EVALUATION OF THE MOST PROMINENT PARAMETERS OF ION EXCHANGE MEMBRANES.

MEMBRANE MODIFICATION FOR ENERGY STORAGE APPLICATION.

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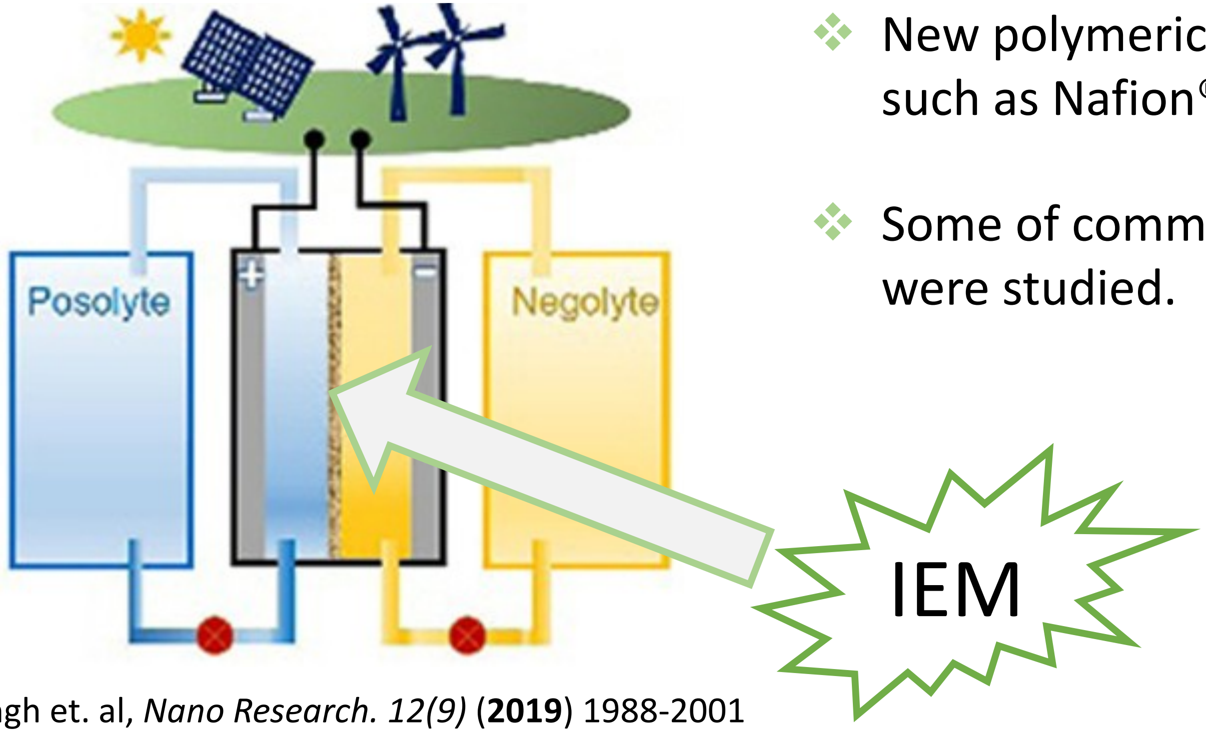
INTRODUCTION & PURPOSE

- 10 Organisations from 5 different countries work together to design, develop and validate an advanced redox flow battery, based on new water-soluble low-cost organic electrolyte compatible with optimized low resistance membrane and fast electrodes kinetics for a high energy density and long-life service.



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

- New polymeric materials to replace highly cost membranes such as Nafion® membranes.

- Some of commercial membranes (both anionic and cationic) were studied.

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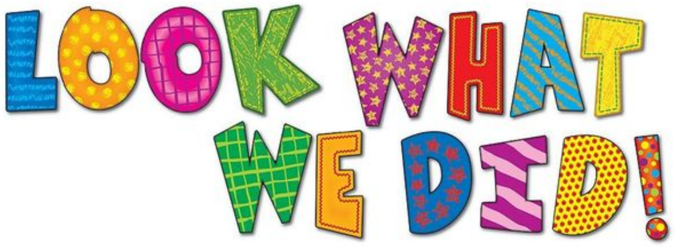

