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New Anion Exchange Membrane Electrolysers

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Anion Exchange Membrane Electrolysis for
Renewable Hydrogen Production on a Wide-Scale

ANIONE – Deliverable Report

<< D3.1 – Supply of 1st generation ionomer dispersions,
reinforcements and additives for manufacturing AEM
electrolysis membranes >>



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Publishable summary

The objective of WP3 of the ANIONE project is the development of novel anion exchange ionomers and membranes with enhanced conductivity, chemical and electrochemical stability, and improved mechanical properties for high-pressure operation having the capability of reducing gas permeation. With this aim, on the one hand, novel perfluorinated short side-chain and hydrocarbon ionomers are synthesized, and on the other hand, additives increasing the chemical and mechanical stability are prepared and investigated. Membrane engineering is addressed to improve conductivity and durability, decrease gas crossover, especially under high differential pressure operation, and expand the operation temperature of AEMWEs.

This deliverable report highlights the results obtained on the first generation ionomer dispersions and reinforcements developed for preparing AEM electrolysis membranes. Furthermore, full characterization of the benchmark membrane for the project, the Fumasep FAA3-50 membrane, is reported.

Perfluorinated anion exchange ionomers are developed, based on short-side chain Aquivion® through the functionalization of the sulfonyl fluoride terminal groups in the side chains of the precursor ionomer. The optimization of the synthetic process for maximization of conversion and selectivity, selection of reactants and dispersants with the lowest environmental impact is one of the objectives of the project.

The use of selected reactants and operative parameters for both reaction steps, allows to remove toxic substances and reduce the energetic consumption of the overall reaction. The increase of temperature from -20 °C up to 5 °C is considered a benefit in terms of energetic balance of the reaction and higher reaction efficiency. The thermal stability of the quaternized polymer renders it a good candidate for operation in the high temperature conditions (up to 90 °C) foreseen by the project.

A complete characterization of the benchmark membrane was carried out. In particular, in-plane and through-plane ion conductivity of the membrane in different ionic forms (Cl^- , OH^- , HCO_3^-) were measured in fully humidified conditions (95-100 %RH) and in a range of temperatures (30-120 °C), as well as ion exchange capacity, water uptake, dimensional stability, hydrogen permeability and thermal stability.

The thermal stability of the Fumasep FAA3-50 membrane is suitable for the targeted application and conditions, with no loss of chemical groups until 200 °C. Furthermore, suitable OH^- conductivity values of about 50 mS/cm were obtained between 90 and 100 °C at 100 %RH. The H_2 crossover at ambient pressure was < 0.1 % that is appropriate for electrolysis operation.

The benchmark membrane and ionomer were used in the first phase for an in situ assessment of the electrocatalysts developed in the project (see D4.1).

Nanofiber membrane reinforcements are prepared by electrospinning of polymer solutions. Two types of polymers are under investigation, with different functional properties, which can lead to chemical interactions with the ionomer matrix with impact on mechanical and dimensional stability. Reinforced membranes were prepared where the fiber webs are homogeneously embedded into the anion exchange polymers. The stability of the fiber webs in alkaline environment was assessed with an ex situ test followed by electron microscopy. The full characterization of the composite membranes for their conductivity, mechanical, thermal and dimensional properties is in progress.

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Abbreviations

Symbol / Shortname	Full Name
AEM	Anion exchange membrane
AEMWE	Anion exchange membrane electrolysis
DMAc	dimethylacetamide
DMSO	dimethylsulfoxide
EIS	Electrochemical impedance spectroscopy
EW	equivalent weight
IEC	Ion exchange capacity
MAS	Magic-angle spinning
NMR	Nuclear magnetic resonance
SEM	Scanning electron microscopy
SPE	Solid-phase extraction
TGA	Thermogravimetric analysis

1 Introduction

The objective of WP3 is the development of novel anion exchange ionomers and membranes with enhanced conductivity, chemical and electrochemical stability, and improved mechanical properties for high-pressure operation having the capability of reduced gas permeation.

With this aim on the one hand novel perfluorinated short side chain (task 3.1) and hydrocarbon ionomers (task 3.2) are synthesized, and on the other hand additives increasing the chemical (task 3.3) and mechanical stability (task 3.4) are prepared and investigated. Membrane engineering is addressed to improve conductivity and durability, decrease gas crossover, especially under high differential pressure operation, and expand the operation temperature of AEMWEs.

This report highlights the results obtained on the first generation ionomer dispersions and reinforcements developed for preparing AEM electrolysis membranes, and characterization of the benchmark of the project, the Fumasep FAA3-50 membrane.

1.1 Perfluorinated short side-chain ionomers

The aim of Task 3.1 is to produce anion exchange ionomers based on perfluorinated ionomer through the functionalization of the sulfonyl fluoride terminal groups in the side chains of the perfluorinated precursor. A di-amine was used at CNR-ITAE to obtain sulfonamide terminal groups, followed by an alkylation reaction to achieve quaternary ammonium ion exchange group [1]. A representation of the chemical synthesis used at CNR-ITAE is shown in Figure 1.

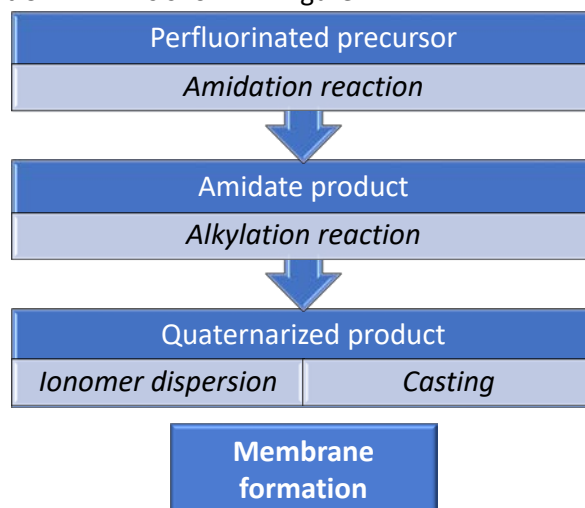


Figure 1. Synthetic approach to perfluorinated anion exchange polymer.

