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Blend membranes from poly(2,5-benzimidazole) and poly(styrene sulfonic acid) as proton-conducting polymer electrolytes for fuel cells

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Abstract Polymer electrolyte membranes were fabricated by blending of poly(2,5-benzimidazole) (ABPBI) and poly(styrene sulfonic acid) (PSSA) at several molar ratios with respect to repeating units. Fourier transform infrared spectroscopy was used to elucidate inter-polymer interactions. Surface morphology was studied through scanning electron microscope. Thermal properties of the membranes were investigated by thermogravimetric analysis and differential scanning calorimetry. The spectroscopic measurements and water uptake (WU) studies indicate a complexation between ABPBI and PSSA where the swelling behavior of membranes increases with the PSSA content. Proton conductivities of the anhydrous and humidified samples were measured using impedance spectroscopy. Proton conductivity of ABPBI:PSSA bend with (1:4) molar ratio was detected as around 10^{-3} S/cm at higher temperatures under anhydrous conditions. On the other hand, the membrane ABPBI:PSSA (1:2) showed the proton conductivity of 0.02 S/cm (ambient temperature, RH = 50%) which is at least five-order of magnitude higher than the anhydrous material.

Introduction

Polymer electrolyte membranes (PEM) are promising materials that can be utilized in electrochemical systems such as fuel cells, electrochromic windows as well as super capacitors [1–8]. During the last decade, there has been an increasing research on the development of proton-conducting polymer electrolytes in order to sustain adequate proton conductivity at low humidity [9–12]. One of the alternative proton-conducting membranes that are considered for working at low humidity or under anhydrous conditions is acid–base complex [10, 13–15]. Homogeneous systems can be produced by strong acid/polymer interaction and proton conduction may occur over the Bronsted acid–base pairs [9]. Although high proton conductivity can only be achieved at higher acid compositions, dopant exclusion is an important drawback during prolonged usage in fuel cells. Therefore, blending high-molecular-weight acidic and basic polymers could be a solution for the leaching out problem due to 'polysalt' formation.

Polybenzimidazole (PBI) is a commercially available polymer and it needs impregnation of phosphoric acid or other acid dopants in order to reach high proton conductivity [16, 17]. In addition, poly(2,5-benzimidazole) (ABPBI) is another benzimidazole polymer which has more simpler structure and can be synthesized from commercially available monomer [8, 18].

Previously, we studied on polymer blends of ABPBI and poly(vinylphosphonic acid) (PVPA). The spectroscopic measurements and WU studies suggested the complexation between ABPBI and PVPA that inhibited dopant exclusion up on swelling in excess water. The proton conductivity of the blends was lower in the anhydrous state such as 1.8×10^{-6} S/cm at 150 °C for ABPBI:PVPA with 1:2 molar ratio. However, it increased to 0.004 S/cm for ABPBI:PVPA membrane with 1:4 molar ratio at 20 °C (relative humidity = 50%) [19].

Poly(styrene sulfonic acid) (PSSA) is a fundamental material in polyelectrolyte chemistry and it can be

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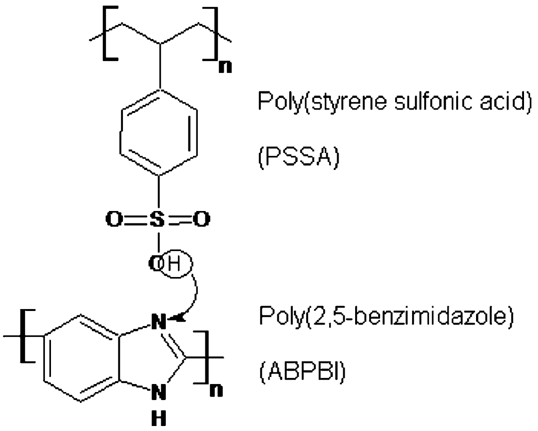

Fig. 1 Chemical structures and interaction of ABPBI and PSSA

produced by direct sulfonation of commercially available polystyrene [3]. From a practical point of view, humidified PSSA demonstrate high proton conductivity and can be used as a PEM in fuel cells for a short period [20]. Nevertheless, high proton conducting PEM that have better thermal, mechanical as well as chemical stability can be prepared by blending PSSA with ABPBI.

