

CRITICAL RAW MATERIALS ELIMINATION BY A TOP-DOWN APPROACH TO HYDROGEN AND ELECTRICITY GENERATION

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DELIVERABLE REPORT

D4.2 – SECOND GENERATION OF AEM AND AEI MATERIALS FOR IMPROVED AEMFC AND AEMEL DEVICES

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DISSEMINATION LEVEL

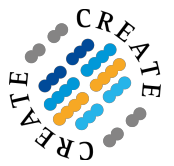
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NATURE OF THE DELIVERABLE

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 second generation of AEI and AEM for testing of AEM fuel cell (AEMFC) and AEM electrolyzers (AEMEL) in combination with benchmark catalysts and novel catalysts developed in CREATE.
Publishable Abstract (If different from above)	

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DELIVERABLE TITLE

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1. INTRODUCTION

Second generation of AEI and AEM were synthesized within CREATE and show sufficient conductivity and stability to be used for testing the catalysts in AEMFC and AEMEL. The conductivity and stability of these AEM and AEI were verified ex situ before being sent to WP5. This second generation of AEM and AEI fulfills the Milestone MS1: AEMs with alkaline stability at 60 °C > 400 h & AEI conductivity > 3 S m⁻¹ at 100% RH.

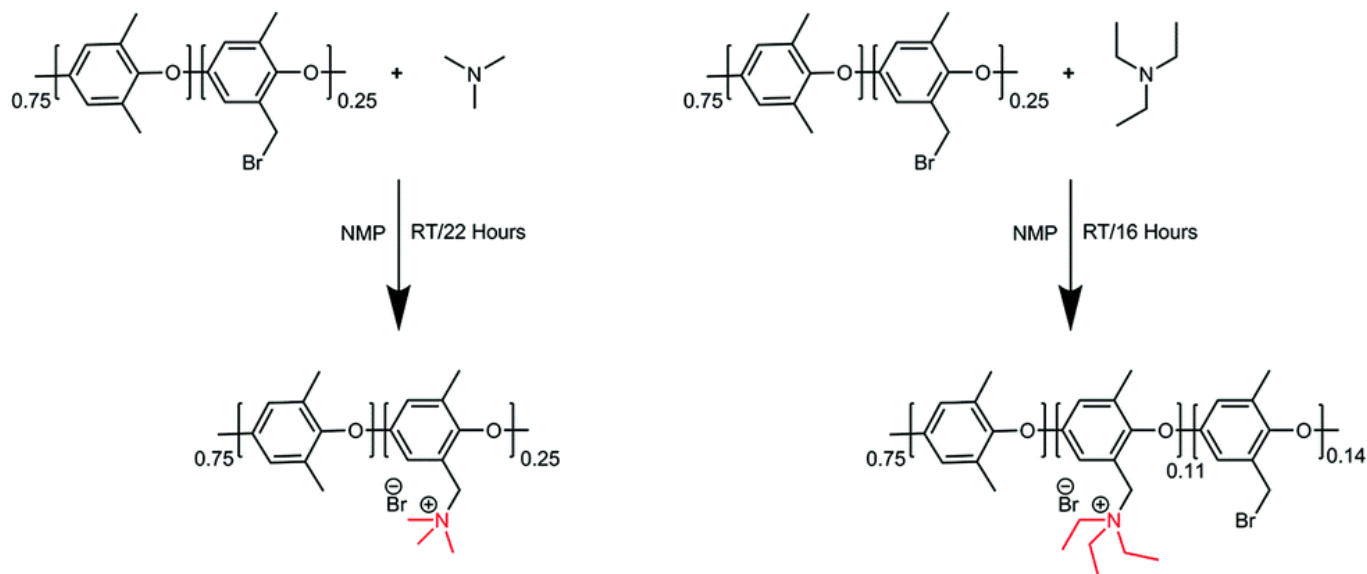
Poly(phenylene oxide) is a great polymeric candidate to be functionalized with cationic groups to serve as an anion-exchange membrane. It has good mechanical properties and high alkaline stability. In addition, PPO synthesis and substitution is relatively simple. Once a trimethylamine group is incorporated as short side chain, in fact a trimethylbenzyl ammonium (TMBA) is formed, known to be a very stable cationic group.

