Analysis of acidic and alkaline alcohol electrolysis and development of optimized membrane-electrode assemblies

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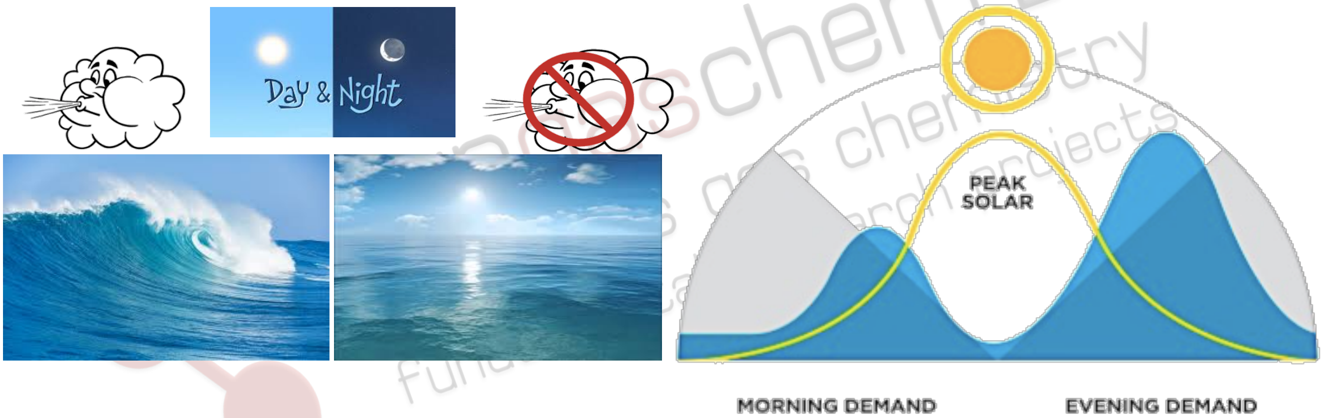
Intermittency of Renewable Energy Sources:

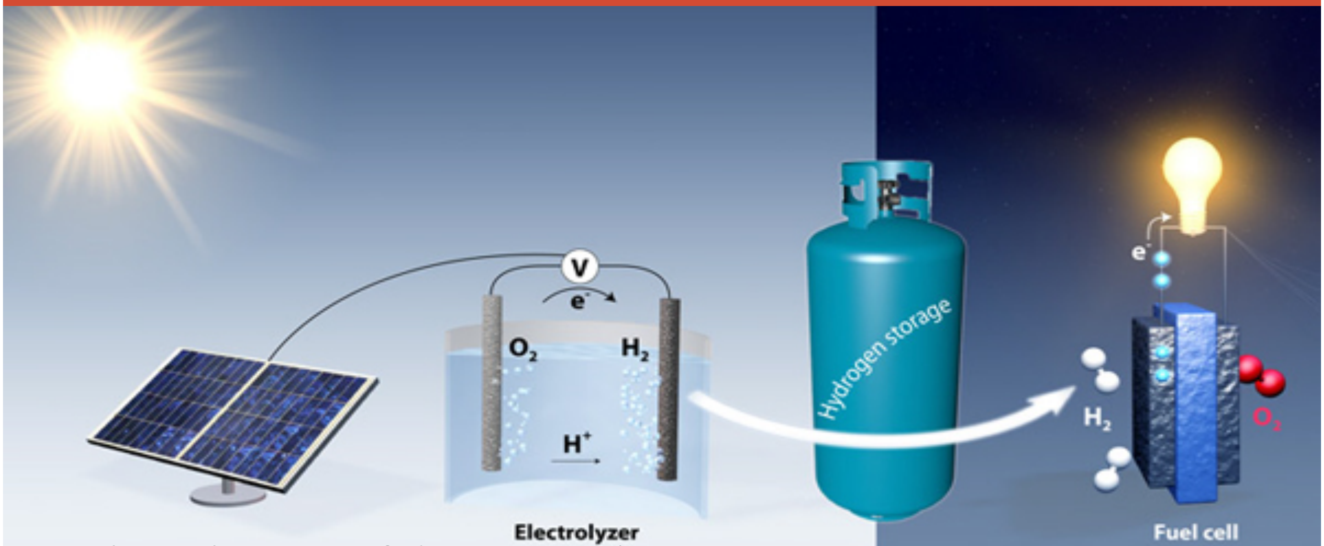
mismatch between availability and demand

wind/solar energy



Storing renewable energy is essential!

