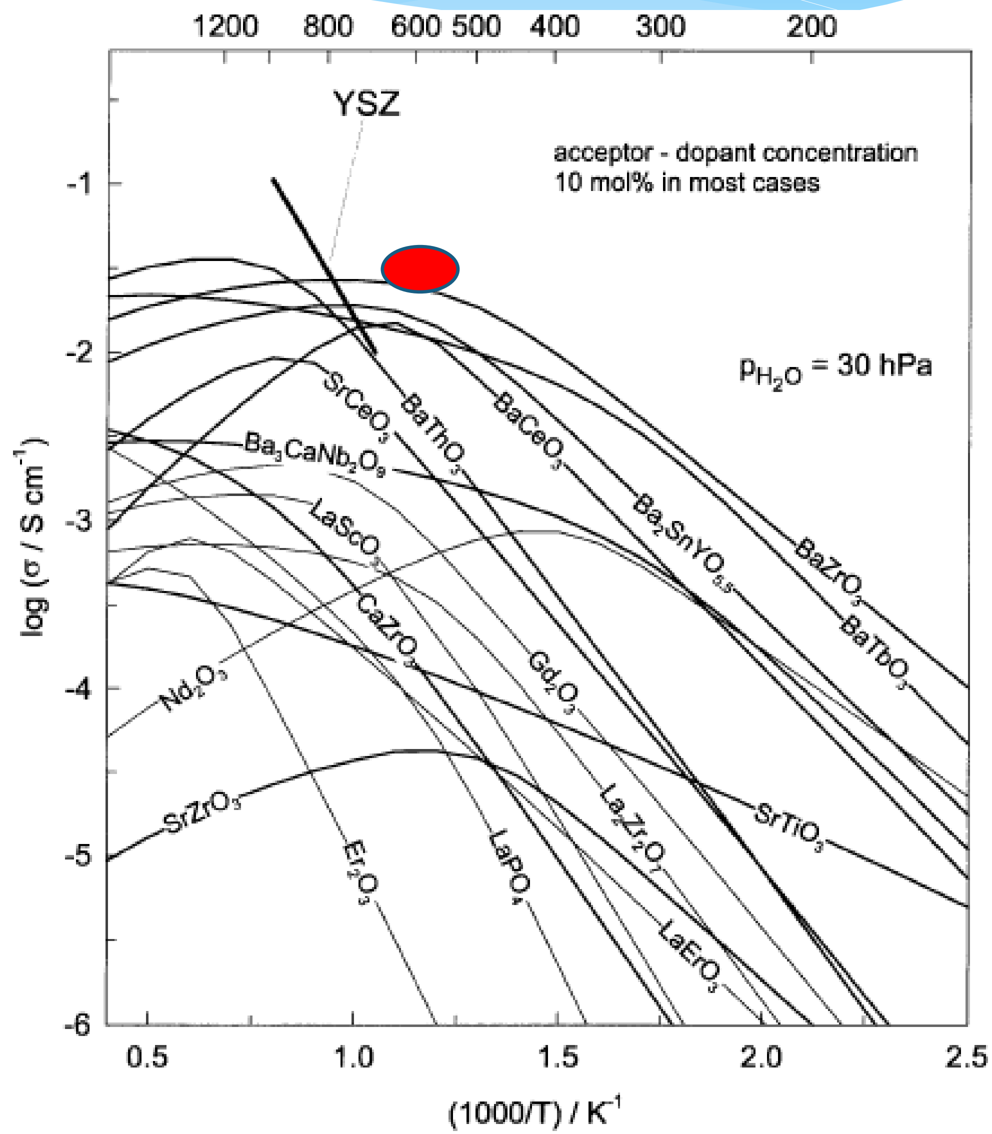
- → $BaZrO_3$ doped
- → $BaCeO_3$-$SrCeO_3$ doped

Rare Earth Oxides Re_2O_3

$LaPO_4$

$LnNbO_4$

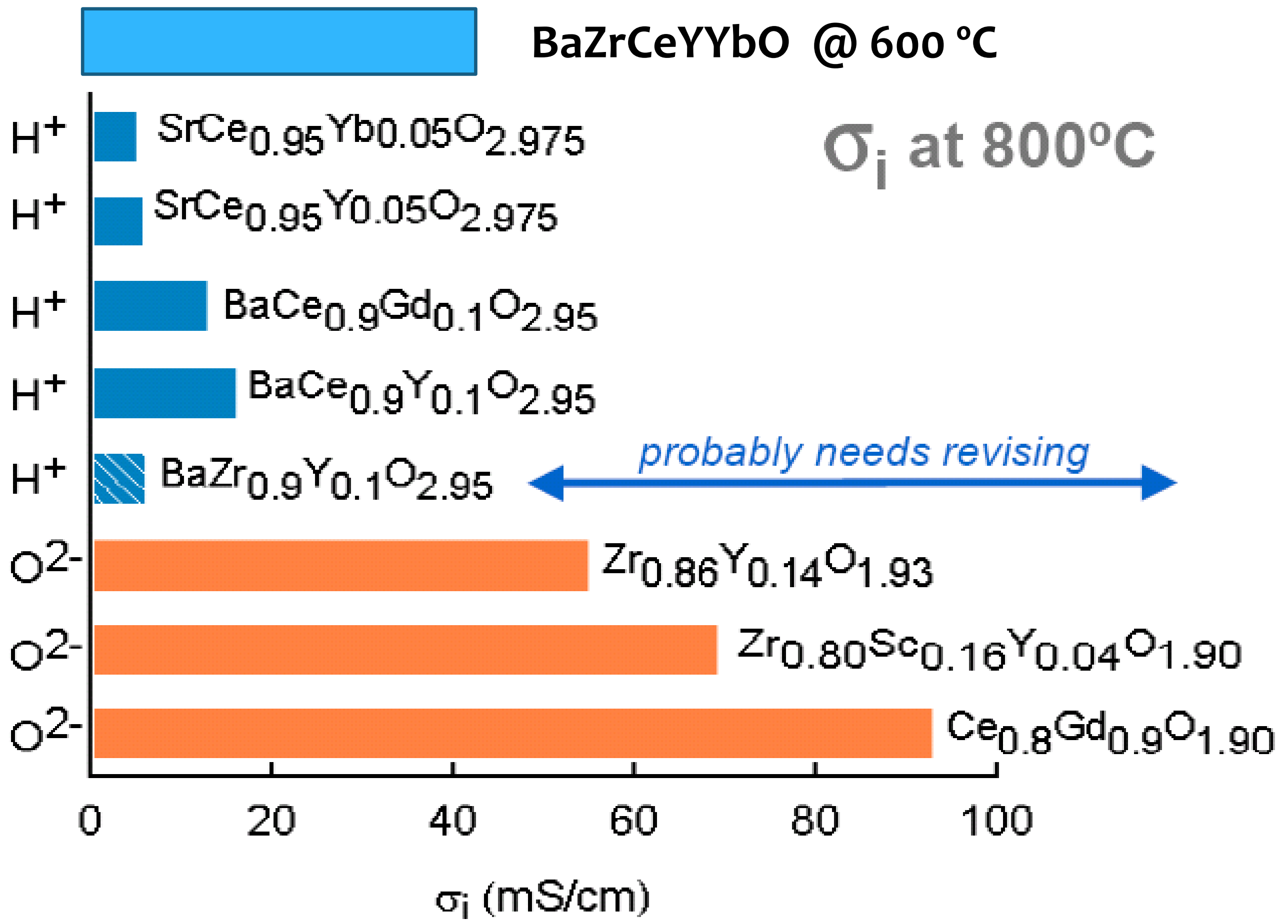
Ln_6WO_{12}



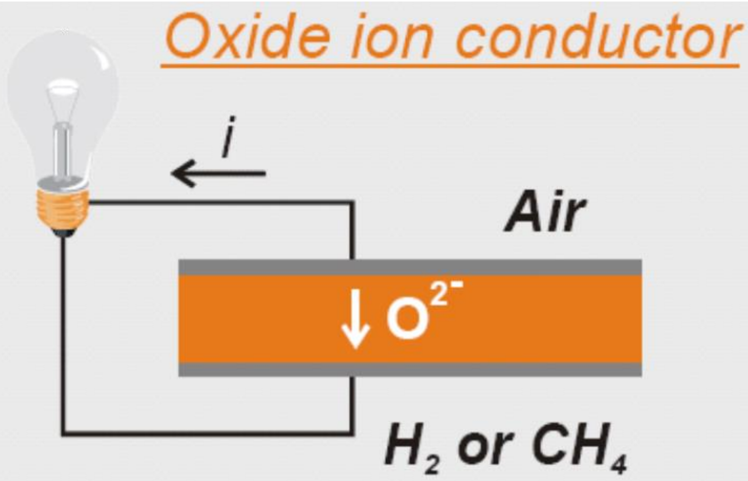
Proton conductivity of various oxides
as **calculated** from data on proton concentrations and mobilities
Norby and Larring, 1999

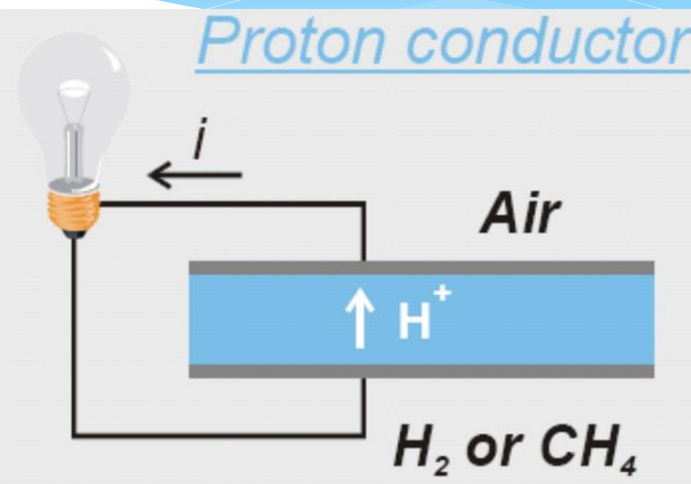
Ion Conduction H$^+$ vs O^{2-}

Overview of Different Solid Electrolytes



Fuel Cells -Electrode Reactions H^+ vs O^{2-}





At air electrode:

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

At fuel electrode:

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

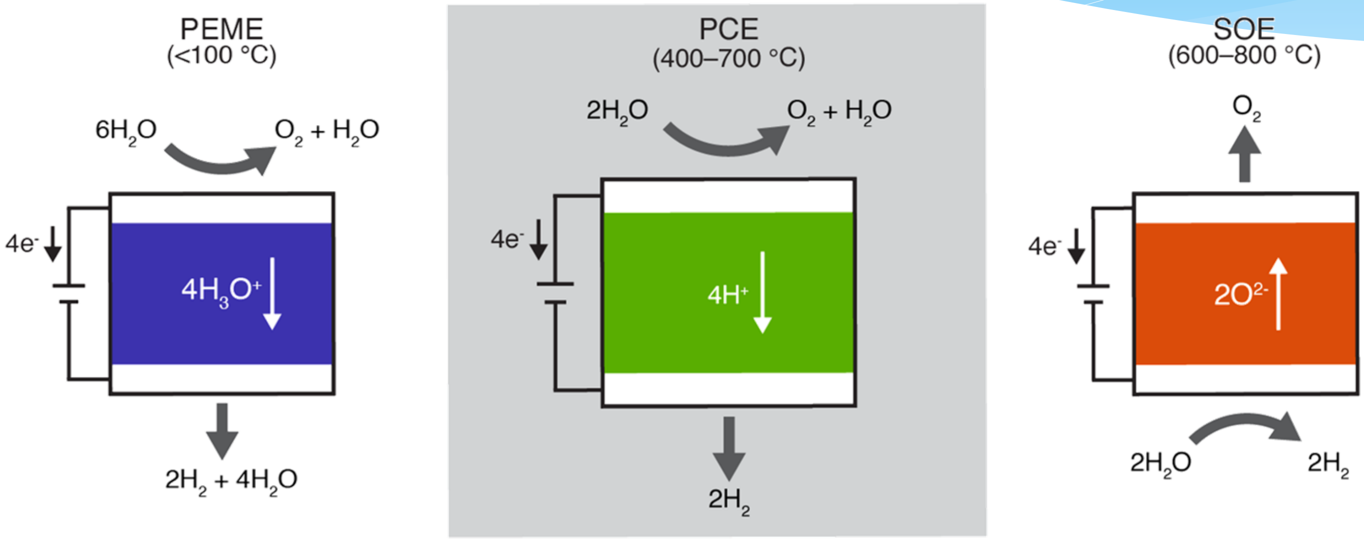
At air electrode:

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

At fuel electrode:

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

Applications - Electrolysis



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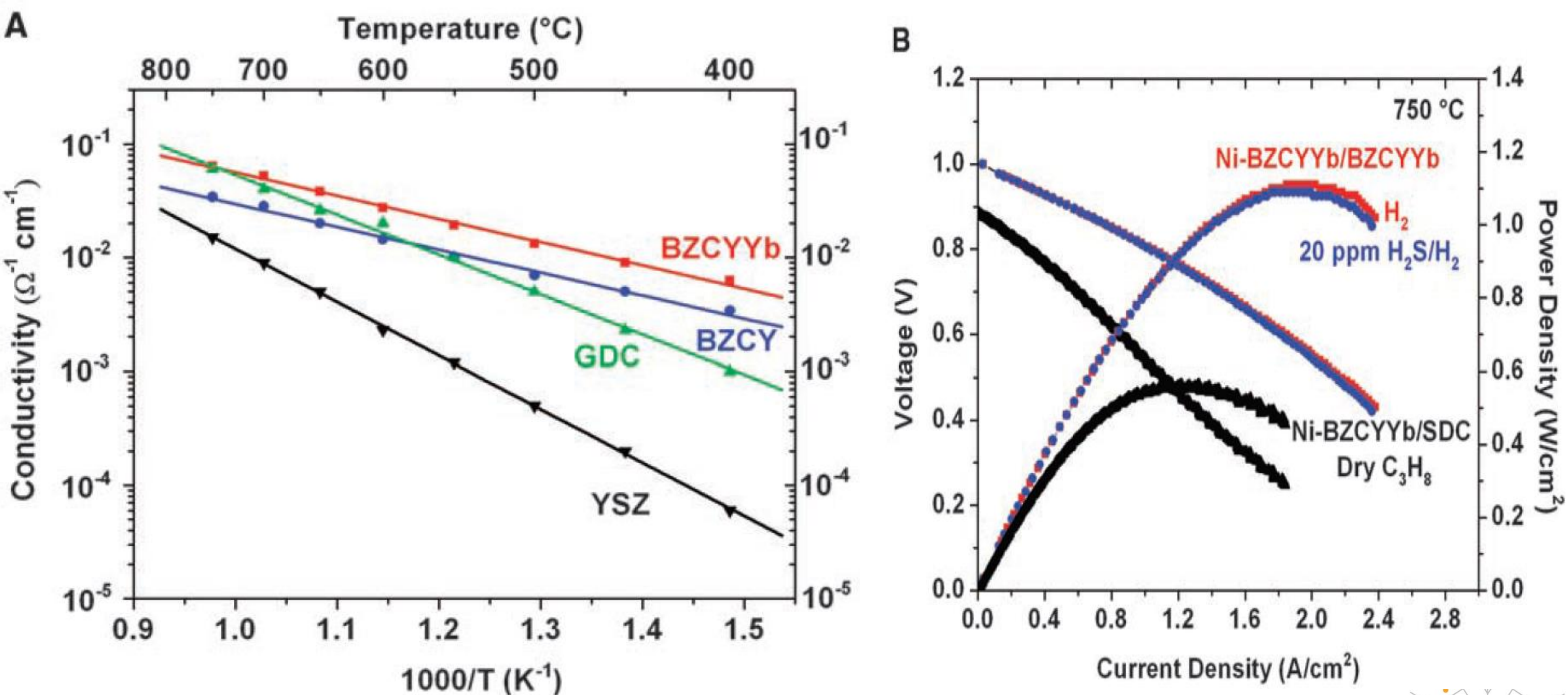
FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