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METHODOLOGY & RESEARCH TASK

A. Physicochemical properties of Ion-Exchange Membranes (IEM). Commercial membranes for the analysis.

B. *Crossover* determination - Modification of commercial membranes

C. Analysis of the morphology and chemical proeperties before and after the membrane modification

D. Ion Transport phenomena in (Modified)-Ion Exchange Membranes

E. Spectroscopic characterization of (Modified)-Ion Exchange Membranes

F. Mechanical properties before and after the membrane modification

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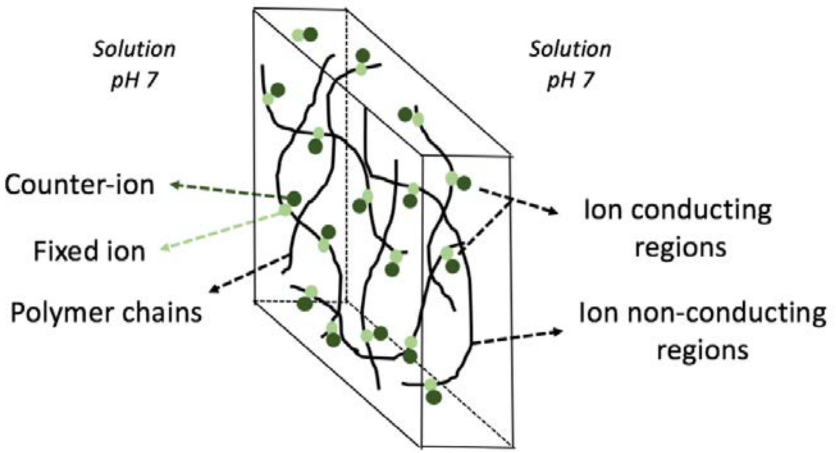
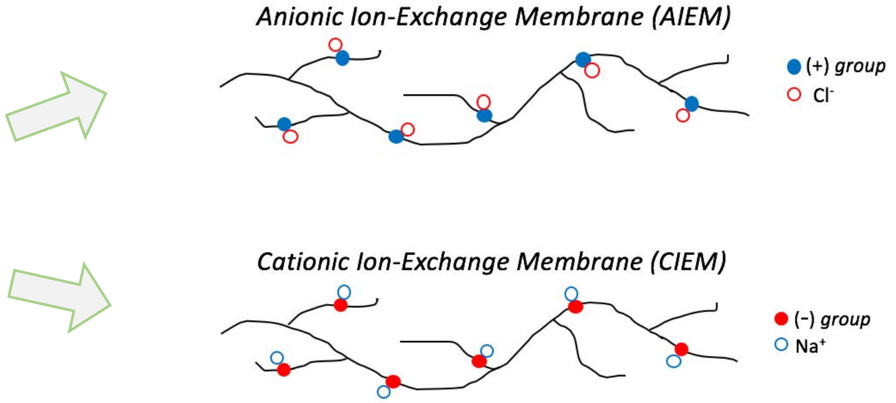
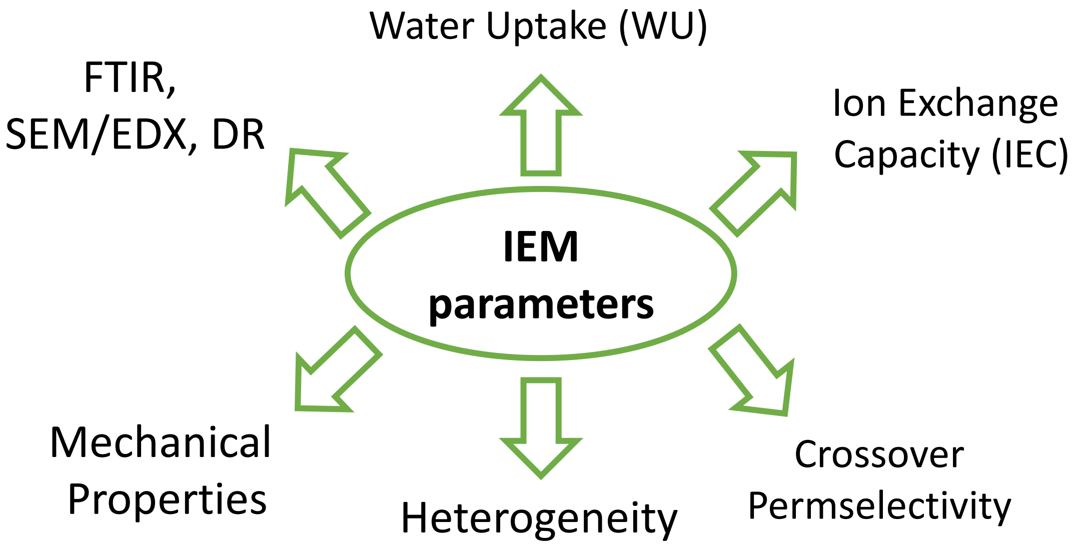
A. Physical-chemical properties of IEMs





Membranes	Provider	Type	Type (Counter-ion)
FAA-3-PE-30	Fumatech BWT	AIEM	Cl^-
FAA-3-50	Fumatech BWT	AIEM	Cl^-
E-630(K)	Fumatech BWT	CIEM	Na^+
FS-950	Fumatech BWT	CIEM	Na^+



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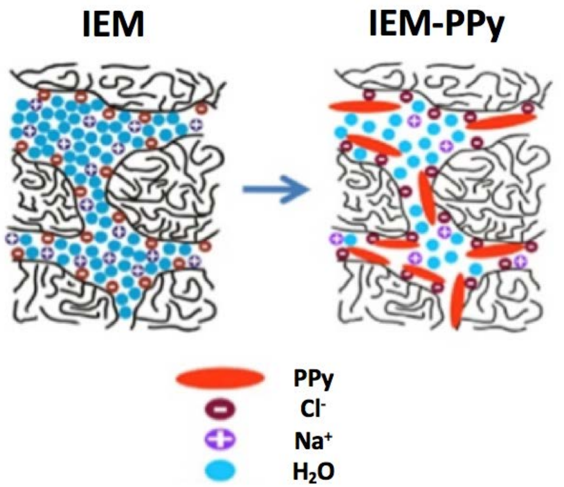
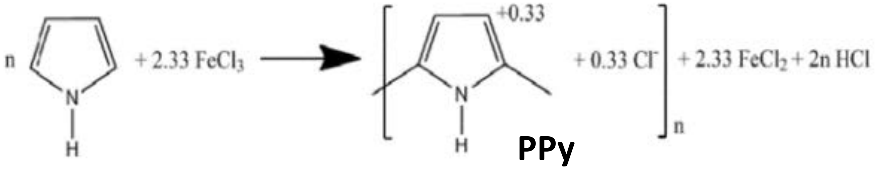
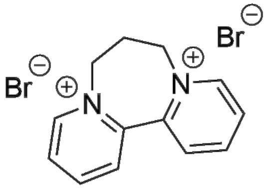
B. *Crossover* phenomena – Modification of IEMs