Storing energy in chemical bonds

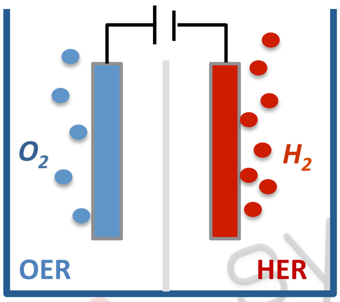


Source: Phys.org, Chris Cesare, Stanford University, November 2014

Syngaschem BV: Storage of energy in H_2, or in synthetic fuels via synthesis gas and Fischer-Tropsch Synthesis

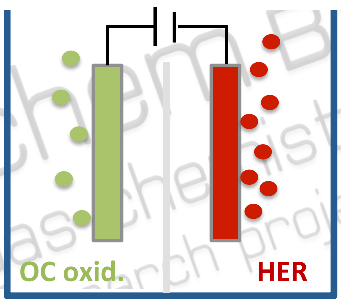
Why alcohol electrolysis?

Conventional H_2O electrolysis



- *High overpotentials due to slow O_2 evolution*
- *Thermodynamic potential: 1.23 V*

Organic solution-assisted H_2O electrolysis or H_2 evolution integrated with organic oxidation



- *Lower thermodynamic potentials (20-200 mV)*

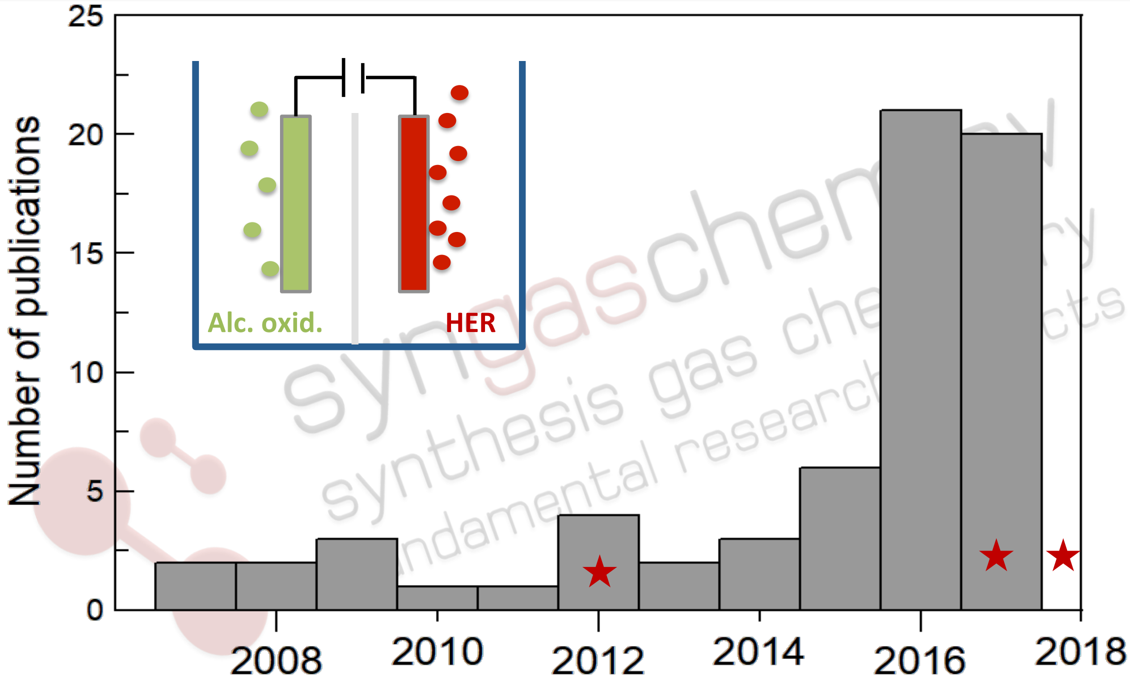
Alcohol electrolysis (or electrochemical reforming of alcohols)

Anodic reaction: OER is replaced by alcohol electrooxidation

1.23 V for OER Vs. **0.016 V for MeOH**, **0.084 V for EtOH**, **0.097 V for n-PrOH**, **0.106 V for i-PrOH**

Simultaneous formation of CO_2 ☹ or added value products ☺ (i.e. oxygenated C_3 chemicals for glycerol electrolysis)

Chemicals-assisted water electrolysis receives attention



★ A.Caravaca, F. Sapountzi,et al. Int J Hydrogen Energy 37 (2012) 9504
F.Sapountzi et al. Int J Hydrogen Energy 42 (2017) 10762
F.Sapountzi et al., Renewable Energy, submitted 2018

