HIGREEW

First Project Workshop

In Pilsen and Online

Membrane developments for RFBs

Towards modified membranes

WP2-Materials and components optimisation

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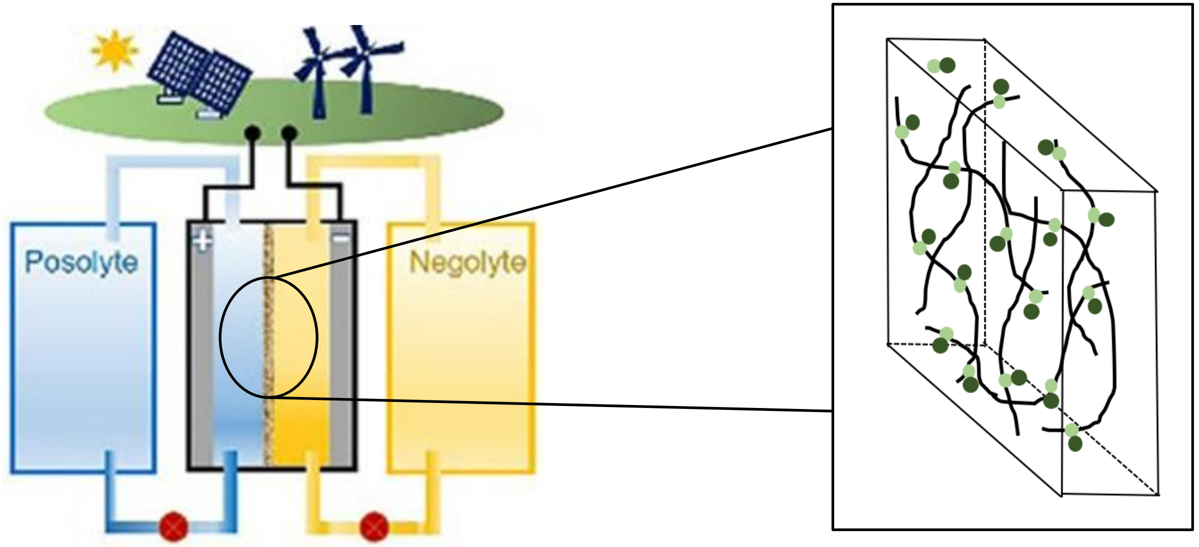
INTRODUCTION

WP2-Membrane Optimization (Task 2.2)



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

Ion Exchange Membrane (IEM)

Chemical stability
Ion conductivity
Mechanical resistance
Permselectivity

Transfer of water
Permeability of active materials
Cost

CATION EXCHANGE MEMBRANES						ANION EXCHANGE MEMBRANES			SEPARATORS		
Fumatech BWT				Solvay (Aquivion)		Fumatech BWT			Amer-Sil		
FS-950	FS-930	E-630(K)	E-620(K)-PE	E98-15S	E87-05S	FAA-3-50	FAA-3-PE-30	FAPQ-330	Sample A	Sample B	Sample C