In this study, the synthesis and characterization of novel blends based on ABPBI and PSSA (Fig. 1) polymer blends are discussed. The blends were prepared by film casting from ABPBI and PSSA solutions. The synthesis of polymers, molecular interactions within the membranes, surface morphologies, thermal and WU properties of the membranes were investigated. Effects of ABPBI and PSSA contents on proton conductivity of final product were discussed.

Experimental

Materials

Polystyrene ($M_n = 140000$ g/mol) was supplied by Aldrich (Munich, Germany). Phosphorus pentoxide and cyclohexane were purchased from Merck (Darmstadt, Germany) as reagent grade. 3,4-Diaminobenzoic acid (DABA) (97%) was obtained from Alfa Aesar (Karlsruhe, Germany). Sulfuric acid (98%), polyphosphoric acid (PPA) (~85%), and trifluoroacetic acid (TFA) were obtained from Merck. All the chemicals were used as-received.

Synthesis of PSSA and ABPBI

PSSA was synthesized through a similar procedure described in the literature [21]. Polystyrene was added into sulfuric acid/phosphorous pentoxide solution. The solution was kept at 40 °C for 1 h after stirring 30 min. Then, crushed ice was added to the solution until PSSA completely precipitated out as a pale yellowish and sticky bulk. Finally, the precipitate was collected and dialyzed against water.

ABPBI was synthesized by condensation of DABA in PPA as reported in the literature [22].

Preparation of the membranes

ABPBI (1.5 g) was dissolved in 60 mL of TFA by stirring at 80 °C for 12 h. Then water was added dropwise into ABPBI/TFA mixture until a uniform solution was obtained. After that ABPBI/TFA and PSSA/water solutions were admixed in order to get ABPBI–PSSA membranes in 2:1, 1:1, 1:2, and 1:4 ABPBI–PSSA molar ratios with respect to monomer repeating units, i.e., molar ratio of benzimidazole to styrene sulfonic acid. Solutions were cast onto the Teflon plates and dried at 70 °C under normal atmospheric pressure. Then, the films were dried further under vacuum at 80 °C, and they stored in a glove box. Film thicknesses were ranging between 150 and 250 μm.

Characterizations

Fourier transform infrared (FT-IR) spectroscopy spectra of dry ABPBI–PSSA membranes were investigated over a wavelength range from 550 to 4000 cm^{-1} with attenuated total reflection module by using Perkin Elmer FT-IR spectrum BX. Prior to FT-IR measurements, the samples were dried under vacuum at 80 °C.

Morphology of polymer films was investigated by using a scanning electron microscope (SEM) with Philips XL30S-FEG. The samples used for SEM analysis were coated with Au layer in order to avoid from charging of samples under the electron beam.

Thermal stabilities of the polymer films were determined by using thermogravimetric analysis (TGA) with Mettler-Toledo TG-50. The analysis was carried out heating the samples from room temperature to 700 °C at a rate of 10 °C/min.

Differential scanning calorimetry (DSC) measurements were performed by using Mettler-Toledo DSC 30 under nitrogen atmosphere heating from 0 to 250 °C at a rate of 10 °C/min. Glass transition temperatures of the membranes were evaluated from the second heating curves.

WU measurements were determined at room temperature by the weight difference between the fully humidified membranes and dried membranes. The dried membranes (W_{dry}) were weighed, and then wetted until the weight remained constant. Wet or saturated weights of the membranes (W_{wet}) were measured quickly after wiping out any remaining surface water with a paper. The WU was calculated according to the formula (1):

$$\text{Water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \qquad (1)$$

Proton conductivity measurements of membranes were performed by using Novocontrol impedance analyzer over a frequency range from 0.1 Hz to 3 MHz with Novocontrol cryosystem-controlled temperature (applicable between −100 and 250 °C). Membranes were placed between two platinum blocking electrodes. Variation of temperatures was from 20 to 180 °C with 10 °C intervals for anhydrous membranes and from 20 to 100 °C for humidified membranes.