New Proton Conductors - PCFC

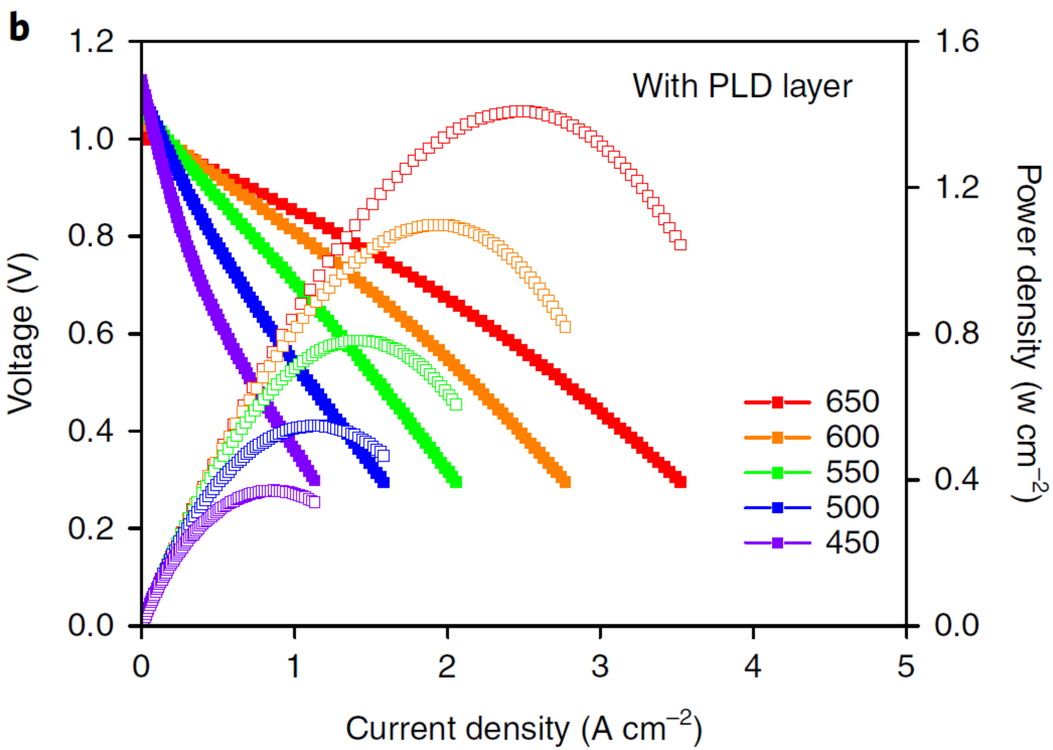
$BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$

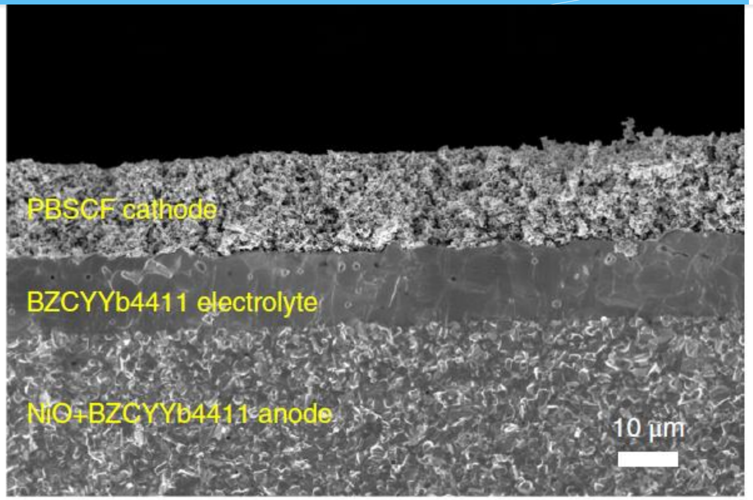


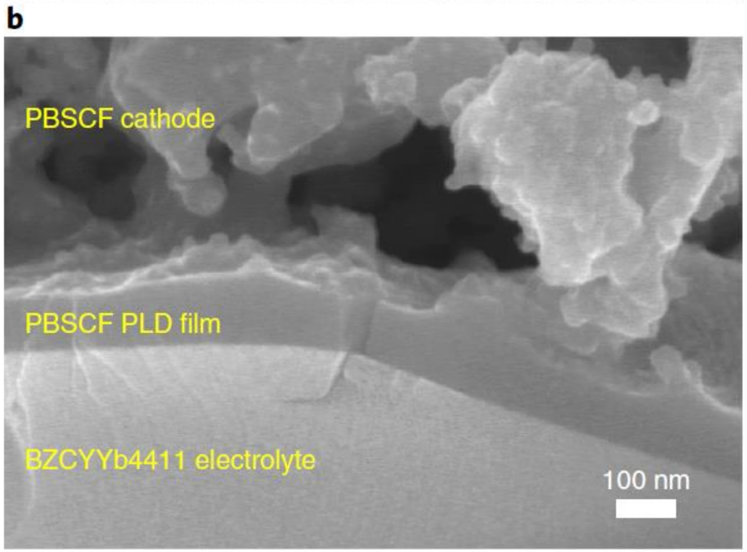
M. Liu et al, **Science** 326 (**2009**) p. 126

New Proton Conductors

$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF)

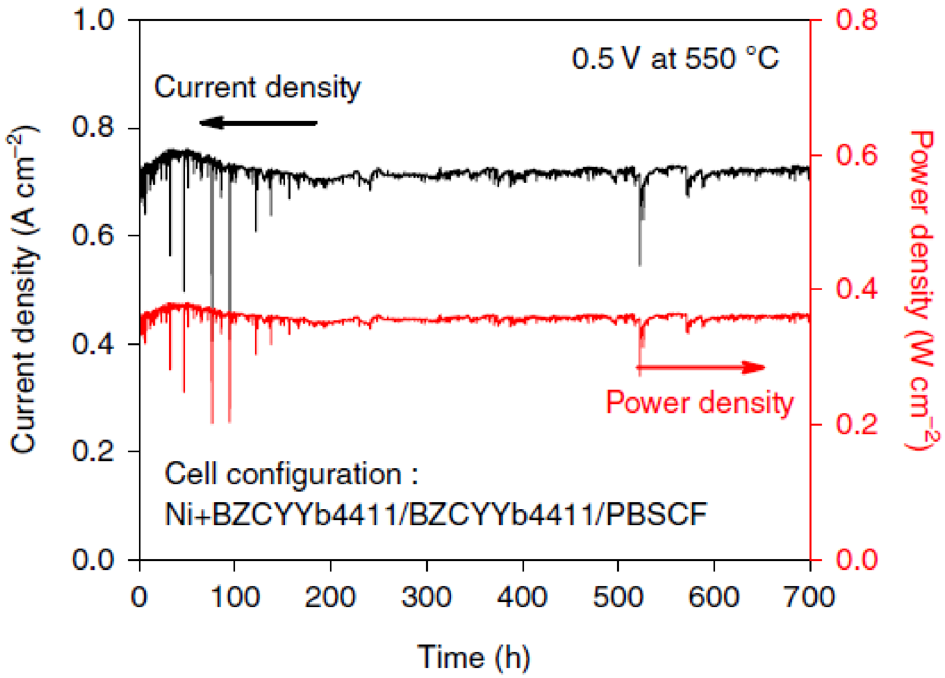






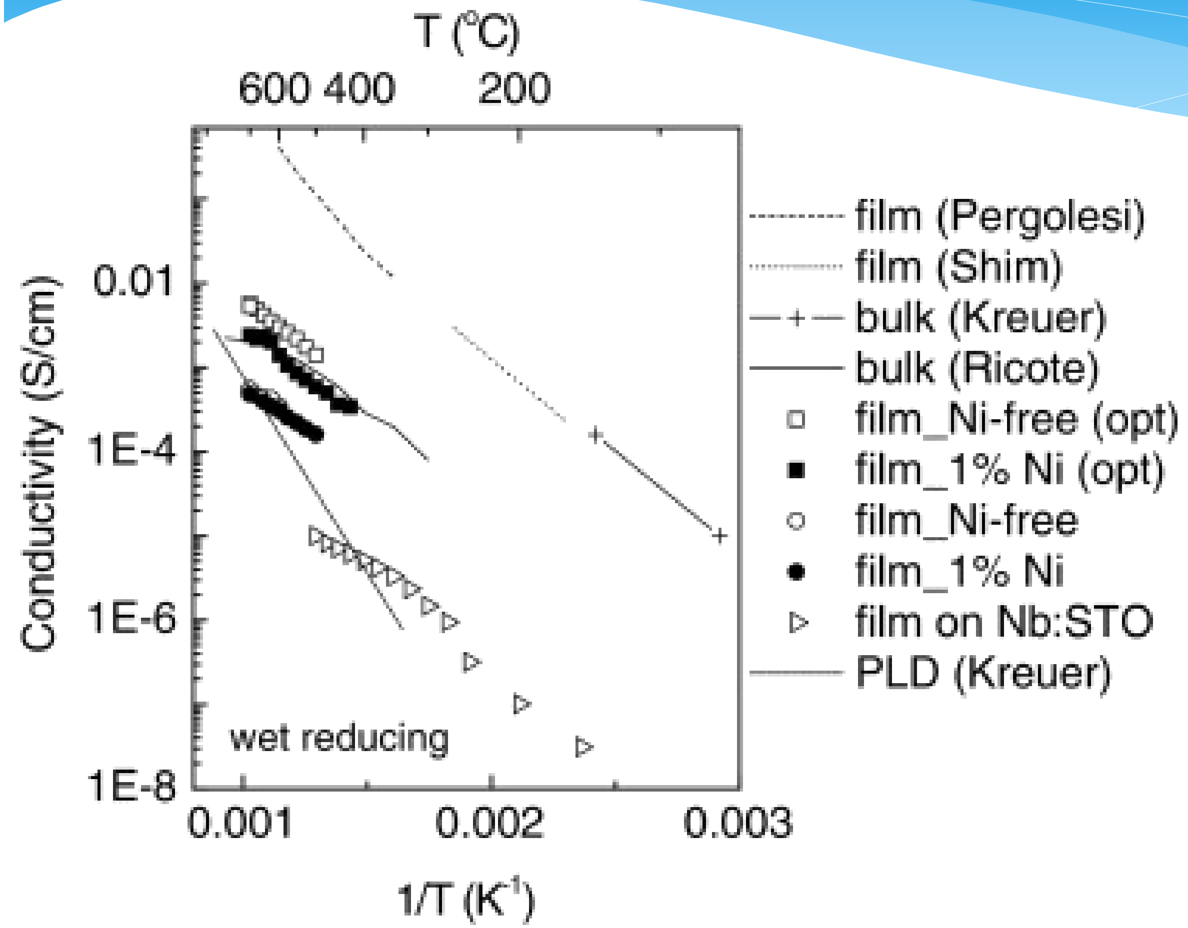
S. M. Haile et al, **Nature Energy (2018)**

New Proton Conductors



S. M. Haile et al, **Nature Energy** (2018)

Proton Conductors – Thin-Films

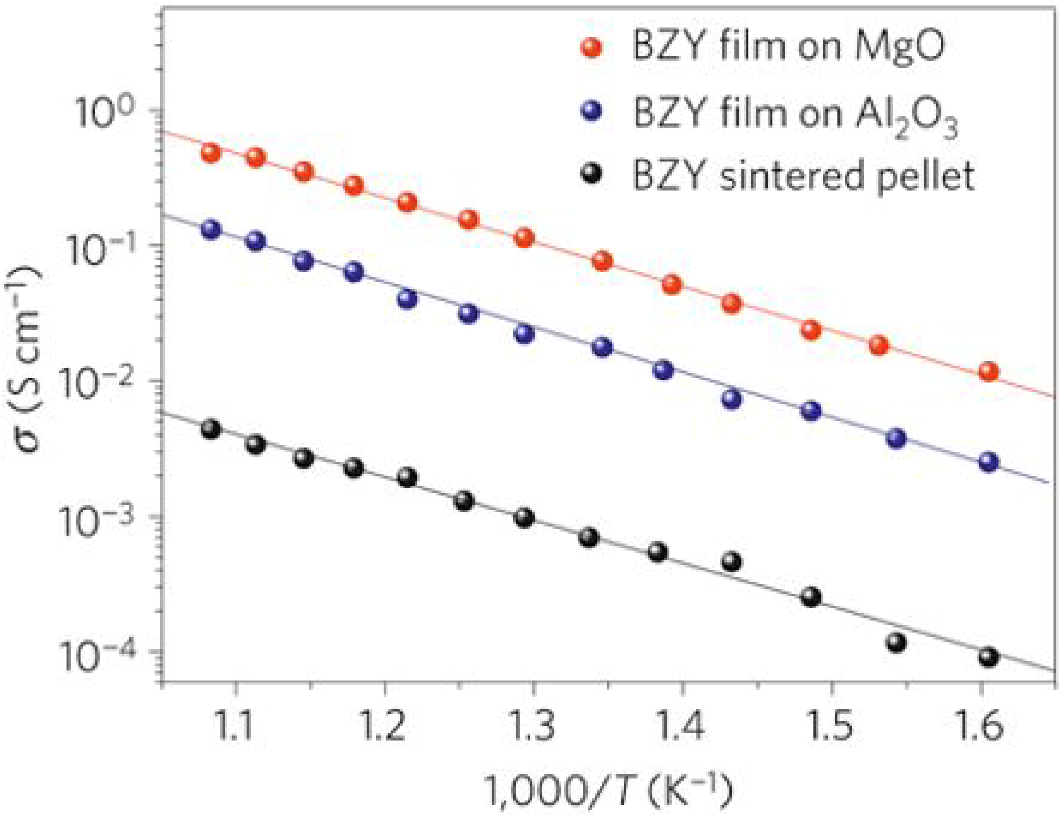


Y-Doped Barium Zirconate (BZY)

- Advantages for SOFC. Decrease of electrode thickness :
  - Enhancement of protonic conductivity
  - Decrease of blocking effects due to resistive grain boundaries

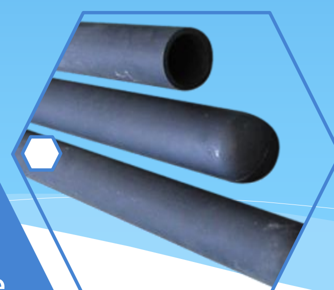
A. Magrasó, et. al. , **Solid State Ionics** 314 (**2018**) 9

Proton Conductors – Thin-Films

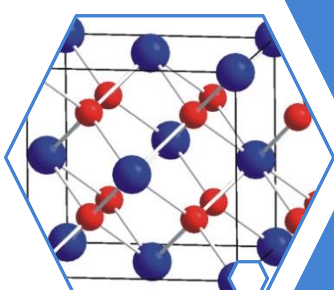


D. Pergolesi, E. Traversa et. al., **Nature Materials** 9 (**2010**), 846-852

Process Intensification
Protonic Membrane Reactors

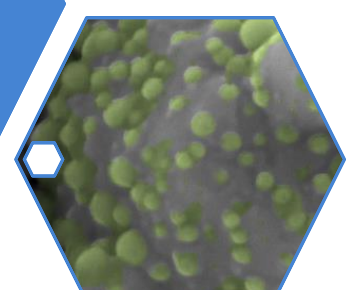


Manufacture
- Synthesis



Surface
Activation

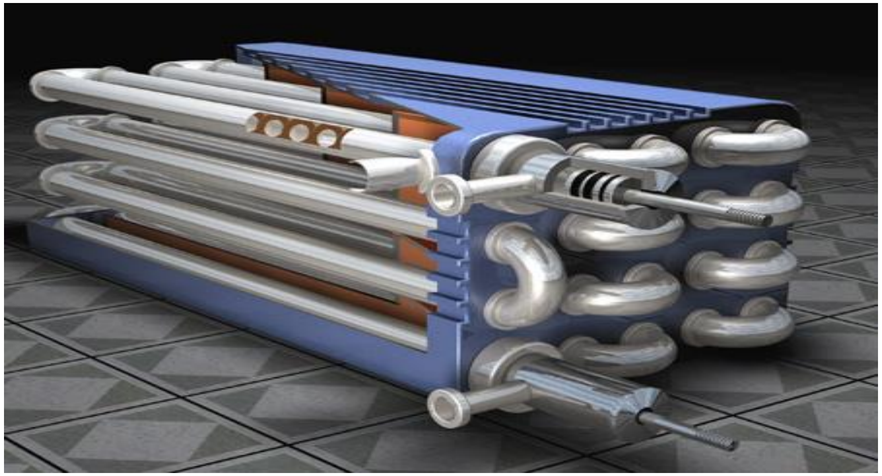
Adjust
Transport
Properties



Process Intensification

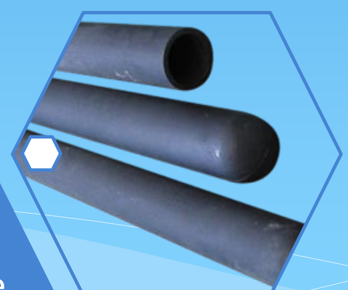
Catalytic Membrane Reactors

- Smaller Equipment & Plant
- Safer Processes
- High Selectivity & Product Purity
- Heat Management
- Major Cost Saving (Capex and Opex)

