

Influence of Electrolyte and Electrode Composition on PEFC Performance in Sulfonated PEKK Systems

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INTRODUCTION

Sulfonated hydrocarbons offer a low cost alternative to Nafion[®] for use in polymer electrolyte fuel cells (PEFC) and direct methanol fuel cells (DMFCs). Sulfonated polyetherketoneketone (SPEKK) has been demonstrated^{1,2} as an alternate electrolyte material. The conductivity of SPEKK is strongly dependent on the degree of sulfonation, and, concomitantly, the water uptake of the membrane. By incorporating heteropolyacid (HPA) additives to SPEKK, the conductivity of the membrane at 80°C 75% relative humidity can be increased over a range of ion exchange capacities (IECs) between 1 and 2.5 meq/g. Membrane electrode assemblies (MEAs) prepared using SPEKK / HPA composite membranes yield adequate performance under these conditions. Two areas that will be addressed in this presentation are: 1. replacing the Nafion[®] based electrodes hitherto utilized with electrodes containing SPEKK and SPEKK / HPA mixtures with varying IECs as the proton conducting phase and 2. Improving the durability of the electrolyte by blending in tough, non – conducting phases such as polyether sulfone (PES) and poly vinylidene fluoride (PVDF). The former study is aimed at minimizing interfacial mismatches in the MEA while the latter is aimed at enhancing the operational lifetime of SPEKK based systems. In each case, MEAs with varying electrode and electrolyte compositions will be prepared and evaluated to yield an optimal structure.

EXPERIMENTAL

PEKK (Oxford Performance Chemicals, Enfield CT) was sulfonated using a mixture of concentrated and fuming sulfuric acid. The degree of sulfonation was controlled by controlling the reaction time. Upon precipitation into water, the resultant SPEKK strands were washed continually with deionized water until a neutral wash water pH was attained. The SPEKK was then dried and dissolved in dimethyl acetamide (DMAc) to yield a 4% by weight solution. Blends were prepared by co-dissolving an appropriate amount of non-conducting polymer (PES or PVDF) with SPEKK. Composite membranes were made by first preparing a precursor solution comprising 4% SPEKK in (DMAc), and appropriate amounts of HPA (typically phosphotungstic acid; PTA). The membranes were cast on flat glass plates by evaporating solvent at 60°C overnight, followed by vacuum drying and washing to remove traces of solvent.

Catalyst ink were prepared by dispersing Pt/C catalyst in methanol and adding an appropriate amount of either solubilized Nafion[®] or dissolved SPEKK followed by vigorous stirring at room temperature. Membrane electrode assemblies (MEAs) were prepared by applying catalyst ink onto the membrane using an airbrush followed by evaporation of solvent. The MEAs were evaluated by obtaining polarization curves at different temperatures and humidities using a fuel cell test system

(Scribner Associates, model 890B) and a flow loop (built in-house). Linear sweep voltammetry and scanning electron microscopy were utilized to study the integrity of the membrane and the membrane electrode interface after fuel cell operation.

RESULTS

The performance obtained from a MEA prepared using a 28 micron thick 1.3 IEC SPEKK membrane containing 20 wt% HPA, with a cathode Pt loading of 0.35mg/cm² and electrodes containing 30% by weight of Nafion[®] on H₂/O₂ and H₂/air at 80°C and 75% relative humidity is shown in Fig. 1. Linear sweep voltammograms (LSVs) obtained before and after operation are shown in Fig. 2. While the MEA yields good performance, the large increase in crossover current and appearance of membrane shorting after operation for 6-8 hours (evidenced by the LSVs) indicated that the lifetime of the MEA is very low. Strategies used to resolve this issue by designing composite electrolyte materials will be presented. Initial results with SPEKK – PES and SPEKK – PVDF membranes are promising, with a two - three fold increase in endurance.

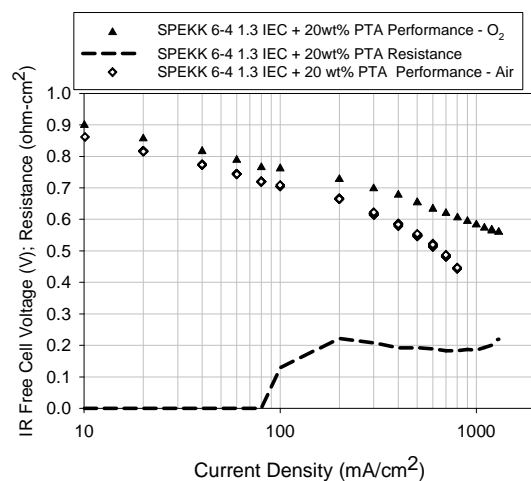


Fig. 1: Performance data at 80°C and a RH of 75%

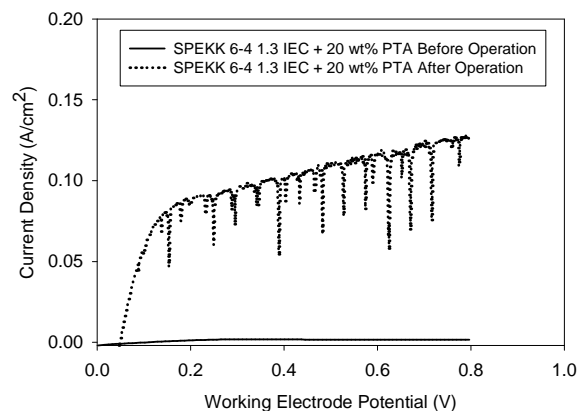


Fig. 2: Room temperature LSVs before and after operation.

REFERENCES

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