An optimization of the synthetic process for maximization of conversion and selectivity, selection of reactants and dispersants with the lowest environmental impact has been performed and evaluated.

1.2 Hydrocarbon ionomers

Hydrocarbon membranes and ionomers as alternative to perfluorinated membranes are also investigated and developed in the project.

The commercial Fumasep FAA3-50 was selected as a benchmark and a complete chemical-physical and electrochemical characterization was carried out. The protocols used for the characterization are reported in detail in the deliverable D.2.1 (Harmonised test protocols for assessing AEM electrolysis components, cells and stacks in a wide range of operating temperature and pressure). *Ex situ*

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characterization was performed to investigate its properties vs. those of other ionomers and membranes prepared in the frame of ANIONE. In particular, POCeITech is working on the synthesis of novel hydrocarbon anion exchange ionomers.

1.3 Membrane mechanical reinforcement

Reducing membrane thickness will allow to reduce ohmic drop with the risk of increasing gas crossover and mechanical failure in the high differential pressures of water electrolysis. To reach the goal of a mechanically robust anion exchange membrane with thickness below 30-50 μm CNRS developed reinforcements using nanofiber webs produced by electrospinning starting from polymer solutions. This approach was already validated for the reinforcement of proton exchange membranes leading to exceptional durability of the membranes upon electrochemical accelerated stress tests. [2, 3]. In particular the role of the interaction (*e.g.* ionic cross-linking, hydrogen bonding...) between the multiple interfaces between the fibers and the ionomer was demonstrated as relevant to increase the mechanical strength and tightness to gas permeation.

A range of variables are under investigation, which take into account the chemical functionalisation of the reinforcement (acidic or basic), the screening of appropriate solvents, the solubility and swelling properties of each polymer type, as well as the properties of the electrospun webs such as base weight, porosity, scalability and ease of handling. CNRS will finally select the appropriate configuration of the membrane needed to reach the project objectives in terms of membrane thickness, polymer equivalent weight, type and volume fraction of fibers.

2 Methods and Results

2.1 Polymer synthesis and characterization

2.1.1 Amidation reaction

Preparation of the perfluorinated membrane at CNR-ITAE included a selection of starting polymer equivalent weight (EW), the diamine, the dispersants and the reaction time and temperature. Amidation, alkylation and membrane preparation processes were carried out at CNR-ITAE, in the first phase of the project, to produce a perfluorinated membrane. In particular, 720 g/eq EW was evaluated for the first phase of polymer preparation; N,N,2,2-tetramethyl-1,3-propanediamine was chosen as a diamine; DMSO, ethanol and NOVEC 7500 were selected as dispersant media; a temperature of 5 °C was used as reaction temperature; different reaction times were investigated. The following synthesis procedure reports the evaluation of dispersants and reaction times during the amidation reaction. In particular, ethanol, dimethylsulfoxide and Novec 7500 dispersants and a time ranging from 30 minutes up to 20 hours were evaluated. The reaction temperature was maintained constant at 5 °C. The reaction time was varied from 30 min. up to 20 hrs.

2.1.2 Alkylation reaction

For the alkylation reaction methyl tosylate was used as an alkylating agent instead of methyl iodide and anhydrous acetonitrile was used as a dispersant. The reaction temperature was maintained at 50 °C for 20 hrs.

2.1.3 Membrane preparation

The alkylated polymer was dispersed in both dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc), placed in a Petri dish and dried at 80 °C until the complete evaporation of the solvents. The membranes were detached from the Petri dish and annealed at 200 °C to improve the mechanical properties.

2.1.4 Ion exchange capacity, slurry pH, water uptake, swelling

A back-titration was carried out as reported [1]. The quaternized polymer with tosylate counter-ions was exchanged in NaCl solution to exchange the tosylate with chloride ions and titrated according the Volhard back-titration reported in the deliverable D.2.1 (Harmonised test protocols for assessing AEM electrolysis components, cells and stacks in a wide range of operating temperature and pressure). The slurry pH was measured by immersing about 0.1 g of dried polymer in 100 ml of H₂O. The water and KOH uptakes, dimensional variation and swelling ($\Delta L/L$) were calculated as reported in D2.1

2.1.5 Solid state NMR

The samples received were characterized by multinuclear (¹⁹F, ¹³C, ¹H) solid state NMR spectroscopy. A 400 MHz instrument with a 1.6 mm probe is used.

2.1.6 Thermal analyses

Thermogravimetric analyses were carried out using a Netzsch (STA 409) thermobalance in air flow from room temperature up to 1000 °C with 5 °C/min scan rate.

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2.1.7 Anion conductivity

The in-plane anion conductivity of samples with tosylate counter-ion was carried out with a four electrodes method by Electrochemical Impedance Spectroscopy (EIS). The EIS parameters for the measurement were: 100 KHz - 1 Hz of frequency range and a 5 mV of amplitude. The measurements were carried out in the range of temperature 80-90 °C, flowing humidified N₂ (100 % RH) at room pressure.

2.2 Hydrocarbon anionic ionomer characterization

2.2.1 Ion exchange capacity

A potentiometric method for measuring the ion exchange capacity (IEC) was used. The membranes were immersed in 1M NaCl solution for 30 min, in order to convert the counter-ion into Cl⁻ form (the solution was refreshed at least 3 times). In the next step, the membranes were washed with DI water in order to remove any excess of Cl⁻ ions (the solution was changed at least 3 times). The membranes were immersed in 0.2 M NaNO₃ solution for 30 min, while collecting the solutions (repeating 4 times). This step confirms that the membranes are in NO₃⁻ form and the Cl⁻ ions are in the beakers. The Cl⁻ ions solution was titrated using AgNO₃ solution. The membrane was exchanged into Cl⁻ form once again and was dry in vacuum oven at 50 °C for 3 hr. The IEC was calculated using the following equation:

$$IEC = \frac{\Delta V_{AgNO_3} C_{AgNO_3}}{m_d}$$

Where, m_d is the mass of the dry membrane (in the Cl⁻ form), ΔV_{AgNO_3} is the consumed volume of AgNO₃ solution and C_{AgNO_3} is the concentration of AgNO₃ solution.