Results and discussion

FT-IR spectroscopy

The molecular structures of the ABPBI–PSSA blend membranes were characterized by FT-IR spectroscopy. FT-IR spectra of ABPBI–PSSA-based polymer blends are shown in Fig. 2. The broad absorption band near 1200 cm^{-1} is attributed to asymmetric O=S=O stretching vibration of $-SO_3^-$ groups [23]. Vibration of phenyl ring attached a sulfonic group leads to the peaks at 1005 cm^{-1} [24]. Deprotonation of the sulfonic acid peak causes broadening of this peak as well as overlapping with phenyl ring attached sulfonic anion peak at 1125 cm^{-1} [23]. Bands at 1628, 1580, and 1460 cm^{-1} could be attributed to the C=N and C=C stretching [25]. Bands detected at 3375 cm^{-1} are assigned to non-hydrogen bonded N–H stretching whose intensity increases with the PSSA content. The shoulder near 3100 cm^{-1} is the result of N^+–H stretching that indicates the protonation of ABPBI, and broad peak between 3000 and 2500 cm^{-1} is due to hydrogen bonding network formation [22].

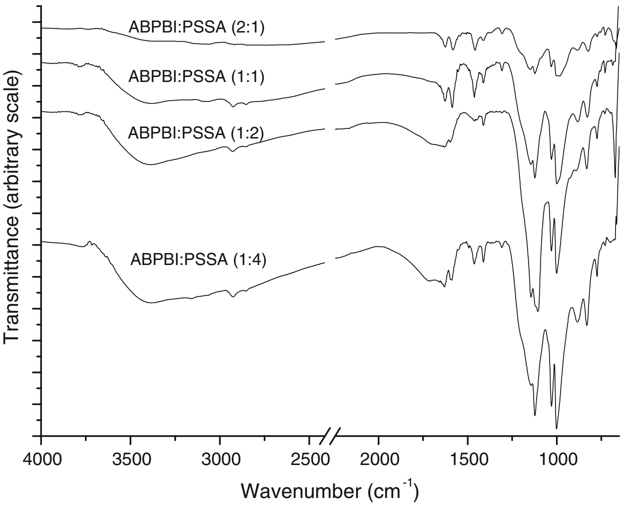

Fig. 2 FT-IR spectra of ABPBI:PSSA blend membranes

Morphology

The surface morphology of ABPBI/PSSA blend membranes was studied by SEM as shown in Fig. 3a–c. Due to strong acid–base interactions between sulfonic acid group of PSSA and imidazole units of ABPBI, complexation occurred immediately, whereas no phase separation