2. EXPERIMENTAL

Br-PPO was prepared in a round-bottom flask (250 mL), charged with chlorobenzene (100 mL). PPO polymer (12 g, ca. 100 mmol of monomer) was slowly added and stirred until completely dissolved. NBS (7.12 g, 40 mmol) and AIBN (0.5 g, 3 mmol) were added to the solution, which was heated under reflux for 3 h. The reaction mixture was cooled to room temperature and the product precipitated by pouring the mixture into a 10-fold excess of ethanol. The polymer was recovered by filtration and washed several times with ethanol followed by drying in a vacuum oven overnight at 60 °C. The polymer was re-precipitated from chloroform / ethanol for further purification. The white powder was dried under vacuum overnight to get the desired Br-PPO with a degree of bromination of 25%, according to ¹H NMR spectroscopy.

Then, trimethylamine and triethylamine were used to functionalize the Br-PPO to achieve PPO–TMA and PPO–TEA, respectively. The functionalized polymers were synthesized via the Menshutkin reaction. NMP was added to a round-bottom flask (25 mL). Br-PPO (0.5 g) was slowly added and stirred until completely dissolved. Trimethylamine in ethanol (4.2 M, 0.6 mL) was added dropwise and the solution was further stirred for 22 hours at room temperature. The dark brown-colored polymer solution was cast on a clean glass plate and dried at 60 °C for 24 h on top of a hotplate. To ensure complete solvent removal, the obtained polymer was further dried under high vacuum for 3 days, until no solvent peaks were seen by NMR. The polymer functionalized with triethylamine (TEA) was synthesized in a similar manner, using pure TEA instead of trimethylamine in ethanol. In this case, a material with partial substitution was used as the polymer with full replacement was insoluble in the test solution.

In addition to PPO-TMA and PPO-TEA, various other amines were tested including dimethylbenzylamine (DMBzA) and fumion[®] FAA-3 (PPO with non-disclosed amine).



3. RESULTS AND DISCUSSION

The stability was tested by two methods:

Method 1: Soluble ionomer treated in non-aqueous solution, with water added to adjust the water content to specific water-to-hydroxide ratio ($\lambda=0, 4, 8$). Stability tested by NMR spectroscopy.

Method 2: Membrane treated in aqueous solution of 2 M KOH at 60 °C with a weekly measurement of conductivity (OH⁻ form, in water at 25 °C).

Results with method 1:

PPO-TMA and PPO-TEA were tested for their stability in water-free solution and with a controlled amount of water (water to hydroxide ratio, lambda $\lambda=0, 4, 8$). The results are shown in Figure 1 for PPO-TMA and in Figure 2 for PPO-TEA. It can be seen that PPO-TEA shows very high degradation rate even at high water content, while PPO-TMA can be stable for more than 1000 hours. However, alkaline stability also depends on water content. In general, at very low water content the stability is limited, even for the most stable PPO-TMA.

