Workshop -Flow batteries, bringing the technology to the market

Vitoria-Gasteiz

Modified anion exchange membranes and other perspectives

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INTRODUCTION

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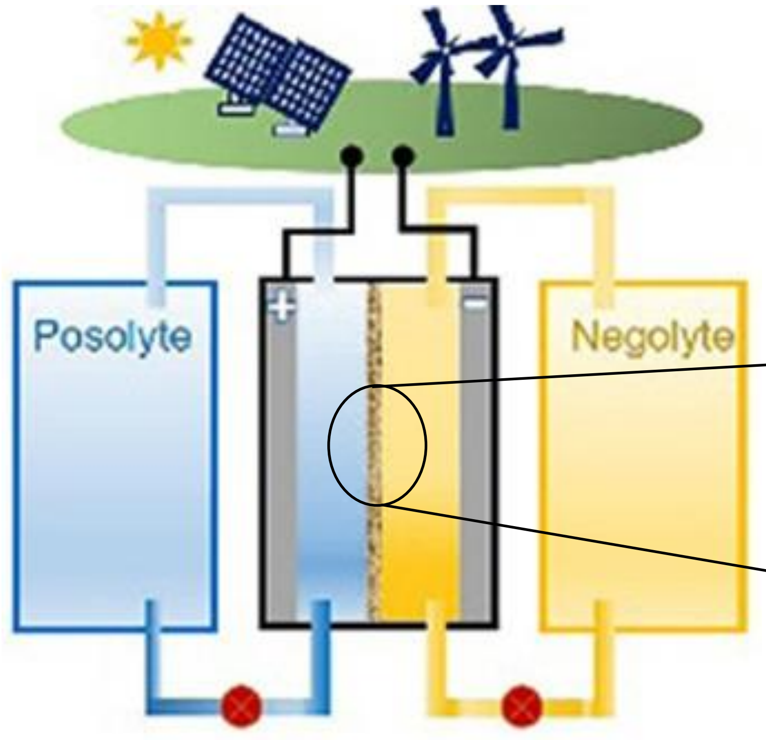
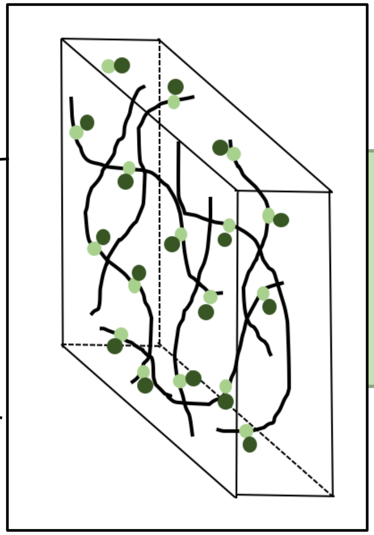
Membrane application: RFB

Chemical stability
Ion conductivity
Mechanical resistance
Selectivity

Permeability of active materials
Cost



V. Singh et. al, *Nano Research. 12(9)* (**2019**) 1988-2001



Ion Exchange Membrane (IEM)

Membrane Modification

IN-SITU POLYMERIZATION

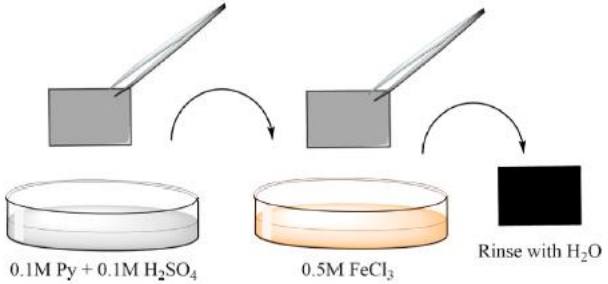
- ✓ Easy to **scale**
- ✓ Cheap
- ✓ Environmentally friendly