2.2.2 Anionic conductivity

Ionic conductivity was measured through-plane using two electrodes in a membrane test station (MTS). The membrane was sandwiched between two GDLs that were enclosed between two electrodes. The membrane impedance was measured over the frequency range from 10 kHz to 10 mHz. The resistance of the membranes was determined from the Nyquist plot of the impedance measurements. The resistance was calculated by extracting the real part of the impedance at the minimum imaginary value. The measurements were done in N₂ environment, in humidified conditions. The in-plane anion conductivity of was carried out as described in paragraph 2.1.7.

2.2.3 Thermal gravimetric analysis

Thermogravimetric analysis (TGA) was used in order to evaluate the thermal properties of the membrane. The thermal stability of the membranes was analyzed using a TGA instrument (TA Instruments Corporation). Temperature was increased from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen environment.

2.3 Preparation and characterization of reinforced membranes

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2.3.1 Preparation of fibrous reinforcement

Polymer nanofibers were prepared by electrospinning their solutions with a standard syringe using a grounded rotating drum collector configuration (Linari Engineering).

2.3.2 Chemical stability of polymer fibers

Polymer fibers were immersed in 0.1 M KOH at 60 °C for 100 hours. SEM micrographs were recorded on the webs before and after this stability test.

2.3.3 Preparation of membranes

Membranes were obtained by casting ionomer dispersions. Reinforced membranes embedding different amounts of polymer fibers were prepared by impregnating electrospun webs with ionomer dispersion. A layer of ionomer dispersion was cast with a doctor blade. The electrospun web was then placed on the top of this layer and another layer of ionomer dispersion was cast onto it. Afterwards, the composite membrane was left to dry overnight at room temperature and then dried to remove remaining solvent.

2.3.4 Morphological characterization of fibers and membranes

Morphology of electrospun nanofibers and membranes was analyzed by field emission-scanning electron microscopy (FE-SEM) using a Hitachi S-4800 microscope after coating with a Pt layer of few nanometers (\approx 2-3 nm) to provide electrical conductivity. Freeze-fractured membrane cross-sections were prepared by immersing and cutting samples in liquid nitrogen. Fiber diameters were calculated using the ImageJ software. For each web, the dimension of more than 100 nanofibers was evaluated.

3 Discussion and Conclusions

3.1 Synthesis of perfluorinated ionomers

Different products were obtained at CNR-ITAE, as reported in Table 1.

Table 1. Synthesized amidated Aquivion®-based products

Sample	Solvent	Reaction time	Yield	pH _{slurry}
Aquivion SO ₂ -F	-	-	-	5.6
DMSO	-	-	-	9.0
AQ720A-1	DMSO	2 hrs	-	9.7
AQ720A-2	DMSO	1 h	90.7	6.6
EtOH	-	-	-	5.5
AQ720A-3	EtOH	2 hrs	-	6.2
Novec			-	5.9
AQ720A-4	Novec	2 hrs	53.6	11.1
AQ720A-5	Novec	30 min.	75.9	11.0
AQ720A-6	Novec	20 hrs	75.0	10.7

The first attempt at CNR-ITAE was performed using DMSO as a dispersant. It is evident that the reaction time affects the final product, in fact a slurry pH of 6.6 and 9.7 was found, higher than the precursor (5.6) and approaching the value of 9 found for DMSO. It was supposed that the slurry pH of the final product was not real but the DMSO dissolved the precursor and remained entrapped into the porosity of the polymer and the washing steps were not enough to remove it.

The second experiment was carried out using ethanol as a dispersant. The final product was in a crystalline form similar to the precursor. The slurry pH of the product is slightly higher than that of ethanol, meaning that no reaction occurred.

Finally, the dispersant used at CNR-ITAE was NOVEC 7500, for the affinity with the fluorine part of the polymer. In this case the reaction conditions of polymer concentration and temperature remained the same and the time was varied from a minimum of 30 minutes to a maximum of 20 hrs. The reaction time does not affect the final product, the slurry pH reported in table 1 is almost the same for the three synthesized products and it is considerably higher than that of the precursor and Novec, meaning that the amidation reaction occurred with a very similar conversion factor.

A solid-state NMR spectroscopy was carried out, to verify the conversion of the -SO₂F to -SO₂NHCH₂C(CH₃)₂CH₂N(CH₃)₂ groups. The AQ720-A1, AQ720-A3, AQ720-A4, AQ720-A5 and AQ720-A6 samples were analyzed.

Figure 2a-c shows the fluorine, carbon and hydrogen spectra recorded for all the samples.

Samples A1 and A3 appear unconverted, while samples A4 and A5 appear completely converted (Figure 2a 40ppm). The ratio between the signals SO₂F and OCF₂ allows to determine the degree of conversion of the two samples A1 and A3 as respectively 6 % and 1 %. The conversion of samples A4 and A5 is 100 %.

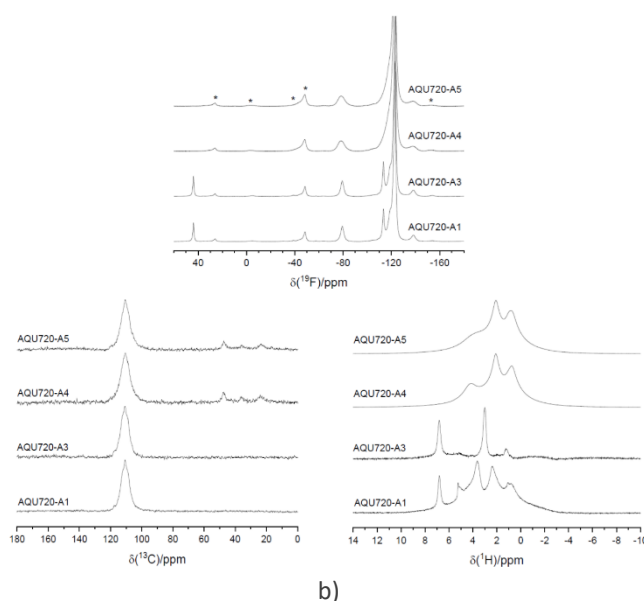


Figure 2. a) ^{19}F MAS spectra, b) ^{13}C (^1H) MAS spectra, c) ^1H MAS spectra for samples A1-A5.

