CRITICAL RAW MATERIALS ELIMINATION BY A TOP-DOWN APPROACH TO

HYDROGEN AND ELECTRICITY GENERATION

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DELIVERABLE REPORT

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NATURE OF THE DELIVERABLE		
R	*Report*	
P	*Prototype*	
D	*Demonstrator*	*D*
O	*Other*	

SUMMARY	
Keywords	Anion exchange ionomer, anion exchange membrane, synthesis, conductivity, stability
Full Abstract (Confidential)	The report presents the preparation, conductivity and stability data for selected anion exchange ionomers (AEI) and anion exchange membranes (AEM) that will be used as a first generation of AEI and AEM for short-term testing of AEM fuel cell (AEMFC) and AEM electrolysers (AEMEL) in combination with benchmark catalysts and novel catalysts developed in CREATE.
Publishable Abstract (If different from above)	

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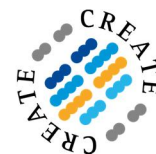
FIRST GENERATION OF AEM & AEI MATERIALS FOR AEMFC AND AEMEL

CONTENTS

First selection of functional groups, AEI and AEM synthesized within CREATE and showing sufficient ionic conductivity and stability for being used as a first generation of materials for short-term testing of the catalysts in AEMFC and AEMEL. The conductivity and stability of this first generation of AEM and AEI have been verified *ex situ* before being sent to WP5.

INTRODUCTION

The purpose of Deliverable D4.1 is to demonstrate the preparation of a first set of AEI and AEM developed in CREATE, with significant anion conductivity and stability, to be interfaced with catalysts inside porous electrodes, processed as membranes, and then integrated in AEMFC and AEMEL devices. Test protocols for anion conductivity and AEI stability measurements were defined in WP2 (Technical Specifications, Cost Analysis & Life Cycle) of CREATE, and reported in Deliverable 2.1. In the following, the material performance is reflected against these criteria as well as relative to recognized state-of-the-art AEI and AEM for anion conductivity in alkaline electrolyte.

1. AEI SYNTHESIS AND AEM PREPARATION

1.1 TYPES OF BACKBONE AND FUNCTIONAL GROUPS DEVELOPED FOR AEI

TECHNION has synthesized several cationic functional groups that were later tested for stability using a novel *ex situ* method closely mimicking AEMFC conditions (see Figure 2). Among these was an imidazolium-class 1,3-di-n-butyl-2-(2,6-dimethylphenyl)-4,5-diphenylimidazolium (BPhIm), whose structure is shown in Figure 1. Another molecule was a tetraarylammonium salt, synthesized for the first time in substantial quantities and with a simplified procedure.
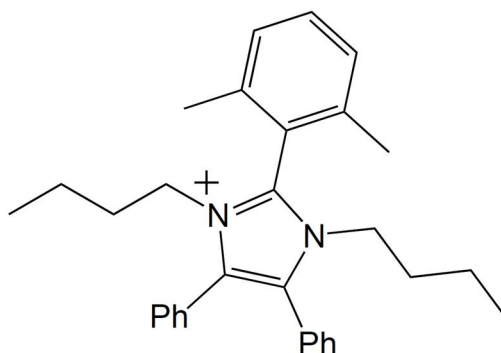

Figure 1. Structure of BPhIm - 1,3-di-n-butyl-2-(2,6-dimethylphenyl)-4,5-diphenylimidazolium.

TECHNION also synthesized several AEIs and cast them as AEMs. They all share a polyphenylene oxide polymer backbone, but differ in the substitutions on the quaternary ammonium in their functional groups. AEI-1 and AEI-2 are functionalized with different alkyl-substituted QAs, AEI-3 with an aryl-substituted QA, and AEI-4 with a cyclic alkyl-substituted QA. All of these were sent to WP5.

FUMATECH has prepared and supplied reference AEI and AEM based on FAA-3 material. FAA-3 consists of a polyaromate with quaternary ammonium group, counter ion = bromide, which can be converted to bicarbonate, carbonate or any other counter ion. FAA-3 membrane is slightly crosslinked, shows high conductivity (40 – 50 mS/cm) but also high swelling in OH-form. FAA-3 shows high conductivity, but does not meet the project target for stability. The benzylic structure of FAA-3 tends to degradation, in particular at elevated temperatures. FAA-3 ionomer is soluble in alcohol, NMP, DMAc and other organic solvents. These solutions can be used for membrane casting, nano-fibre electrospinning, and electrode preparation. Best procedure for electrode preparation with FAA-3 ionomer is not yet developed.