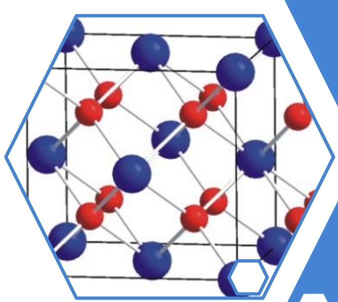


Engineering future ion-transport membranes for gas separations in energy and chemistry applications

Direct Conversion of Methane to Aromatics in a co-ionic CMR

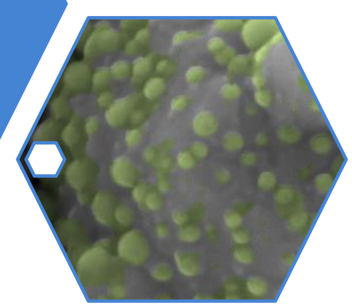


Manufacture - Synthesis



Surface Activation

Adjust Transport Properties



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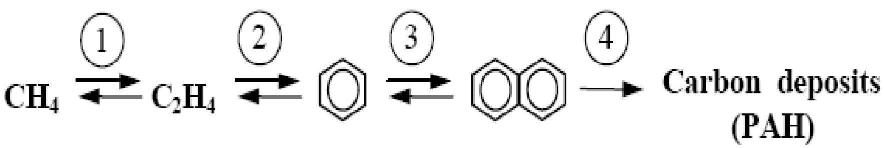
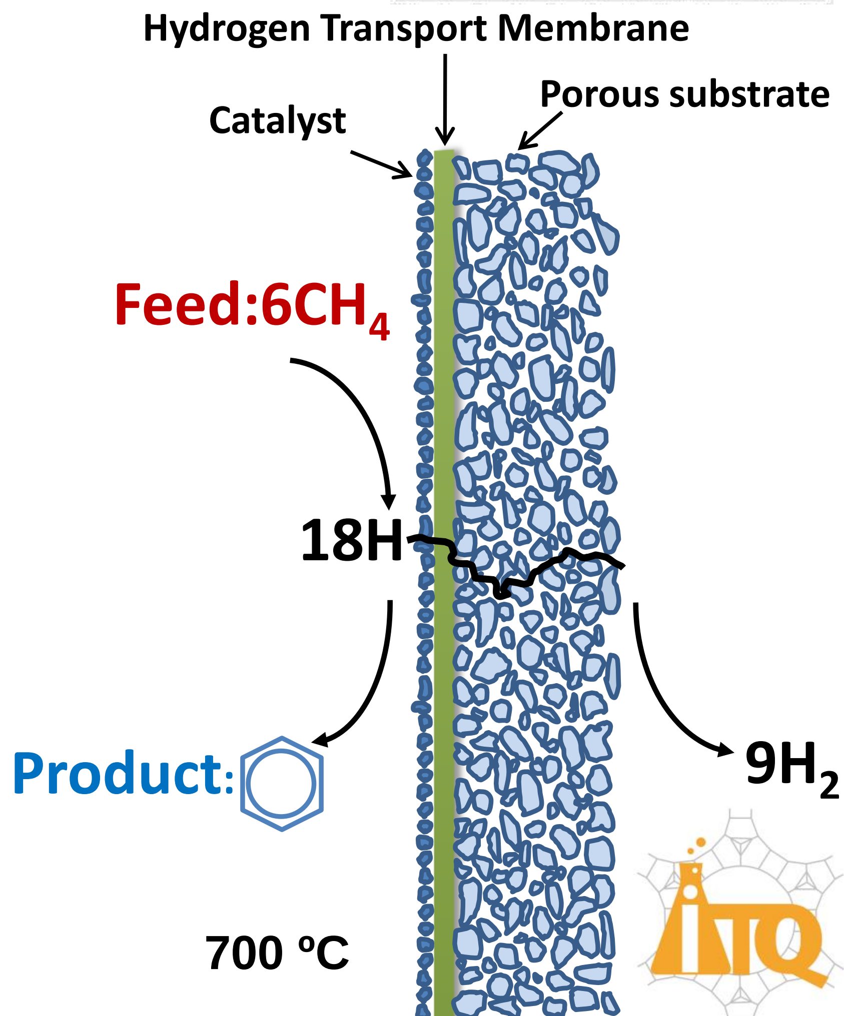
Ceramic Membrane Reactors – Intensified Processes

Gas-to-Liquids:
Non-Oxidative Methane Dehydro-Aromatization (MDA)

In-situ H_2 removal using ceramic membranes
- **Equilibrium shift**
- Surface Kinetic Improvement

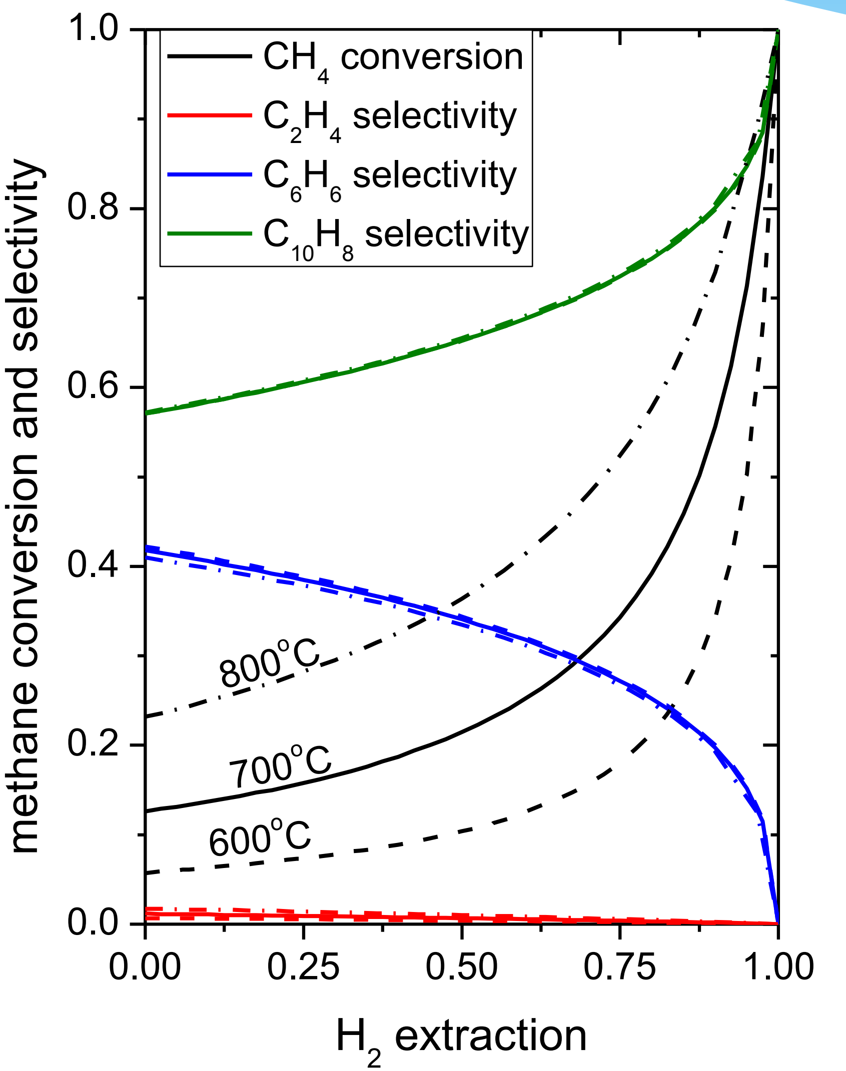


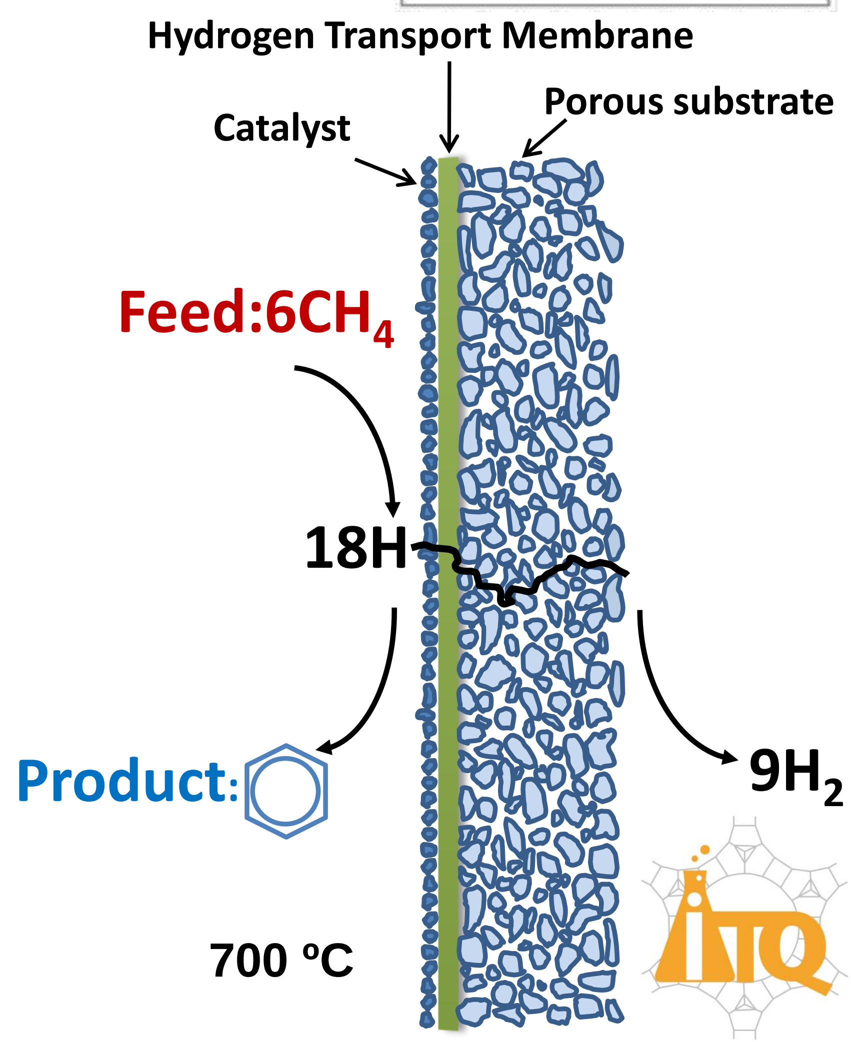
Bifunctional Catalyst for CH_4 conversion:
- CH_4 coupling to produce C2
- Aromatization to produce Benzene
- **Prevent coking**



S. H. Morejudo et al, **Science** 353 (**2016**) p. 563

Ceramic Membrane Reactors – Intensified Processes





S. H. Morejudo et al, **Science** 353 (**2016**) p. 563

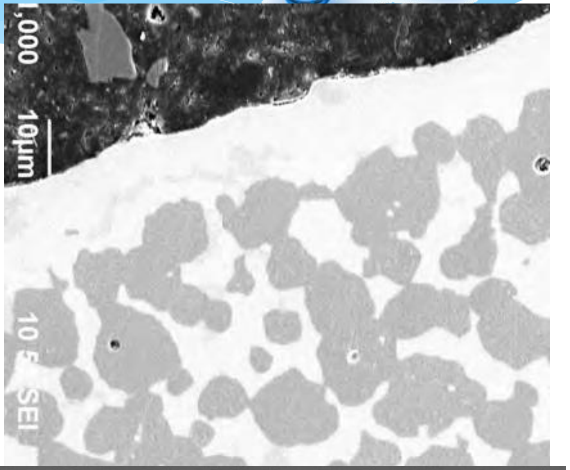
Ceramic Membrane Reactors – Intensified Processes

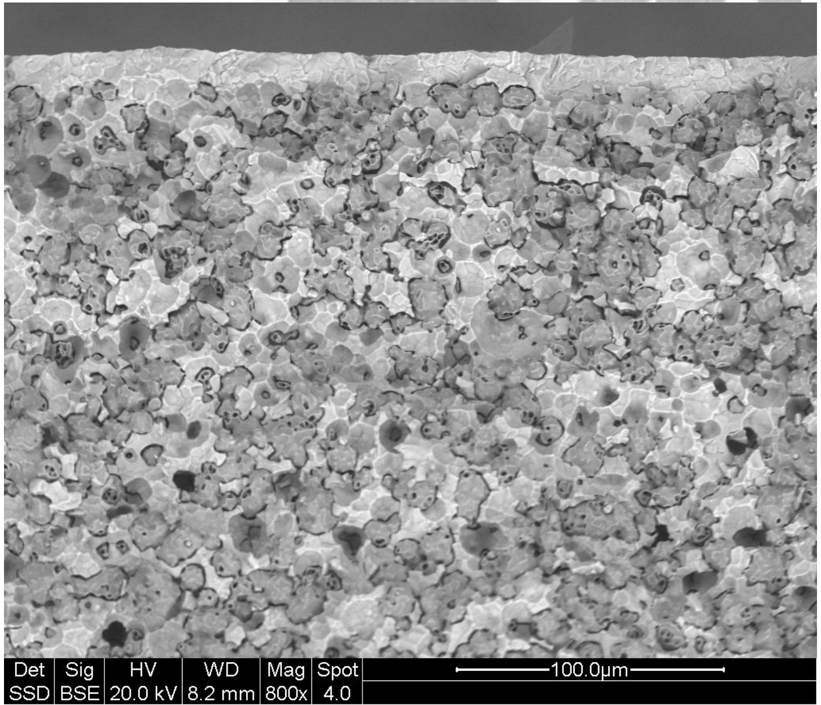
Gas-to-Liquids:
Non-Oxidative Methane Dehydro-Aromatization (MDA)

Hydrogen Removal (700 °C): H2 Pumping

MANUFACTURE:

- Slip-cast/extrude BZCY-NiO composite
- Spray/dip on BZCY electrolyte precursor
- Co-sinterinng
- Sufficient porosity upon NiO reduction
- Size: 10 mmØ, 1 mm wall, 20 μm BZCY, 30 cm
- Development of CH_4-side electrodes





S. H. Morejudo et al, **Science** 353 (**2016**) p. 563

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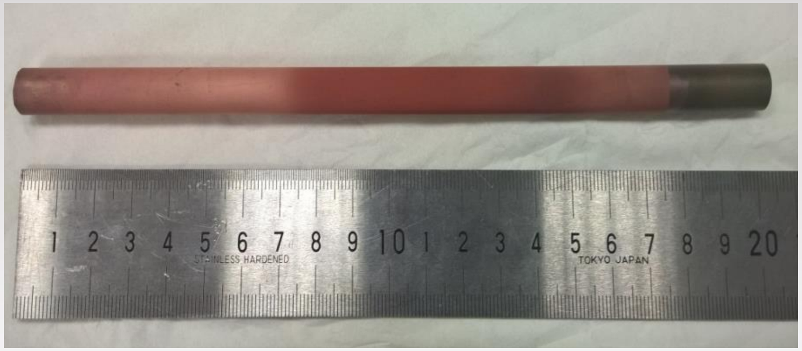