In all spectra the wide signal at 111 ppm related to CF_2 was observed (Figure 2b). For samples A4 and A5, additional signals are also observed at 44, 36 and 24 ppm that are compatible with the structure - $\text{SO}_2\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$.

Figure 2c shows the proton NMR spectra recorded for the four samples. It seems difficult to associate any signal with the formation of any SO_3H groups, especially in the A3 sample. For samples A4 and A5 the signals are intense, however their chemical shifts 0.8, 2.1, and 4 ppm could correspond to those expected for structures such as $\text{SO}_2\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$. If the conversion had been to SO_3H , it would have been expected a broad signal at 7 ppm related to the SO_3H groups interacting with water, but this is not observed, so the conversion did not lead to the formation of such groups.

The same spectrum of A4 and A5 sample was also recorded for sample A6 (below reported), meaning that the synthesis kinetics is very fast and a complete conversion can be obtained after 30 minutes. After a longer time, the conversion is the same and no by-products formation or secondary reactions occur meaning a stability of the product even after about one day (20 hrs).

In conclusion, samples A1 and A3 show no changes with respect to the perfluorinated precursor and there is a low or no conversion of the SO_2F groups. A complete evolution of the SO_2F groups is observed for the A4, A5 and A6 samples, validating the conversion to $\text{SO}_2\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$. The spectra suggest that the reaction has occurred and is not a simple conversion to SO_3H .

Regarding the ion exchange capacity of the polymer, the measure was carried out following the back-titration procedure reported in the previous section (Table 2).

Table 2. IEC measured for samples produced with different reaction times and dispersant

Sample	Solvent	Reaction time	IEC _{NMR} , meq/g	IEC _{tit-back} , meq/g
AQ720A-1	DMSO	2 hrs	0.08	0.05
AQ720A-2	DMSO	1 h	N.M.	0
AQ720A-3	EtOH	2 hrs	0.01	0
AQ720A-4	Novec	2 hrs	1.13	0.92
AQ720A-5	Novec	30 min.	1.13	0.80
AQ720A-6	Novec	20 hrs	1.13	0.90

N.M. not measured

It is evident that the ion exchange capacity of the samples measured through NMR are higher than those measured through back-titration. This result is not surprising for this kind of polymer because the error in the titration method is higher than in NMR measurements [4], in addition the titration method reveals the anions easily exchanged from the powder sample and it is limited respect anions coordinated into the inner part of the polymer. The back-titration procedure should be further optimized to reduce the incongruence found with NMR results and to limit the errors. It can be concluded that the back-titration leads to underestimated values.

The second part of the synthesis carried out at CNR-ITAE consists in the alkylation of the amidate group to form a quaternary ammonium, as depicted in the step 3 of the Figure 1. The synthesis was carried out starting from sample A5.

Solid state NMR was used to verify the structure obtained after quaternization (A5-Q1). The spectra of sample AQ720-A5, A6 and A5-Q1 were compared (Figure 3a-b)

For all samples the ^{19}F MAS spectrum does not show any signal from the SO_2F groups.

As above reported, the spectra ^1H and ^{13}C of sample A6 are very similar to those obtained for sample A5, therefore the two samples they have the same structure.

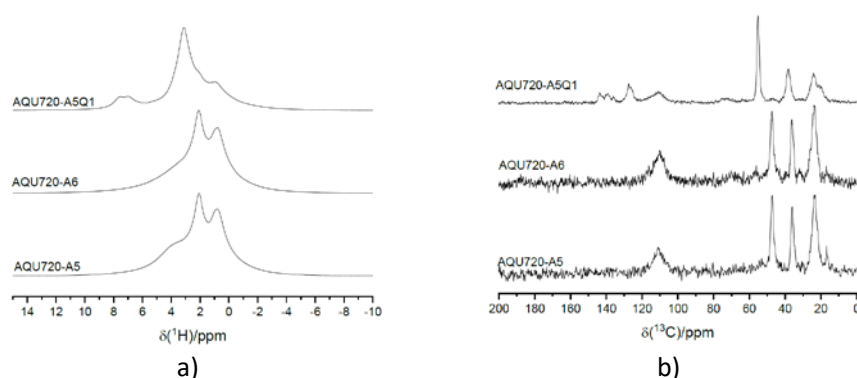


Figure 3. a) ^1H SPE MAS spectra, b) ^{13}C (^1H) CP MAS spectra.

In sample A5 and A6 it was observed a signal at 0.8 ppm attributable to CH_3 on C^{IV} , a signal at 2.1 ppm which presumably includes the CH_3 on Nitrogen and the CH_2 group in alpha to Nitrogen. In sample A5-Q1 the signal at 0.9 ppm is still clearly observed, while the signal at 2.1 ppm is shoulder to the more intense signal at 3.1 ppm. This last signal it is compatible with $(\text{CH}_3)_3\text{-N}^+$ groups. The peak at 7.6 ppm is attributable to the protons of the aromatic ring.

The ^{13}C one pulse MAS spectrum is reported in Figure 3b. The spectrum of the sample after quaternization shows many additional signals and a shift of some of the signals already present in A5. The signals between 144 and 127 ppm are related to the carbon atoms of the aromatic ring, while the CH_3 of the toluene group resonates at 20 ppm. The presence of a derivative of p-toluenesulfonic acid can be confirmed. The SO_3H alpha C^{IV} appears to exhibit two resonances at 139 and 136 ppm. Most of the CH_3 is now around $(\text{CH}_3)_3\text{-N}^+$ and resonates at 55 ppm. There is also a not very intense and broad contribution of 73 ppm which could be related to CH_2 in alpha to Nitrogen.