- Modifications on IEMs are essential to mitigate the *crossover* phenomena.
- One strategy of modification was performed on IEMs:

Chemical in situ polymerization







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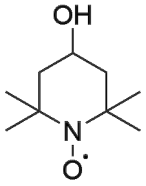

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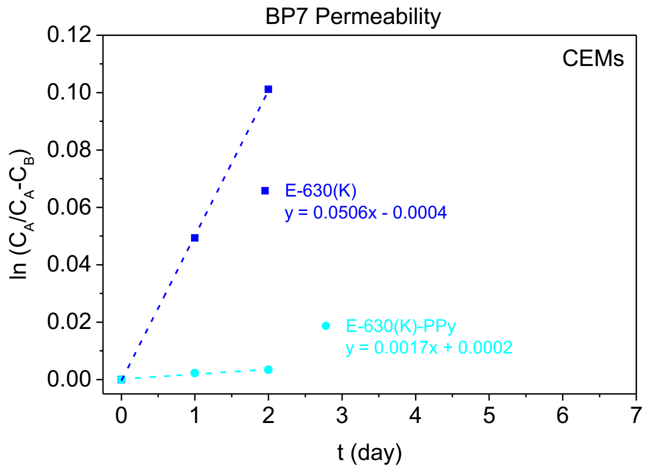

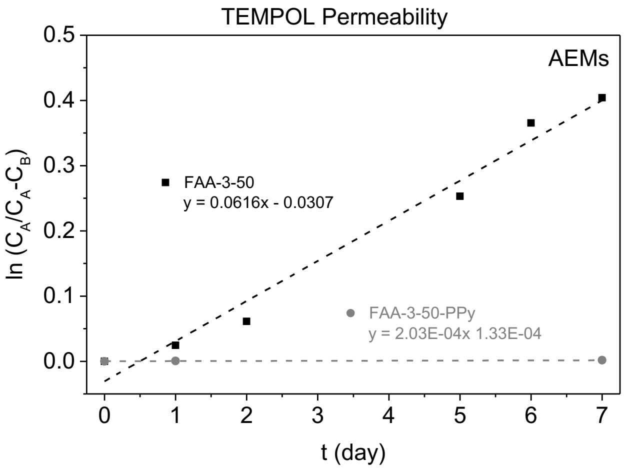

In situ polymerization significantly reduces the *Crossover* phenomena

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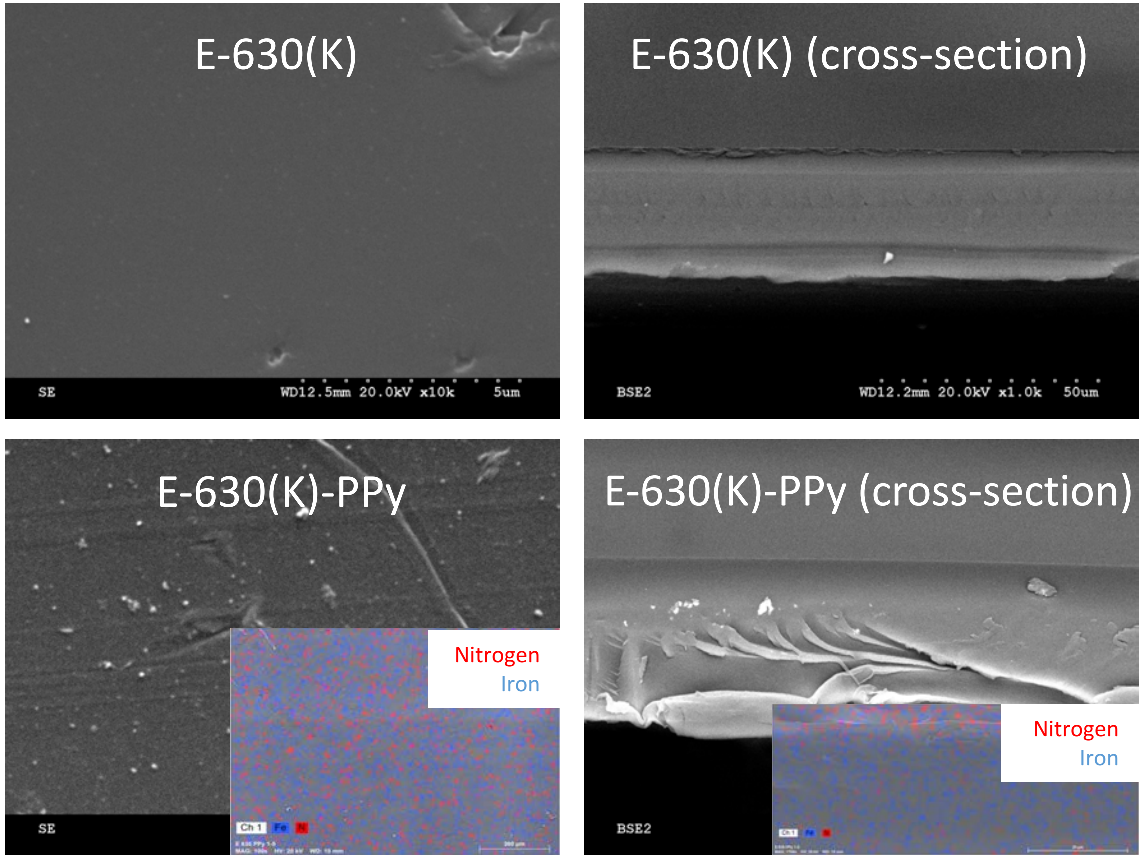
C. Morphological Properties of modified IEMs