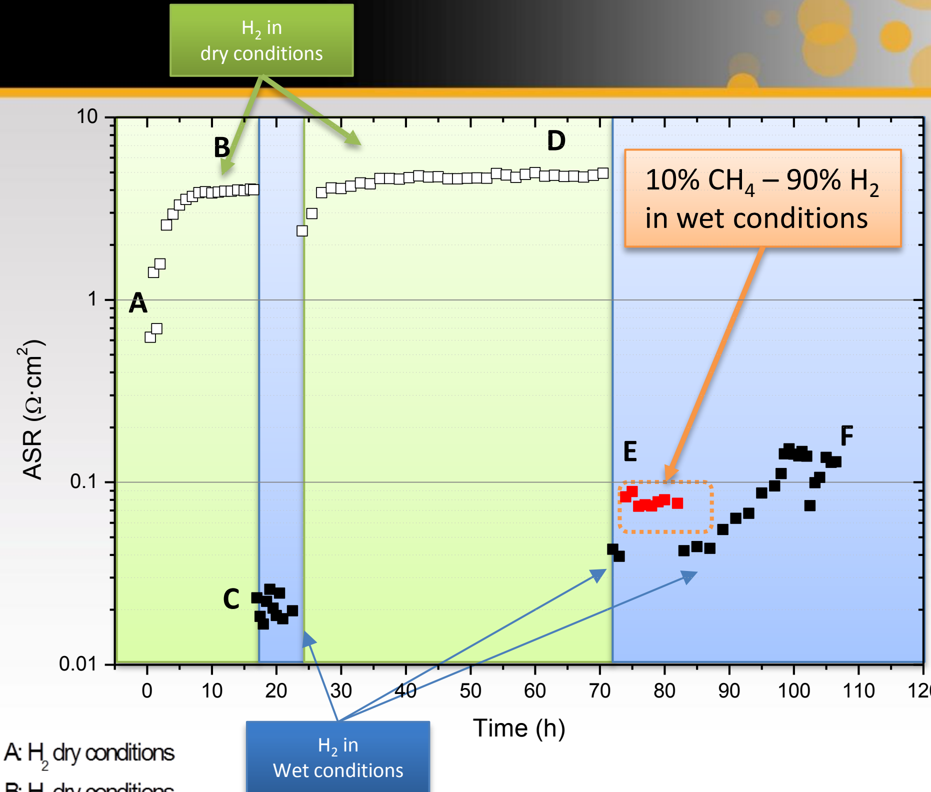

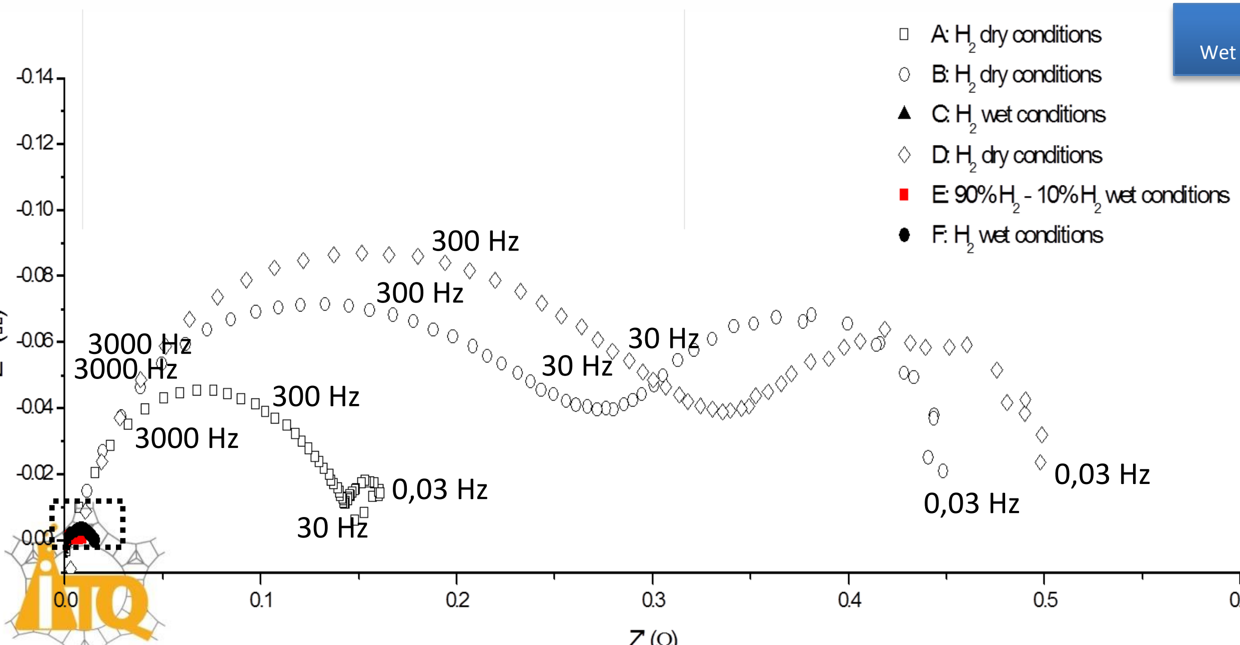

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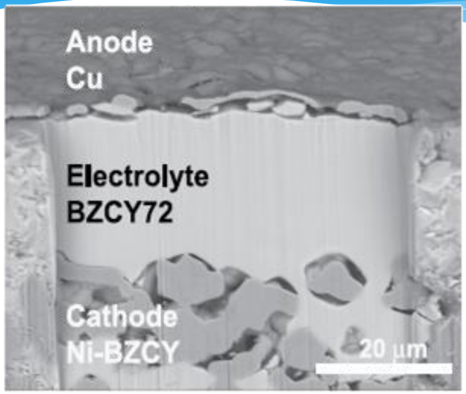
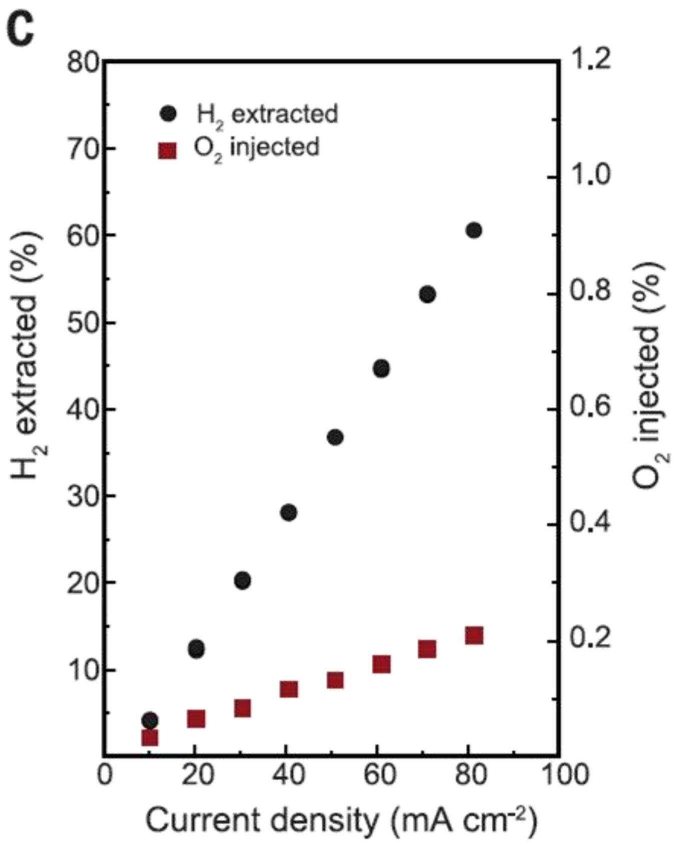
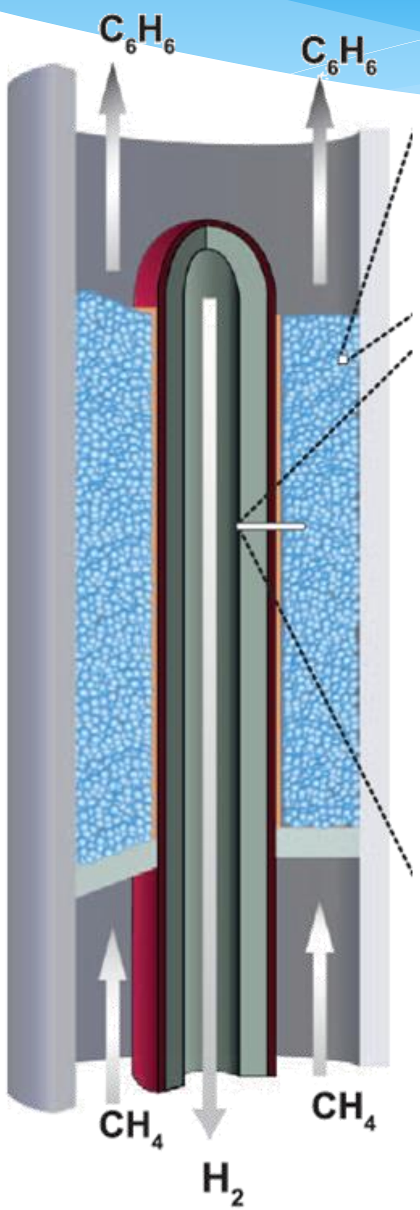
Ceramic Membrane Reactors – Intensified Processes





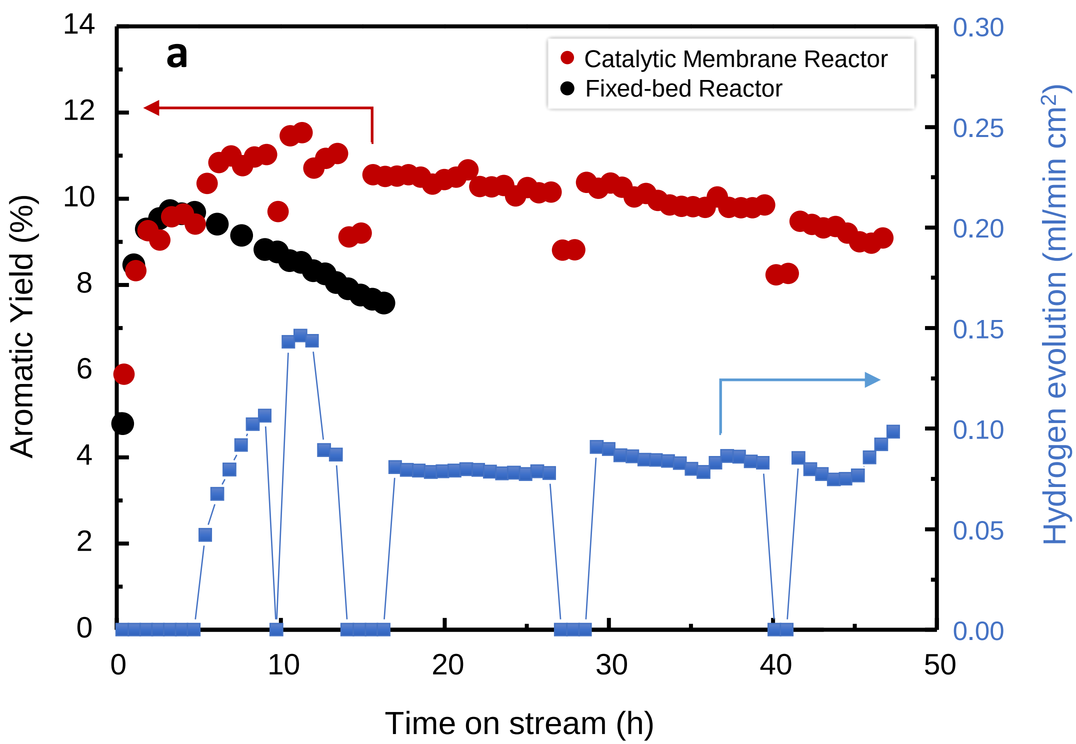


S. H. Morejudo et al,
Science 353 (**2016**) p. 563

Ceramic Membrane Reactors – Intensified Processes

Gas-to-Liquids:
Non-Oxidative Methane Dehydro-Aromatization (MDA)

Hydrogen Removal (700 °C): H2 Pumping



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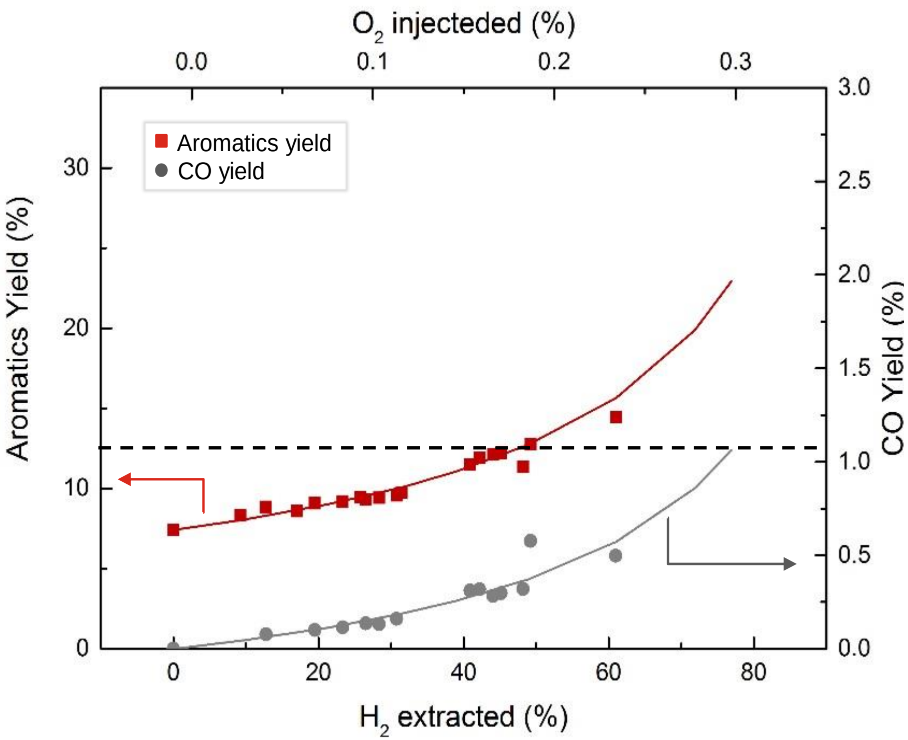

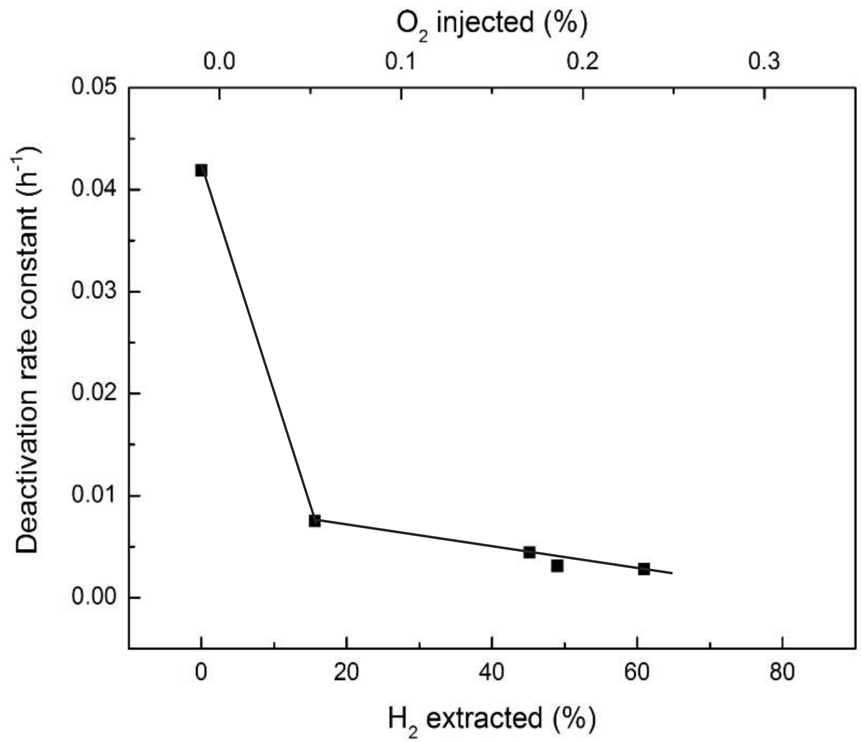

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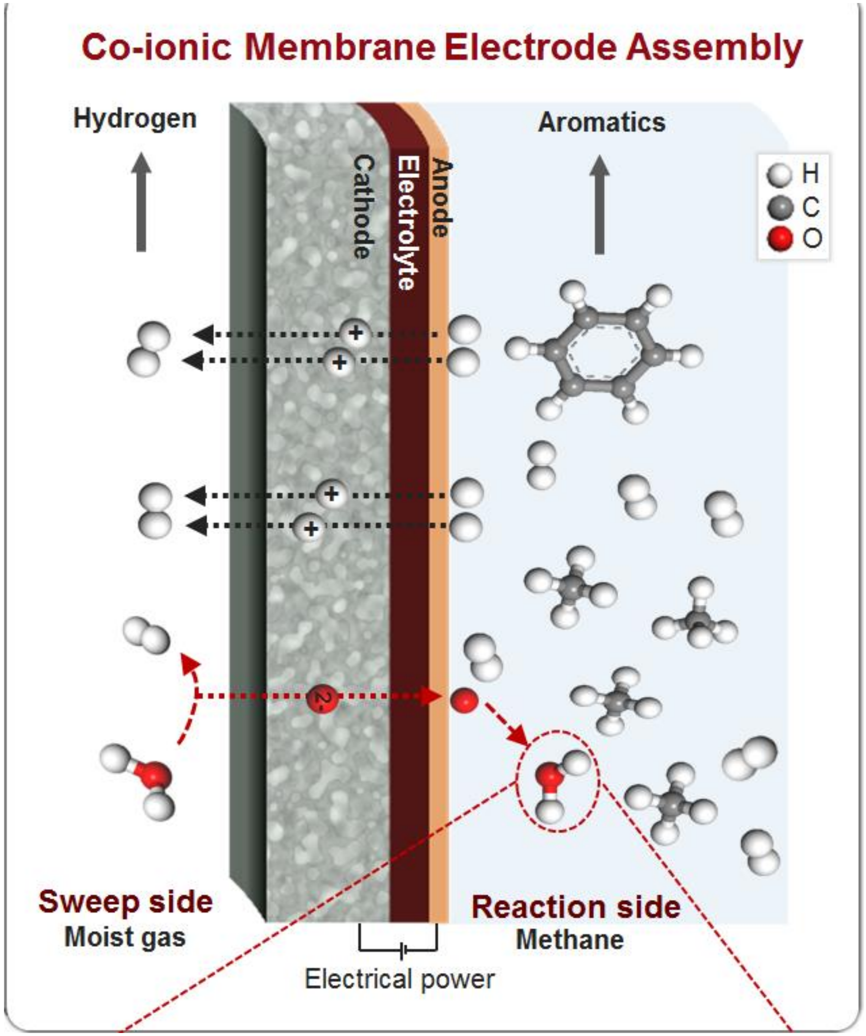