IEC

WU

SR

ASR

t_{app}

HIGREEW INNOVATIONS & EXPECTED TARGETS

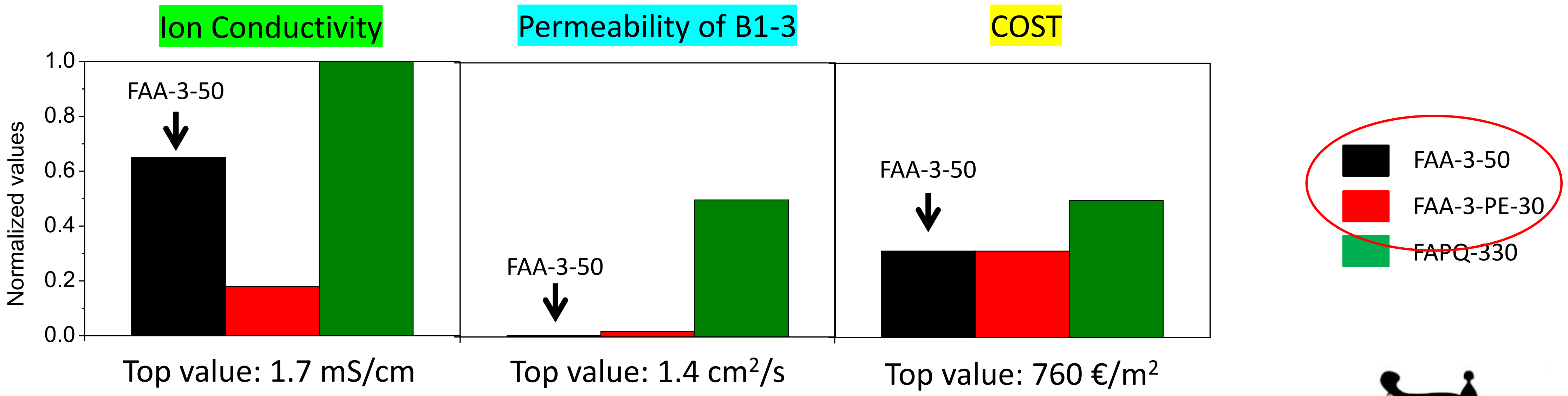
INNOVATIONS AND EXPECTED TARGETS

Evaluation of commercial membranes (Cation and Anion Exchange Membranes) to select the most promising materials based on the targets of HIGREEW.

Objectives	Current state in VRFB targets	HIGREEW targets
Type	Nafion™ membrane	Low-cost separator
Cost	500-750 €/m²	< 150 €/m²
Conductivity	0.5 mS/cm	> 0.5 mS/cm
Ion Exchange Capacity	2 meg/g	2 meg/g
Area specific resistance	1 Ω·cm²	< 1 Ω·cm²
Coulombic Efficiency	~ 90 %	95 %
Voltage Efficiency	~ 83 %	85 %
Self-discharge process from 75 % to <50 % SOC	10-30 h (from 1.4-1.5V to 0.8V)	> 50h

INNOVATIONS AND EXPECTED TARGETS

ANION EXCHANGE MEMBRANES (**AEMs**): SCREENING SELECTION

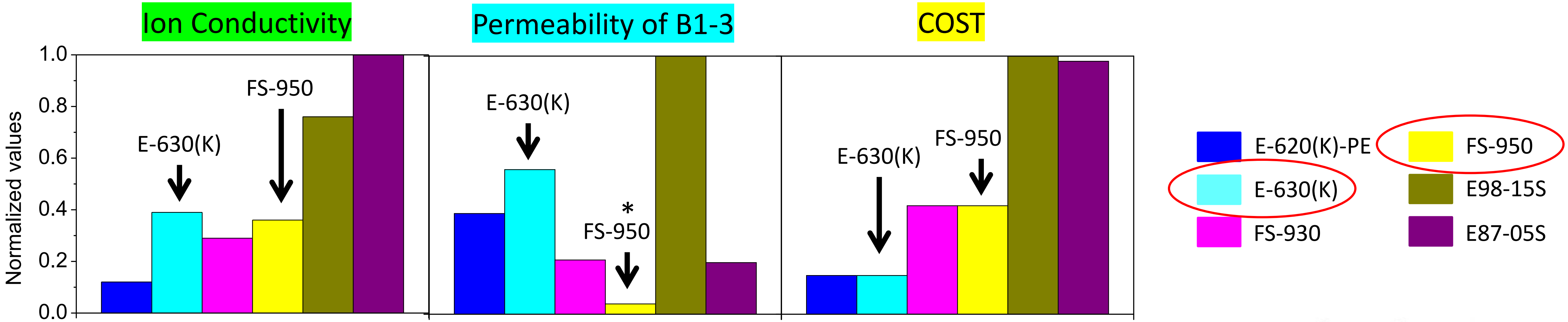


Two promising candidates were found in case of using AEMs according to targets:

- FAA-3-50 → 45.0 µm / non-fluorinated
- FAA-3-PE-30 → 23.0 µm / non-fluorinated with PE as reinforce / Difficult to handle!