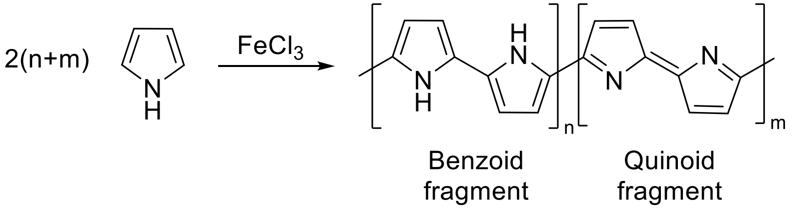
FAA-3-50
FAA-3-PE-30

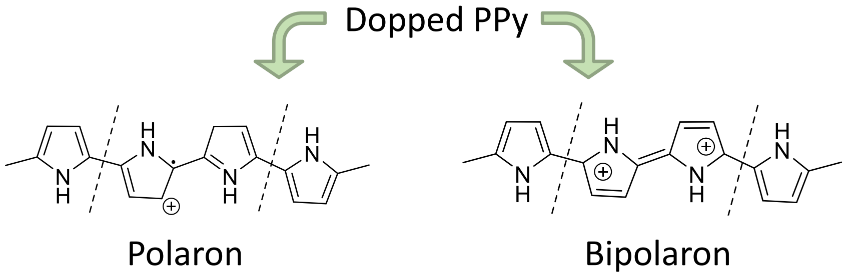
HIGREEW INNOVATIONS & CURRENT RESULTS

HIGREEW Innovations & Current Results

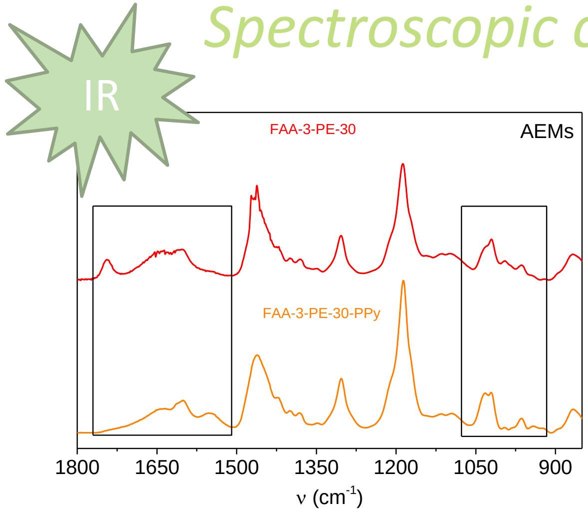
Chemical modification

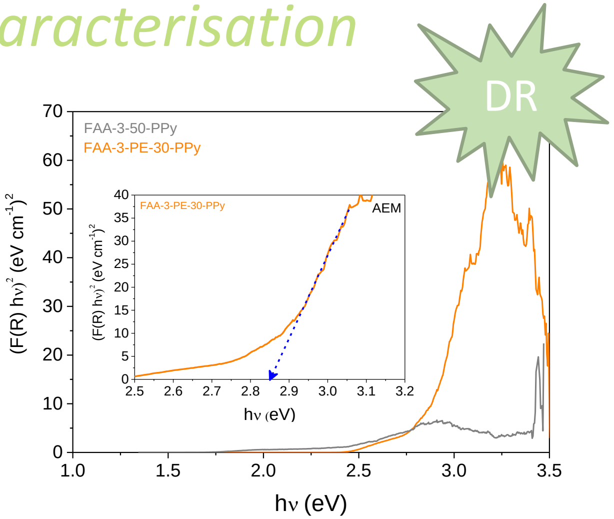




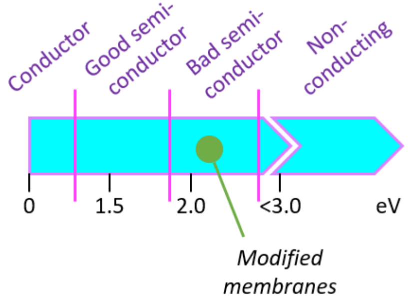


Spectroscopic characterisation





Sample	Estimated oxidation degree (%)	Estimated band gap (eV)
FAA-3-50-PPy	37	>2.0
FAA-3-PE-30-PPy	72	>2.5