FUMATECH also synthesized new AEI and AEM based on an aliphatic backbone and quaternary ammonium groups with cyclic aliphatic structure (labelled FUMA-2). The main target of this development is to avoid the benzylic structure linked to the ammonium group. Different degrees of functionalisation and crosslinking have been tested. The aliphatic based material with very high ion-exchange capacity (IEC > 10 mmol/g) requires blending with inert matrix polymers such as alkaline-stable polysulfones. Among others (IEC, degree of crosslinking) the blend ratio is the main factor that controls swelling and conductivity.

1.2 EXPERIMENTAL CONDITIONS AND PROTOCOL FOR CONDUCTIVITY AND STABILITY MEASUREMENTS

In Deliverable D2.1, a general description of the set-up and conditions for conductivity measurements and alkaline stability tests have been defined. In general, the following pre-treatment is recommended before any measurement on a new membrane sample:

The membranes should be converted into OH form before characterisation according to the following prescription:

- Immerse in 0.5 M NaOH solution at room temperature for 12 hours (3-time exchange)
- Rinse in demineralized water for 30 min
- Start characterisation method

For all measurements, it is important to keep in mind that the OH-form of the membrane is very sensitive to CO_2 from the environment (air). Conversion from OH-form into (bi)carbonate form may take place within hours. It is recommended to carry out the measurements in a CO_2-free glove box. In case a glove box is not available and some carbonatation occurs or is suspected to occur, a routine procedure can be established that guarantees reproducible and comparable results, *e.g.* by characterising the membranes always exactly at the same time after the conditioning so that the fraction of cationic groups in OH-form and in carbonate form is always the same for all membrane samples.

The conductivity measurement is performed in an in-plane configuration using a four-electrode set-up. The membrane is placed in demineralized water at 25 °C. Also, measurements at different relative humidity and temperature are defined in Deliverable D2.1. The conductivity is determined by ac impedance spectroscopy.

Two protocols for the alkaline stability have been defined: (1) Treatment in 0.01 M KOH at 80 °C and (2) treatment in 2.0 M KOH at 80 °C. Properties like IEC and conductivity of the as-prepared membrane and

of the membrane after exposure to the alkaline media are used for assessing the alkaline stability. The internal pass criterion is defined as a drop of no more than 20 % in conductivity after one month exposure to the alkaline electrolyte.

TECHNION has developed a novel stability test method for functional groups. The testing is performed in an alkaline, non-aqueous solution developed for this purpose. To simulate various ultra-low water concentrations prevailing in an operating AEMFC (especially at the cathode side), small amounts of water were added in a rigorously controlled way. The method was published recently.[1,2] Solid potassium chunks are added to crown ether (CE) and titrated with an exact amount of water to produce a dry KOH-CE complex *in situ*. This complex is then added to DMSO with the quaternary ammonium (QA) to be tested, in an NMR test tube. QA degradation is monitored using ^{1}H-NMR analysis.
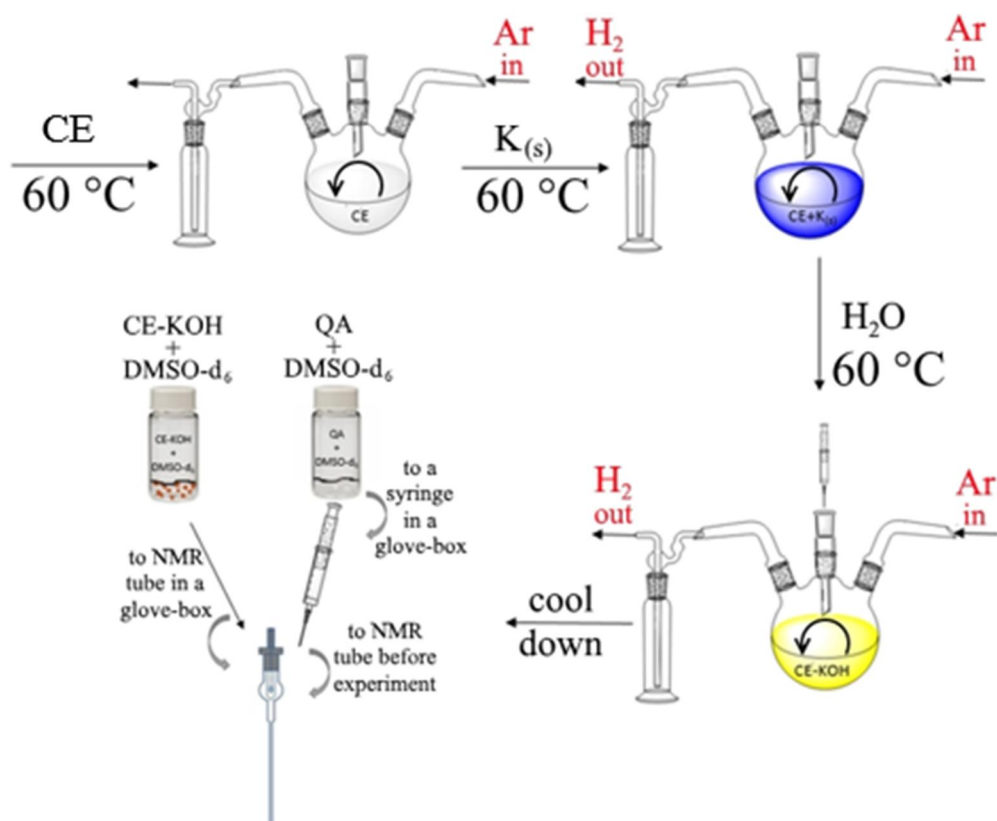