According to these results it can be concluded that a quaternarization reaction occurred, but it is not quantitatively determined. Further characterizations will be carried out to confirm the amount of quaternized polymer.

Back-titration based on Volhard method was carried out on the quaternized polymer and compared with the precursors, as reported in Table 3. Also in this case the back-titration is very low, probably due to the presence of alcohol in the solution that produces a high error during the measurement. The object of the next period of the project will be the optimization of the back-titration methods. In any case, the slurry pH suggests the formation of quaternary ammonium salt and not the unreacted p-toluenesulfonic acid because the value is typical of a salt sample.

Table 3. Comparison of chemical-physical characteristics

Sample	Yield, %	pH _{slurry}	IEC _{NMR} , meq/g	IEC _{tit} , meq/g
AQ720SO2F	-	5.6	1.39	-
AQ720A-5	75.9	11.0	1.13	0.80
AQ720A5-Q1	78.3	6.5	1.10	0.112

To understand the thermal stability of the polymer after each step of the reaction, thermogravimetric analyses were carried out at CNR-ITAE from room temperature up to 1000°C in air flow with 5 °C/min scan rate.

In Figure 4 is reported the comparison of the thermal profile of the precursor, the amidated product and the quaternized one.

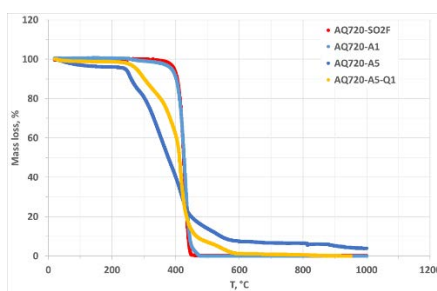


Figure 4. Thermal profile of the synthesized polymers compared to the precursor.

In agreement with IEC, pH_{slurry} and NMR results, the thermal profile of the precursor and sample AQ720-A1 is the same and no mass loss is detectable before the decomposition temperature of the main chain at about 400 °C confirming that no amidation reaction occurs when DMSO is used as a reaction dispersant.

Regarding the amidated products, it is reported as an example the sample AQ720-A5 because the others shows the same thermal profile. The graph highlights that the first mass loss from room to about 150 °C is attributable to the water loss (3.8 % and 1.2 % for AQ720-A5 and AQ720A5-Q1, respectively), the second in the range 230-350 °C is due to the functional groups decomposition and the third, over 350 °C, is the polymer main chain decomposition process. The conversion of the sulfonyl fluoride group decreases the decomposition temperature from about 400 °C down to about 250 °C (AQ720-A5). The curve of the AQ720-A5 sample presents a residual mass over the decomposition temperature of the polymer backbone, this mass can be attributed to the formation of a potassium salt, it was hypothesized. K₂SO₄, formed during the decomposition process, a similar behavior was found for a polyaromatic in sodium salt form and for perfluorosulfonic salt membrane [5, 6]. The alkylation synthesis increases the decomposition temperature of the functional group of about 20°C, due to the quaternary ammonium salt formation having tosylate as a counter-anion [7]. In addition, the absence of a residual mass at high temperature indicates that no residual K⁺ is present and means a complete conversion of the polymer to the quaternary form. This result makes the polymer a good candidate for the application at 90 °C.

The sample AQ720A5-Q1 was used for the very first tentative of membrane formation and solubility test at CNR-ITAE. In particular, the polymer (10 wt%) was dispersed in both dimethylsulfoxide and dimethylacetamide at 80 °C under stirring for 2 hrs. The DMSO was not able to dissolve the polymer and with the increase of temperature a gel formation occurred. The dispersion was placed in a Petri dish and dried at 80 °C until the complete evaporation of the solvent. A big size agglomerate of undissolved polymer was visible. On the contrary, the DMAc was able to dissolve the polymer and the obtained cast membrane was more homogeneous than that prepared with DMSO. The membranes were detached from the Petri dish by dipping in water and left to dry between filter papers. The membrane prepared with DMSO was very brittle and it was impossible to detach it from the Petri

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without damage it. The membrane prepared with DMAc was fragile but with better mechanical characteristics than DMSO-based one. This membrane was thermally treated at 200 °C for 30 minutes to improve the mechanical properties. The membrane was exchanged in 5 wt% KOH aqueous solution for 24 hrs at room temperature to measure the water uptake at 90 °C. After the 24 hrs, the membrane was rinsed with deionized water until the neutral pH and placed in an oven at 70 °C under vacuum to determine the dry mass. Successively it was placed in water at 90 °C for 2 hrs and then the wet mass was measured.

A very low KOH and water uptake values of 2.3 % and 4 % was found, respectively, with a corresponding swelling ($\mu\text{L/L}$) of 2.6 %. Considering that the water loss reported in TGA for the polymer in tosylate form was 1.2 wt%, the value of 4 % is probably due to a poor exchange from tosylate to hydroxide ions and it should be further optimized. Consequently, the corresponding value of swelling is underestimated.

Conductivity measurements on membrane in tosylate and hydroxide form were carried out at CNR-ITAE and roughly values of about 10 mS/cm and 18 mS/cm can be calculated at the same temperature (90 °C), respectively. The slight increase could be due to the exchange of the ions from tosylate to hydroxide. This behavior is in accordance with the data above reported and could be attributable to the difficulty of ion exchanging and to the very low water uptake of the membrane. These data can be considered the first tentative of an estimation of the properties of the quaternized polymer. These results suggest that the procedure for membrane preparation needs to be improved. In particular, the polymer concentration, time and temperature to improve the solubility of the polymer and reduce the tendency to gel formation. In addition, the annealing process should be evaluated. Moreover, anion exchange process will be investigated using hydro-alcoholic solutions as in the case of IEC measurements, to permit the swelling of the polymer and favoring the exchange of the ions.

