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A Novel Proton-Conducting Membrane

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A family of novel proton-conducting membranes (PCMs) has been prepared from low-cost, thermally stable materials and has been preliminarily characterized. These PCMs consist of electronic nonconductive nanosize ceramic powder, polymer binder, and an acid. They have the appearance of plastic, good mechanical properties, nanosize pores (typically smaller then 1.5-3 nm) filled with the acid, and room-temperature conductivity of up to 0.21 S cm^{-1} (twice that of Nafion). Their thickness ranges from 40 to 400 μm. These PCMs are considered to be excellent and low-cost candidates for many electrochemical applications, including fuel cells, electrolyzers, supercapacitors, sensors, and batteries.

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Proton-conducting membranes (PCMs) are found in many electrochemical applications, including fuel cells, electrolyzers, supercapacitors, sensors, and batteries. Nafion is the most commonly used membrane in fuel cells operating at near-room temperature (up to 100°C). Nafion, a solid polymer electrolyte, has two major disadvantages, it is very expensive and it dries during fuel cell operation as a result of water dragging by the proton.[1,2]

In recent years, there has been an intensive effort to develop a low-cost solid polymer electrolyte to replace Nafion, with significant progress being made.[3,4] Room-temperature, proton-conducting materials are reviewed in Ref. 5. None of them has a room-temperature conductivity higher then 0.18 S cm^{-1}.

The goal of this work is to develop and characterize a low-cost, highly conductive PCM. It basically consists of nanosize ceramic powder with good acid adsorption capacity, a polymer binder, and an acid absorbed, by the nanosize ceramic powder, in nanosize pores.

Experimental

The PCMs were formed by a solvent casting technique with the use of K control coater (R K Print, Coat Instruments). A viscous paste was formed by mixing nanosize ceramic powder with Kynar poly(vinylidene difluoride)(PVDF) 2801-00 (ELF Autochem) and a solvent mixture, typically cyclopentanone and propylene carbonate (PC). This paste was poured into the coater to form a wet film. Upon drying, a flexible film was obtained. The film was washed several times with double-distilled water to remove the residual organic solvents. Following this wash, the film was doped by immersion in the desired acid for 3 h. This doping was done either at room temperature or at 90-100°C. Using this procedure we prepared PCMs with the following nanosize powders: amorphous fumed 150 nm particle size silicon dioxide, 99.8% (Alfa Aesar, Johnson Matthey), micropolish 50 nm alumina (Buehler), 21 nm particle size Degussa titanium dioxide P25, 99.5%, and TiO_2/SiO_2 mixed powder. The thickness of the PCM ranged from 40 to 200 μm. Thicker films (400 μm) were formed by casting the paste on a Teflon tray. The volume fraction of the ceramic powder was between 0.5 and 15%. The ionic conductivity of the PCM was measured at room temperature (25 ± 3°C) with the use of a 1 cm^2 spring-loaded stainless steel (SS) disks cell and a Solatron model SF 1260 AC analyzer (four-electrode measurement). The conductivity test cell is described in Ref. 6. The pore-size distribution of dry (with no acid) PCMs was carried out with the use of a Quantachrome NOVA 2200 surface area analyzer. Scanning electron microscopy (SEM) photographs were taken with the use of a JEOL JSM-3600 scanning electron microscope.

Results and Discussion

In this paper we present preliminary results regarding a narrow range of PCM composition. PCMs which consist of 5-10 vol % ceramic powder have good mechanical and acid absorption properties. They have the appearance of plastics and can be bent 180°, with no damage to the film. Qualitatively, mechanical strength follows the order: $Al_2O_3 \approx TiO_2 > SiO_2/TiO_2 > SiO_2$. SEM images reveal no cracks or holes larger then 0.1 μm (Fig. 1). The Barrett-Joyner-Halerda (BJH) method for measuring pore-size distribution (PSD) (Fig. 2) for a dry PCM which consists of 10 vol % SiO_2 and 15 vol % PVDF shows that the dominant pore volume is due to pores smaller than 2 nm. In other PCM samples (depending on composition) a small peak in the PSD curve was found at about 1.5-2.5 nm. For comparison, Nafion has a wide spectrum of pore sizes ranging from 1 to 100 nm with an average value of about 2 nm.[7] We believe that

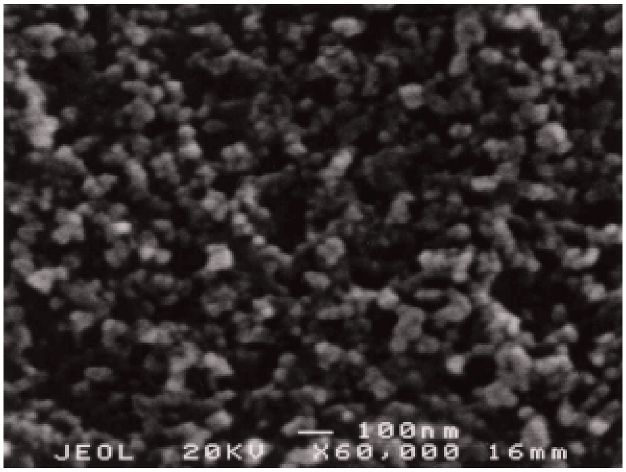

Figure 1. SEM photograph of gold plated, 75% porous dry PCM, consisting of 10% (v/v) SiO_2, 15% (v/v) PVDF.