Figure 2. Novel ex situ method for testing the stability of functional groups in conditions closely mimicking those encountered during AEM fuel cell operation.

TECHNION measured the membrane conductivity using a four-point electrical impedance spectroscopy with frequency ranging from 1 Hz to 1 MHz, with the high-frequency resistivity taken as the reported value. The measurement was performed through the plane of the membrane (*i.e.* through-plane measurement). Following D2.1, the conductivity of a membrane impregnated in 1 M KCl was measured at 90 % RH and in the temperature range 35-60 °C.

1.3 AEM PREPARATION METHODS

TECHNION prepared polymeric membranes by a solution casting method. After the reaction was over, a thick polymer solution was cast on top of a clean glass plate and heated at 60 °C for 24 hours in order to obtain a transparent thin film. Finally, those thin films were peeled off from the glass plate and used as required.

For ionomer synthesis, reaction terminated polymer solution was precipitated in a desired solvent and the precipitate was collected as a crude product through Buchner funnel. The precipitate was cleaned further with solvent and dried at ambient temperature prior to further use.

In general, FUMATECH's membrane production is based on a solution casting method. Accordingly polymer / ionomer solutions of FAA-3 and FUMA-2 were prepared in appropriate solvents and cast on a continuous backing foil (*e.g.* PET foil) using a reverse-roll-coater (RRC). Then the solvent was evaporated in several subsequent dryers at defined temperatures. The final membranes were obtained in roll form.

2. CONDUCTIVITY RESULTS AND DISCUSSION

2.1 AEM CONDUCTIVITY

The conductivity of AEI-2 measured at 90 % RH and as a function of temperature is presented below in Figure 3. The curve shows an expected rise of the conductivity with rising temperature from 35 to 60 °C. At 60°C, which is in the lower working range for current AEMFCs, the conductivity is 18 mS·cm^{-1}. This value allows initial investigation in other WPs, as defined in the project.
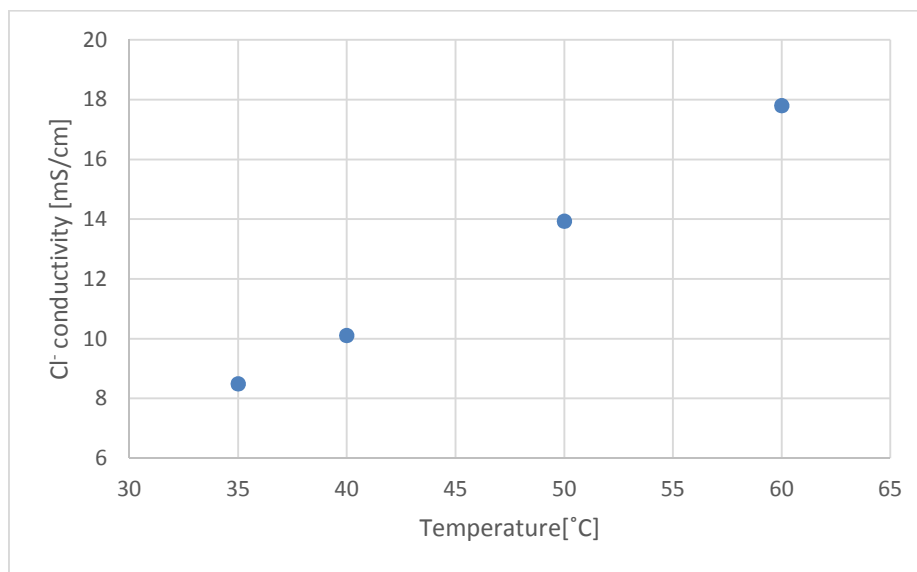