INNOVATIONS AND EXPECTED TARGETS

CATION EXCHANGE MEMBRANES (CEMs): SCREENING SELECTION



Top value: 6.6 mS/cm

Top value: $6.2 \cdot 10^{-8}$ cm^2/s

Top value: 2700 €/m^2

*This value was 10 times increased to be able to visualize the bar

Two promising candidates were found in case of using CEMs according to targets:

- FS-950 → 52.0 µm / perfluorinated
- E-630(K) → 34.0 µm / partially-fluorinated

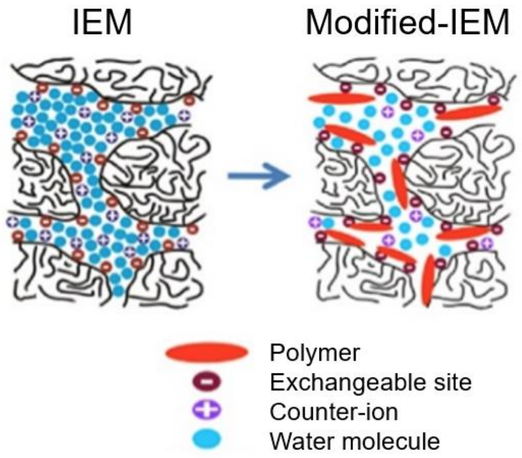
CURRENT RESULTS

INNOVATIONS AND EXPECTED TARGETS

Cost-effective materials are a bit far from the targets of HIGREEW: permeability is an important transport phenomena that needs to be considered and overcome.

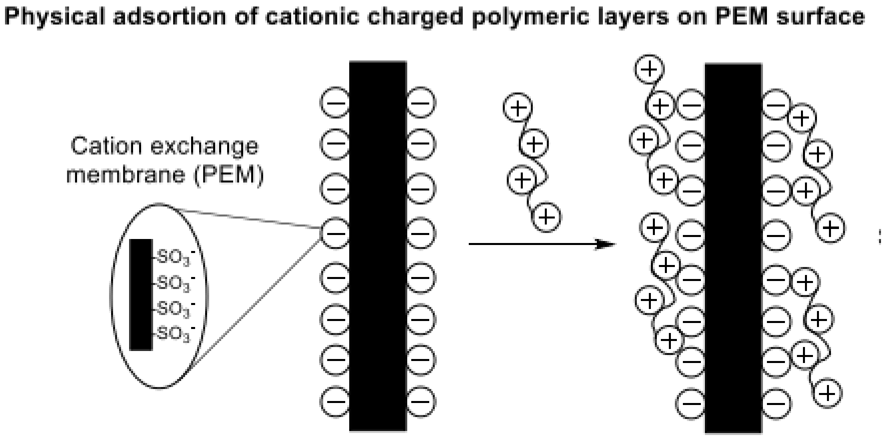
Membrane modification strategies

IN-SITU POLYMERIZATION



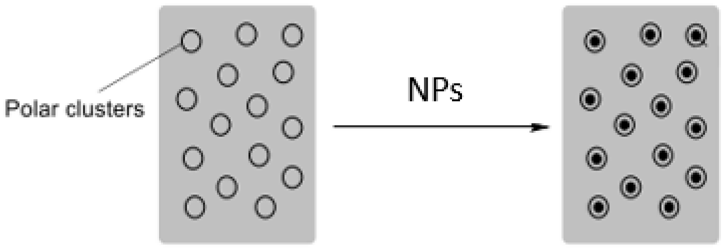
- ✓ Easy to **scale**
- ✓ Cheap
- ✓ Environmentally friendly

LAYER-BY-LAYER



- ✓ Enhanced conductivity
- ✗ Difficult to scale
- ✗ **Homogeneity** compromised

INCORPORATION OF NANOPARTICLES



- ✓ Cheap
- ✗ Requires membrane dissolution
- ✗ Difficult to **re-cast**
- ✗ No green chemistry

