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MacKinnon, Sean; Mokrini, Asmae; Robitaille, Lucie

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Publisher's version / Version de l'éditeur:

Meeting Abstracts - Electrochemical Society, 1101, 593, 2011-05-01

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Strategies to Incorporate Sulfonation Resistant Aromatic Hydrophobic Segments to Facilitate Hydrophobic-Hydrophilic Domain Segregation in PEMs

Sean M. MacKinnon*, Asmae Mokriani, Lucie Robitaille
National Research Council Canada
Industrial Materials Institute

75 boul. de Mortagne, Boucherville, Québec Canada
sean.mackinnon@nrc-nrc.gc.ca

The successful development of proton exchange membranes requires the efficient segregation of a percolated protonic phase from an anhydrous hydrophobic domain providing desirable morphologies to facilitate the concentration of the aqueous protonic domain while concurrently mechanically reinforcing the membrane.^{1,2} This has been successfully demonstrated over recent years with the development of a series of design rules appropriate for formulating new proton exchange membranes. Of the series, three specific guidelines can be simultaneously employed, namely (1) block copolymers are preferred to random or alternating copolymers, (2) when choosing a hydrophobic domain chose the most hydrophobic domain possible to promote efficient sequestering of water in the hydrophilic domain and (3) the hydrophilic domain should be highly sulfonated to ensure high acid concentrations in the absorbed water phase. Therefore, the objective to deliver improved aqueous based performance under low humidity conditions; we provide various strategies to incorporate a sulfonation resistance aromatic hydrocarbon into the hydrophobic domain of block copolymers containing very high concentration of protonic conductors in the aqueous domain.

In this paper we report on the use of a unique aryl hydrocarbon based hydrophobic unit which can withstand very aggressive sulfonation conditions, such as fuming sulfuric acid at 120°C for 24 hours. This approach leads to the selective and complete sulfonation of the hydrophilic domain and encompasses the outlined guidelines resulting in a series of polymerization and sulfonation strategies. Synthetic methods will be disclosed including a classical polymerization of telechelic oligomers, followed by solution sulfonation (Method 1), an *in-situ* one pot sulfonation-polymerization (Method 2) or a sequential polymerization (Method 3) whereby a pre-sulfonated telechelic oligomer is polymerized with the unique hydrophobic monomer. The attributes of each method will be discussed through the characterization of the membrane IEC, proton conductivity, water content and *in-situ* hydrogen fuel cell performance. Where appropriate, further comparisons will be discussed to compare the various methods of membrane preparation as a result of post sulfonation of either classical unsulfonated melt-extruded membranes or solution cast block copolymers.

References

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