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D4.3 – Supply of BMs with proven ex situ properties for testing in BMFC and BMEL	
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Nature of the Deliverable		
R	*Report*	
P	*Prototype*	
D	*Demonstrator*	***D***
O	*Other*	

SUMMARY

Keywords	Bipolar membrane, resistance, stability
Full Abstract (Confidential)	The report presents the preparation and characterisation of bipolar membranes (BM) with improved ex situ properties with respect to stability and resistance. The BM will be supplied for testing in bipolar membrane fuel cells (BMFC) and bipolar membrane electrolysers (BMEL).
Publishable Abstract (If different from above)	

SUPPLY OF BMs WITH PROVEN EX SITU PROPERTIES FOR TESTING IN BMFC AND BMEL

CONTENTS

1. INTRODUCTION

In Figure 1 are presented two different types of bipolar membrane architectures (type I and type II). Both designs have a dense proton exchange layer (PEL), but they differ from the architecture of the Anion Exchange Layer (AEL). Type I presents a porous AEL. The porosity allows fast transport of water to the PEL-AEL junction during electrolysis, preventing build-up of gas pressure at the PEL-AEL junction in a bipolar membrane fuel cell (BMFC) and permitting the evacuation of CO_2 formed at the junction (when BMFC is operated with air) in order to avoid mechanical stress arising from possible CO_2 evolution at the junction. Type II presents a dense AEL in order to prevent cation crossover from the AEL- to the PEL-side. The dense AEL must be thin to reduce the overall electrical resistance. This deliverable report describes the preparation and characterization of bipolar membranes based on the design of type II, with improved ex situ properties with respect to stability and resistance.

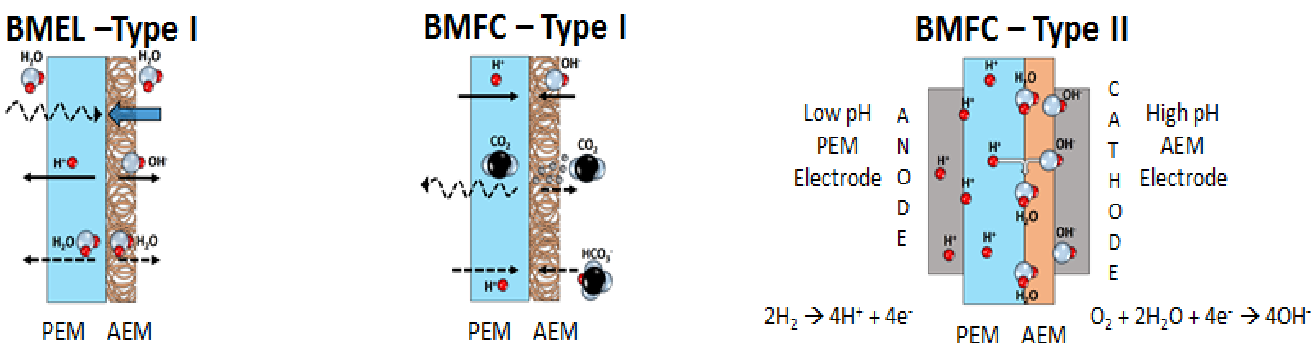

Figure 1. Design of bipolar membrane.

These bipolar membranes will be supplied for testing in bipolar membrane fuel cells (BMFC) and bipolar membrane electrolysers (BMEL), and the reactions and ion migration paths and recombination at the CEM-AEM interface in these two devices are shown in *Figure 2*.

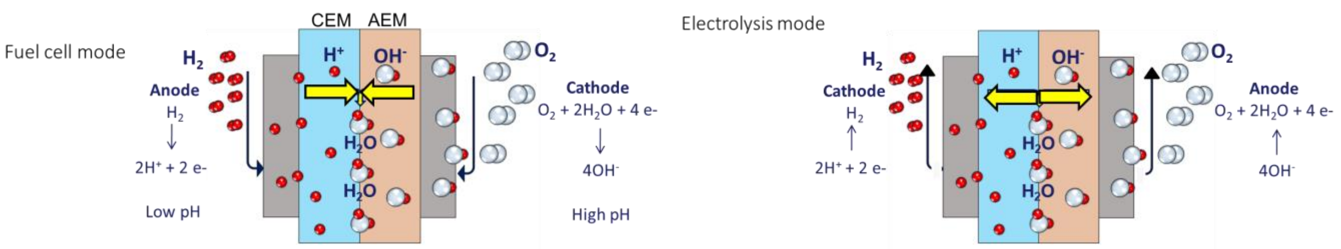

Figure 2. Bipolar membrane type II in FC and EL mode.