CURRENT RESULTS

COMMERCIAL MATERIALS

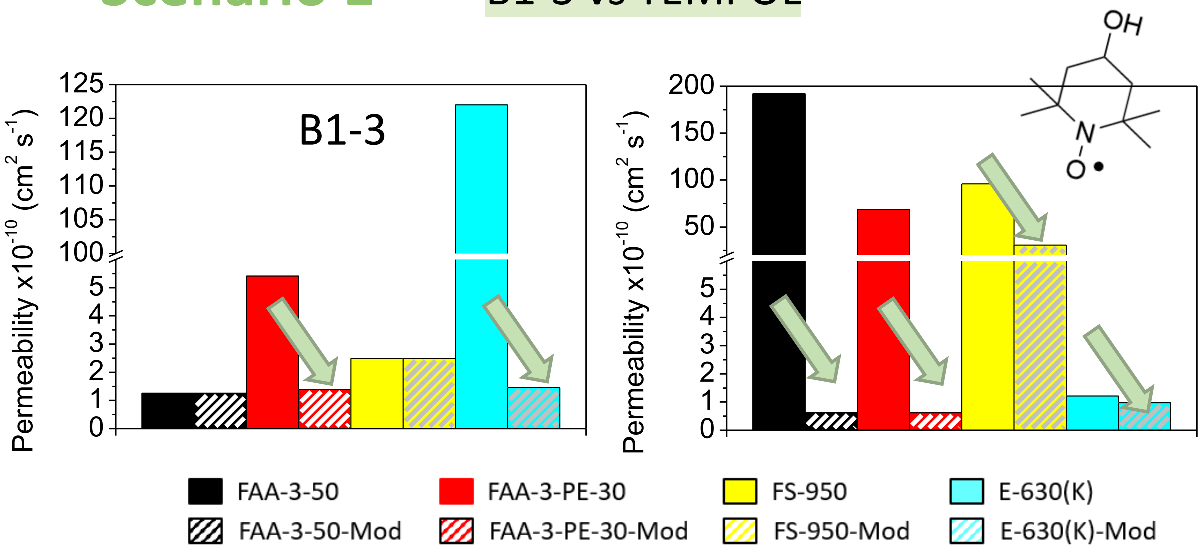
Screening selection based on: **permeability** (B1-3 and TEMPOL) and **conductivity** (1M NaCl)

Two promising candidates of **CEM** and **AEM** were selected for the different redox active material

	AEM (Cl^-)		**CEM (Na^+)**	
Membrane	**FAA-3-50**	**FAA-3-PE-30**	**FS-950**	**E-630(K)**
Thickness (µm)	45.0	23.0	52.0	34.0
WU (%)	<35	<35	<35	<35
SR (%)	<30	<30	<30	<30
IEC (mmol/g)	1.9	1.1	1.5	1.1
Conductivity (mS/cm)	1.1	0.3	2.4	2.6

Scenario 1

B1-3 vs TEMPOL

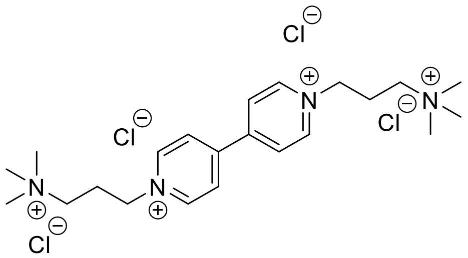


*Permeability in H-cells with no current (7-15 days)