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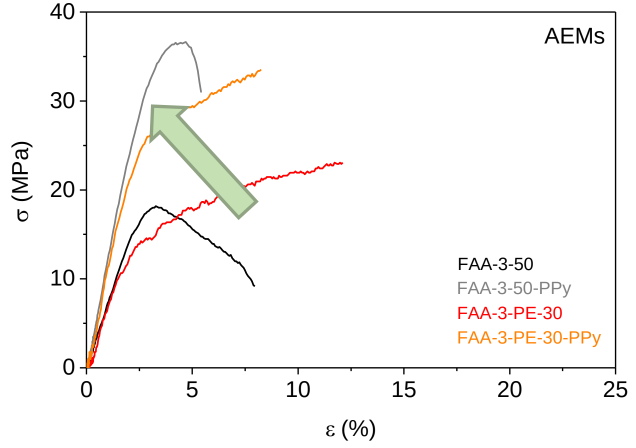
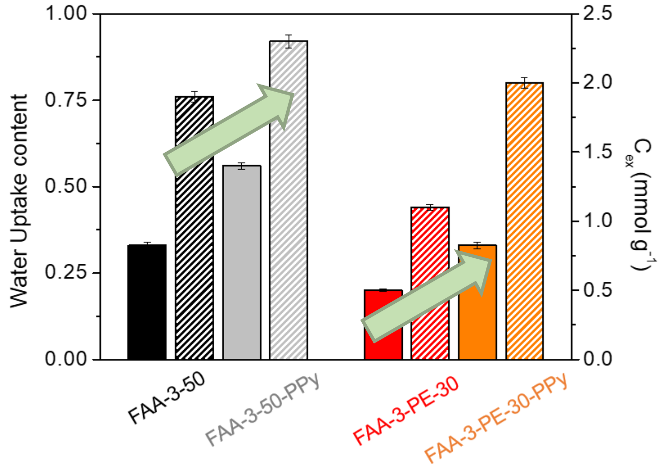
Membrane properties





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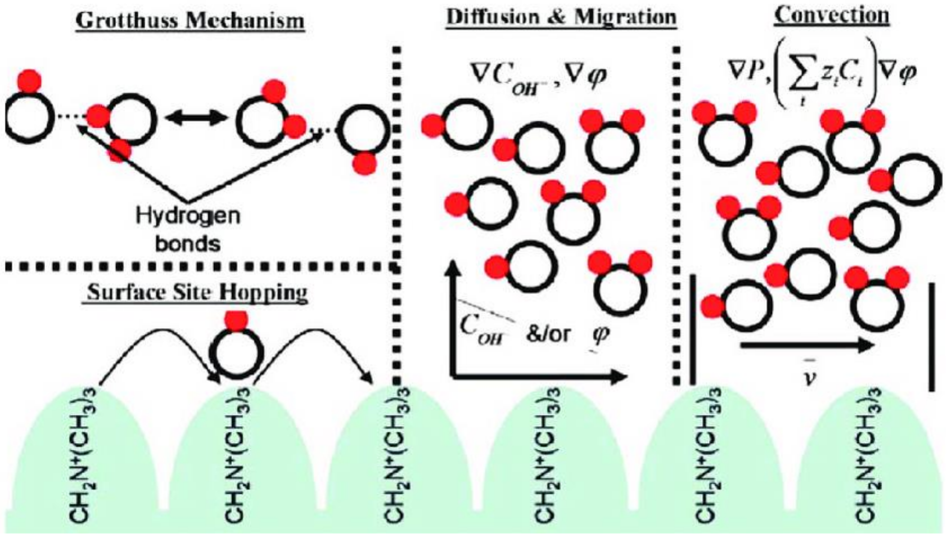
- Mechanical properties were improved after membrane modification.
- Both **WU** (<u>filled columns</u>) and **C_{ex}** (<u>partially filled columns</u>) highly increased in modified-AEMs due to positively charged PPy segments.