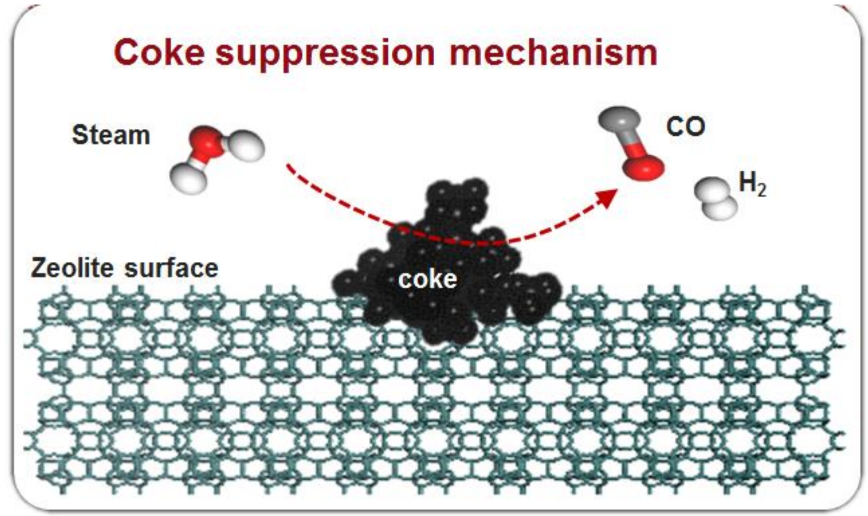

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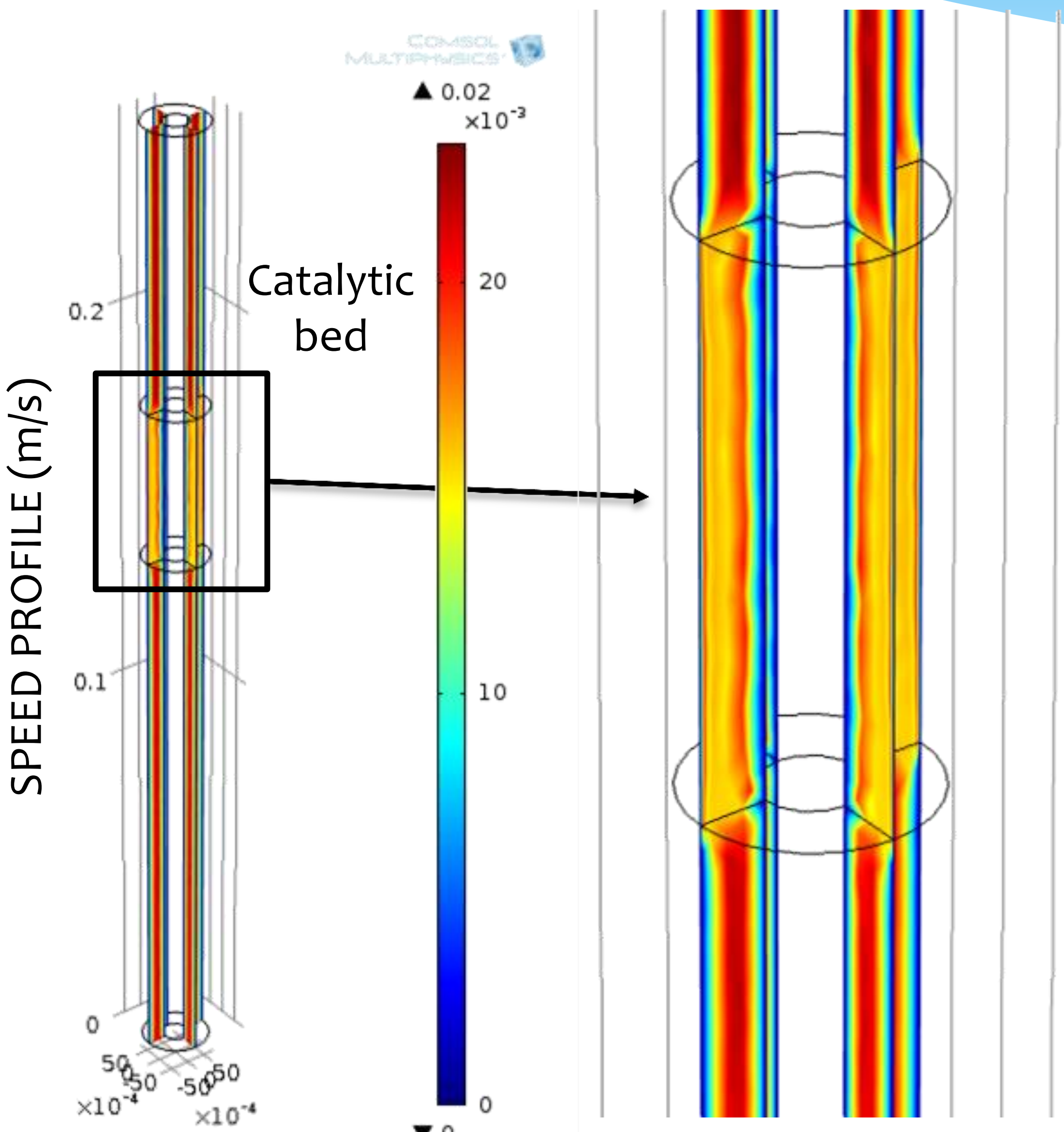

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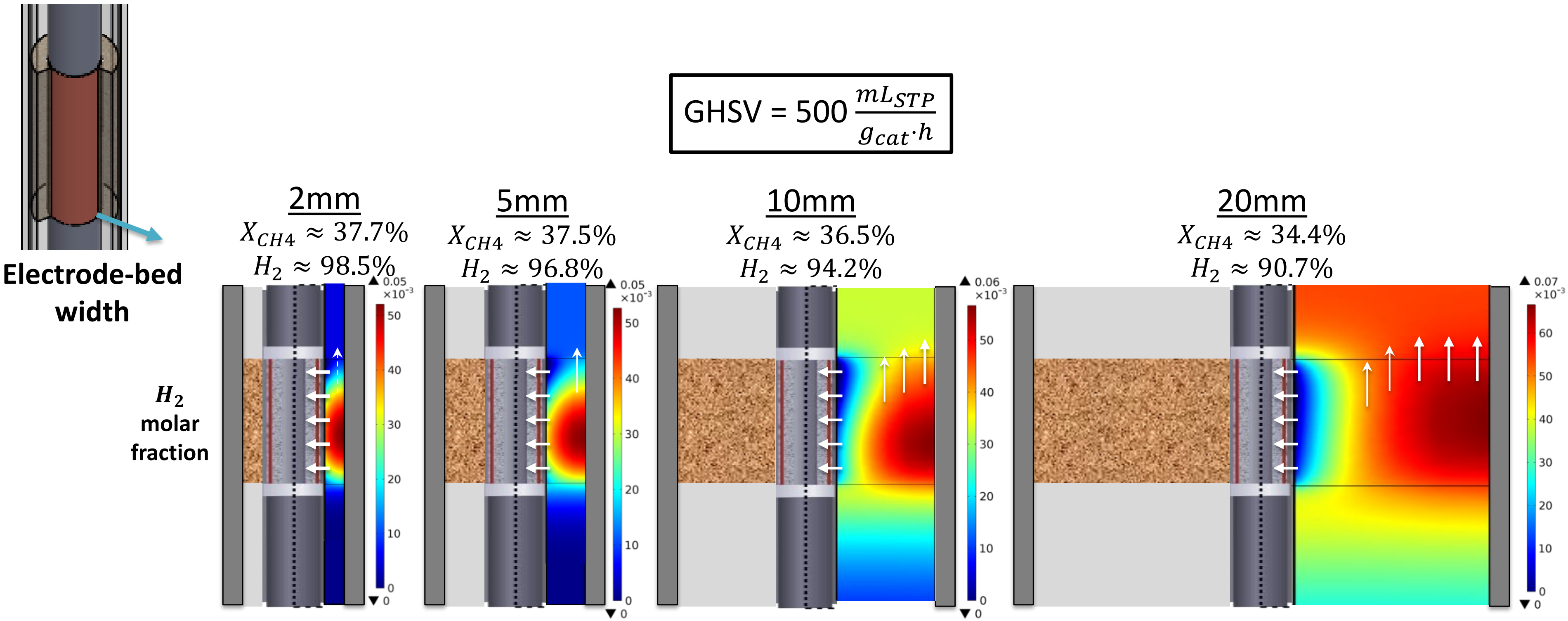

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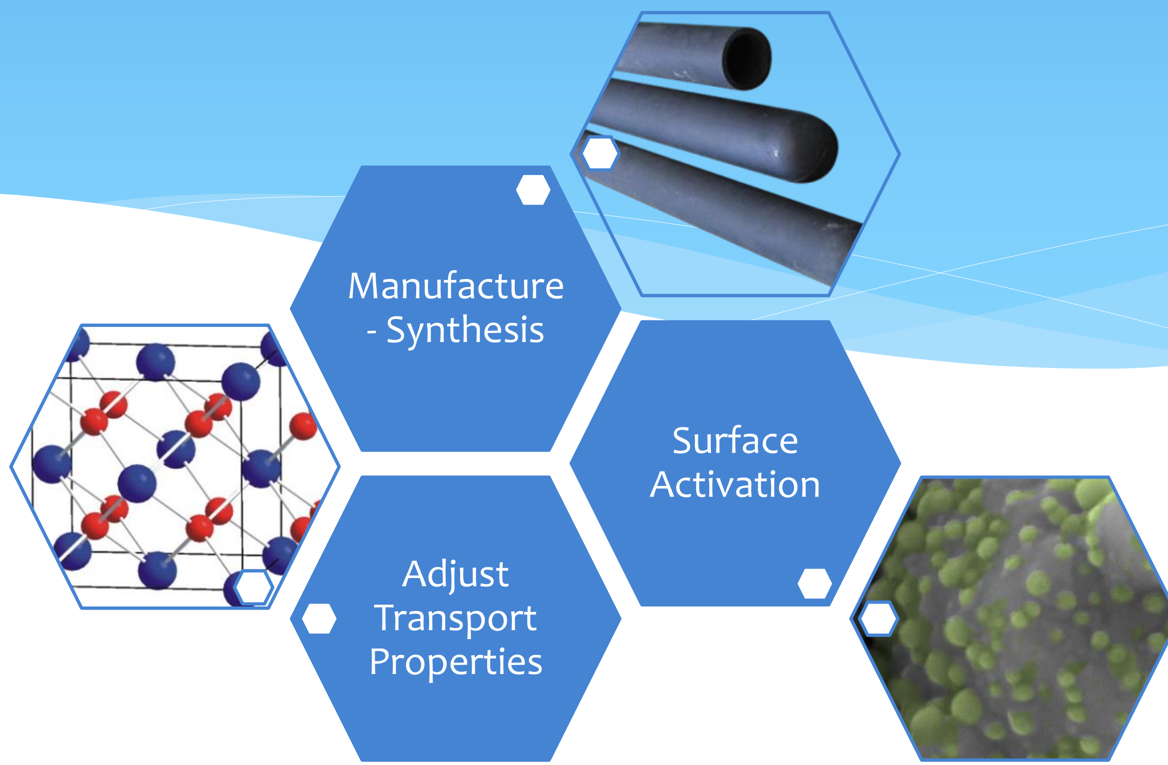
Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss



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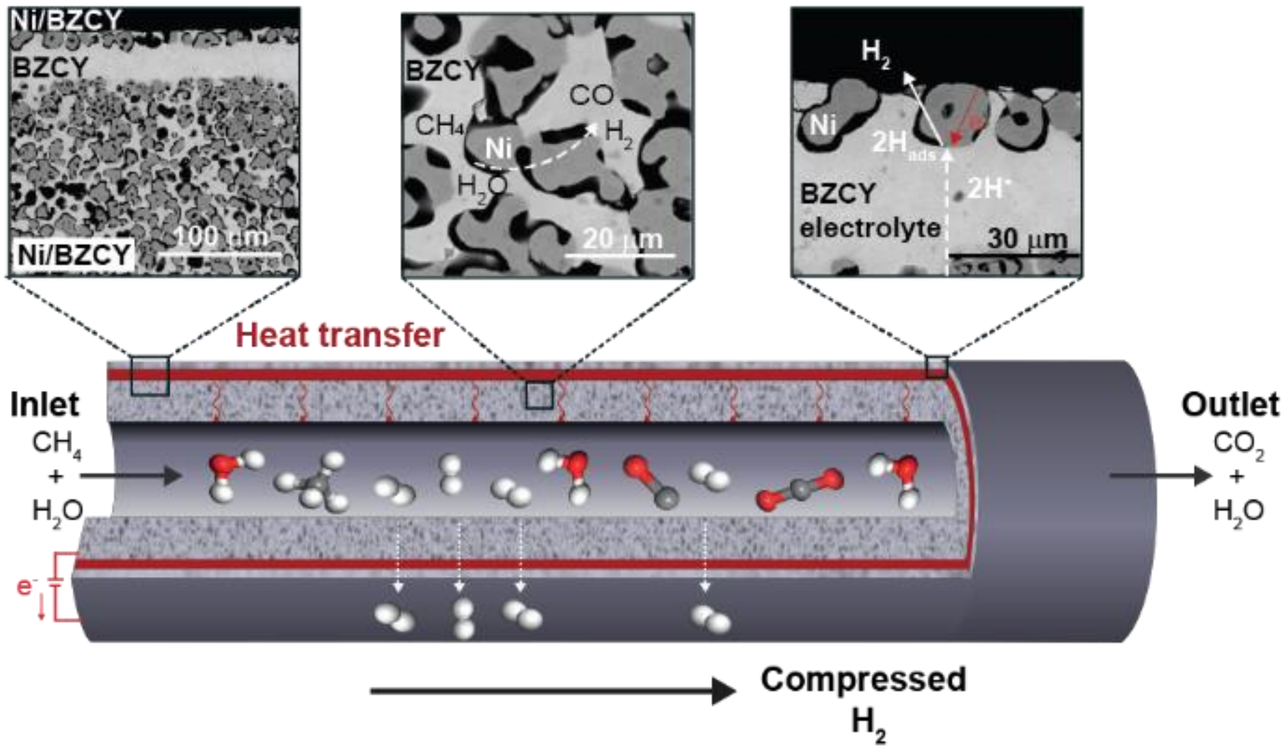
Proton Membrane Reformer (PMR) – EC Compression !!