CURRENT RESULTS

Scenario 2

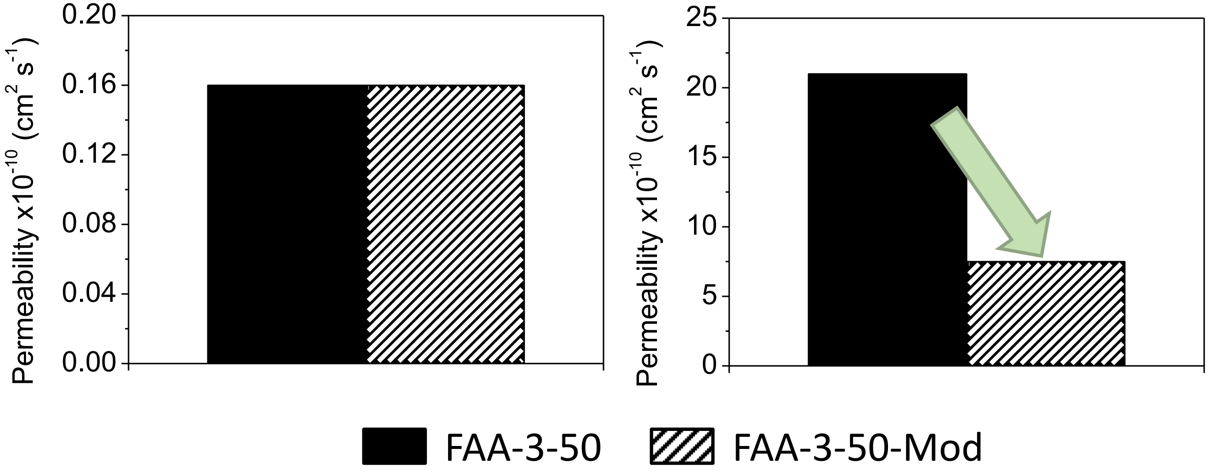
B2-1 vs C1-1



TEMPOL derivative

B2-1

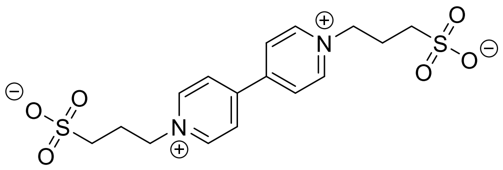
C1-1

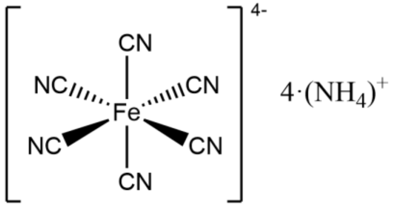


*Permeability in H-cells with no current (7-15 days)

Scenario 3

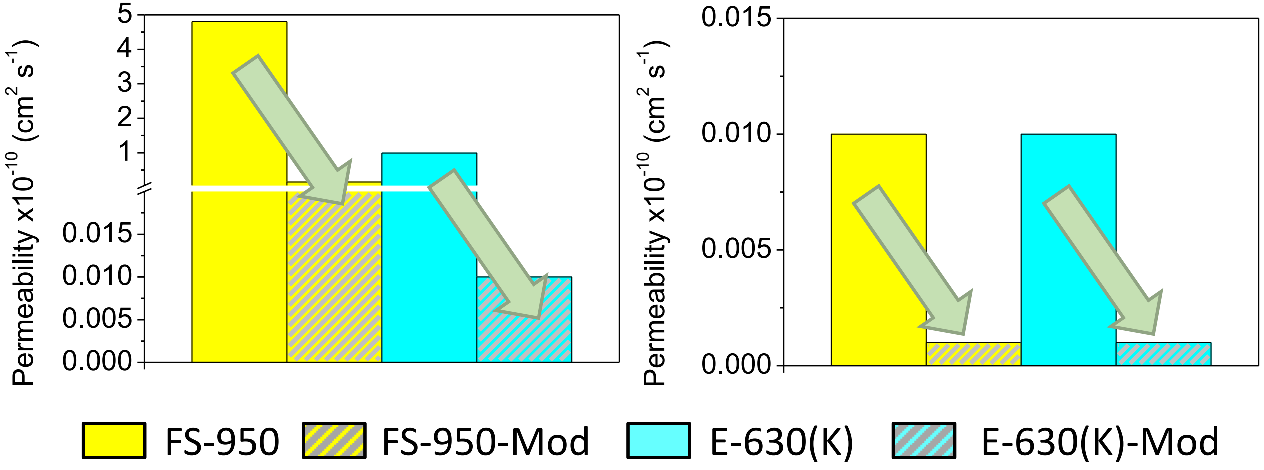
B2-2 vs C3-1





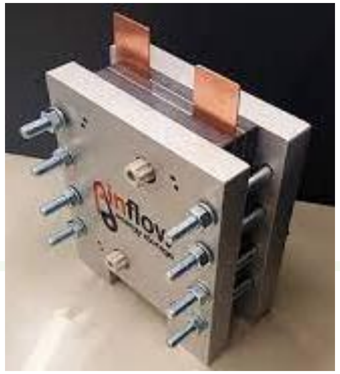
B2-2

C3-1



*Permeability in Pinflow cell with current (15-30 days)

CURRENT RESULTS



WP2-Testing at single cell lab-level (Task 2.5)

Battery prototype (single cell) for scenario 3: membrane evaluation

Anolyte: **0,9 M** of **B2-2** in **1M NH_4Cl**
Catholyte: **0,9M** of **C3-1** in **1M NH_4Cl**
Flow rate: 40 mL/min