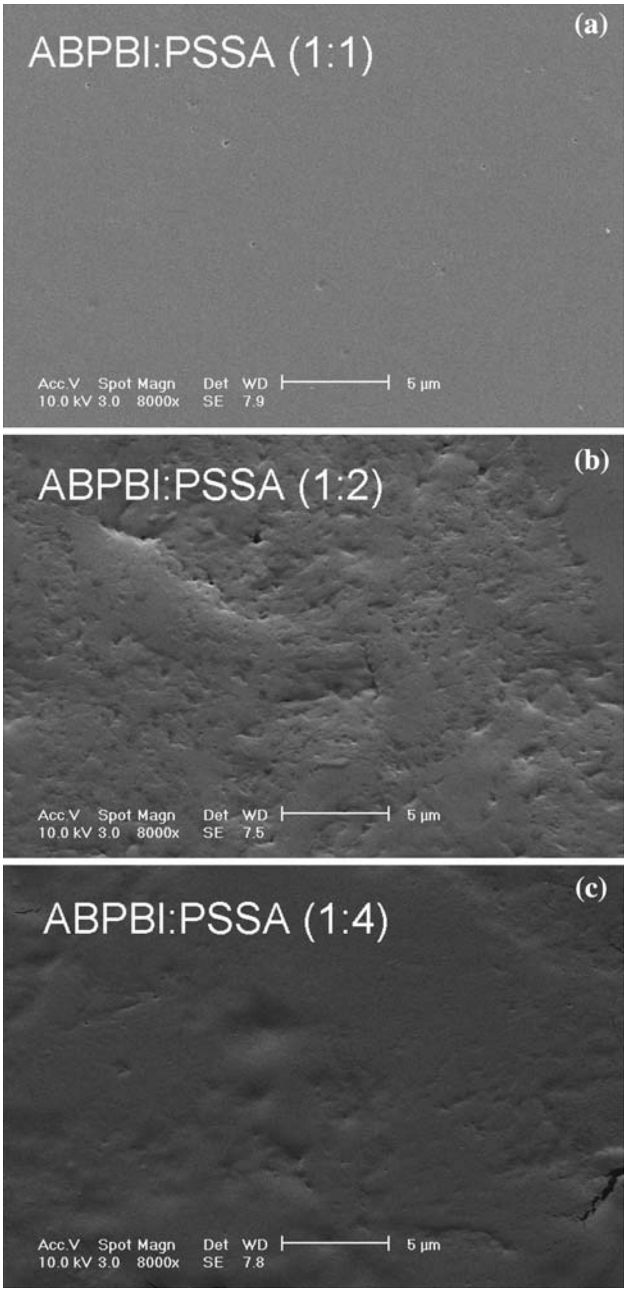

Fig. 3 The SEM micrograph for the surface of ABPBI:PSSA blend membrane with **a** 1:1 molar ratio, **b** 1:2 molar ratio, **c** 1:4 molar ratio

observed during solvent evaporation. In fact, extensive phase separation was prevented by strong ionic interactions and homogeneous films were produced. Figure 3 shows a very good compatibility between ABPBI and PSSA.

Thermal analysis

Thermal properties of ABPBI/PSSA blend membranes were studied by TGA and DSC. In a previous study, decomposition of poly(4-styrene sulfonate) was studied through TGA [26]. It was reported that the first slight weight change that occurs from 100 to 280 °C was attributed to absorbed water [26]. The second weight loss, which was observed over the temperature interval 300–400 °C, was due to degradation of the polymer [26]. In this study, a similar degradation pathway for all the ABPBI/PSSA blend membranes was observed where the first weight change up to 150 °C was due to absorbed humidity in these hygroscopic materials (Fig. 4). Then the ABPBI:PSSA membranes with 1:2 and 1:4 begin to decompose above 160 °C. On the other hand, ABPBI:PSSA blend with 2:1 starts to degrade at about 250 °C and has better stability. As can be seen from Fig. 4, thermal stability of the membranes increases with increasing ABPBI content. Materials also have long-term thermal stabilities within the operating temperature range.

The DSC thermograms were obtained by heating–cooling cycles from 25 to 200 °C, and T_g values of the blends were evaluated from the second heating curves. T_g of pristine PS is nearly 108 °C. The glass transition temperature of the blends increased after blending with ABPBI, which are determined as 153, 178, and 180 °C for ABPBI:PSSA blends with 2:1, 1:1, and 1:2 molar ratios, respectively. The increase in the glass transition temperatures could be attributed to the restriction of PSSA polymer segmental motions that may result from the ionic complexation [23].

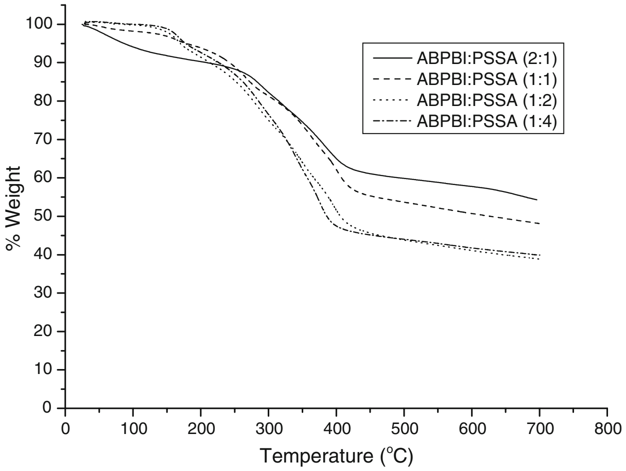

Fig. 4 TG thermograms of ABPBI:PSSA blend membranes at a heating rate of 10 °C/min