3.2 Characterization of benchmark membrane

3.2.1 FAA3-50 Benchmark

Complete chemical-physical and electrochemical characterization was carried out by CNR-ITAE, CNRS and POCeITech. The membrane is supplied in bromide form and exchange in 1 M NaCl solution for 72 hrs is needed before the utilization, as suggested by Fumatech.

In Table 4 are reported the ion exchange capacity (IEC) of the membrane with different counter-ions measured at CNR-ITAE.

Table 4. IEC of FAA3-50 membrane having different counter-ions.

Membrane	IEC _{exp.}	IEC _{nom.}	% active groups
FAA3-50 (Br)	2.28	1.85	123
FAA3-50 (Cl)	1.85	1.85	100
FAA3-50 (OH)	1.59	1.85	86

The ion exchange capacity is higher than the nominal one due to the residual of synthesis reactants and membrane production. After the exchange in NaCl solution the nominal value is reached meaning that the exchange does not produce only the anion exchange but also a purifying effect and the removal of excess of bromides. A further exchange in 1 M KOH solution produces a hydroxide counter-ion presence and a reduced IEC respect the nominal, meaning that a possible degradation occurs in alkaline environment. These data are also confirmed by the percentage of conversions of active groups reported in the table 1 in which is evident that 14 % of functional groups are degraded during the alkaline exchange. POCeITech also performed the potentiometric determination of the IEC of the FAA3-50 membrane in Cl⁻ form. A value of 1.53 mmol/gr was recorded, slightly lower than the nominal.

In Table 5 are reported the other chemical-physical data related to the properties of liquid uptake, swelling, number of molecules of water per functional groups, anion concentration, mobility and diffusion coefficient of the anions determined at CNR-ITAE.

Table 5. Physical-chemical data of FAA3-50 membrane.

Membrane	Up, %	$\Delta L/L$, %
FAA3-50 (OH) (H ₂ O)	17	9
FAA3-50 (OH) (KOH 1M)	70	19

As evident, the water uptake carried out at 30 °C is lower than the hydroxide uptake. This is due to the strong affinity of functional groups of the membrane for the alkaline solution. Such property is useful for the alkaline electrolyzer application because the membrane acts as a reservoir for the OH⁻ electrolyte. The swelling is 10 % higher for the KOH uptake than water, and consequently the λ value is higher than in pure water.

The anion conductivity of FAA3-50 membrane with different counter-anions was measured in-plane at CNR-ITAE as a function of temperature from 30 up to 120 °C at 100 %RH (Figure 5).

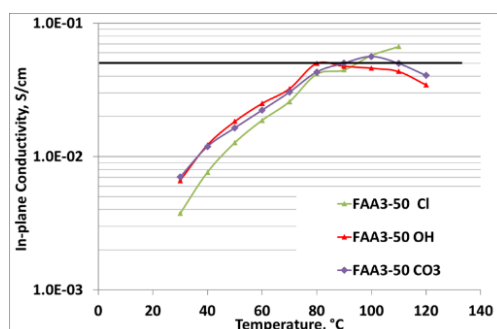


Figure 5. In-plane conductivity of different anions in FAA3-50 as a function of the temperature at 100 %RH.

The conductivity increases by increasing the temperature, a maximum value is recorded between 90 and 100 °C with values of about 50 mS/cm and then a decrease is detected due to the mechanical degradation of the polymer caused by the excessive swelling at high temperatures. The conductivity of Cl⁻ anions is lower than the others until 80 °C due to the low mobility of this ion respect the other two. The conductivity of Hydroxide and Carbonate ions is similar and values of 50 mS/cm and 56 mS/cm are reached at 90 °C and 100 °C, respectively. The value of 50 mS/cm is reported in the milestone MS2 of the project and we can consider it achieved.

The conductivity of the benchmark membrane in OH⁻ and HCO₃⁻ form was measured through-plane at POCeITech as a function of temperature at 95 %RH. The membrane in the HCO₃⁻ form (Figure 6) presents a maximum of conductivity of 9 mS/cm at 70 °C. At a slightly higher temperature (80 °C) a small decrease in conductivity is observed.

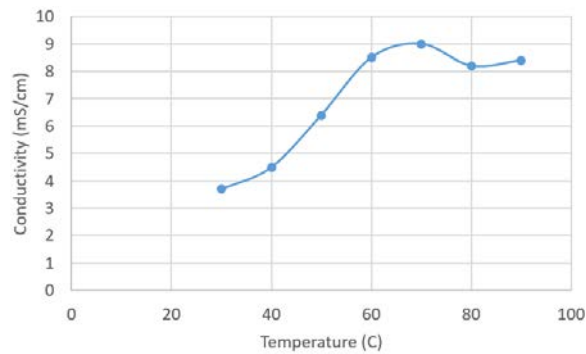


Figure 6. Through-plane conductivity of FAA30-50 membrane in HCO₃⁻ form.

The through-plane conductivity of the FAA3-50 membrane in OH⁻ form was characterized in the same conditions (between 40 and 90 °C, 95 % RH) (Figure 7). Around 80 °C the membrane reaches its maximum conductivity of 43 mS/cm. At higher temperature of 90 °C lower conductivity values are observed, which could be attributed to chemical degradation of the membranes, since the OH⁻ environment could cause to loss of IEC and consequently of ionic conductivity.

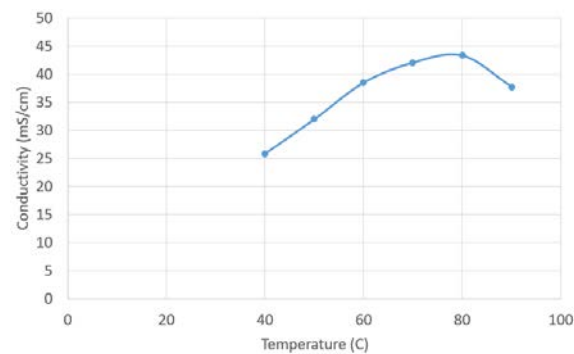


Figure 7. Through-plane conductivity of FAA30-50 membrane in OH⁻ form.