Transport phenomena



S. Castañeda-Ramirez et. al, *New Trends in Ion Exchange Studies (2018), ISBN 978-1-78984-248-7*

$$J_i = -D_i \frac{dC_i}{dx} - D_i \frac{F z_i C_i}{RT} \frac{d\varphi}{dx} + v C_i$$

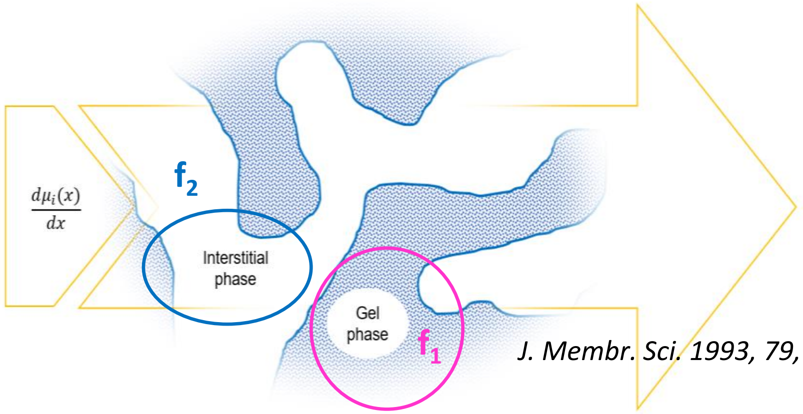
HIGREEW Innovations & Current Results

Membrane microstructure

V. I. Zabolotsky et. al. provided a description of IEMs based on **Nernst-Planck approximation** and by considering **membrane conductivity** as a measurable property, the following expression would describe the membrane as:

$$\kappa_i^* = \left(f_1 \bar{\kappa}_i^{\ \alpha} + f_2 \kappa_i^{\ \alpha}\right)^{1/\alpha}$$

where [−1 < α < +1]

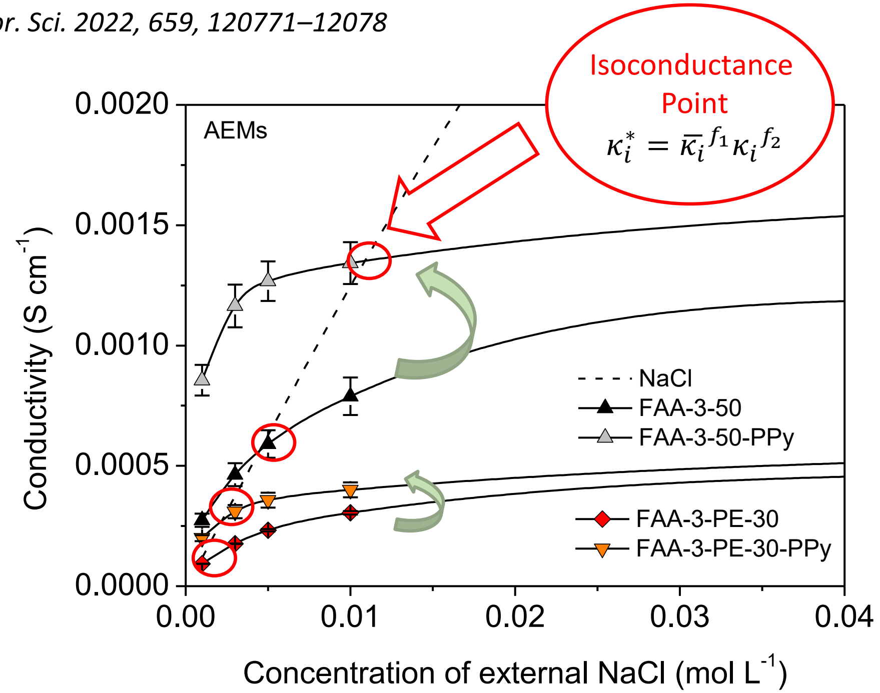


J. Membr. Sci. 1993, 79, 181–198

where $\boldsymbol{\kappa}^*$ is the overall **membrane conductivity** (mS cm^{-1}); $\bar{\kappa}$ and κ are the conductivities of the gel (assumed to be constant) and interstitial phase (same as the external solution in mS cm^{-1}), respectively.