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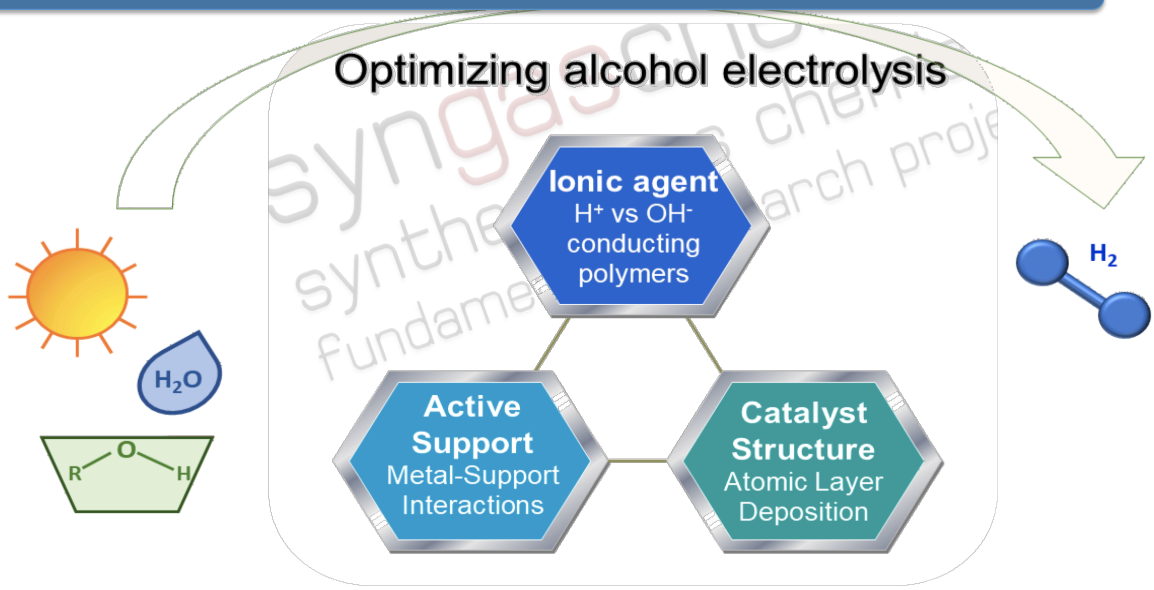
Motivation of this work

Alcohol electrolysis-Current status:

- **30-70% less energy** than H_2O electrolysis
- current densities are low (few mA/cm^2) → **optimization** is required

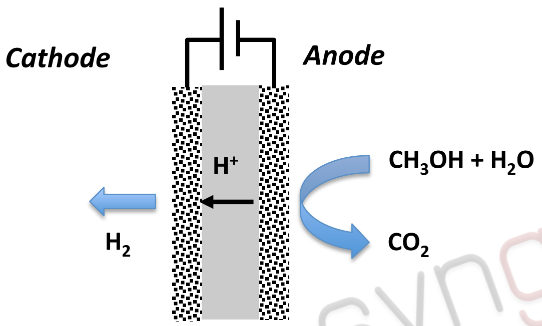
Our question:

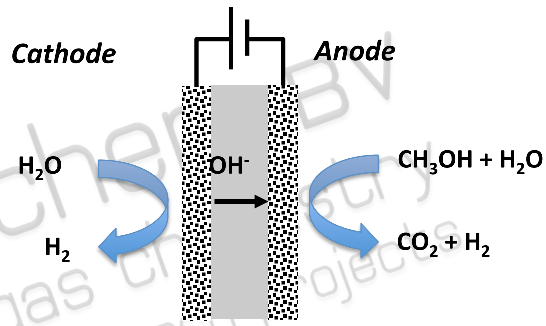
What limits the performance of acidic and alkaline alcohol electrolysers?