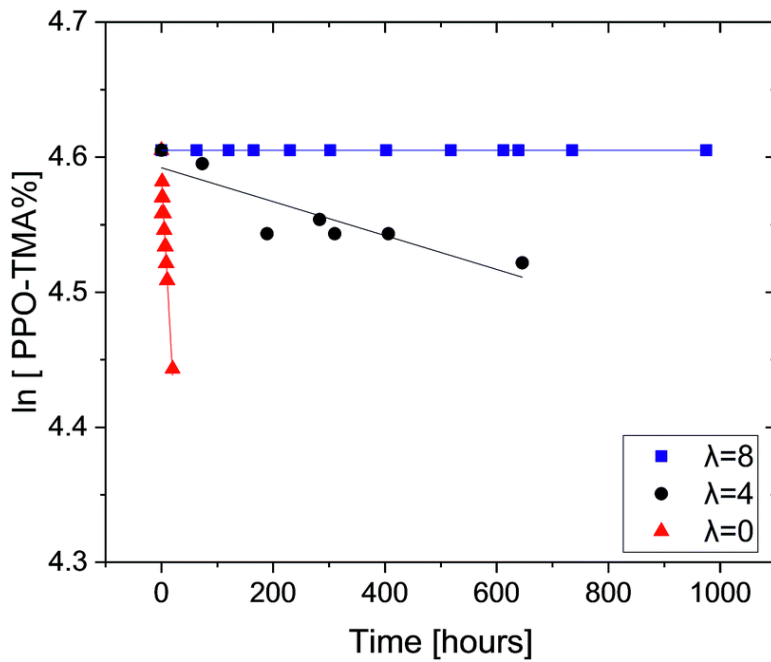


Figure 1. AEI stability of PPO-TMA in non-aqueous solution with specific water content ($\lambda = 0, 4, 8$), Y-axis represents percentage of decomposition determined by NMR.

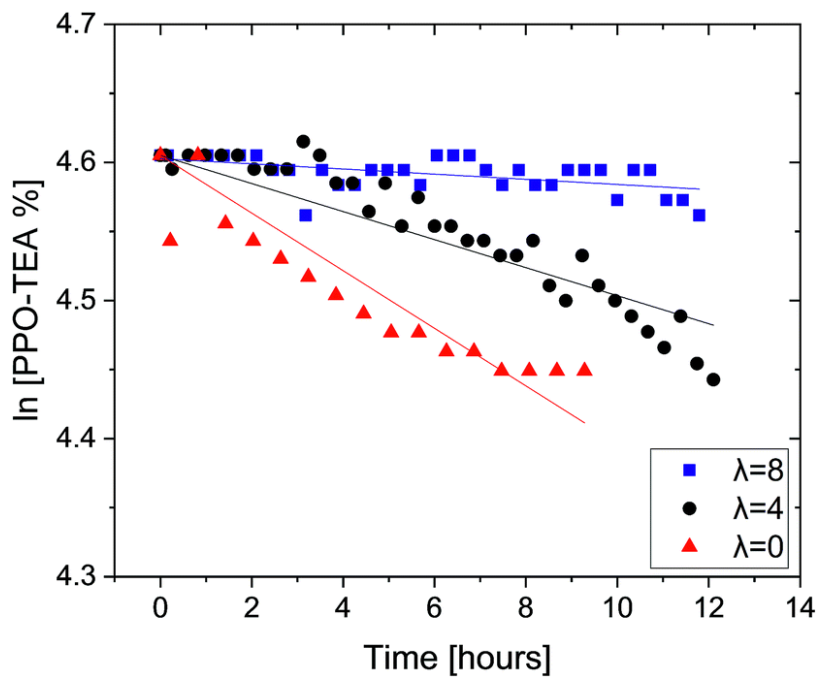


Figure 2. AEI stability of PPO-TEA in non-aqueous solution with specific water content ($\lambda = 0, 4, 8$), Y-axis represents percentage of decomposition determined by NMR.

Results with method 2:

Many PPO polymers functionalized with various amines were tested by method 2. Among them, only PPO-TMA and fumion® FAA-3 show conductivity $> 3 \text{ S/m}$ and stability $> 400 \text{ h}$, indicated by very small decrease in conductivity within more than 800 h (Figure 3). All other tested amine-functionalized PPO show lower initial conductivity and higher degradation rate (decomposition of the functional group), as shown by the strong decay in conductivity within 500 h, depicted in Figure 3 for PPO-DMBzA as an example. This also proves the high alkaline stability of the PPO-polymeric backbone, which results in combination with a suitable quaternary ammonium group (e.g. TMA) in a stable AEI and AEM.