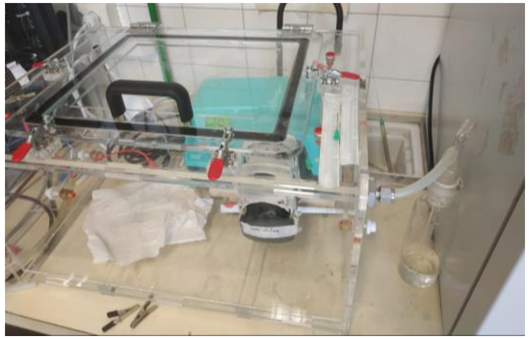
Felts: SGL 4.6 EA activated
Home-made glovebox / O_2 permeation

Procedure by UWB:
1) EIS 0% SOC
2) CC-CV 10 cycles (Capacity evaluation)
3) EIS 50% SOC + LC at different flow rates
4) CC cycling (stability test)
5) EIS 50% SOC + LC at different flow rates
6) CC-CV 10 cycles (change capacity evaluation)

		E-630(K)	E-630(K)-Mod	FS-950	FS-950-Mod
ASR 0% SoC (Ω cm²)		4.400* (UWB)	4.200	1.800	2.990
ASR 50% SoC (Ω cm²)		4.100* (UWB)	5.400	1.847	4.118
CE (%)		90-100	99	99	99
VE (%)		40-49	36	65	52
EE (%)		36-49	36	65	52
Capacity decay (%)		90	35	32	56
Permeability (cm²/s)**	B2-2	9.9E-11	<E-12	4.8E-10	1.5E-11
	C3-1	<E-12	<E-12	<E-12	<E-12

*With 3M NH_4Cl in the anolyte and 1M NH_4Cl in the catholyte / **Tests carried out during 15-30 days of evaluation

Higher resistance leads to lower VE. Modified membranes present low crossover but lower energy efficiencies.



Home-made glovebox

CURRENT RESULTS

Anolyte: **0,9 M** of **B2-2**
Catholyte: **0,9M** of **C3-1**
Flow rate: 40 mL/min

DATA PROVIDED BY THE **UWB**!

Felts: SGL 4.6 EA activated
Glovebox

C3-1 composition
[a]NH_4^+/Na^+: 71/29
[b]NH_4^+/Na^+: 83/17

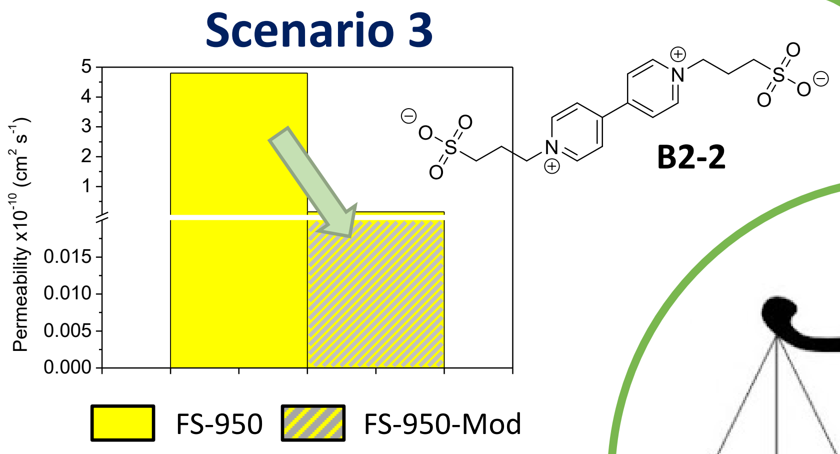
- Resistivity depends strongly on the electrolyte configuration
- Diluted compositions decrease the resistivity due to membrane swelling