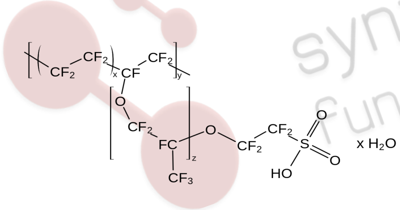
Our methodology: *polymeric membranes*

Acidic membrane **VS** ***Alkaline membrane***

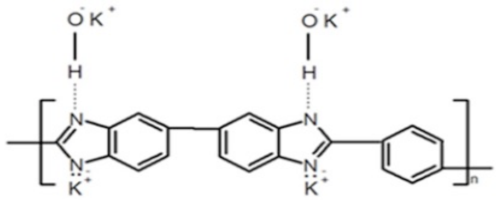




Commercial Nafion 117 with H^+ conductivity

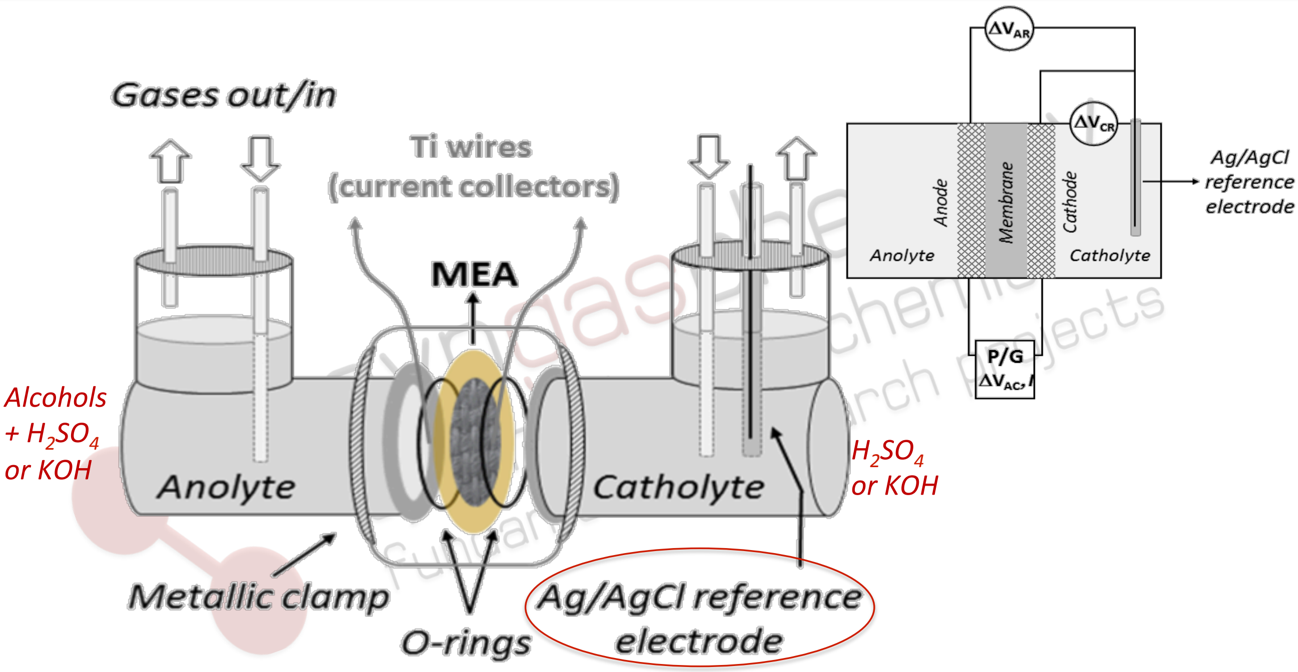


KOH doped-PBI with OH^- conductivity



Collaboration:
H. Penchev et al., Materials Letters 221 (2018) 128-130

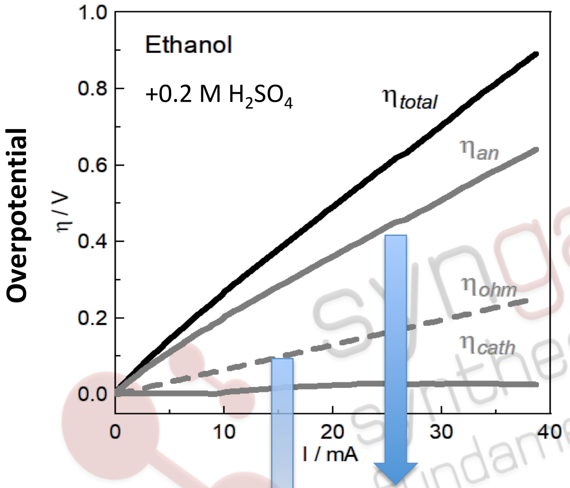
The electrochemical cell



F. Sapountzi et al., Int. J. Hydrogen Energy 42 (2017) 10762-10774

Ethanol electrolysis with commercial Pt/C gas diffusion electrode: Potential losses

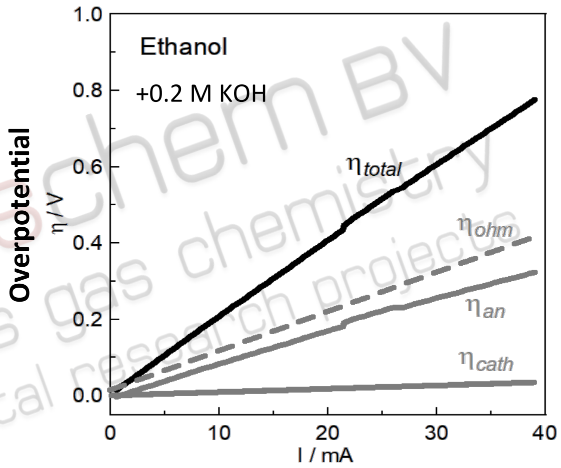
Acidic membrane



~75 % of potential losses due to the anodic reaction (alcohol electrooxidation)

~25 % ohmic losses

Alkaline membrane



anodic losses are lower but... ohmic losses larger !

