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Electrochimica Acta 53 (2007) 1372–1378
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Structural and transport effects of doping perfluorosulfonic acid polymers with the heteropoly acids, $H_3PW_{12}O_{40}$ or $H_4SiW_{12}O_{40}$

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Received 17 November 2006; received in revised form 31 May 2007; accepted 1 June 2007
Available online 24 June 2007

Abstract

A perfluorosulfonic acid (PFSA) polymer with pendant side chain $–O(CF_2)_4SO_3H$ was doped with the heteropoly acids (HPAs), $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$. Infrared spectroscopy revealed a strong interaction between the HPA and the PFSA ionomer. Modes associated with the peripheral bonds of the HPA were shifted to lower wave numbers when doped into PFSA membranes. Small-angle X-ray scattering (SAXS) measurements showed the presence of large crystallites of HPA in the membrane with *d* spacings of ca. 10 Å, close to the lattice spacing observed in bulk HPA crystals. Under wet conditions the HPA was more dispersed and constrained the size of the sulfonic acid clusters to 20 Å at a 5 wt% HPA doping level, the same as in the vacuum treated ionomer samples. Under conditions of minimum hydration the HPA decreased the E_a for the self-diffusion of water from 27 to 15 kJ mol^{-1}. The reverse trend was seen under 100% RH conditions. Proton conductivity measurements showed improved proton conductivity of the HPA doped PFSAs at a constant dew point of 80 °C for all temperatures up to 120 °C and at all relative hummidities up to 80%. The activation energy for proton conduction generally was lower than for the undoped materials at RH $\leq$80%. Significantly the E_a was 1/2 that of the undoped material at RHs of 40 and 60%. A practical proton conductivity of 113 mS cm^{-1} was observed at 100 °C and 80% RH.

Keywords: Heteropoly acid; Ionomer; Proton conduction; PFSA; PEM

1. Introduction

Proton exchange membrane (PEM) fuel cells have many attractive attributes including high operating efficiencies, power densities and system versatility. However, widespread commercial introduction of the PEM fuel cell is still hampered by issues such as durability, cost, the need for membrane hydration and the low operating temperatures (e.g., 80 °C) achievable for this promising device. Higher temperature operation would deliver the benefits of relaxed fuel purity requirements and simpler heat exchange systems. The properties of current state of the art perfluorosulfonic acid (PFSA) ionomers, which are necessary to achieve a reasonable level of oxidative stability, drive the need for the low operating temperature and supplemental hydration of the PEM fuel cell [1,2]. This is because sulfonic acid derived proton transport only delivers sufficient proton conductivity when the membrane is fully hydrated, which becomes less practical as the operating temperature exceeds 100 °C. One strategy for preserving hydration at high temperature involves cell pressurization, but the energy cost of pressurization diminishes the overall system efficiency. Thus, there is a need for a low cost, durable PEM that will operate at temperatures >100 °C on dry inlet gases without pressurization [3].

One approach to the improvement of PFSA ionomers is to form composites with inorganic particles [4]. We and others

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doi:10.1016/j.electacta.2007.06.047

have shown that the proton conductivity and durability of the PFSA ionomers and fuel cell performance of membrane electrode assemblies (MEA) can be improved by the addition of heteropoly acids (HPAs) [5–11]. The HPAs, a subset of the polyoxometallates, are an extensive class of structurally well-defined inorganic metal oxide clusters that contain a central heteroatom [12]. These superacidic inorganic oxides are synthetically versatile, exhibit redox catalyst activity, and have very high proton conductivity in the solid state. The HPAs are known to have strong interactions with the sulfonic acid groups of ionomers [13] into which they are doped, resulting in morphological changes, as compared with the undoped ionomers. Additionally, the HPAs may interact with catalyst layers in an MEA. In order to shed light on these complex interactions we report here the results of studies on the structural features of an HPA doped PFSA ionomer, using two different HPAs.

The HPAs chosen were the commercially available 12-phosphotungstic acid, $H_3PW_{12}O_{40}$ (HPW) and 12-silicotungstic acid, $H_4SiW_{12}O_{40}$ (HSiW). We have shown that doping HSiW into PFSA membranes improves fuel cell performance under hot and dry operating conditions and can reduce the rate of F^- release from the fuel cell membranes by 50% [6]. HPW is not stable under the harsh fuel cell operating conditions of our previous study, but nevertheless is used here as it gave interesting data that is used to further interpret the complicated interactions between superacidic HPA and the PFSA ionomer. These two HPAs, HPW and HSiW, have the well known and commonly encountered Keggin structure. Keggin HPAs have the general formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ in which a central heteroatom X (where X = B, Zn, Si, Ge, As, P, etc.) is surrounded tetrahedrally by four groups of three MO octahedra (where M is commonly W or Mo) (Fig. 1). The PFSA ionomer chosen in this study is the polymer available from 3M, which is similar to the well known Nafion® material, in that it has a PTFE backbone, but differs by having a shorter side chain $–O–(CF_2)_4SO_3H$. In this study a polymer with an equivalent weight (EW) of 1000 was used (ion exchange capacity of 1.0 meq g^{-1}). In general, experimental conditions where chosen that avoided contact between liquid water and the HPA doped membranes, to avoid HPA leaching. A preliminary account of this work, concerning only the interaction of HPW with the 3M ionomer, has been published [14].