H. Malerød-Fjeld et al., *Nature Energy,* **2,** p. 923–931 (2017)

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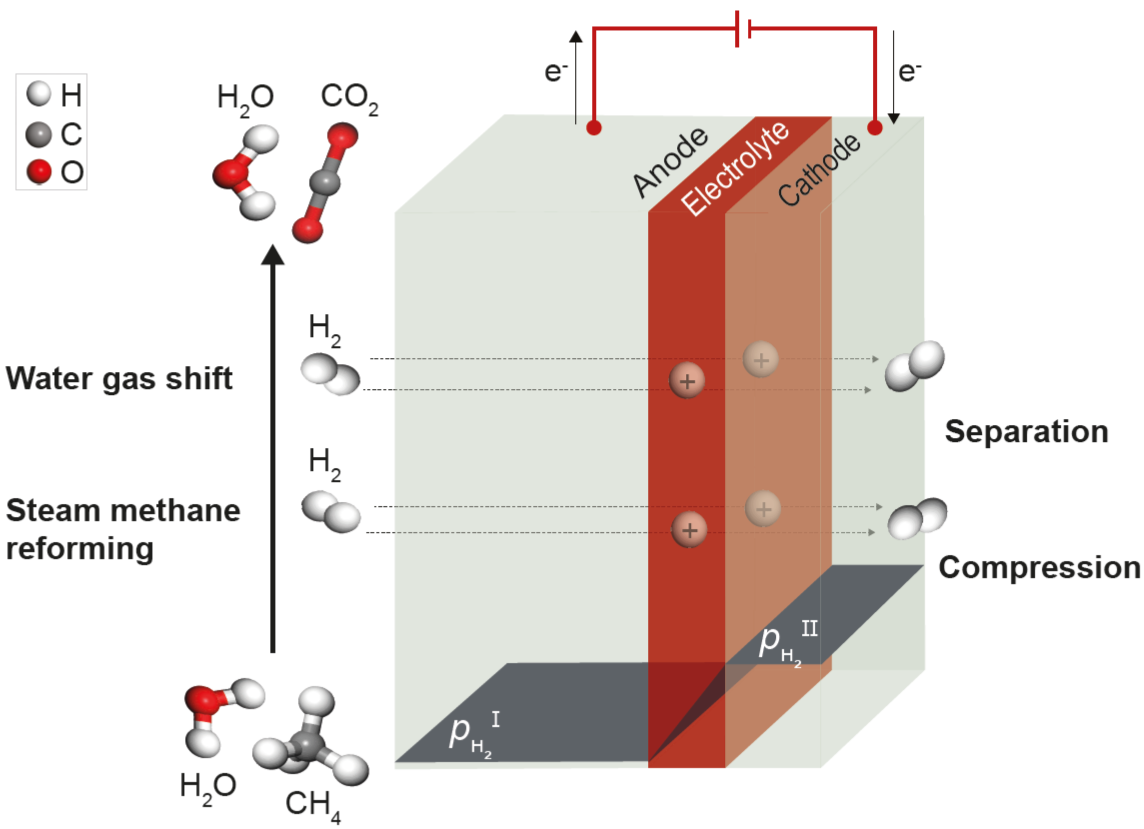

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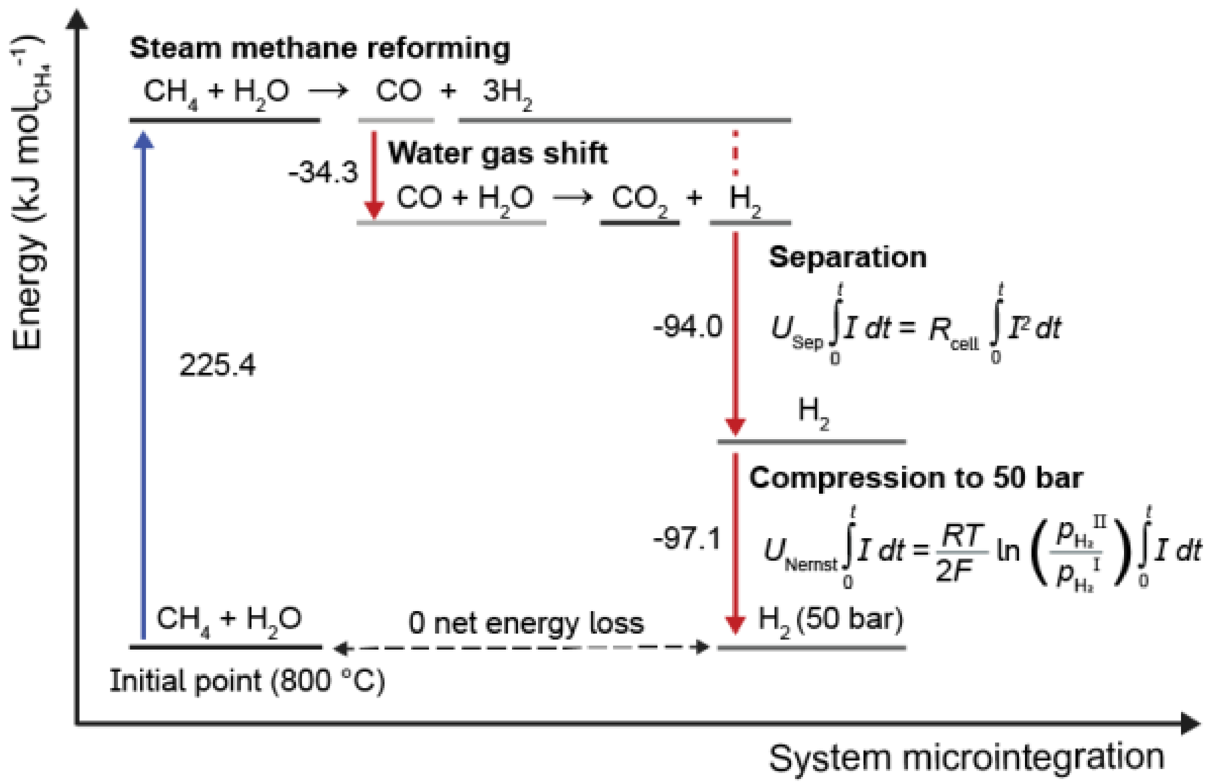

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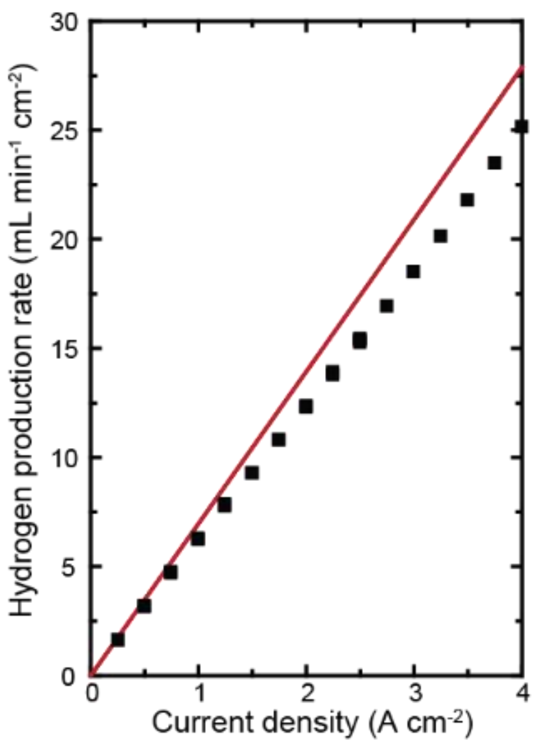
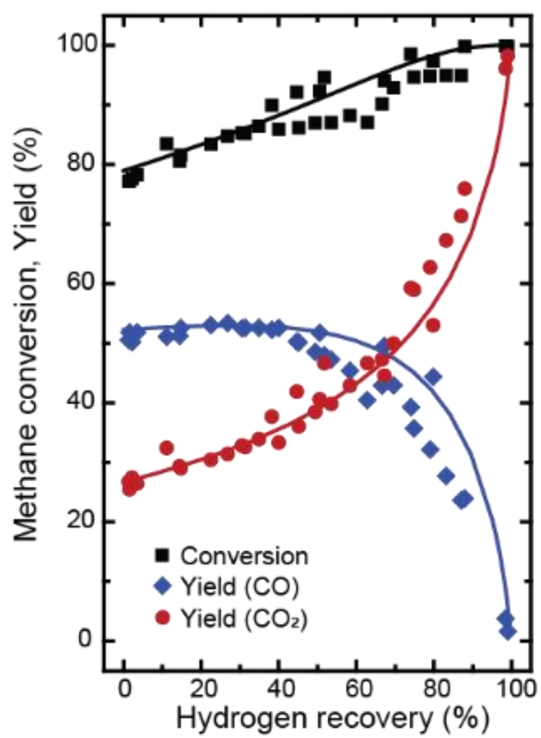
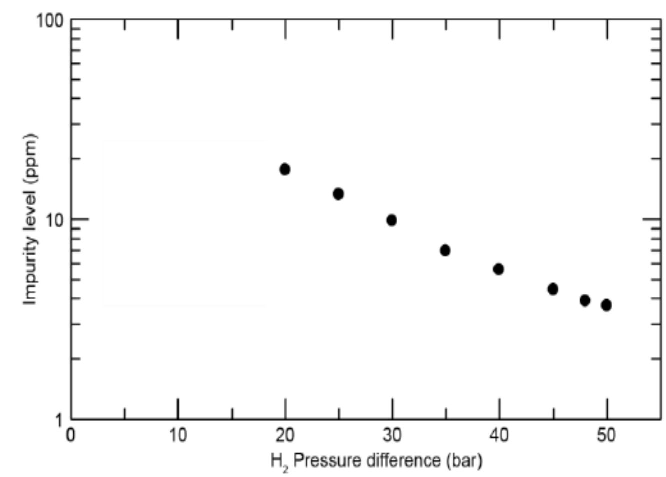




Impurity Level



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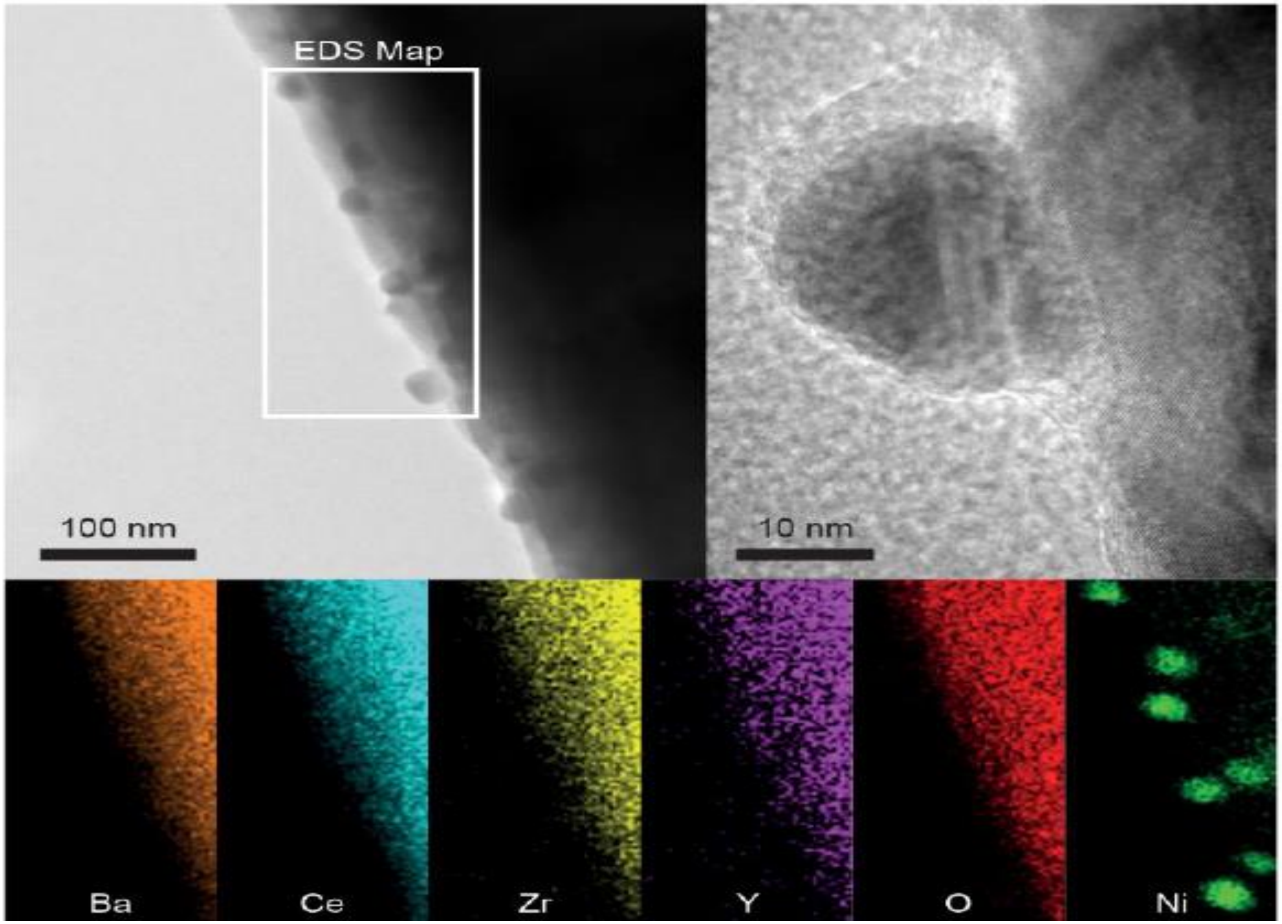
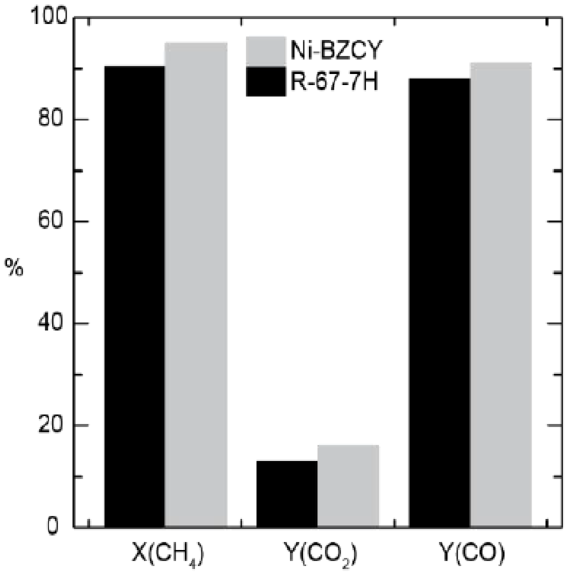
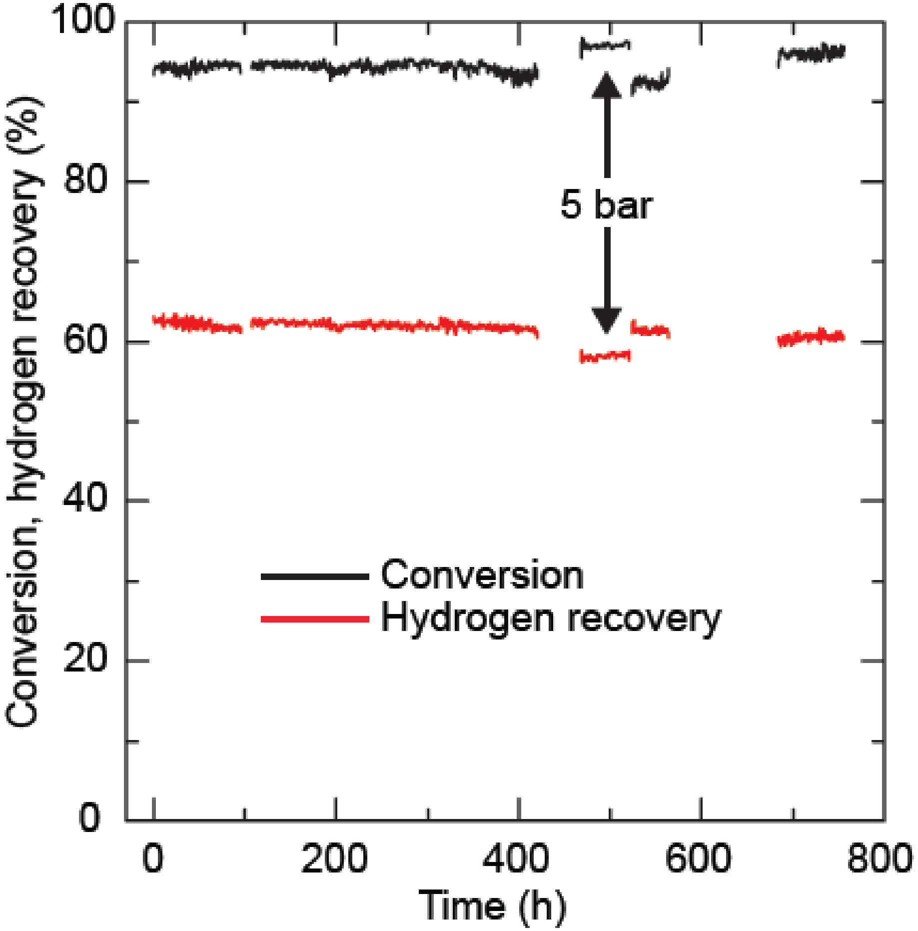
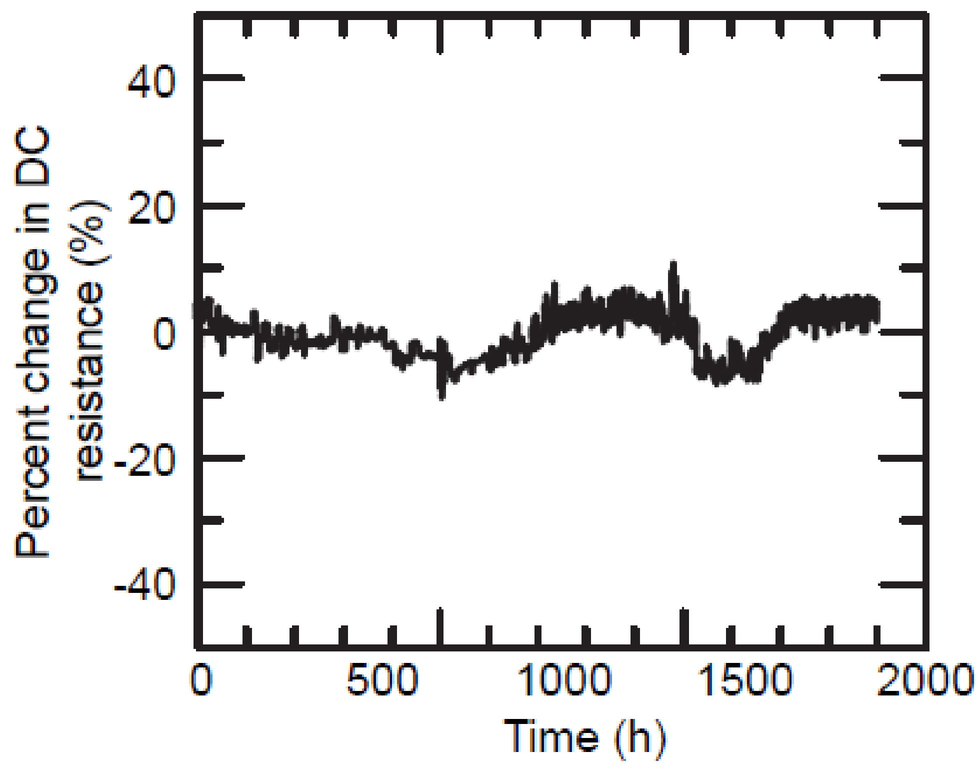




