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#329 Oral

## Design of High-Performance Anion-Exchange Membrane for Fuel Cells and Electrolysers

Hydrogen Uses and Applications / Other Fuel Cells: materials, components and stacks

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### Introduction

Proton-exchange membrane (PEM) fuel cells performance has known enormous progress due to decades of research in electrocatalysts, ionomers, especially perfluorinated sulfonic acid (PFSA), membranes-based ionomers and catalysts layers, as well as effective integration of these individual components to fabricate a membrane electrode assembly (MEA) [1]. The major challenges in PEM Fuel Cells to be overcome prior to widespread deployment are related to cost minimization without affecting performance and durability. The high costs are related to the need of precious metal based on Platinum (PGM (Platinum Group Metal)) as catalyst for oxygen reduction reaction (ORR) and hydrogen oxidation reduction (HOR) and PFSA membrane and ionomers. There is significant effort related to the development of non-PGM catalysts, less expensive, for PEM Fuel Cells. However, their durability is far from the targets and replacing PGM in the PEMFC catalyst layers seems to be unlikely.

Therefore, today, Anionic-Exchange Membrane Fuel Cells (AEMFCs) receive ever-increasing attention, because of their overwhelming superiority in comparison to PEM Fuel Cells: quicker electrochemical kinetics, lower catalysts cost and weaker corrosion. In comparison, the alkaline medium rendered by AEMFCs provides the potential to use non-precious-metal catalysts [2], which can facilitate commercialization.

However, the promise of AEMFCs to lead to a PGM-free and high-performance Fuel Cells still need to be realized. The development of AEMFCs is significantly hampered by a lack of high performance and highly stable alkaline exchange membranes (AEMs) and ionomers (AEIs). Both the backbones and the cations of the polymer in AEMs and AEI are prone to nucleophilic attack by hydroxide ions. This leads to reduced mechanical strength, decreased ion exchange capacity (IEC) and conductivity with time/operation of the device. Polymer backbone degradation in AEMs primary occurs via aryl ether bonds cleavage [3], motivating a recent change in research focus towards aryl-ether free backbones [4]. A more serious issue is the alkaline stability of the tethered cationic groups, generally ammonium cations. These quaternary ammoniums (QAs) are used because of their low cost and ease synthesis. Nevertheless, some degradation on alkaline conditions at 60°C can occur such as Hofmann elimination [5] or nucleophilic substitution [6].

Similar to what is observed in PEMs, the ionic conductivity of AEMs increases with increasing water content. Therefore, the development of polymeric structures that can provide a well-connected ion-conducting water channel is essential, especially at low relative humidity (RH). A successful approach to maximize the utilization of water molecules without sacrificing other physicochemical

properties is the synthesis of a well-defined hydrophilic-hydrophobic phase separated morphology through the introduction of a multiblock structure and/or a spacer between the backbone and ionic function.

Another drawback of AEMFCs consist in the imbalance in water during the system operating. Since molecules of water are consumed at the cathode and produced at the anode, the water migrate from the cathode to the anode due to electro-osmotic drag [7], the anode is flooding and cathode is drying.

### **Objectives Materials and Methods**

This work aims at developing AEI and AEM composed of poly-aryl ether-free backbone that demonstrate high alkaline stability [8], bearing stable quaternary ammonium side chain spaced from the backbone by an alkyl chain with different lengths. The objective is to study the impact of monomer structure on the polymerization reaction and the influence of copolymers structure on membranes and ionomers properties, especially on anionic conductivity, water up-take, thermo-mechanical properties and alkaline stability. The alkaline stability was evaluated ex-situ by immersing the membranes in 2M KOH at 80°C. The structure of copolymer and its evolution after degradations were assigned by FT-IR, Raman and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR. The pristine membranes and those submitted to degradation tests were characterized by thermal and thermo-mechanical measurements (TGA, DSC, DMA), ionic conductivity (impedance spectroscopy), water up-take and ion exchange capacity measurements (IEC).

The polymers from this work are synthesized through an acid catalyzed condensation (Friedel-Crafts Figure 1). It was demonstrated that the lengths of the spacer between the polymer backbone and ionic function play a significant role in the hydrophilic-hydrophobic nano-phase separation as well on the alkaline stability [9]. Therefore, monomers such as 7-bromotrifluoroheptan-2-one ( $x = 5$ , noted BrTFK5) and 6-bromotrifluorohexan-2-one ( $x = 4$ , noted BrTFK4) are first synthesized with high purity and good yield (>40%). Their structures and purity are confirmed by Infrared spectroscopy (FT-IR) and nuclear resonance ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR) analysis. These monomers are copolymerized with different aromatic commercial monomers, the resulting copolymers are then functionalized with different ammonium (Figure 2).