- SEM and SEM/EDX mapping images show the PPy attached to the membrane surface on both types (AEM and CEMs).



EDX Analysis for the modified membranes.

Membranes	Type	Fe content (%)	N content (%)
FAA-3-50-PPy	AEM	0.16%	1.91%
FAA-3-PE-30-PPy	AEM	1.27%	5.08%
FS-950-PPy	CEM	5.30%	10.34%
E-630(K)-PPy	CEM	3.46%	2.24%

PPy was attached throughout the membrane materials.

CEMs retained higher amounts of Fe than AEMs.

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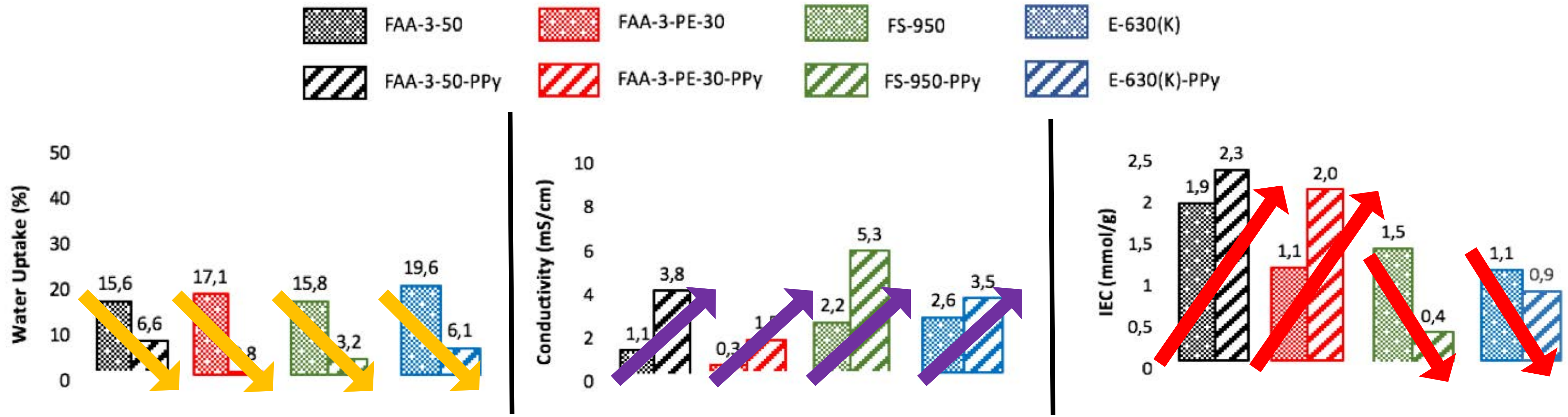
C. Chemical Properties of modified IEMs



PPy modification significantly reduces the water absorption of the final material.

PPy modification increased the ionic conductivity of all materials due to the PPy oxidized species.

Different behaviour in terms of IEC when considering AEM or CEMs.

$$WU\ (\%) = \frac{w_{wet} - w_{dry}}{w_{dry}} \cdot 100$$

$$\sigma_i = \frac{l}{R \cdot A}\ \left(\frac{mS}{cm}\right)$$

$$IEC = \frac{n_{displaced\ ions}}{w_{dry}}\ \left(\frac{mmol}{g}\right)$$

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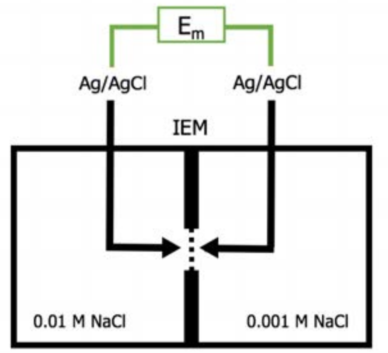
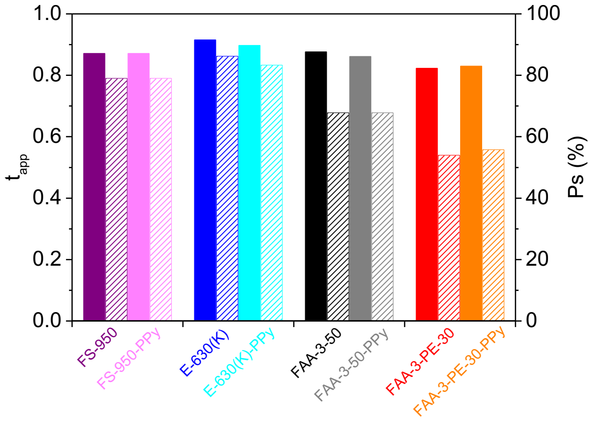
D. Ion Transport phenomena through IEMs

- Transfer of ions through IEMs are essential to complete the electrical circuit. **Ion Transport phenomena**
- Coulombic efficiency and energy density may differ depending on how the processes are taking place when using IEMs or modified-IEMs.