Further characterization was performed at CNR-ITAE to evaluate the effect of CO₂ on the conductivity. A sample was exchanged in 1 M KOH solution for 24 hrs, exposed to the ambient air for more than 6 months (aged sample) and the conductivity was measured. After this period, another piece of the same membrane was again exchanged in KOH solution for 1 h (regenerated sample) and the conductivity measured. The comparison of conductivity plot is reported in Figure 8.

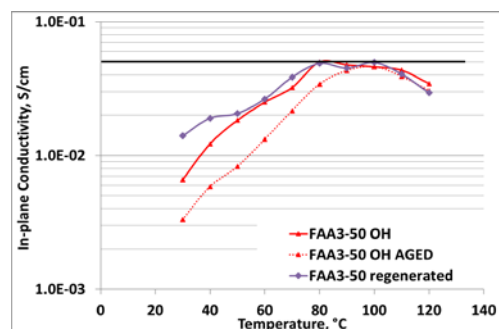


Figure 8. Effect of CO₂ on the conductivity of the FAA3-50 membrane.

The difference between the fresh and the aged sample is more pronounced at temperature lower than 80 °C, in fact the conductivity of the fresh sample is almost twice of the aged one. When the aged sample is regenerated in the potassium hydroxide solution the conductivity was restored reaching the values of the fresh one.

The ambient pressure H₂ crossover (Table 6) was measured. The crossover was in the order of magnitude of 10⁻⁹ mol/s cm², one order of magnitude lower than the target suggested by DoE (10⁻⁸ mol/s cm²). Considering that the cell was fed with 0.173 mol/s cm² H₂ flow during the measurement, the crossover percentage (last column of Table 6) can be determined to evaluate the amount of H₂ permeated through the membrane, less than 0.1 % of H₂ fed to the cell is permeated through the membrane.

Table 6. Ambient pressure H₂ crossover for FAA3-50 membrane.

T, °C	Crossover H ₂ , mA/cm ²	Crossover H ₂ , mol/s cm ²	H ₂ crossover, %
40	0.64	3.32 10 ⁻⁹	0.037
50	0.56	2.90 10 ⁻⁹	0.035
60	0.68	3.52 10 ⁻⁹	0.046

In order to have insight on the thermal stability of the benchmark membrane, the thermal degradation of the FAA3-50 membrane in Cl⁻ form was characterized by TGA at POCeITech (Figure 9). Five decreasing steps were observed: the first one, around 56 °C could be attributed to water evaporation, then at 200 °C the functional groups are being released, and the last stages that ends at 600 °C with a loss of 40 % of the weight the backbone of the membrane is degraded. The benchmark membrane presents suitable thermal stability for its use in AEMWE at 90 °C as foreseen in ANIONE.

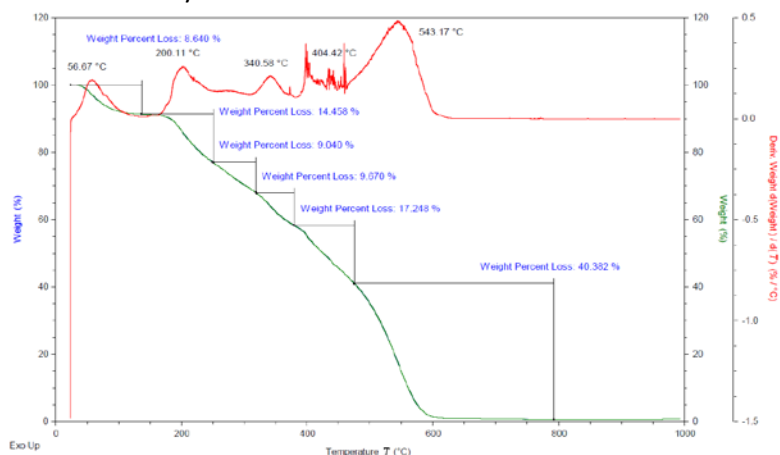


Figure 9. Thermogram obtained on FAA3-membrane in Cl⁻ form.

3.2.2 Ionomer formation

Regarding the ionomer formation different typologies of ionomer formulation were investigated varying the solvent composition. The first formulation consisted in n-propanol and 2-propanol solution but the solubilization of the polymer was not stable during the time.

The second formulation based on n-propanol and ethanol solution produced a stable ionomer during a long time and it was used for the electrodes preparation and the electrochemical tests in the WP4.

The third formulation consisted in a hydro-alcoholic solution, in particular ethanol and water. Also in this case it was produced a stable ionomer solution.

The last formulation was the same of the second, but the polymer was previously treated in 1 M KOH solution to have the ionomer in OH⁻ form. This formulation was also stable during time.

The benchmark membrane and ionomer were used in D4.1 for an in situ assessment of the electrocatalysts.

3.3 Nanofiber reinforcement

CNRS developed membrane reinforcements using nanofiber webs produced by electrospinning of polymer solutions. Two types of polymers are under investigation leading to different chemical interactions with the ionomer matrix. These polymers were successfully electrospun into fibers of homogeneous thickness (Figure 10).