### **Results**

Among all the synthesized copolymers those obtained by the copolymerization of BrTFK5 with p-terphenyl give the higher molecular mass ( $M_n = 45\ 000\ \text{g/mol}$ ) and allow to obtain membrane with very good mechanical properties, low water uptake and conductivity close to the commercial reinforced membrane A15R. When the p-terphenyl is replaced by biphenyl, the water uptake and the conductivity increase, due from a site to the higher IEC and from other site to lower molecular mass that is obtained ( $M_n = 30\ 000\ \text{g/mol}$ ). The lower molecular mass affects the mechanical strength; however, it exhibits better mechanical strength than sustainion commercial membrane with very close  $\text{Cl}^-$  conductivity trough the membrane, at 95% RH and 30°C i.e. of 2.60 mS/cm and 2.88 mS/cm respectively.

### **Conclusions and Acknowledgments**

To perform membranes with good mechanical properties and different water uptake and conductivities, the p-terphenyl copolymer was modified with different quaternary ammoniums (Figure 2). The membrane obtained from polymers functionalized by methylmorpholinium and methylpyridinium show higher hydration number (Table 1), their conductivities and alkaline stability are under investigation.

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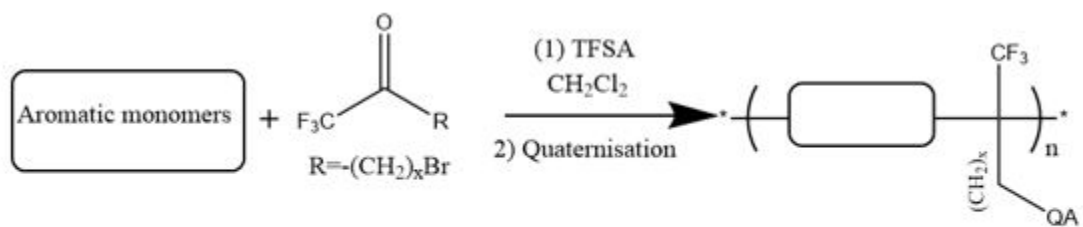


Figure 1: Acid catalyzed condensation reaction

Figure 1 : Catalyzed condensation reaction

Table 1: Properties of polymers study in this work

Aromatic Backbone	Cationic group	Thermal stability <sup>a</sup> (°C)	IEC <sup>b</sup> (mmol.g <sup>-1</sup> )	Water up-take <sup>c</sup> (%)	Hydration number
biphenyl	Trimethylammonium	260	2.64 (±0.07)	50(±3)	10.5
p-terphenyl	Trimethylammonium	245	2.16 (±0.04)	17(±1)	4.37
p-terphenyl	Methylpyridinium	230	2.07 (±0.05)	19(±2)	5.1
p-terphenyl	Methylmorpholinium	225	2.03 (±0.07)	29(±2)	7.9

<sup>a</sup> Determined by TGA measurement

<sup>b</sup> Determined using Mohr Titration and <sup>1</sup>H NMR analysis

<sup>c</sup> Determined after 48h immersed in water in Cl<sup>-</sup> form at 30°C

Table 1 : Properties of polymers study in this work

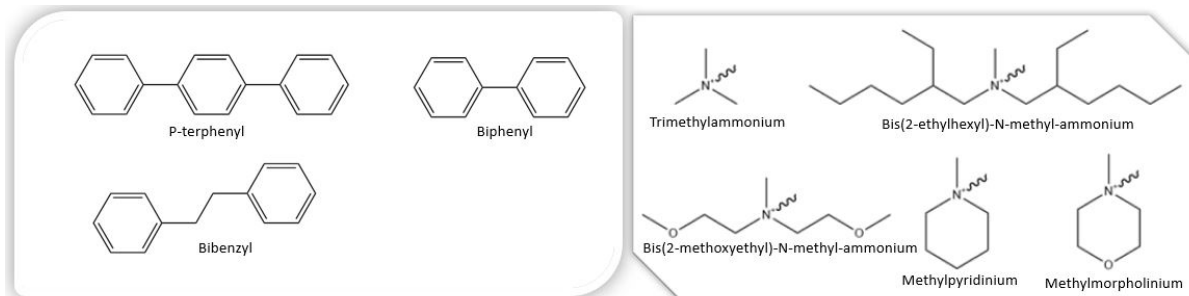


Figure 2 : Several aromatics monomers and quaternary ammonium study on this work