Each phase can be found experimentally when equilibrating the membrane with the electrolyte solution (NaCl, in this work) and then measuring the conductivity of the external solution and the membrane conductivity by means of EIS technique.

J. Membr. Sci. 2022, 659, 120771–12078



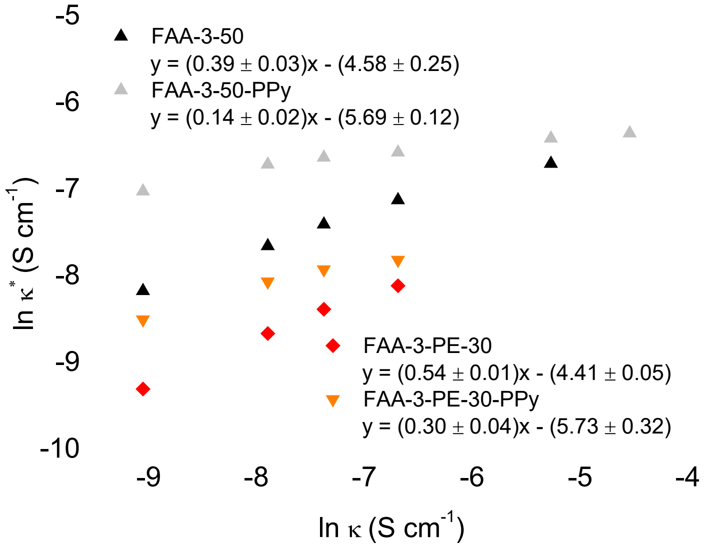
HIGREEW Innovations & Current Results

Membrane microstructure

The **two-phase model** can be **linearized** by the following expression in order to obtain the volume fractions of the corresponding phase **near isoconductance region**:

constant

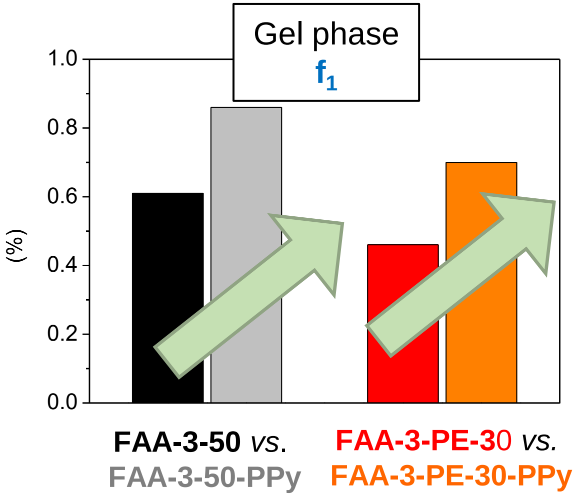
$$\ln \kappa^* = f_1 \ln \bar{\kappa} + f_2 \ln \kappa$$