Water uptake

WU of the membranes is a major parameter influencing proton conductivity, mechanical property, and stability. WU of the ABPBI:PSSA and ABPBI samples are shown in Fig. 5. As can be seen, WU with increasing PSSA content is due to swelling of PSSA in the blend. The sample with 1:2 composition has the highest WU value (375%). Although the mechanical strength of the swelled membrane decreased to a certain extent, almost no PSSA dissolved in the solution. The result showed that complexation of ABPBI with PSSA prevented the loss of guest polymer (PSSA) to the solution.

Proton conductivity

Frequency-dependent proton conductivity of the samples was measured by AC impedance method over 0.1 Hz to 3 MHz frequency range at various temperatures, under dry nitrogen flow. AC conductivities ($\sigma_{ac}(\omega)$) were measured using Eq. 2:

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega)\omega\varepsilon_o \tag{2}$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_o is the vacuum permittivity ($\varepsilon_o = 8.852 \times 10^{-14}$ F/cm), and ε'' is the imaginary part of complex dielectric permittivity (ε^*).

The samples were dried under vacuum at 80 °C for 24 h. AC conductivity, σ_{ac}, versus frequency curves are shown in Fig. 6a for anhydrous ABPBI:PSSA blend with 1:4 molar ratio. Additionally, Fig. 6b shows AC conductivity for the 50% humidified ABPBI:PSSA blend with 1:2 molar ratio.

The curves for all the samples involve the frequency dependent and independent areas which are typical in ion