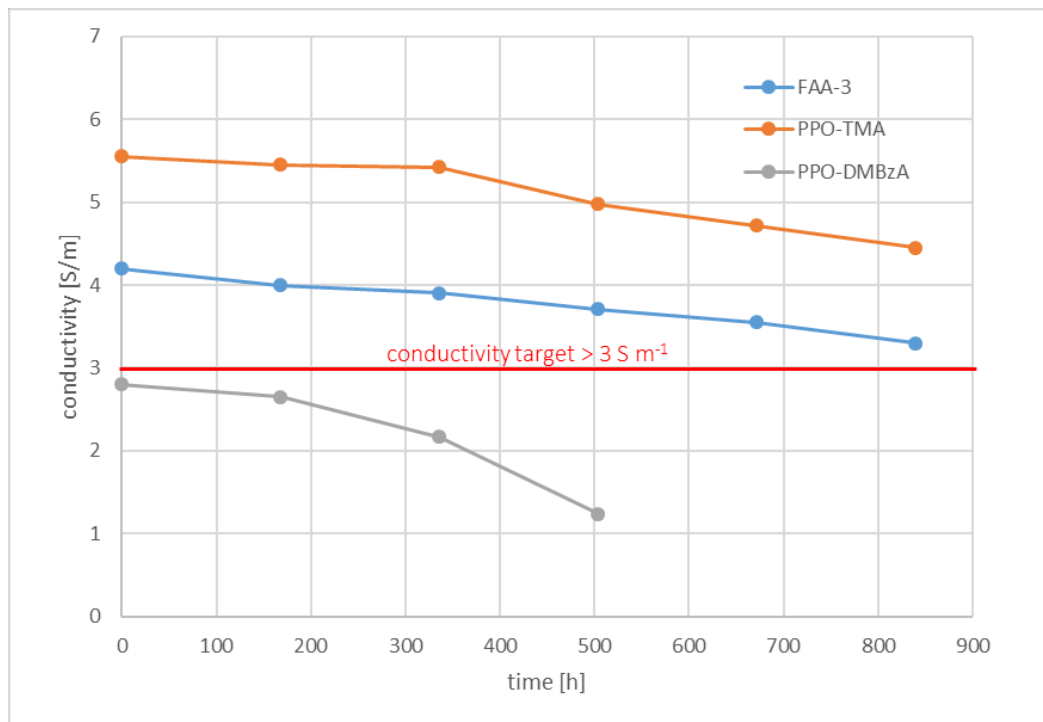


Figure 3. Conductivity during stability test by method 2: Membrane is exposed to an aqueous solution of 2 M KOH at 60 °C, the conductivity is checked weekly (in OH form in water at 25 °C).

4. CONCLUSIONS

A second generation of AEI and AEM was identified within CREATE that show sufficient conductivity and stability to be used for testing the catalysts in AEMFC and AEMEL. This second generation of AEI and AEM is based on PPO functionalized with TMA and fulfills the MS1: AEMs with alkaline stability at 60 °C > 400 h & AEI conductivity > 3 S m⁻¹ at 100% RH.

5. RECOMMENDATIONS AND FUTURE WORK

Functionalize the PPO and other backbones with other, even more stable functional groups, in particular for obtaining better stability at low water content.

6. REFERENCES

- [1] S. Willdorf-Cohen, A.N. Mondal, D.R. Dekel, C.E. Diesendruck, Chemical stability of poly(phenylene oxide)-based ionomers in anion exchange-membrane fuel cell environment, *J. Mater. Chem. A*. (2018) Advance Article.

7. APPENDIX

Acronyms

Br-PPO	brominated poly(phenylene oxide)
DMBzA	dimethylbenzylamine
PPO	poly(phenylene oxide)
TEA	triethylamine
TMA	trimethylamine
TMBA	trimethylbenzyl ammonium