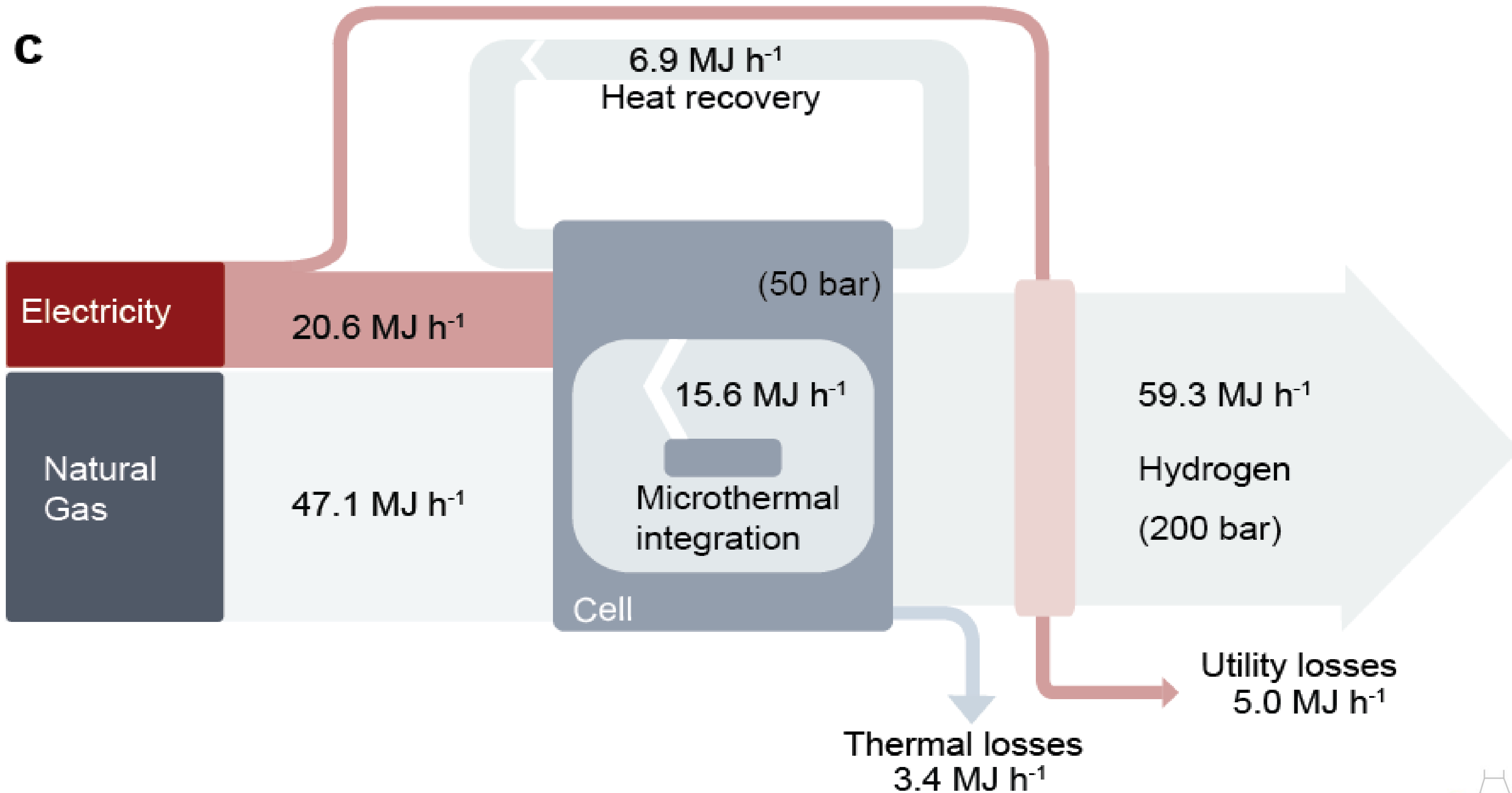
Proton Membrane Reformer (PMR) – Stability





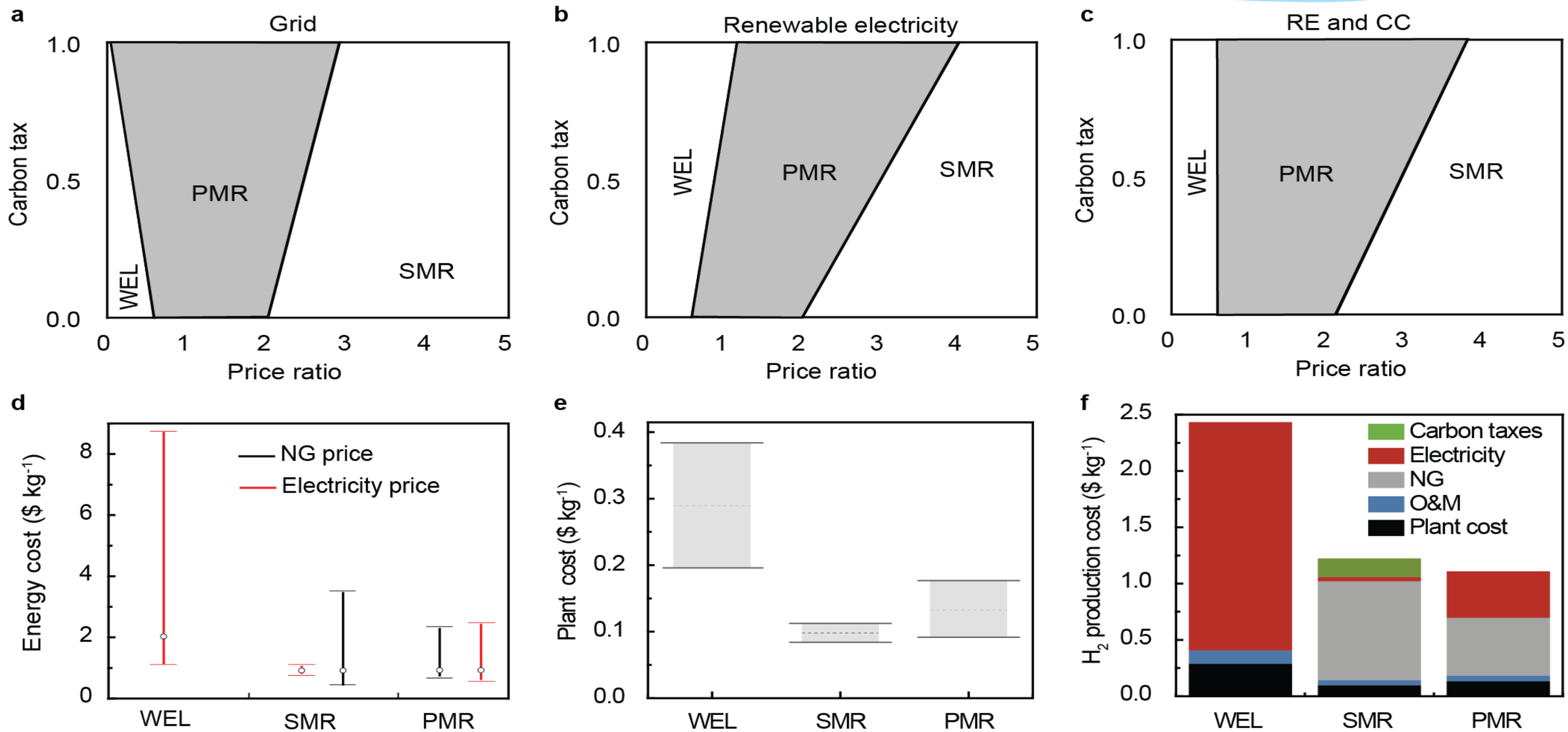
H. Malerød-Fjeld et al., *Nature Energy,* **2,** p. 923–931 (2017)

Proton Membrane Reformer (PMR) – Energy Balance



H. Malerød-Fjeld et al., *Nature Energy*, **2**, p. 923–931 (2017)

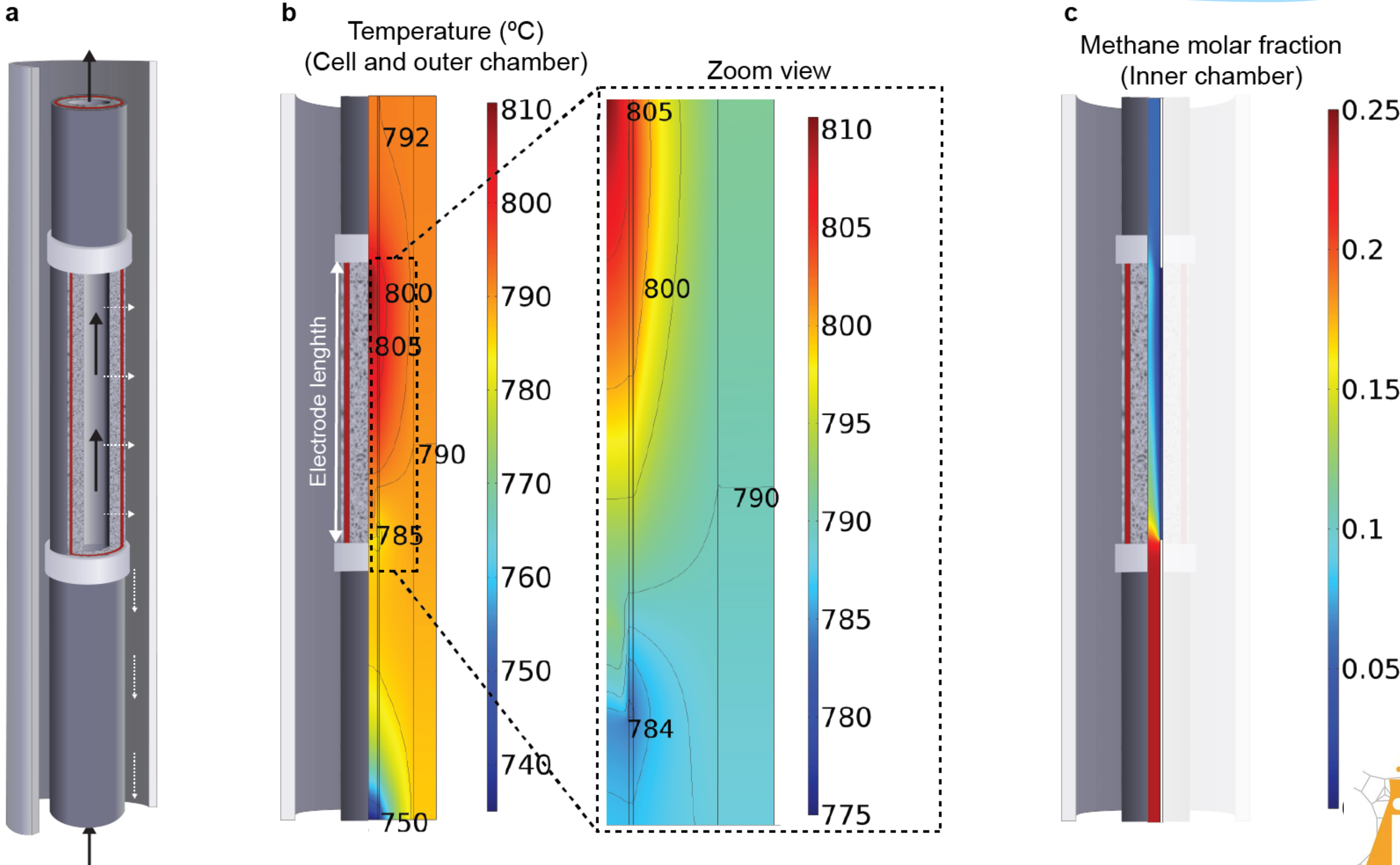
Proton Membrane Reformer (PMR) – Techno-economics



H. Malerød-Fjeld et al., *Nature Energy,* **2,** p. 923–931 (2017)

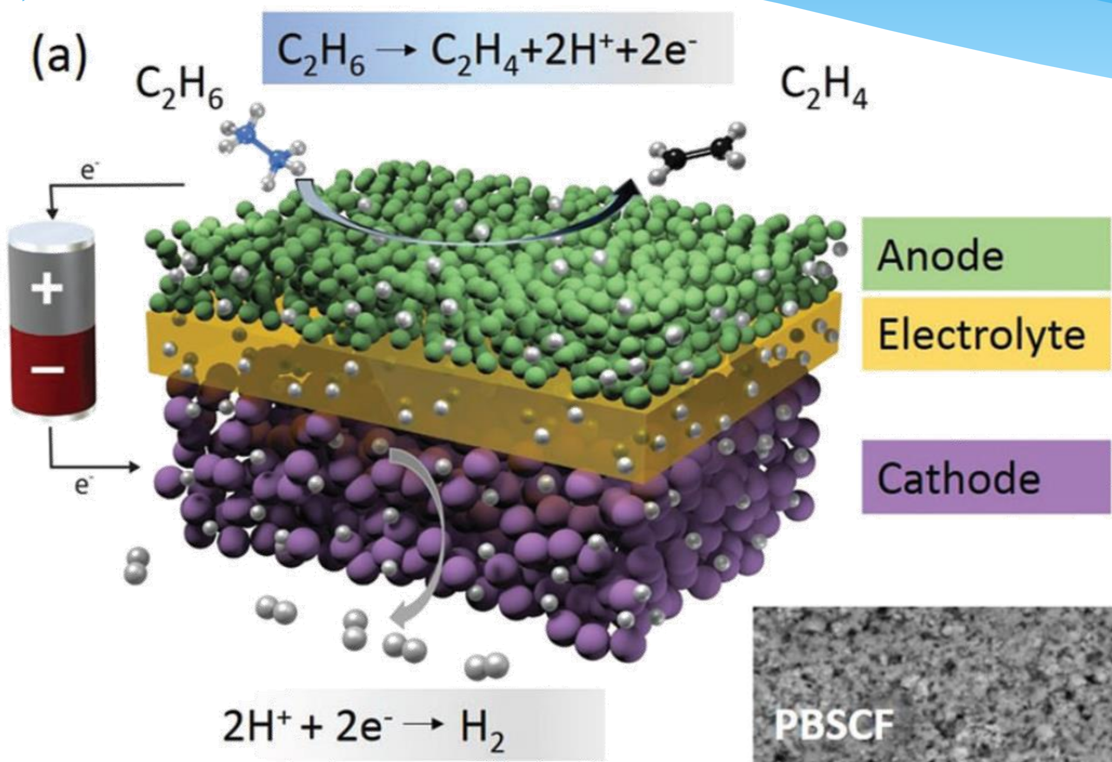
Proton Membrane Reformer (PMR) – EC Compression !!