The exact design of the bipolar membrane based on type II is shown in Figure 3. At the junction between the dense AEL and PEL, an interface region is introduced, consisting of a network of nano-fibres, nano-particles or amphoteric polymers. This interlayer provides mechanical interlocking of the anion and cation exchange ionomers preventing delamination and providing an extended bipolar reaction zone intended to facilitate the water splitting and proton-hydroxide recombination.

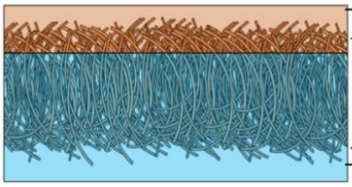

Figure 3. Design of a bipolar membrane type II consisting of an anion exchange layer (AEL), an interface layer and a cation/proton exchange layer (PEL).

Commercially available bipolar membranes (e.g. fumasep® FBM, supplier FUMATECH), intended for use in the production of acid and base from salt solutions, have normally a thickness of at least 150 µm and are reinforced with a woven textile. The resistance is usually above 5 Ω cm^2 (determined at current densities of about 25 $mA{\cdot}cm^{-2}$). Starting from this commercially available bipolar membrane, following measures have been taken in order to reduce the overall resistance of the membrane and to improve the chemical stability needed for FC and EL applications:

- Reduction of thickness of CEM layer and increased IEC of CE polymer
- Reduction of thickness of AEM layer
- Remove / replace woven textile to minimize area resistance
- Substitution of cation-exchange polymer by a chemically more stable PFSA polymer
- Optimized interlayer composition and thickness

2. Results and Discussion

As a first step, the thickness of the cation exchange layer of a standard bipolar membrane (woven-reinforced version) was gradually reduced. As a consequence, the resistance of the bipolar membranes could be significantly reduced starting from approx. 5 Ω cm^2 for a standard membrane with 150 µm thickness down to below 2 Ω cm^2 for a membrane with 85 µm thickness (see Figure 4), determined at current densities of about 25 mA/cm^2.

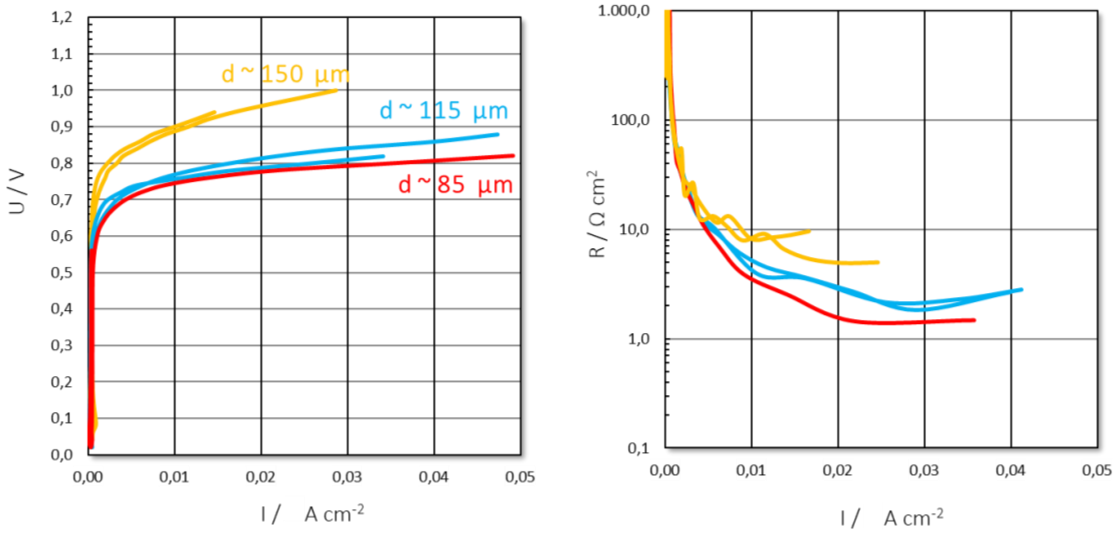

Figure 4: U-I Characteristics (left) and R-I curves (right) of bipolar membrane with gradual reduction of the thickness of the cation exchange layer.

	Thickness µm	Resistance Ω cm^2
Standard bipolar membrane FBM (woven-reinforced)	150	4.9
reduced thickness of CEL (woven-reinforced)	115	1.8
reduced thickness of CEL (woven-reinforced)	85	1.4

In a second step, the following non-reinforced bipolar membranes were prepared comprising (i) a cation exchange polymer with increased ion exchange capacity (IEC) using sPEEK with IEC 1.7 mmol/g, and (ii) complete replacement of the standard CE polymer used in the standard bipolar membrane by the more stable PFSA ionomer as CE layer.