Schematic experimental set of the two-compartment electrochemical cell used to obtain the apparent transport number and therefore, the permselectivity.



$$E_m = \left(2t^m_{app,i} - 1\right)\frac{RT}{nF}\ln\frac{a_1}{a_2}$$

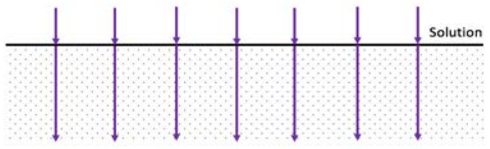
$$Ps = \frac{t^m_{app,i}}{1 - t^s_i}$$

Modified Sand's eq.*

$$\tau = \varepsilon^2 \frac{\pi D_s}{4}\left(\frac{z_i v_i F}{\left(t^m_{app,i} - t^s_i\right)}\right)^2 \left(\frac{C_0}{i}\right)^2$$

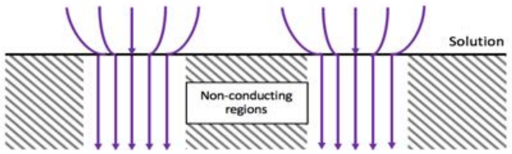
"τ vs. $\left(\frac{C_0}{i}\right)^2$"

$\varepsilon \rightarrow 1$

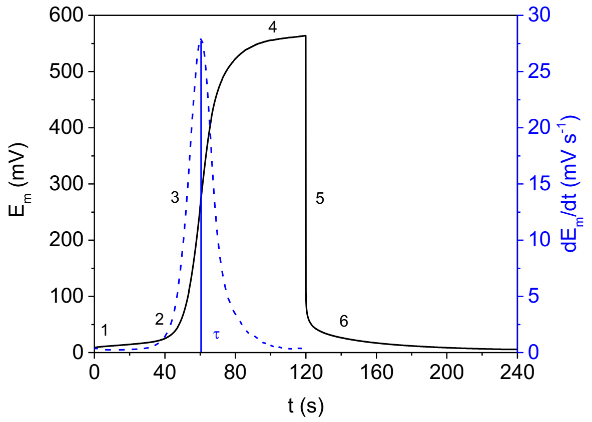


Homogeneous IEM

$\varepsilon \rightarrow 0$



Heterogeneous IEM



Chronopotentiometry

*Modified by J. H. Choi et. al, *J. Colloid Interface Sci.* 241 (**2001**) 120-126

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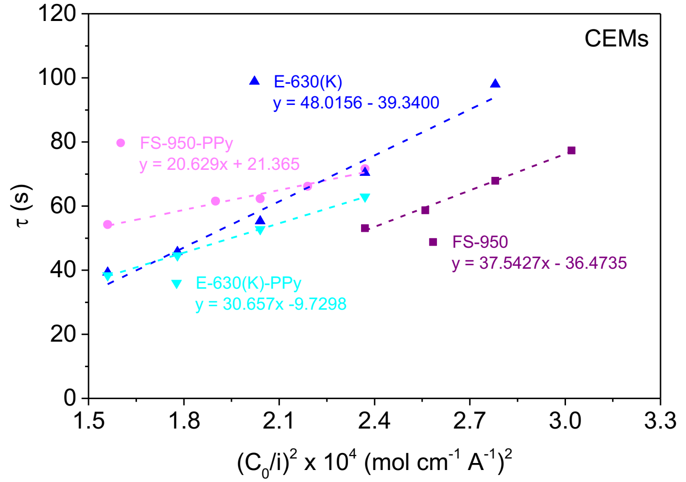
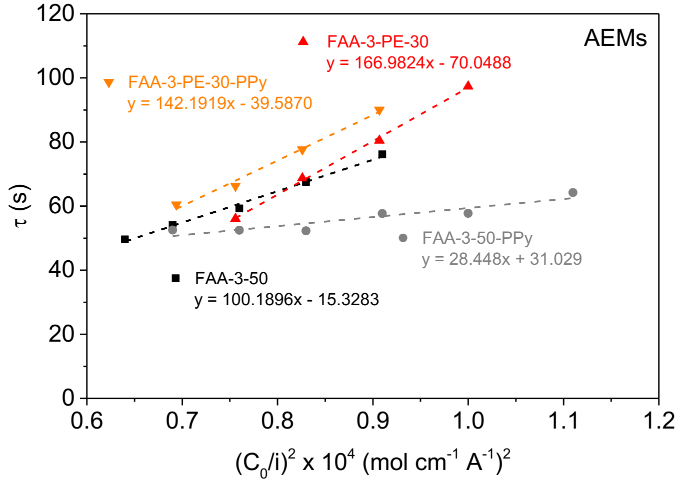
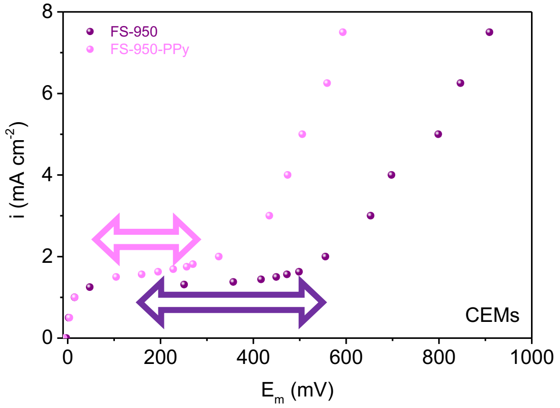
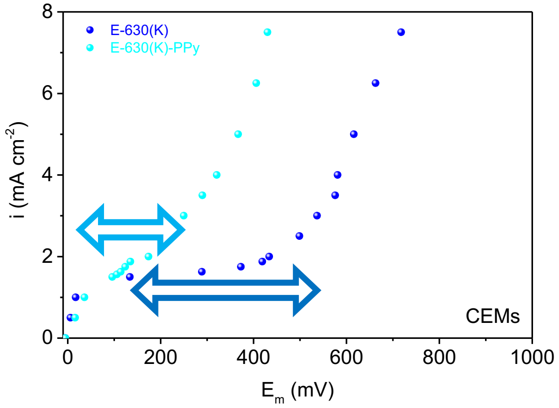
D. Ion Transport phenomena through IEMs