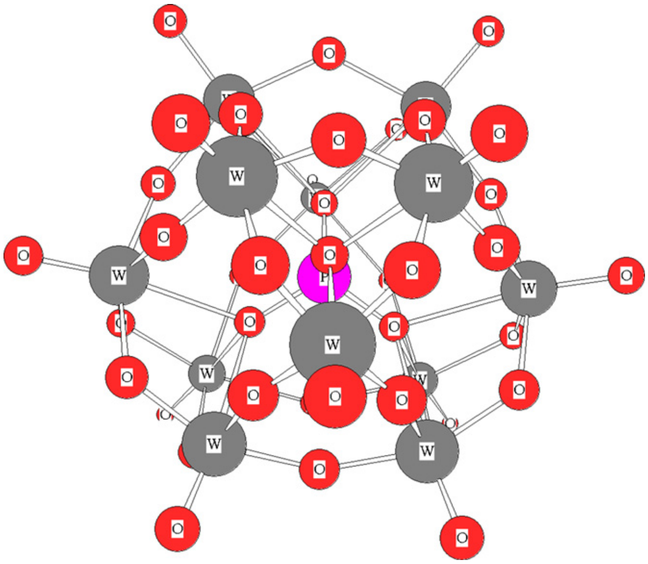

Fig. 1. Ball and stick representation of a typical Keggin structure $[PW_{12}O_{40}]^{3-}$.

2. Experimental

12-Silicotungstic acid (HSiW) and 12-phosphotungstic acid (HPW) (Aldrich) were dried in an oven at 110 °C overnight prior to use. A casting dispersion of the 1000 EW 3M ionomer in a solvent of mixed alcohols and water was obtained from 3M. An appropriate amount of the dried HPA was dissolved in the casting dispersion, which was in turn cast on a glass plate, to a uniform dried thickness of 40 μm, using a multigap applicator yielding membrane films.

Attenuated total reflectance (ATR) infrared spectra were taken at room temperature using a Specac GS11000 ATR attachment in a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a liquid N_2 cooled MCT detector. Samples were measured both equilibrated at ambient conditions, and after vacuum drying.

Small-angle X-ray scattering (SAXS) measurements were performed with a Kratky slit-collimation SAXS system [15] attached to a Rigaku rotating Cu anode X-ray generator utilizing the Cu Kα X-rays (wavelength, $\lambda = 0.154$ nm) selected by a graphite monochromator. An angular range of scattering angles (2θ) from 0.1° to 8°, corresponding to a momentum transfer $[q = (4\pi/\lambda)\sin\theta \approx (2\pi/\lambda)2\theta]$ range from 0.1 to 6.2 nm^{-1} was used. This range allows detection of features in the size range from about 1 to 20 nm. The SAXS intensity was converted to absolute units (cross-section per unit volume = cm^{-1}) using the measured sample thickness and following literature procedures [16]. SAXS patterns of the membranes were recorded under dry helium atmosphere, vacuum and wet conditions. Vacuum condition spectra were taken both before and after the sample was hydrated. Wet condition experiments were performed by sealing the samples with two drops of liquid water in thin polyethylene bags. Background scattering intensity of the empty plastic bag was measured separately and subtracted from the samples. No free-flowing liquid water was visible in the bags at the time of the measurements, and the bags and membranes looked dry afterwards.

Pulsed-field gradient spin-echo (PGSE) NMR proton diffusion measurements were obtained on a Chemagnetics Infinity 400 NMR spectrometer operating at 400 MHz for ^1H using a 5 mm Doty Scientific Inc. #20–40 z-gradient pulsed-field gradient NMR probe. The stimulated-echo pulse sequence was used [17]. The temperature of the sample was calibrated using a type-T thermocouple inserted into a sample of alumina in the NMR probe. To maintain a steady hydration state of the membrane, samples were sealed with a torch under vacuum in an NMR tube either under conditions of minimum hydration or with enough liquid water at the bottom of the tube to provide 100% RH; a gap of 27 mm between the bottom of the NMR tube and the lower end of the membrane sample permitted the sample to be placed