Alkaline alcohol electrolysis performs better than acidic, but ohmic losses should be suppressed

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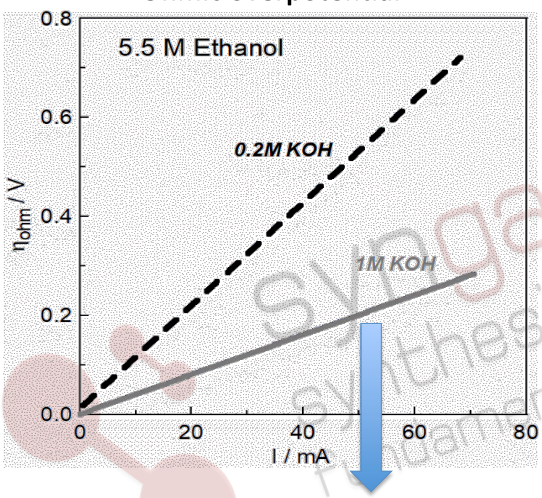
F. Sapountzi et al., Int. J. Hydrogen Energy 42 (2017) 10762-10774

Can we tune ohmic losses in alkaline electrolysers by varying parameters?

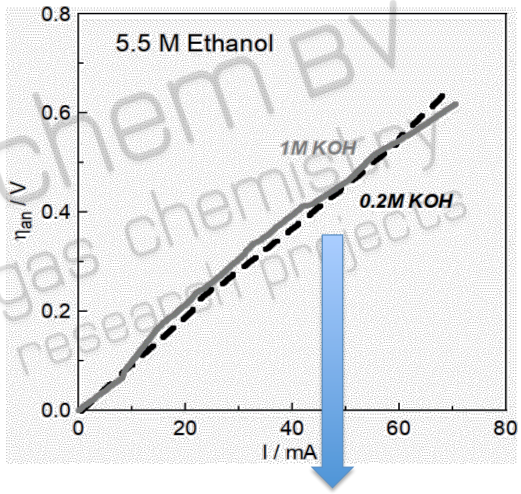
Alkaline membranes

Ohmic overpotential



Increased KOH concentration: ohmic losses decrease by 70%...

Anodic overpotential



...while electrocatalysis remains unaffected (anodic overpotential is stable)

Alkaline alcohol electrolysis is more efficient under appropriate operational conditions (high pH)

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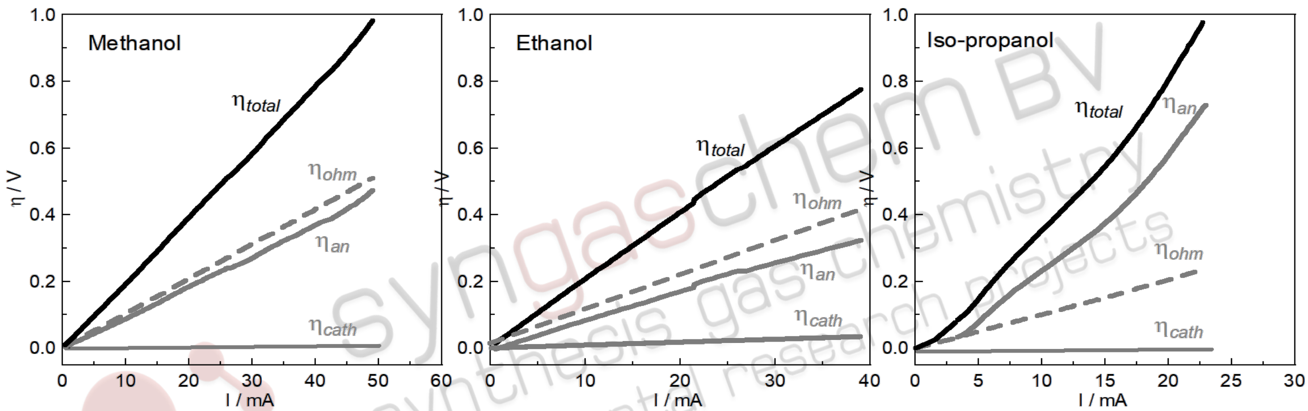
What about other alcohols?