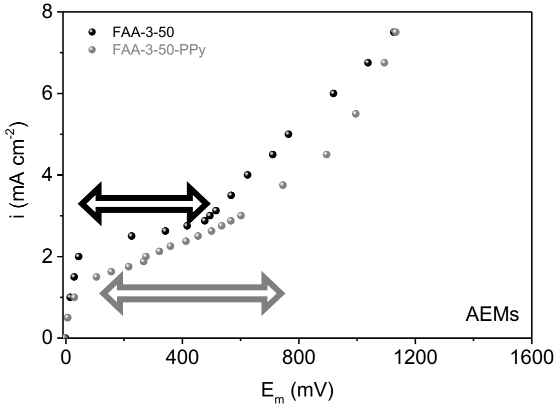


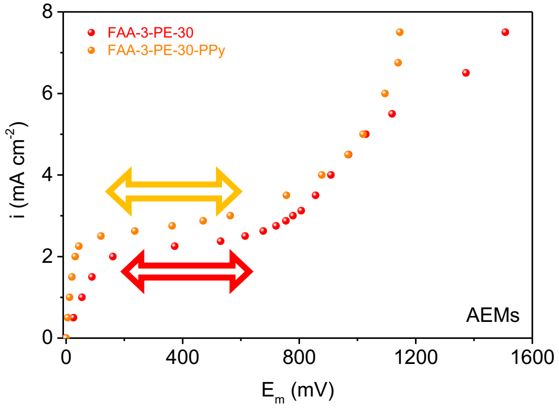


Samples	slope x 10^4 s·(A·cm)² mol⁻²	ε
FS-950	37.54	0.77
FS-950-PPy	20.63	0.57
E-630(K)	48.02	0.95
E-630(K)-PPy	30.66	0.73
FAA-3-50	100.19	0.67
FAA-3-50-PPy	28,45	0.34
FAA-3-PE-30	166.98	0.69
FAA-3-PE-30-PPy	142.19	0.66