Figure 3. Through-plane conductivity of AEI-2 at 90 % RH *(in 1 M KCl)* as a function of temperature

The conductivity of the new AEM FUMA-2 as a function of blend ratio is shown in Figure 4. Within a blend ratio of 30 – 45 % of inert matrix polymer, the conductivity is sufficiently high (20-45 mS·cm^{-1}), while swelling is still acceptable. Blend ratio higher than 45 % leads to a strong decrease of the conductivity, while a blend ratio below 30 % results in high dimensional swelling.
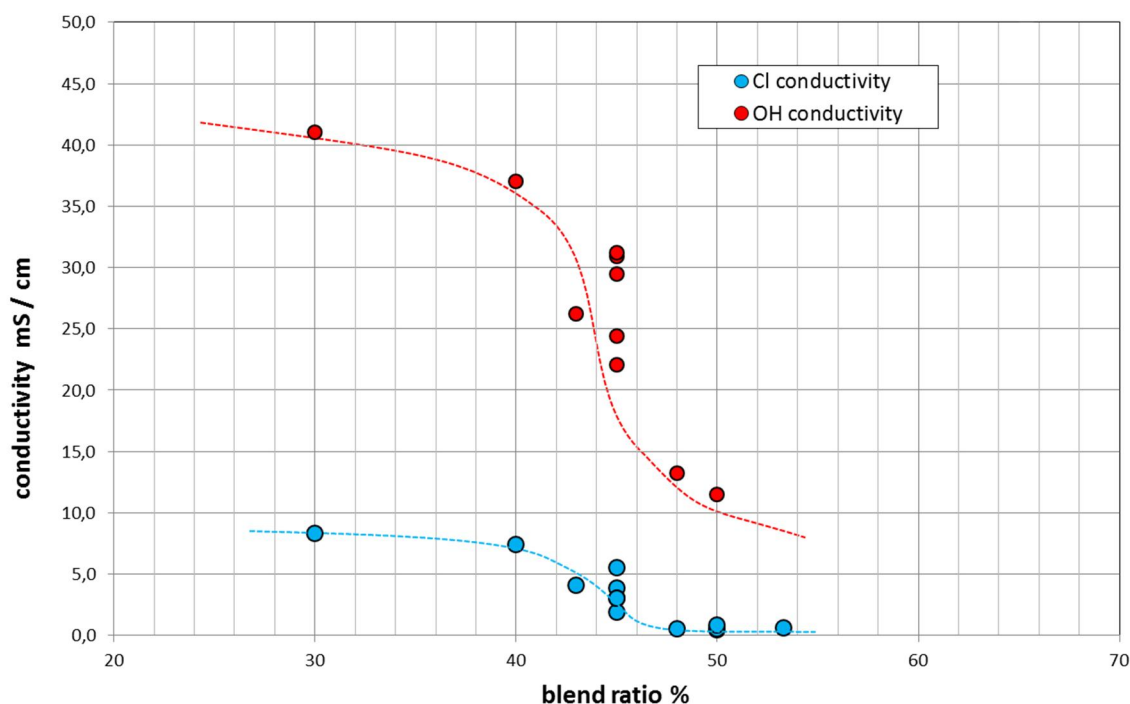
Figure 4. Conductivity of new AEM FUMA-2 as a function of blend ratio (in water at 25 °C).

2.2 COMPARISON TO INTERNAL PROJECT TARGET AND FAA-3 BENCHMARK

AEI-2 (TECHNION) is based on a stable polyphenylene oxide backbone. Its stability towards alkaline conditions is currently being investigated. The conductivity presented above is promising and allows follow-up work in other WPs (WP3, catalysts and WP5, cells).