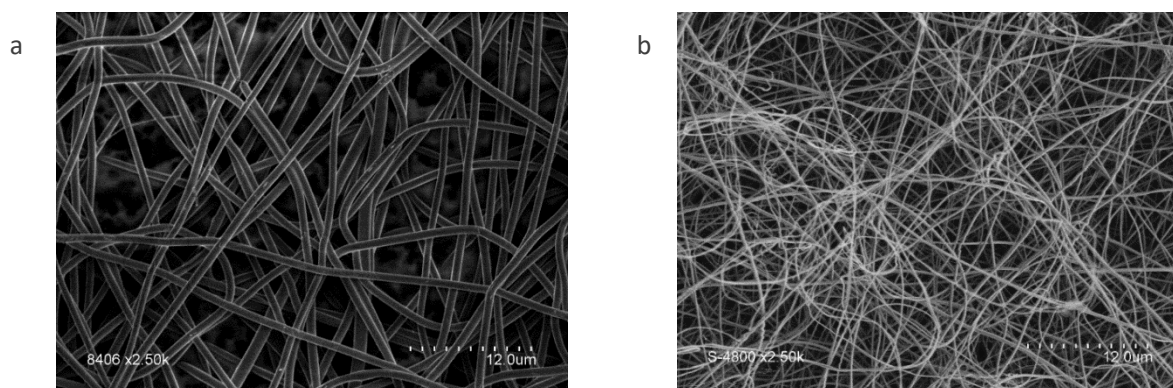


Figure 10. SEM micrographs of electrospun fibers of acidic (a) and basic (b) polymers.

The ionomers were cast on the nanofiber webs to obtain reinforced membranes. As observed in Figure 11, this approach allowed spreading of the nanofibers all over the membrane thickness.

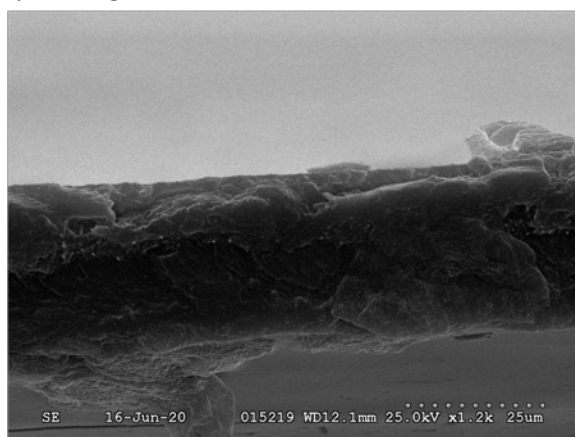


Figure 11. SEM micrograph of the cross-section of the anion exchange membrane reinforced with polymer nanofibers.

CNRS work is focusing on developing the appropriate configuration of the membrane. In particular, the effect of the volume fraction of nanofibers on the ion conductivity and mechanical and dimensional stability is currently investigated.

Another relevant aspect to be considered is the stability of the reinforced membranes in the alkaline environment of electrolysis. It was established that the basic fiber reinforcement is stable in 0.1 M KOH at 60 °C for 100 hours: no fiber welding or damage were observed by scanning electron microscopy after such treatment (Figure 12).

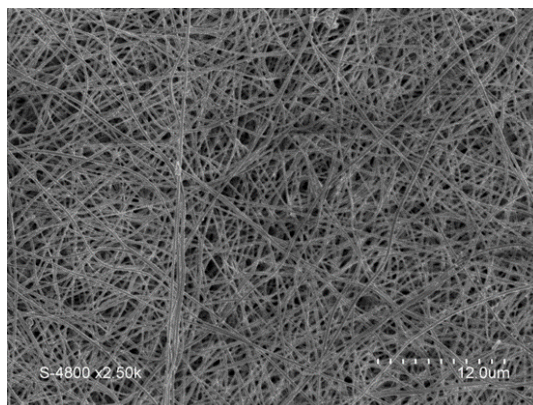


Figure 12. SEM micrograph of electrospun fibers of the basic polymers after treatment in 0.1 M KOH at 60 °C for 100 hours.

3.4 Conclusion

Regarding the perfluorinated ionomer synthesis at CNR-ITAE, the use of selected reactants and operative parameters for both reaction steps, allowed to remove toxic substances and reduced the energetic consumption of the overall reaction. The increase of temperature from -20 °C up to 5 °C was beneficial in terms of energetic balance of the reaction. The lower energy consumption, the higher reaction efficiency also due to the reaction shortened time. The thermal stability of the quaternized polymer makes it a good candidate for operation in high temperature conditions (up to 90 °C), as foreseen by the project.

POCellTech worked on the synthesis of novel hydrocarbon anion exchange ionomers showing promising properties for electrolysis operation.

A complete characterization of the benchmark membrane was carried out at CNR-ITAE, CNRS and POCellTech. Its thermal stability is suitable for the targeted application, with no loss of chemical groups until 200 °C. An OH⁻ conductivity of 50 mS/cm and H₂ crossover, at ambient pressure, < 0.1 % were determined. The benchmark membrane and ionomer were used in the first phase for an in situ assessment of the electrocatalysts developed in the project (see D4.1).

Nanofiber membrane reinforcements were prepared by electrospinning of polymer solutions at CNRS. Two types of polymers are under investigation. At CNRS, reinforced membranes were prepared where the fiber webs are homogeneously embedded into the anion exchange polymers. The full characterization of the composite membranes is in progress.

The Covid-19 situation produced some delays in receiving reactants from the suppliers and the access to the laboratories was reduced. This leads to a limited production of anion exchange polymer and delay in the optimization of membrane and ionomer preparation.

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5 Risk Register

Risk No.	What is the risk	Probability of risk occurrence ¹	Effect of risk ¹	Solutions to overcome the risk
WP3	Achieving high conductivity and stability (chemical, thermal and mechanical) for the thin reinforced anionic membranes.	Low	Medium	This is mitigated by having different routes for membrane development that have already provided good indication in terms of hydroxide conductivity and chemical stability

¹) Probability risk will occur: 1 = high, 2 = medium, 3 = Low

6 Acknowledgement

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Project partners:

#	Partner	Partner Full Name
1	CNR-ITAE	CONSIGLIO NAZIONALE DELLE RICERCHE
2	CNRS	CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
2.1	UM	UNIVERSITE DE MONTPELLIER
3	POCELLTECH	POCELL TECH LTD (HYDROLITE)
4	PV3	PV3 TECHNOLOGIES LTD (TFP Hydrogen Materials Limited)
5	IRD	IRD FUEL CELLS A/S
6	HYDROGENICS	HYDROGENICS EUROPE NV
7	UNR	UNIRESEARCH BV



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