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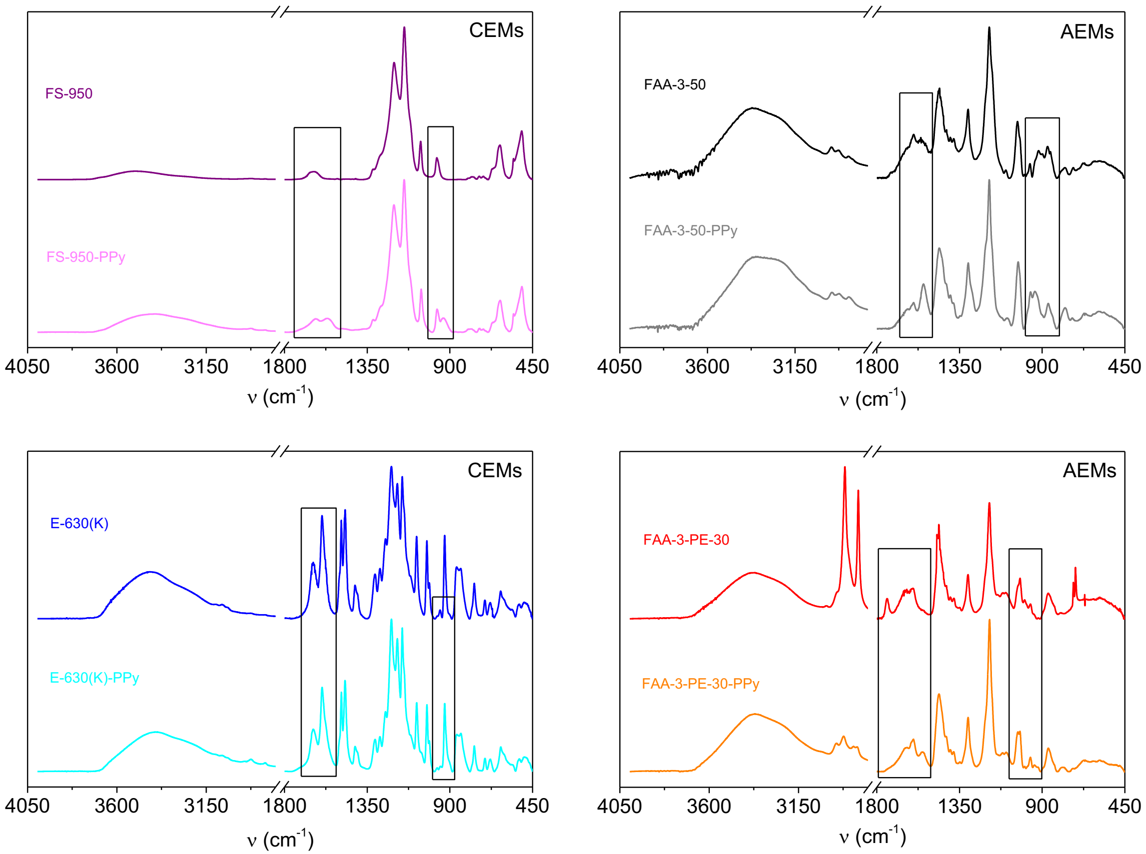
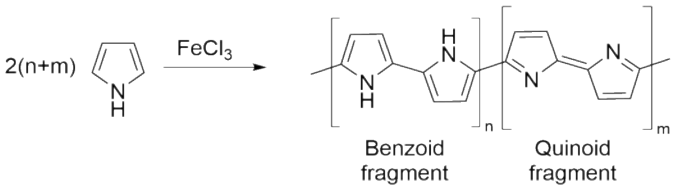
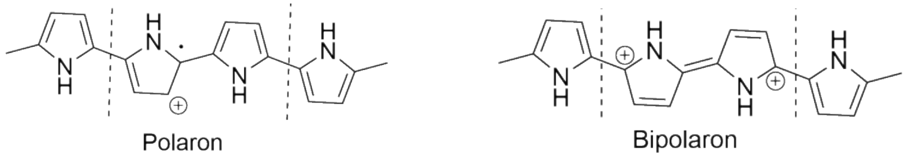
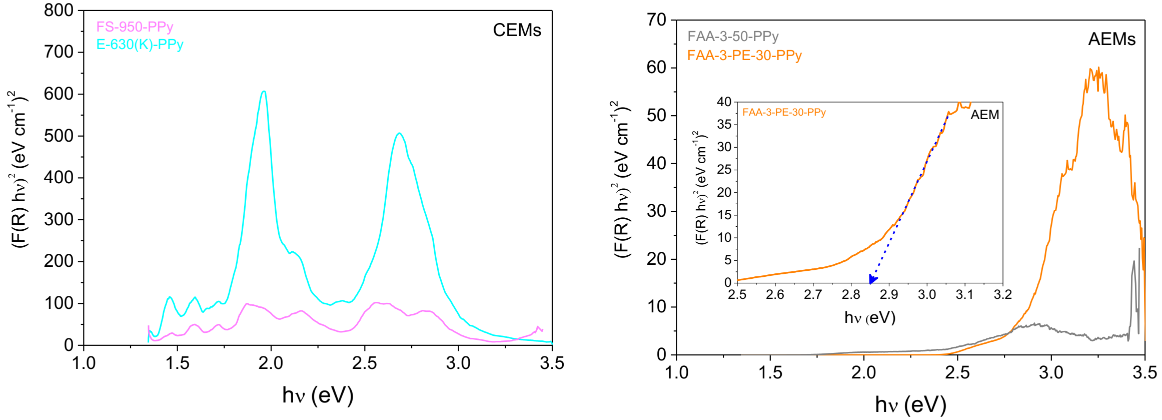
E. Spectroscopic Characterization of (modified)-IEMs







Samples	Estimated oxidation degree (%)	Absorption max. energies (eV)	Estimated band gap (eV)
FS-950-PPy	60%	1.8 and 2.5	1.75 and 2.40
E-630(K)-PPy	--	2.0 and 2.7	1.75 and 2.50
FAA-3-50-PPy	37%	2.1 and 2.9	1.75 and 2.35
FAA-3-PE-30-PPy	72%	2.8 and 3.2	2.45 and 2.85