The novel AEM FUMA-2, based on an aliphatic polymeric backbone, shows comparable conductivity data to the reference membrane FAA-3, ranging between 35 – 45 mS / cm at 25°C and at blend ratio of less than 35 % (Fig. 4). This conductivity value meets the project target of conductivity planned for Month 20 (30 mS·cm^{-1} at room temperature, Milestone 1 – the latter also involves a stability criterion). Due to the aliphatic backbone of the novel AEM, it is expected that the alkaline stability will however be significantly improved relative to FAA-3. Initial tests on the alkaline stability at elevated temperature (80 °C, 2 M KOH) already indicate better stabilities. More tests will be performed to confirm these initial results.

3. STABILITY RESULTS AND OUTLOOK

TECHNION has tested functional groups synthesized in-house and others for their stability under non-aqueous conditions using the novel method described above.

We have tested a trimethylbenzylammonium (TMBA) salt for stability. The results with 0-4 and 8 water molecules per OH⁻ at room temperature are presented below in Figure 5. We have shown that TMBA stability is challenged by the decrease in water content. The stability data is presented in

Table1 , showing TMBA half-life to be 109 hr. In an additional experimental campaign, we have shown that higher temperature increases the degradation rate of TMBA.
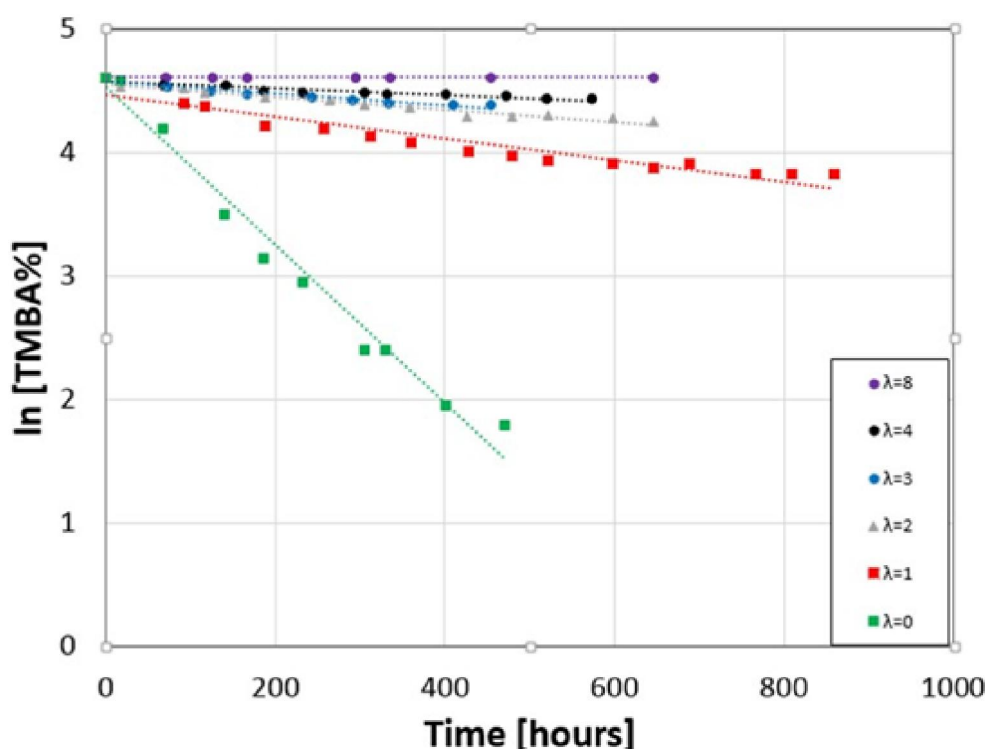

Figure 5. Remaining TMBA fractions (on logarithmic scale) as a function of time with different number of water molecules per OH⁻ (λ=0–8), in 0.6 M OH⁻ DMSO-d₆ solutions at room temperature. The experimental data is fitted with linear trends (dotted lines).

Table1. Fitting parameters for degradation results of TMBA shown in

Figure, and the calculated half-life time.

λ	Degradation rate constant, h^{-1}	Calculated half-life, h
0	6.38×10^{-3}	109
1	8.75×10^{-4}	792
2	5.10×10^{-4}	1360
3	4.75×10^{-4}	1460
4	2.82×10^{-4}	2460
8	~0	∞

TECHNION keeps synthesizing and screening additional functional groups to reach enhanced stability. In parallel, we are working on the synthesis and testing of the respective (but also other) AEIs.

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