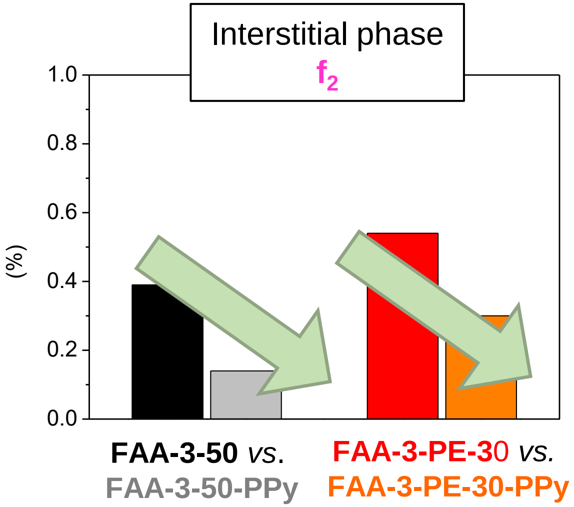


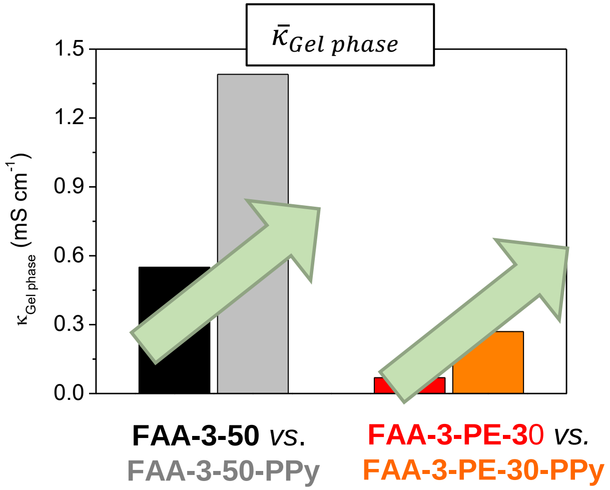
AEM

vs.

AEM-PPy







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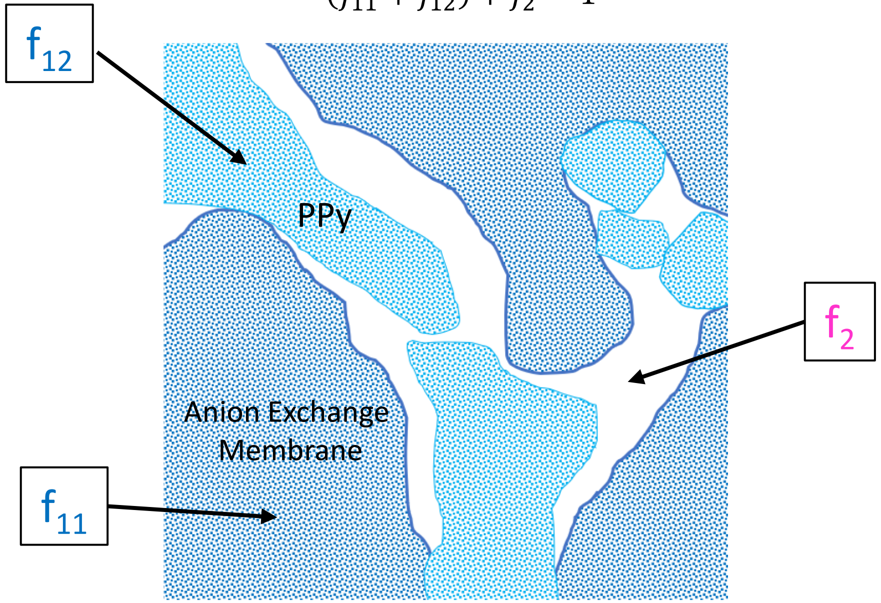
HIGREEW Innovations & Current Results