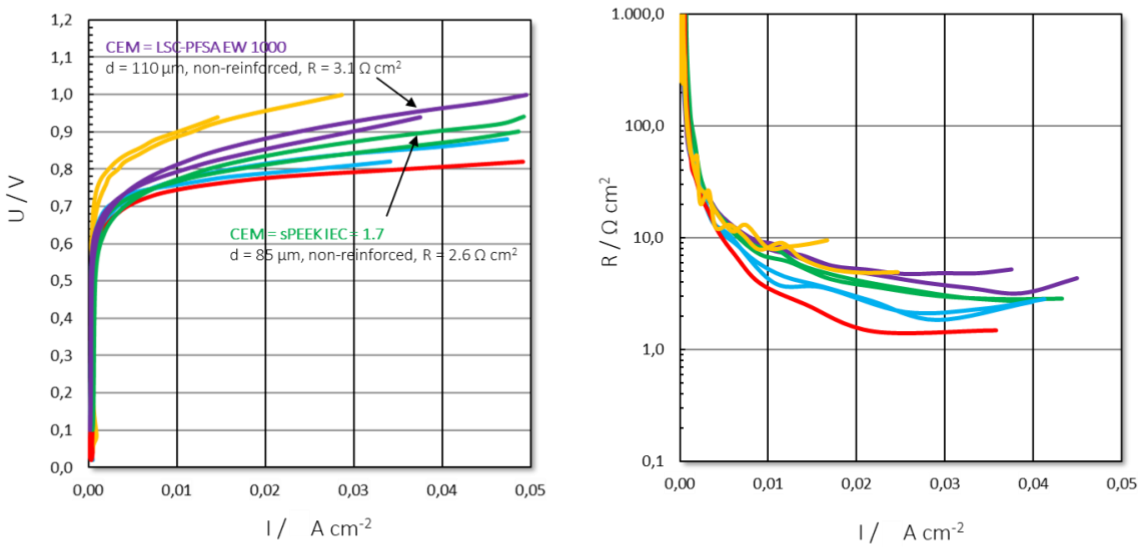

Figure 5: U-I characteristic (left) and R-I curves (right) of bipolar membrane with gradual reduction of the thickness of the cation exchange layer (150, 115 and 85 µm / reinforced versions), and replacement of CE layer by sPEEK IEC 1.7 mmol / g (green curve) and by PFSA ionomer (violet curve).

Although the replacement of the standard CEL by PFSA ionomer was successful (high water-splitting capability could be demonstrated), the overall membrane resistance could not be reduced further.

Therefore, in a third step, the thickness of the anion exchange layer was also significantly reduced, and additionally the interlayer composition and thickness were optimized. A very thin fumapem® FAA-3-10 membrane with thickness of 10 µm was used as anion exchange layer. This layer is based on fumion® FAA-3 ionomer, which shows sufficiently high conductivity and reasonably high stability (proven in Deliverable report 4.2). Several interlayer compositions and thicknesses were tested, applied by spray-coating on the AEM fumapem® FAA-3-10. As cation exchange layer, highly stable and highly conductive PFSA ionomer was applied onto the interlayer. Total thickness of the bipolar membranes is ranging between 30 and 50 µm. No reinforcement was used in order to avoid any contribution to the area resistance.

Current – Voltage characteristics / resistance measurements were carried out up to current densities of 300 mA/cm² using following set-up (Figure 6):

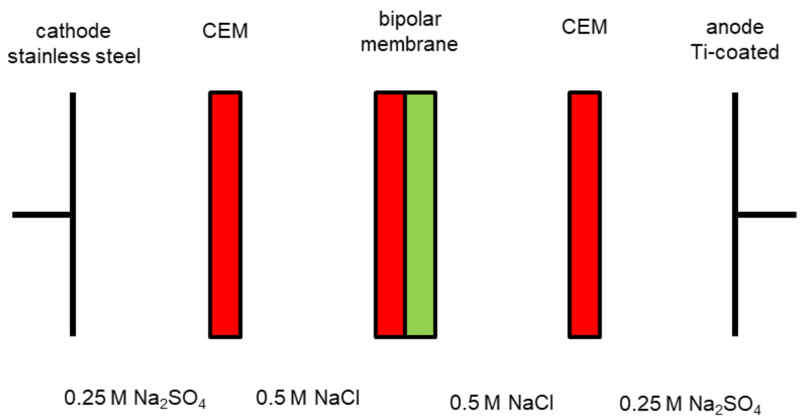

Figure 6: Set-up for the measurement of U-I Characteristics of bipolar membrane.