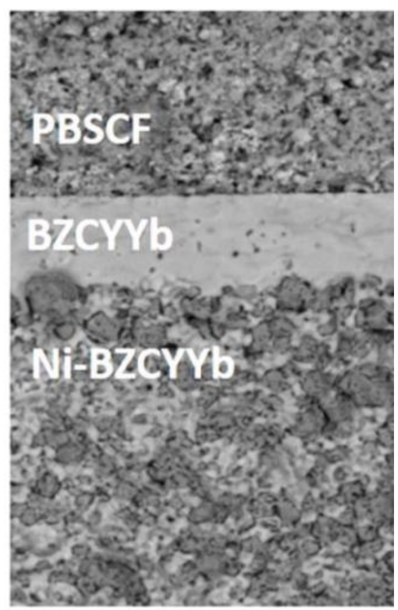
Thermoneutral regime



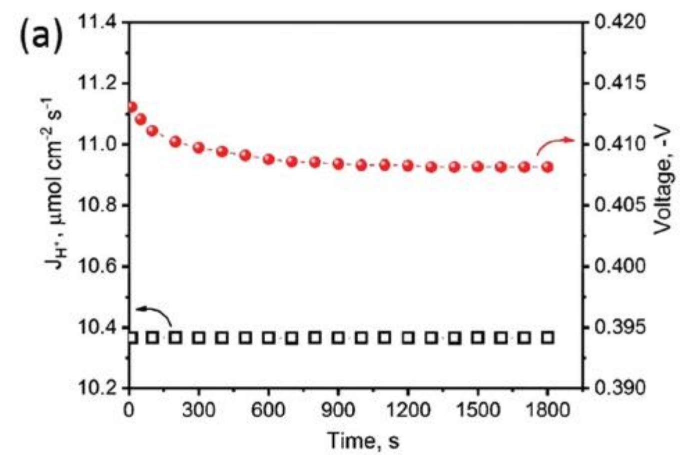
H. Malerød-Fjeld et al., *Nature Energy*, **2,** p. 923–931 (2017)

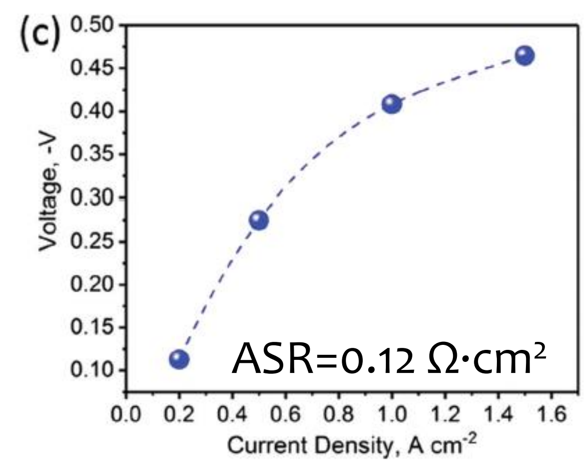
Ethane dehydrogenation at low temperatues





400 °C



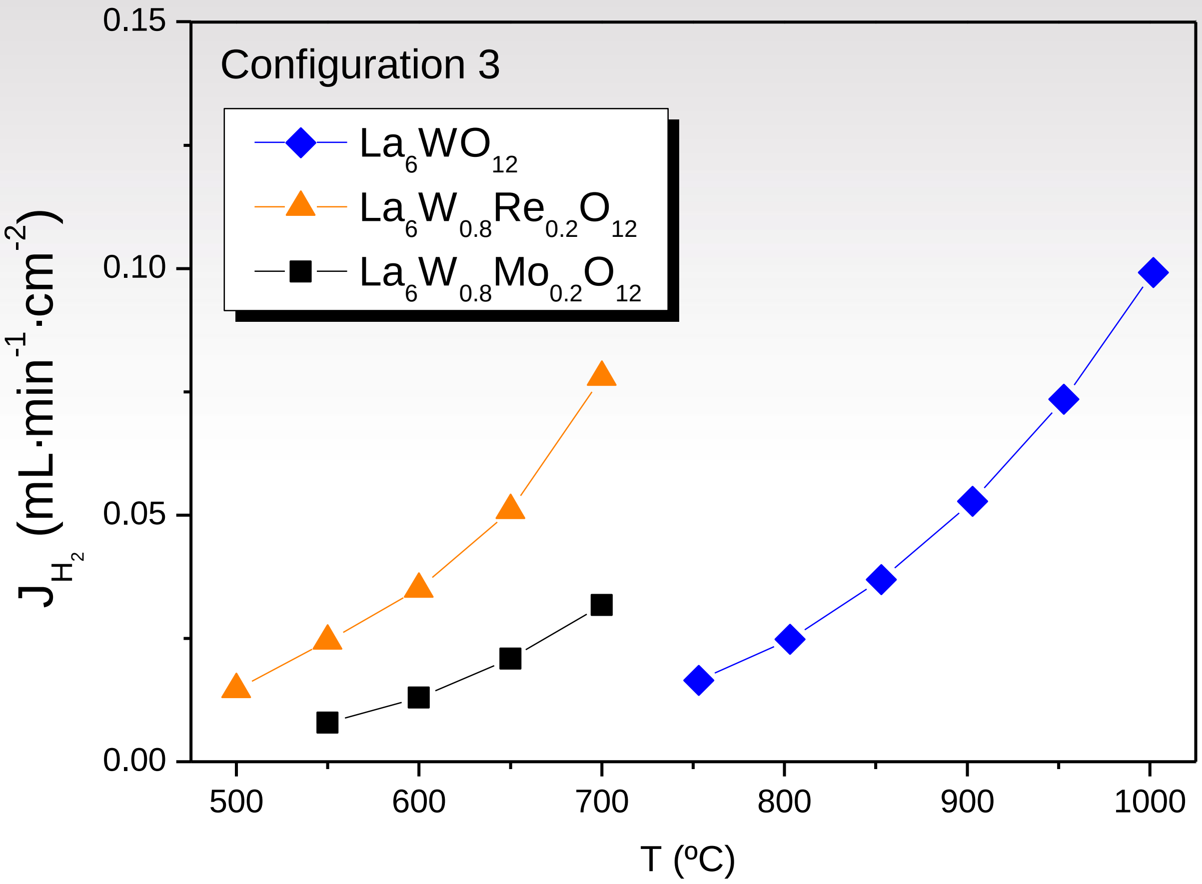


D. Ding et al.. ***EES** (**2018**)*
DOI: 10.1039/c8ee00645h.

Optimized Compositions

Doped $La_{5.5}WO_{12-\delta}$

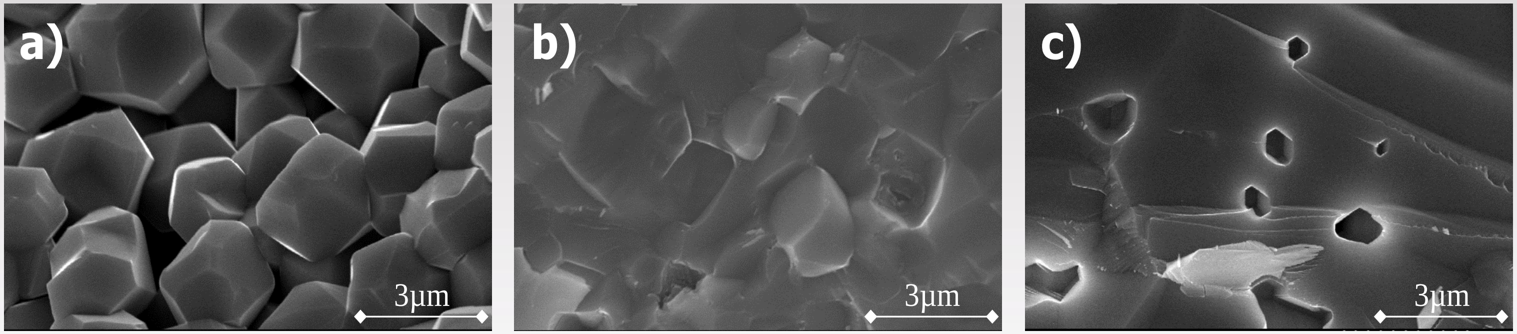
0.9mm-thick membranes



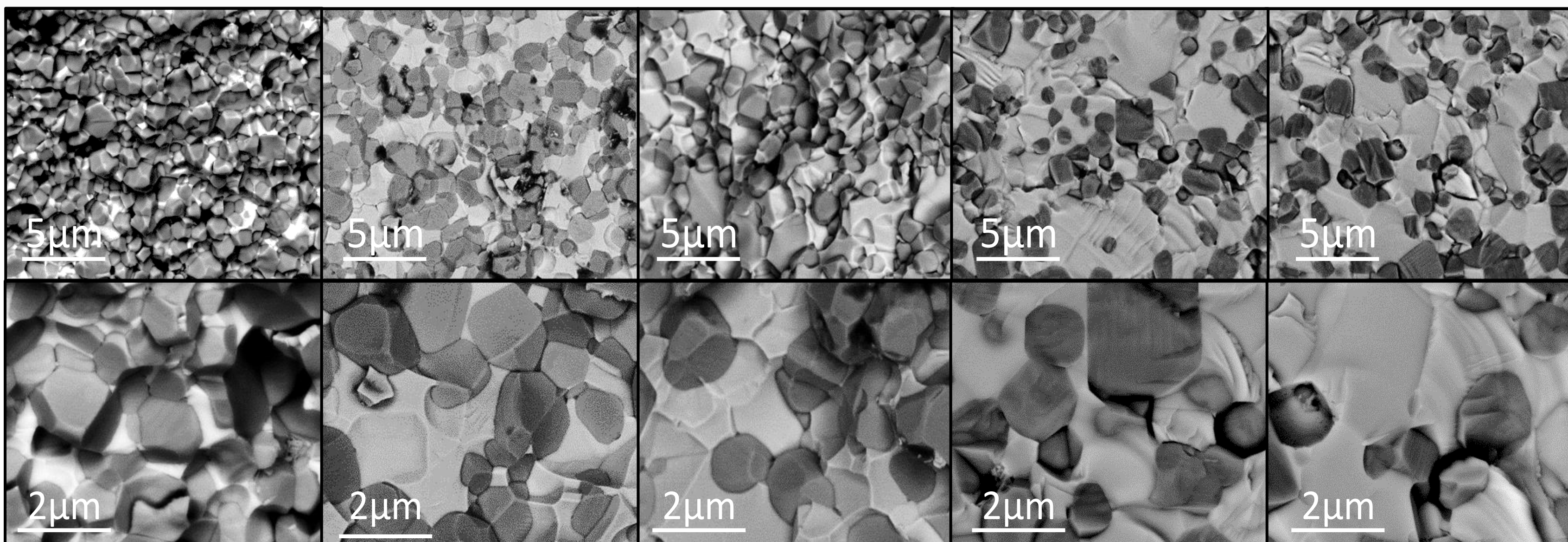
Escolástico, Seeger, Serra et al**. ChemSusChem** 6 (**2013**) 1523
J.M. Serra et al. **Patent Appl. (2010)** WO2012/010386A1

Composite Approach

$La_{0.87}Sr_{0.13}CrO_{3-\delta}$ LWO/LSC $La_{5.5}WO_{11.25-\delta}$

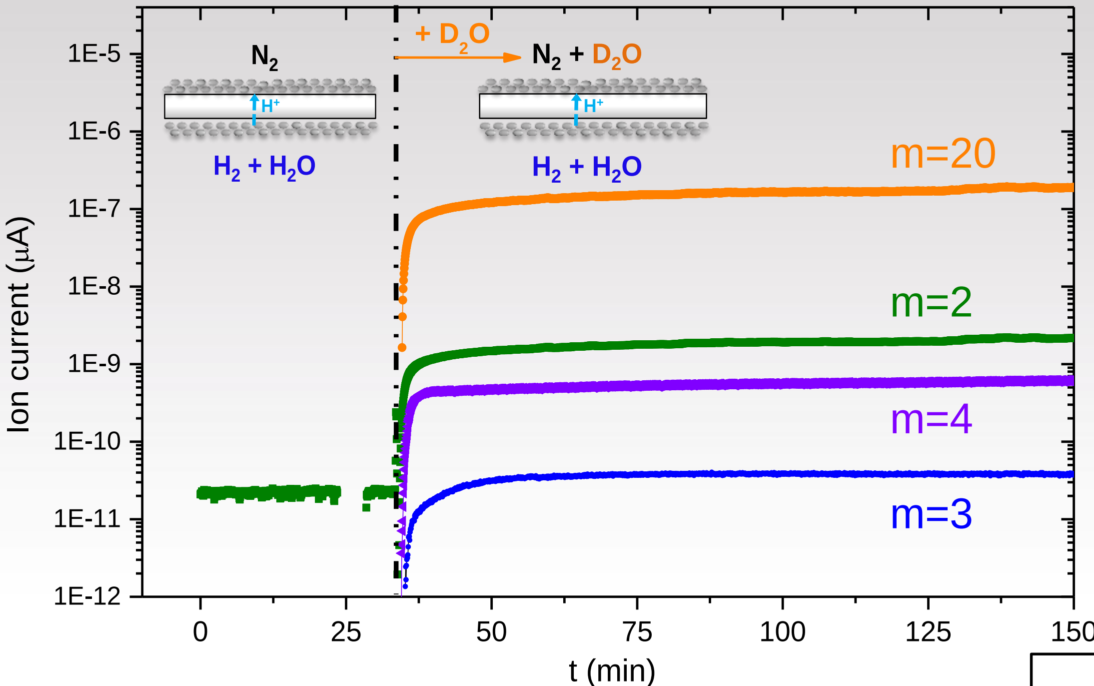


10/90 20/80 30/70 40/60 50/50



J. M. Serra et al, International (PCT) Patent Application No. PCT/EP2014/060708
S. Escolastico, C. Kjølseth, J. M. Serra et al, EES 7 (2014) 3736

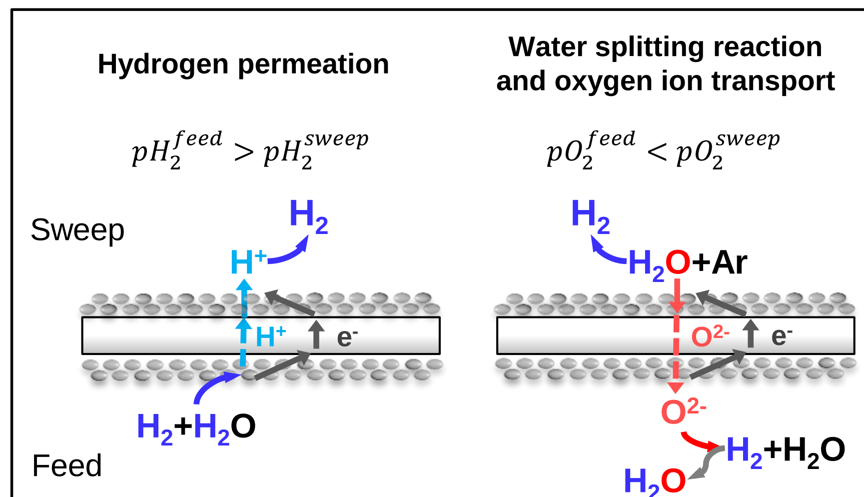
LSC-LW Composite Approach



700ºC

Permeation test

H/D EFFECT



J. M. Serra et al, International (PCT) Patent Application No. PCT/EP2014/060708

S. Escolastico, J.M. Serra et al. EES 7 (2014) 3736

Messages to take home

PROTON Conducting Membranes offer excellent opportunities in chemical production and energy sector: cleaner, safer & more efficient

Functions: **H_2 extraction**/injection | **O_2 Injection**/extraction | **H_2O extraction**

Proton Ceramics are matured for the game!

Hot /Emerging topics (playing with protons)

- Enable the Use of Renewable Electricity in Chemical Industry
- Selective Dehydrogenation / Oxidation (Equilibrium Shift)
- Reversible operation (FC, EC, PMR)

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UiO

DTU

SINTEF

JÜLICH FORSCHUNGSZENTRUM

KERIONICS

H2020 Project GAMER

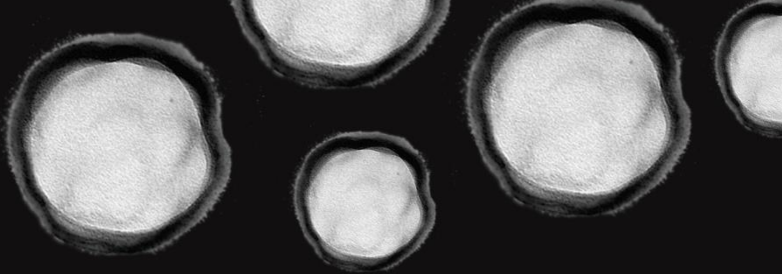
FCH | FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

GAMER

ITQ

Thank You for your Attention

INSTITUTO DE TECNOLOGÍA QUÍMICA



Thank you for your atention.

Jose M. Serra

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