Membrane microstructure

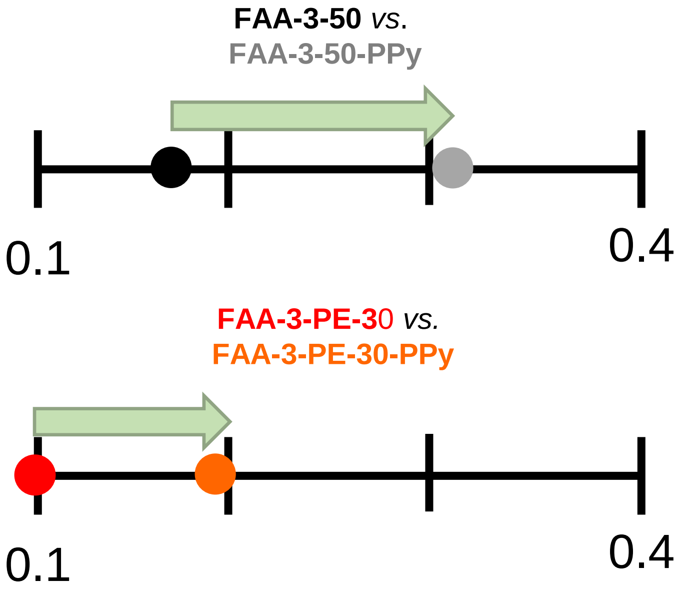
$$(f_{11} + f_{12}) + f_2 = 1$$



Schematic representation of modified-AEMs with reduced interstitial phase (f2) and gel phase 1 (membrane) and gel phase 2 (charged PPy).

- But… How would the new **α** look like?
- What about the **ion transport** of the resulting material?

Structural parameter (α)



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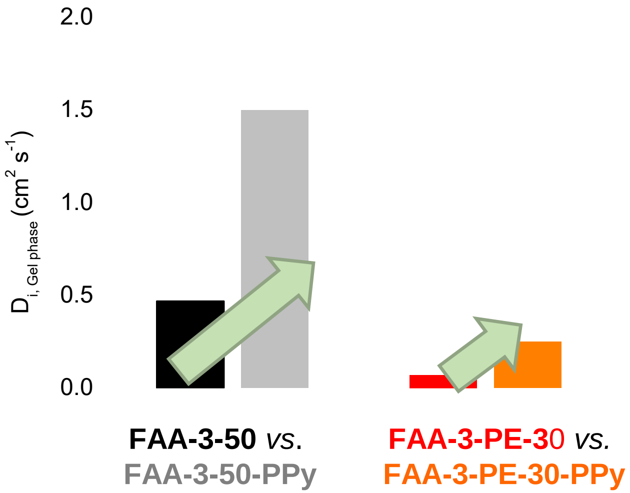
Diffusion coefficient in the gel pase ($\overline{D}_{Cl^-}$)

$$\overline{D}_i = \frac{RT}{F^2}\frac{\kappa_{iso}}{C''_{ex}} f'_1$$

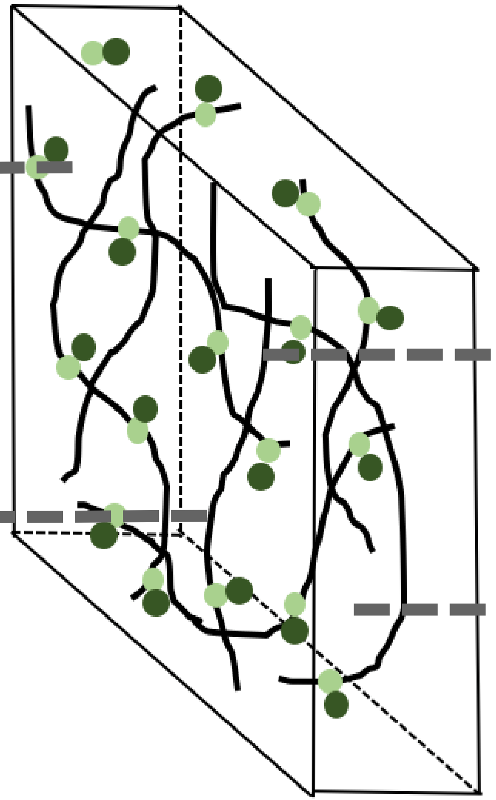


CONCLUSIONS

Conclusions

Modified membranes showed outstanding properties

Ion transport was improved after PPy modification



The two-phase model was useful for AEM microstructural description

RFB expertise from HIGREEW + UAM membrane experience

UAM has acquired knowledge on RFB field from the rest of HIGREEW partners and has offered his knowledge on membrane field. UAM has successfully achieved 2 PhD thesis, several JCR publications and performed many dissemination activities during the project.

Thank you!

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