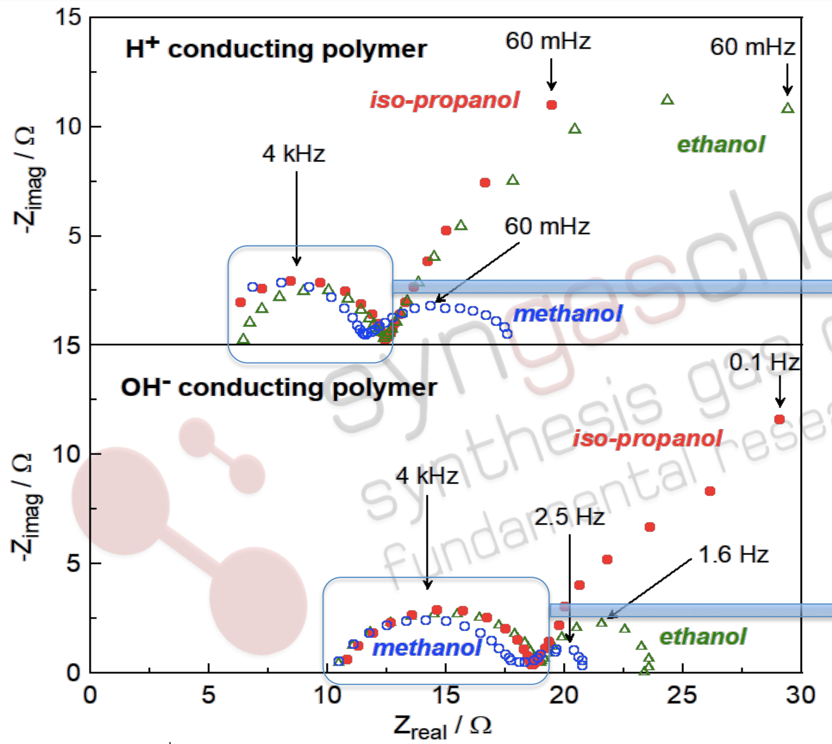
Alkaline membranes



Methanol and ethanol electrolysis show qualitatively the same behavior

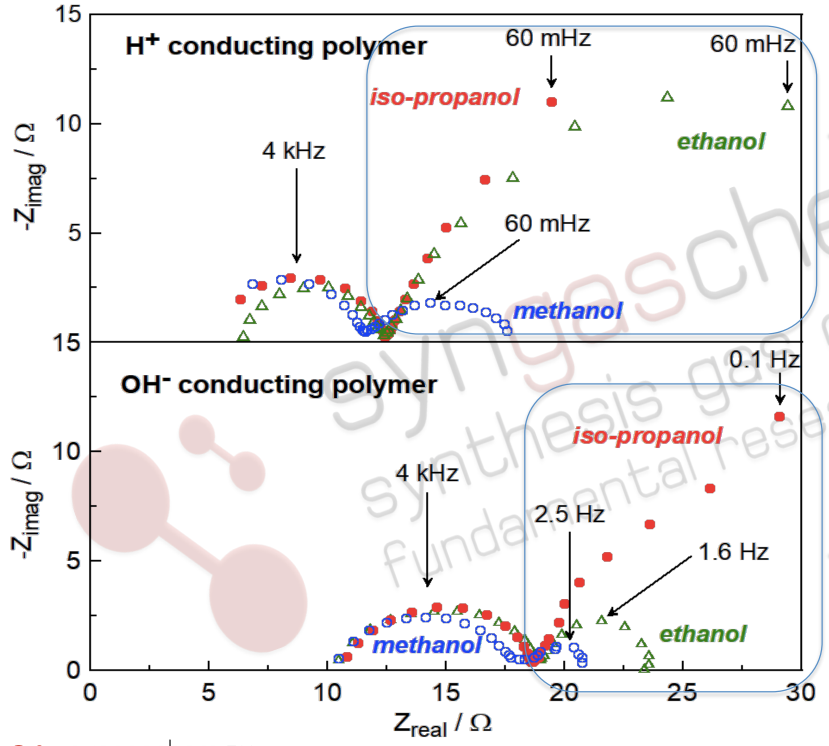
Propanol-assisted water electrolysis shows poor performance under the tested conditions: anodic overpotential is too high
Methanol and ethanol assisted electrolysis work well

