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PREPARATION OF HYBRID PROTON EXCHANGE MEMBRANES BASED ON HPA/CLAY COMPLEXES AND THERMOPLASTIC POLYMERS

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1. INTRODUCTION

Heteropolyacids (HPAs) are becoming an increasingly popular proton conducting additives in ionomer composite membranes for use under dry and/or elevated temperature conditions [1]. Several advantages result from operating a proton exchange membrane fuel cell (PEMFC) at elevated temperatures (above 100 °C), such as faster heat rejection rates, easier and more efficient water management, higher reaction rates, improved CO tolerance by the anode electrocatalyst, etc. In recent studies [2], it has been demonstrated that the high proton conductivities of HPAs can be translated into impressive currents in PEMFC at room temperature with no external humidification. Unfortunately, the extremely 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]. This strategy has been extensively employed in the heterogeneous catalysis field [4].

In this work, we investigated the immobilization of phosphotungstic acid (PTA), a strong Brønsted heteropolyacid (Fig. 1) with good thermal stability and high intrinsic proton activity, on a synthetic clay Sumecton (SSA) (Fig. 2.) 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 polystyrene(ethylene-co-butylene) block copolymer (SEBS) and PVDF by melt extrusion will be described

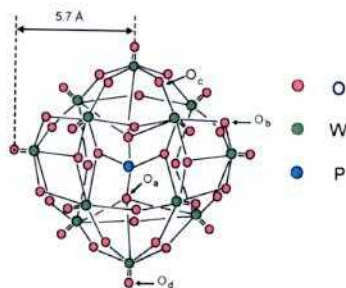


Fig. 1. Schematic representation of the Keggin unit of phosphotungstic heteropolyacids (PTA)

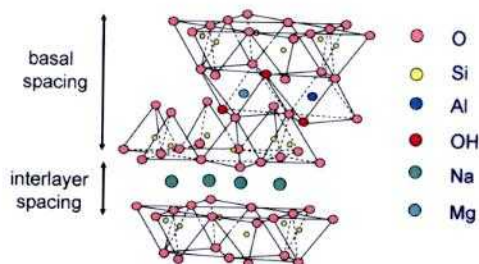


Fig. 2. Schematic representation of a Saponite-like smectite clay Sumecton (SSA)

2. EXPERIMENTAL

To prepare PTA/SSA complexes, the clay was first dispersed in water, then added to a concentrated aqueous solution of 12-phosphotungstic acid. Relatively high PTA-SSA weight ratios were used, namely 2, 3 and 5. The large amount of PTA in the mixture used was higher than the cation exchange capacity of the SSA (99.7 meq/100 g). Consequently, most Na ions are expected to be exchanged. The dispersion was sonicated at 60 °C for 1 hr and water was rotary evaporated. The obtained white powder was further dried under vacuum at 125 °C for 1h. The complex was washed by stirring vigorously two times with methanol during 30 min, filtered and dried overnight at 60 °C.

For nanocomposite preparation, a two step compounding procedure was used. In a first step, 5, 10 and 15 wt.% of the PTA/SSA complex was melt mixed in a matrix of modified SEBS using a 5cc Haake MiniLab microextruder operating at 200°C and 100 rpm under nitrogen atmosphere. In a second step, semi-fluorinated blend were compounded using a 5 cc DSM research twin-screw microcompounder at 230°C and 100 rpm under nitrogen atmosphere. Different compatibilizers have been used, since melt-processed nanocomposites require

optimized interface between the functional clay and polymer to ensure proper dispersion during the mixing process.

PTA/SSA complexes and nanocomposites were characterized by energy-dispersive X-ray spectroscopy (EDX), FTIR diffuse reflectance spectroscopy (DRIFT) and X-ray diffraction (XRD). Nanocomposite proton exchange membranes were prepared by hot-pressing. The obtained films were characterized in terms of ion exchange capacity, water uptake and conductivity.

3. RESULTS AND DISCUSSION

For PTA/SSA complex, EDX results confirm the presence of tungsten in the complex and the quasi-substitution of Na counterions when a large excess of PTA is used. EDX measurements carried out before and after methanol washing indicate that the amount of PTA immobilized onto the clay varies with the amount of PTA/SSA weight ratio used for the complex formation.

DRIFT measurements provide support that complexation occurs between SSA and PTA through electrostatic interactions, and indicate the formation of robust PTA/SSA complexes. The Keggin structure of PTA is preserved within the complexes and is thermally stable up to 450°C (Fig. 3).

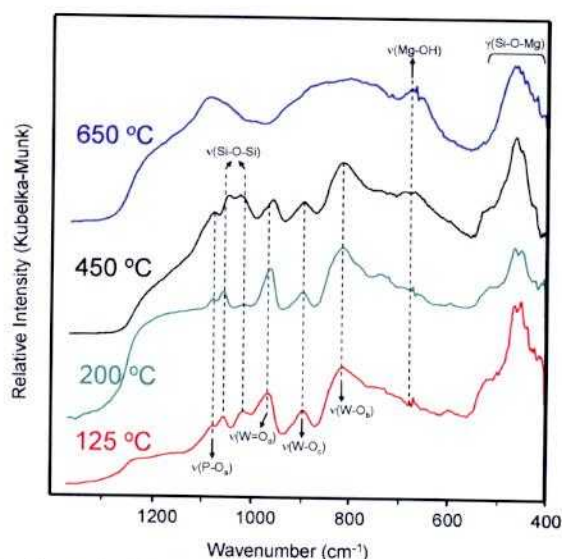


Fig 3. Fourier Transformed Diffuse Reflectance Spectroscopy (DRIFT) spectra obtained for PTA/SSA complexes at different temperatures

Melt compounding and characterization of nanocomposite PEMs based on PTA/SSA complexes will be discussed.

4. ACKNOWLEDGEMENTS

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