Preparation and Characterization of Semi-fluorinated Composite PEM with Phosphotungstic Acid Immobilized on Clays Using Melt Processing Technologies

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Title:

Preparation and Characterization of Semi-fluorinated Composite PEM with Phosphotungstic Acid Immobilized on Clays Using Melt Processing Technologies

Authors & affiliations:

A. Mokrini*[a], P.Y. Vuillaume[a], L. Robitaille[a], K. Shi[b] and S. Holdcroft[b]

[a] *Industrial Materials Institute, National Research Council Canada, 75 de Mortagne, Boucherville, Québec, Canada. J4B 6Y4*

[b] *Institute for Fuel Cell Innovation, National Research Council, 4250 Wesbrook Mall, Vancouver, B.C, Canada. V6T 1W5*

asmae.mokrini@cnrc-nrc.gc.ca

Abstract:

Melt blending is a potentially cost-effective route toward phase-segregated materials compared to recast techniques commonly used, and offers an interesting approach towards a solvent-free process for PEM materials preparation. Several melt-processing technologies, such as twin-screw extrusion, melt blowing and calendering were used to prepare advanced composite polymer blends based on fluoropolymers in this case poly(vinylidene fluoride) (PVDF) and a thermoplastic elastomer; polystyrene(ethylene-co-butylene) block copolymer (SEBS). The properties of these polymer blends are mainly determined by the processing history and the interfacial properties. Blend membranes preparation and interface modification were addressed in a previous work [1] to obtain optimized semi-fluorinated composite membranes. Functionalization of the membranes was achieved by grafting sulfonic acid groups on the styrene blocks of the elastomers. PEM membranes with thicknesses between 40 and 200 microns, presenting good mechanical properties and high ionic conductivities, were prepared for hydrogen and methanol fuel cell applications.

Figure 1 compares the polarization curves measured in a single cell fuelled with H_2/air at 70 °C, with Nafion 112 and a semi-fluorinated membrane with 70wt% PVDF, 50 microns thickness and a conductivity of 8.10^{-2} S/cm. The measured membrane showed a performance similar to that of Nafion and produced a current of ~660 mA at 0.6V.

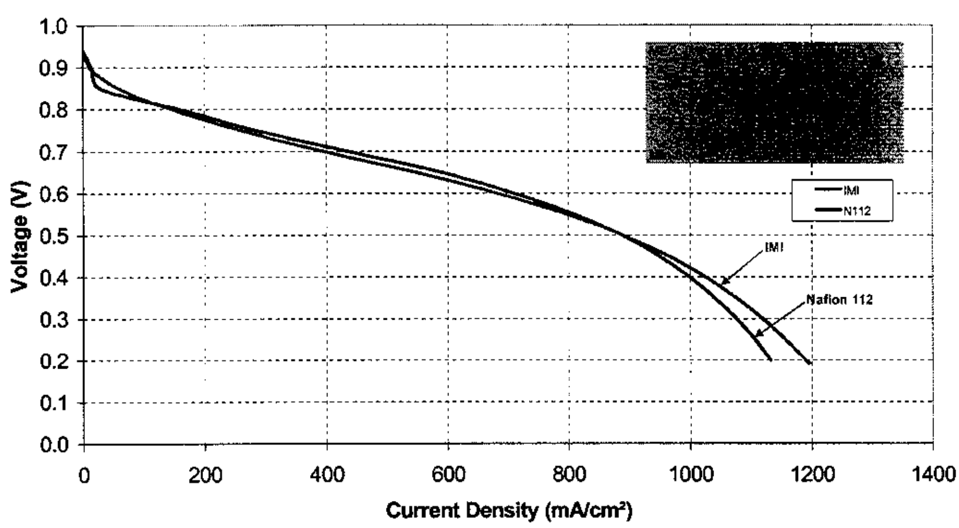

Fig.1. Cell polarization curves obtained for Nafion 112© and IMI semi-fluorinated PEM (70wt% PVDF) at 70°C with H_2/air.

In order to further improve the performance, hybrid (organic-inorganic) membranes were prepared. It has been reported that this approach results in reduced fuel permeability, increased proton conductivity and enhanced water retention characteristics of the membranes at higher temperatures and/or lower humidity conditions.

In recent studies [2], it has been demonstrated that the high proton conductivities of heteropolyacids (HPA) can be translated into impressive currents in PEMFC at room temperature with no external humidification. Unfortunately, the high solubility of the HPA additives in aqueous media has a detrimental effect on long term stability. To prevent HPA leaching during fuel cell operation, a common technique has been to support the HPA additive on commercially available metal dioxide supports such as silicon dioxide and zirconium dioxide [3]. In this work, we investigate the immobilization of 12-phosphotungstic acid (PTA), a strong Brønsted heteropolyacid (Fig. 2) with good thermal stability and high intrinsic proton activity, on a synthetic smectite clay (saponite-like), Sumecton SA (Fig 3.), a layered mineral material which possesses negatively charged layers neutralized by exchangeable Na counterions. The preparation and the characterization of HPA/clay complexes, as well as their incorporation in semi-fluorinated polymer blends based on modified SEBS and PVDF by melt extrusion will be described.

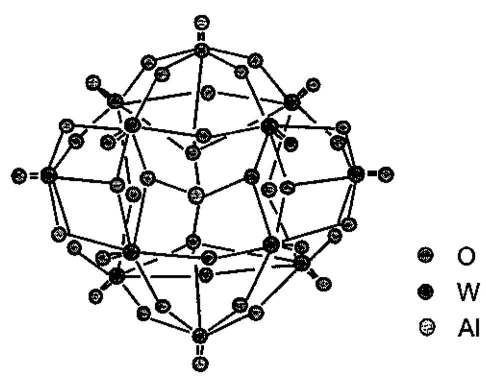

Fig.2. Schematic representation of the 12-phosphotungstic heteropolyacid Keggin structure.

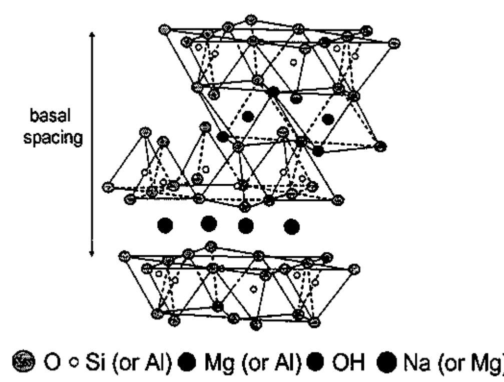

Fig. 3. Schematic representation for the Sumecton SA structure.

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