Acidic vs Alkaline membranes: Common impedance characteristics



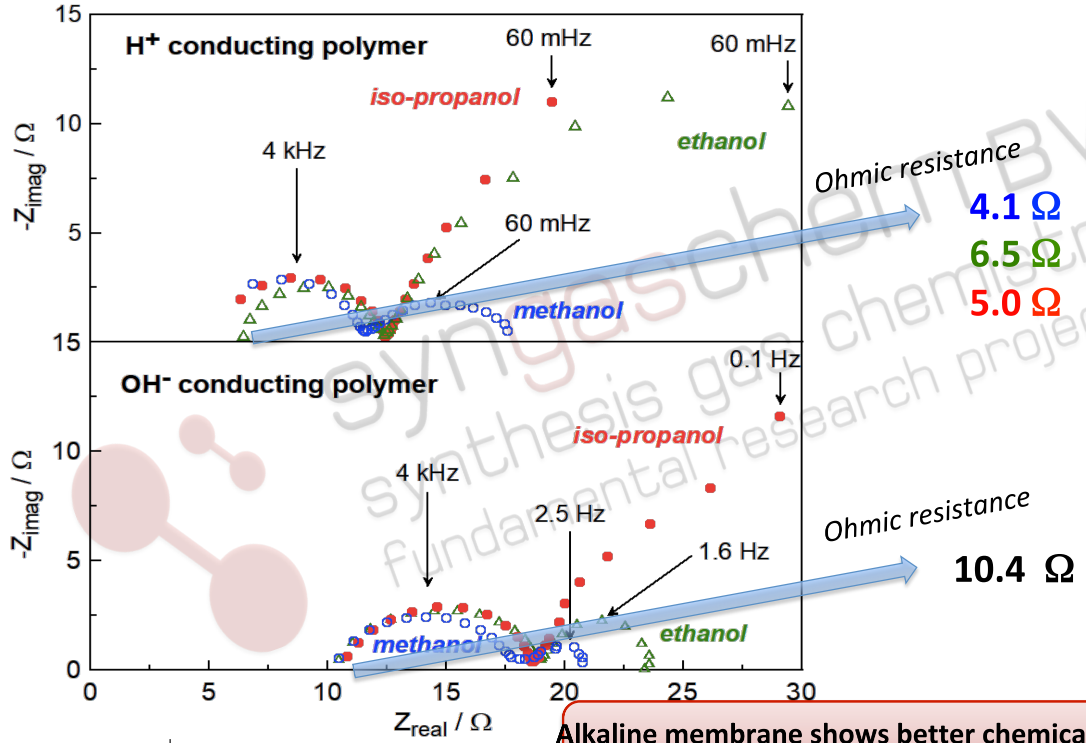
High-frequency arc:
Fast cathodic reaction

Acidic vs Alkaline membranes: Common impedance characteristics



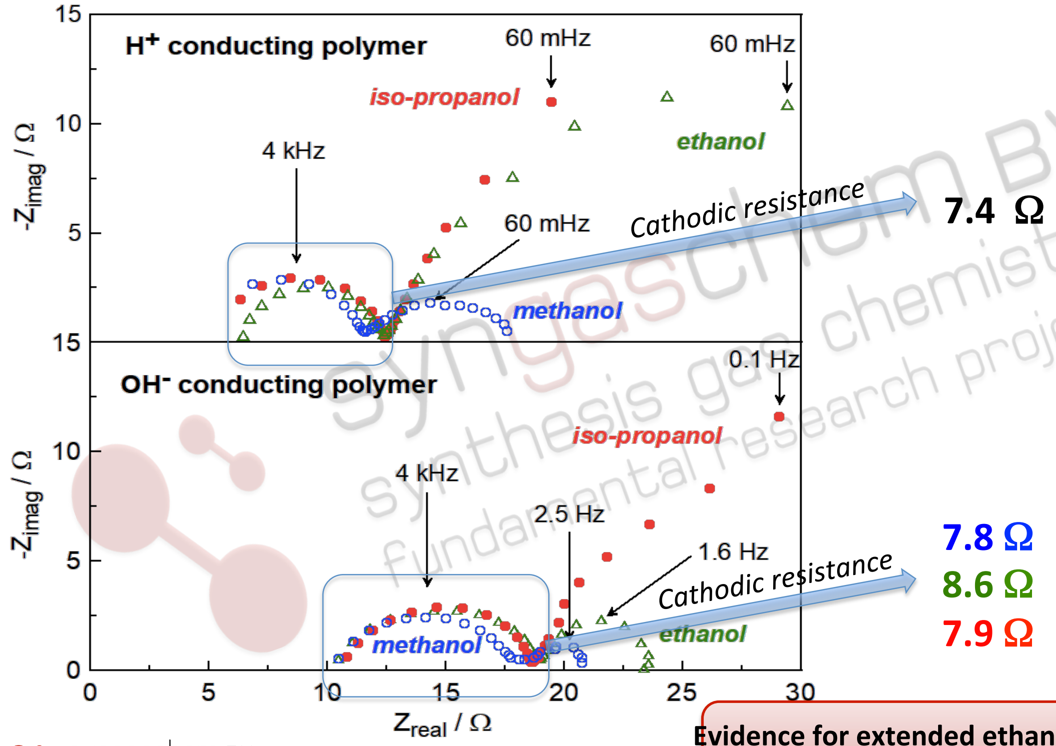
Low-frequency arc is larger for heavier alcohols

What EIS can tell us about the stability of membranes in alcohols?



Alkaline membrane shows better chemical stability under alcohol electrolysis conditions

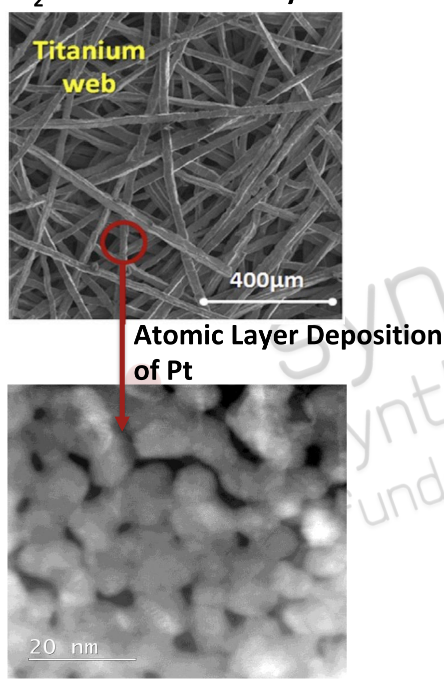
What EIS can tell us about alcohol crossover?