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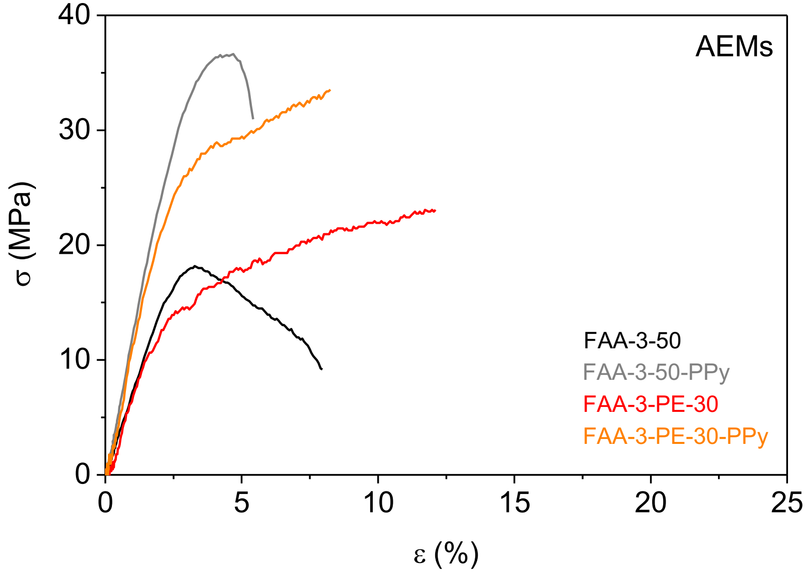
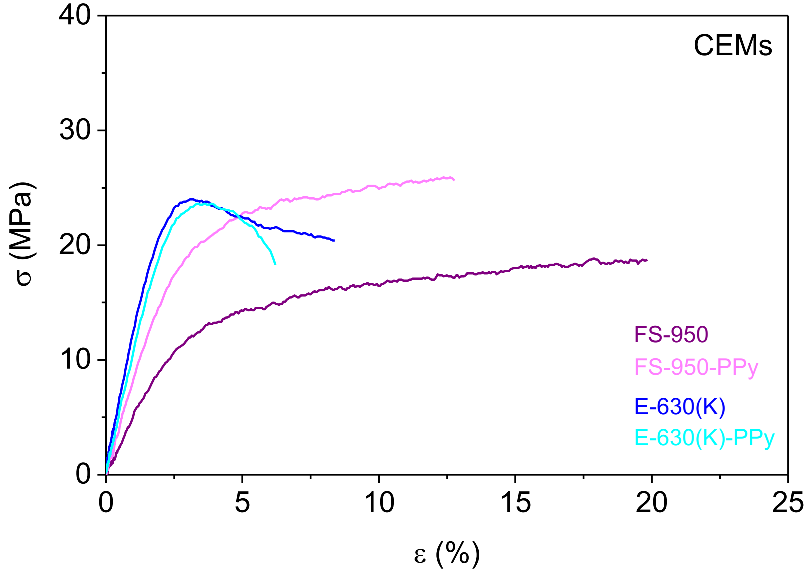
F. Mechanical Properties of (modified)-IEMs





Samples	E (MPa)	σ_S (MPa)	L_e (MPa)	ε (%)
FS-950	399.6 ± 56.2	16.81 ± 3.4	9.9 ± 3.1	≈18
FS-950-PPy	768.8 ± 42.7	23.3 ± 1.3	17.0 ± 0.3	≈12
E-630(K)	1097.0 ± 64.0	24.1 ± 0.6	19.3 ± 1.1	≈8
E-630(K)-PPy	1031.4 ± 44.5	25.6 ± 1.9	23.9 ± 1.7	≈6
FAA-3-50	634.2 ± 37.5	18.1 ± 1.3	15.3 ± 0.3	≈6
FAA-3-50-PPy	1093.5 ± 77.1	34.2 ± 3.7	26.0 ± 1.3	≈4
FAA-3-PE-30	492.2 ± 78.5	21.8 ± 4.3	11.5 ± 0.7	≈11
FAA-3-PE-30-PPy	797.8 ± 77.6	31.9 ± 5.1	17.4 ± 2.5	≈7

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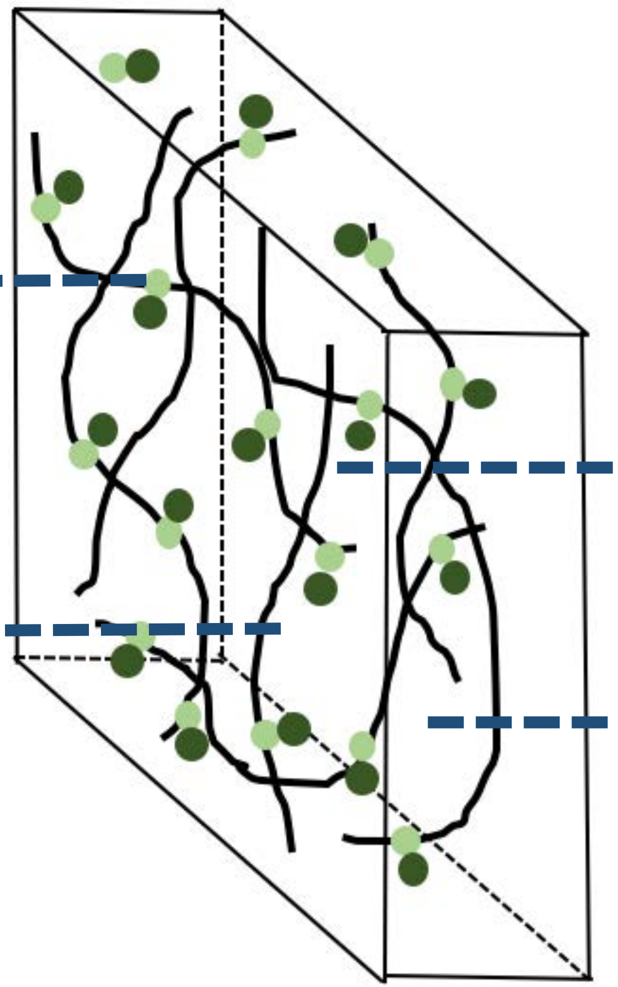
CONCLUSIONS

SEM, EDX and visual analysis confirmed the presence of PPy in the final material

The ion conductivity was enhanced in all IEMs



PolyPyrrole mitigates crossover

Microheterogeneity was increased while keeping the effectiveness of exchange in modified IEMs.

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