- 4-chamber set-up: cathode / Na_2SO_4 / CEM / NaCl / bipolar membrane / NaCl / CEM / Na_2SO_4 /anode
- 4-probe measurement: Haber-Luggin capillary (3 M KCl) with Ag / AgCl reference electrodes
- Electrolyte loop: 0.5 M NaCl solution / recombined
- Electrode loop: 0.25 M Na_2SO_4 / recombined
- Resistance is compensated by conductivity of electrolytes and temperature

The results are shown in Figure 7. The membrane resistance measured with above set-up depends on the applied current density, even standard bipolar membranes show a resistance close to 1 Ω cm^2 @ 300 mA / cm^2. The results also show that the membrane resistance is mainly affected by the interlayer composition and interlayer thickness, as long as the thickness of the AEL and CEL is not dominant. By optimization of the interlayer an overall resistance below 0.3 Ω cm^2 @ 300 mA / cm^2 could be achieved.

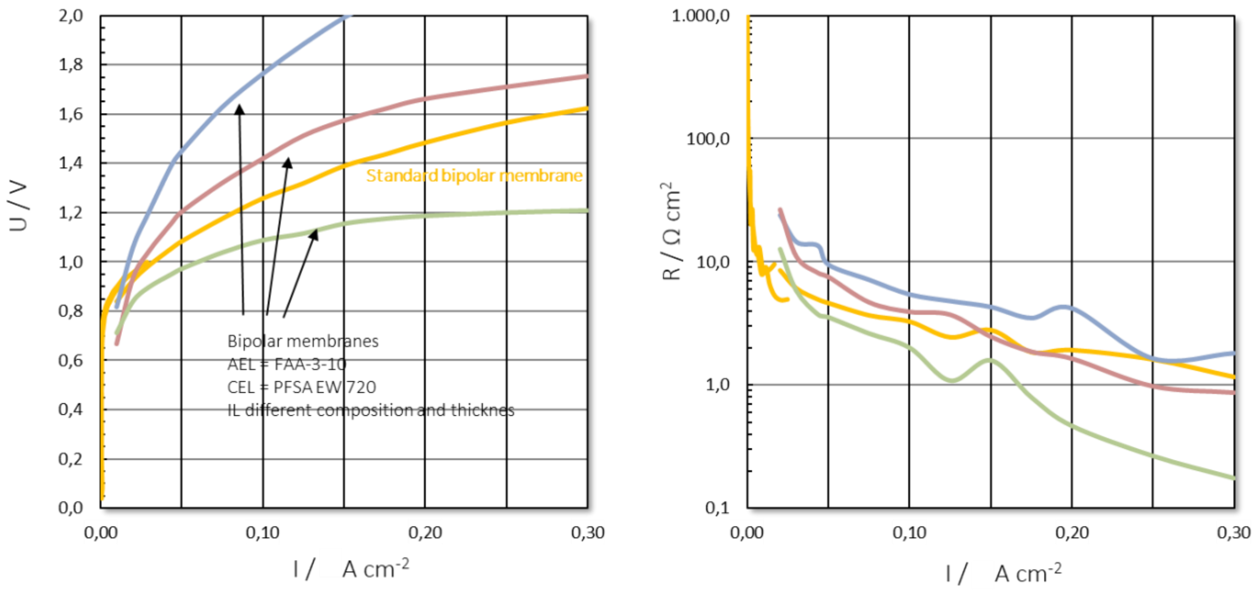

Figure 7: U-I Characteristics (left) and R-I curves (right) of bipolar membrane based on AEL = FAA-3-10, different interlayer compositions and thickness, CEL = PFSA, @ current densities up to 300 mA/cm^2.

3. Conclusions

Improved bipolar membranes (BM) were synthesized within CREATE showing low resistance and anticipating improved stability intended for testing in BMFC and BMEL. It could be shown that the resistance is mainly affected by the composition and thickness of the interlayer between AEL and CEL. The resistance of these BMs were verified ex situ before being sent to WP5. This bipolar membrane generation fulfills the Milestone MS2: Novel bipolar membrane designed for electrolyser with resistivity < 0.3 Ω cm^2 & improved water transport to AEI-PEM junction.

4. Recommendations and Future Work

Replace AEL of the bipolar membrane by more stable AEI.

5. Appendix

Acronyms

BM	bipolar membrane
AEM	anion exchange membrane
AEL	anion exchange layer
CEM	cation exchange membrane
CEL	cation exchange layer
IL	interlayer
IEC	ion exchange capacity in mmol/g
EW	equivalent weight in g/mol
PFSA	perfluoro sulfonic acid