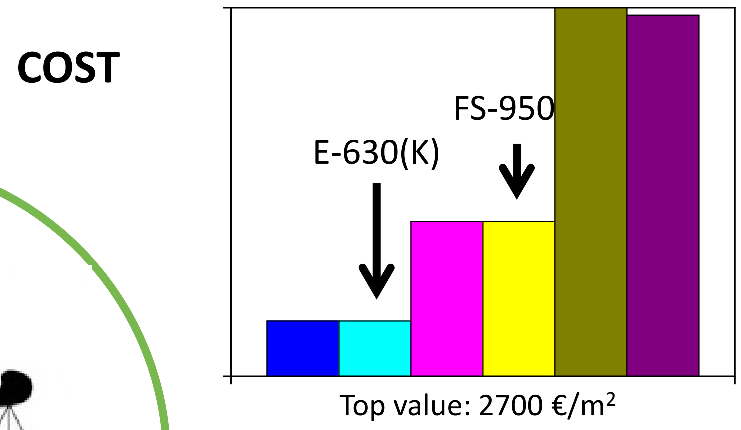
	↓ [NH_4Cl]				↑ [NH_4Cl]	
	B2-2 in **2M NH_4Cl** C3-1 in **1M NH_4Cl**		B2-2 in **2M NH_4Cl** C3-1 in **1M NH_4Cl**		B2-2 in **3M NH_4Cl** C3-1 in **1M NH_4Cl**	
	[a]FS-950	[b]FS-950-Mod	[a]FS-950	[b]FS-950-Mod	[a]FS-950	[b]FS-950-Mod
ASR 0% SoC (Ω cm²)	1.380	2.240 (+40%)	1.480	2.480 (+51%)	1.560	2.840 (+92%)
ASR 50% SoC (Ω cm²)	1.340	1.880 (-17%)	1.400	2.120 (-18%)	1.450	2.790 (-19%)
CE (%)*	99.9	99.9	99.5	99.2	99.2	99.3
VE (%)*	67.2	56.0	66.1	54.5	63.3	51.0
EE (%)*	67.1	56.0	65.8	54.1	62.8	50.7
Qteo/c (%)*	-0.05	-0.06	-0.09	? -0.36	-0.03	-0.06

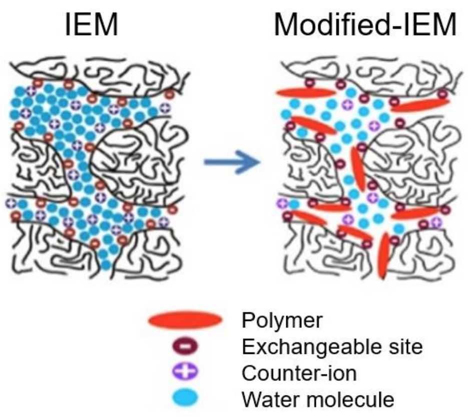
*Data of mid-term stability tests from UWB procedure for battery cycling tests – 50 cycles

- ✓ Mod-Membrane slightly recovers the conductivity upon cycling
- X Mod-Membrane more resistive than pristine one
- ✓ Membrane selectivity is apparently not compromised
- X Energy density is compromised but… Should we ignore further losses in long-term battery cycling tests? Mod-membrane could help us in that situations.
- X Crossover needs to be analysed at long-term experiments with a defined electrolyte configuration

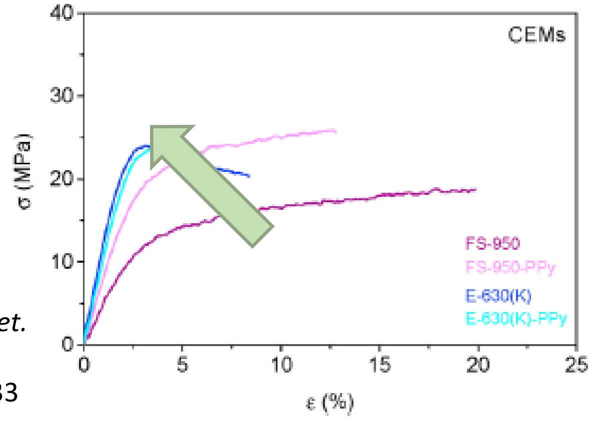
CONCLUSIONS







I. Salmeron-Sanchez, Juan Asenjo-Pascual *et. al, J. Membr. Sci.* 643 (2022) 120020-120033



NEXT STEPS

NEXT STEPS

Membrane evaluation (Fumatech + Aquivion + Selemion if proceed)

Non-mixed electrolyte battery prototype (home-made glovebox)

0,6M K-FeCN (**C3-1**) + 0,5M NH4Cl // 0,6M SPr2V (**B2-2**) + 2M NH4Cl → Scenario 3

by following the procedure proposed by UWB!

(The rest of partners will evaluate other membrane families under glovebox as well as mixed electrolyte battery prototype)

Modified membrane alternative

New formulations of membrane modification

Composite membranes with other polymer derivatives to reduce the crossover while keeping an eye on membrane conductivity

Thank you!

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Disclaimer/ Acknowledgment

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