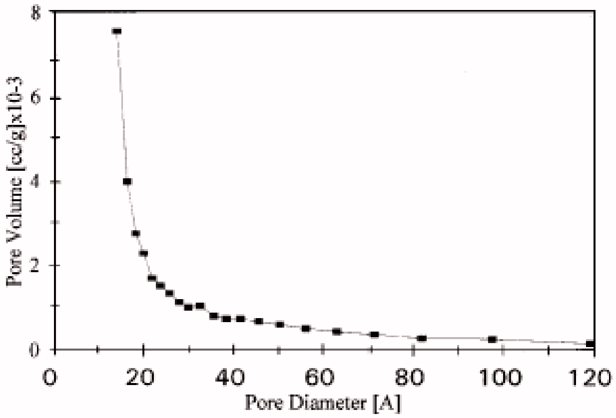

Figure 2. Pore size distribution (BJH method) for dry PCM (for composition see Fig. 1).

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Table I. PCM Room-temperature[a] conductivity.

PCM composition (vol)	Dipping temperature (°C)	Acid (vol. ratio)	Conductivity (S cm^{-1})
8% SiO_2 (12% PVDF)	25 ± 2	Pure H_2SO_4	0.04
8% SIO_2 (12% PVDF)	25±2	1:3 H_2SO_4:H_2O	0.18
10% AL_2O_3	100	1:3 H_2SO_4:H_2O	0.07
10% TIO_2	100	1:3 H_2SO_4:H_2O	0.19
10% SIO_2	100	1:3 H_2SO_4:H_2O	0.21
10% SIO_2	25 ± 2	1:1 H_3PO_4:H_2O	0.06
10% SIO_2	25 ± 2	1:2 CF_3SO_3H:H_2O	0.14
10% SIO_2	25 ± 2	1:3 CF_3SO_3H:H_2O	0.12
10% SIO_2	25 ± 2	1:1.5 CF_3SO_3H:H_2O	0.13
10% SIO_2	25 ± 2	1:1 CF_3SO_3H:H_2O	0.11
10% SIO_2	90	1:2 CF_3SO_3H:H_2O	0.18
Nafion[b]			0.10

[a] 25±2°C
[b] Ref. 2, at 30°C.

the pores of the PCM are small enough to prevent H_2 or O_2 gas bubbles from crossing the PCM, when it is used in a fuel cell. For conductivity measurement, PCMs which consist of 10 vol % ceramic powder and 15 vol % PVDF were doped by several acids at room temperature, 90, and 100°C. The results (taken at room temperature) are summarized in Table I. Several aqueous solutions of the superacid (SA) CF_3SO_3H were doped at room temperature in the PCM. This acid is considered[8-10] a promising candidate for fuel-cell applications. Changing the SA/water volume ratio from 1:1 to 1:3 has little effect on the PCM conductivity which has a maximum at the 1:2 ratio. Doping the acid at 90°C (for 3 h) caused a 20% conductivity rise (up to 0.18 S cm^{-1}). The conductivity of the same PCM which was doped (at 100°C) by H_2SO_4:H_2O 1:3 (volume ratio) is 0.21 S cm^{-1}. For comparison the maximum conductivity of Nafion is 0.10 S cm^{-1} (Table I). The conductivities of H_2SO_4:H_2O 1:3 and SA:H_2O 1:2 solutions were measured at 25°C (with a platinized-platinum electrode cell). The values obtained were 0.734 and 0.624 S cm^{-1}, respectively. The labyrinth factor (λ) of the PCM can be calculated by comparing the conductivity of the PCM with that of the appropriate acid solution (λ = solution conductivity/PCM conductivity). Values of λ are 3.5 for both the SA-doped PCM and the H_2SO_4-doped PCM.

A 0.3 F/cm^2 double-layer capacitor was assembled with the use of porous carbon electrodes. Two porous carbon electrodes were hot pressed on both sides of the PCM. The equivalent series resistance of a carbon-PCM double-layer capacitor was 0.05 Ω cm^2. The results will be published elsewhere.[11] It should be mentioned that other aqueous electrolytes can be doped into this membrane to form thin ionic-conductor films.

Summary

A family of 40-400 μm thick novel PCMs was developed with the use of low-cost, thermally stable materials. They exhibited room-temperature conductivity higher than any other PCM and double that of Nafion. They are believed to be excellent candidates for many applications, including fuel cells, electrolyzers, supercapacitors, sensors, and batteries.

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