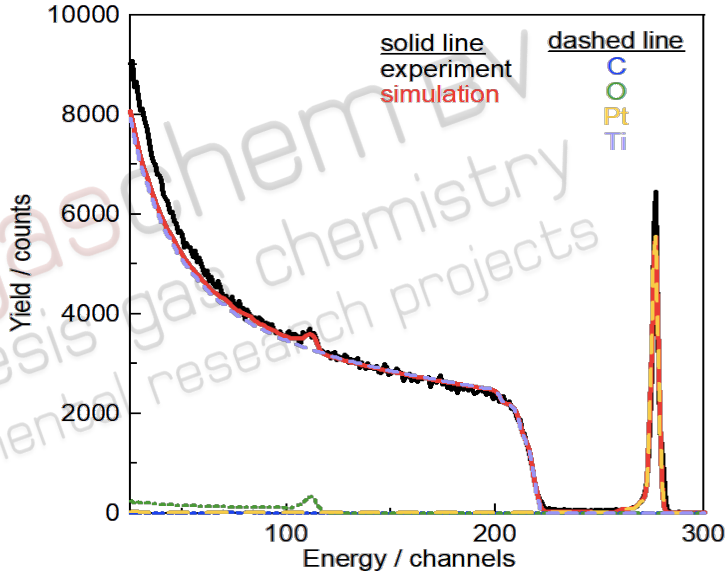
Evidence for extended ethanol crossover through the alkaline membrane

Optimized anode architecture: Pt/TiO_2-Ti

TiO_2-Ti Gas Diffusion Layer

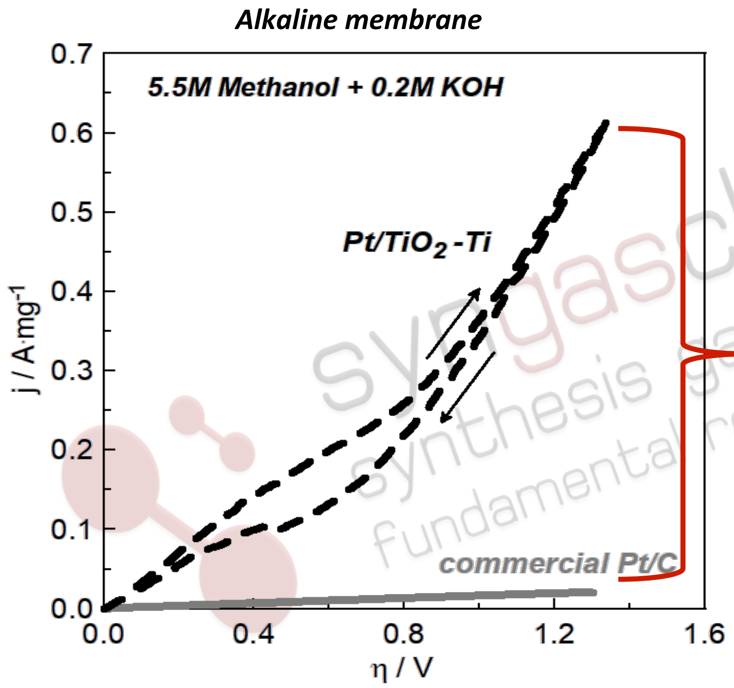


Rutherford backscattering spectrometry



Quantitative analysis: 0.025 mg Pt/cm^2

Methanol electrolysis with optimized anode architecture



30 times larger mass-normalized current

- uniform distribution of Pt, even in the porosity of the GDL, owing to the ALD technique
- open structure of the substrate facilitates mass transport
- metal-support interactions between nanosized Pt particles and the TiO_2-Ti substrate affect electrocatalysis

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Conclusions

- Methanol and ethanol assisted water electrolysis to form hydrogen are promising processes; isopropanol electrolysis is less efficient under these conditions and may need further optimization.
- Alcohol electrolysis for hydrogen production is more efficient under alkaline (high pH) than under acidic conditions.
- We developed optimized membrane-electrode-assemblies by combining ALD of Pt on porous TiO_2-Ti Gas Diffusion Layers : 10-30 times more efficient catalyst utilization per Pt mass.
- In order to be CO_2-neutral, the alcohol has to come from bio-sources or from waste.

Slides available on our website www.syngaschem.com