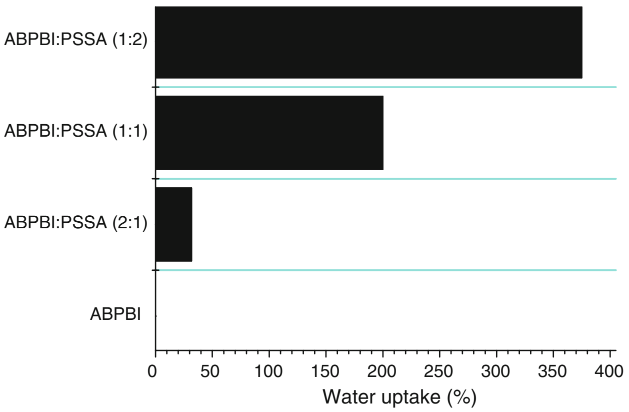

Fig. 5 WU of the blend membranes

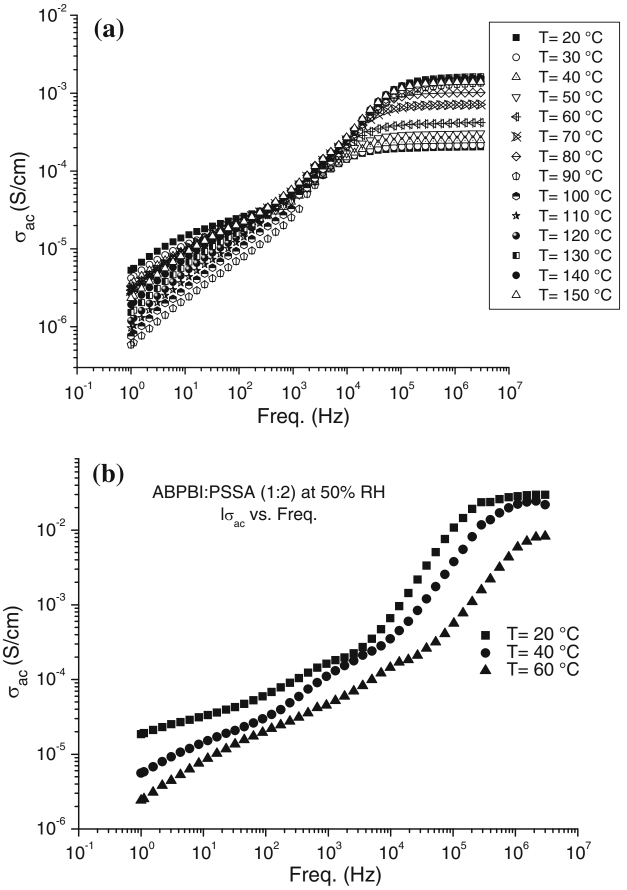

Fig. 6 **a** AC conductivity versus frequency of ABPBI:PSSA (1:4) blend membrane at several temperatures. **b** AC conductivity versus frequency of 50% relatively humidified ABPBI:PSSA (1:2) blend membrane at several temperatures

conducting polymers. At lower frequencies, an increase in conductivity up to a certain level is due to electrode polarization. Then a frequency-independent region over two to three decades was observed at higher frequencies. The DC conductivity, σ_{dc}, of the samples was derived from those plateau regions by linear fitting.

The temperature dependence of proton conductivities for anhydrous ABPBI:PSSA blends is shown in Fig. 7. As a matter of fact, the conductivity of the ABPBI:PSSA system depends on the composition, temperature as well as the RH. The proton conductivity of the samples mainly increases with increasing temperature. The sample with 1:4 molar ratio has conductivities at around 1.0×10^{-3} S/cm at high temperatures. The effect of relative humidity on conductivity was studied on (1:2) blend composition with 50% RH. For the anhydrous state of the sample, the highest conductivity of the sample detected as 1.4×10^{-6} S/cm at 160 °C. On the other hand, the proton conductivity of the sample increases with increasing humidity. The highest conductivity was achieved as around 0.02 S/cm at ambient temperature with 50% relative humidity. For the humidified samples, the conductivity gradually decreases due to the loss of absorbed humidity above 100 °C. The optimum composition as an anhydrous polymer electrolyte is the membrane with 1:4 molar ratio. The amount of PSSA in the blend samples played an effective role on the proton conductivity. The proton conductivities of the ABPBI:PSSA PEM increase with increasing PSSA content.

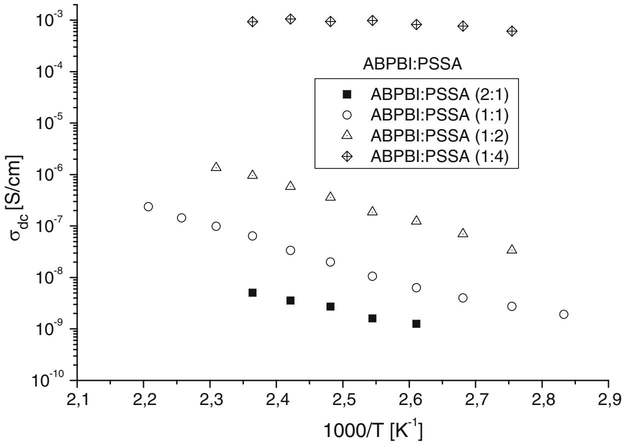

Fig. 7 The DC conductivity versus reciprocal temperature for the ABPBI:PSSA blend membranes

Actually, the conduction of the proton can occur through the transition of proton from protonated guest molecules to a non-protonated neighbor host molecule [27–29]. As was reported in the literature, anhydrous polymer systems facilitate the formation of protonic defects and provide strongly labile proton donor and acceptor functions. In addition, acidic molecules such as sulfonic acid could also act as proton donors and acceptors [30]. Protonated and non-protonated nitrogen in heterocyclic group of ABPBI and sulfonate group of PSSA can act as donors and acceptors in proton transfer reactions. Therefore, benzimidazole groups of ABPBI and sulfonate groups of PSSA act as proton charge carriers. Considering the FT-IR spectra of polymer blend composition as well as conductivity data, Grotthuss mechanisms (structural diffusion) cause a pathway for the total proton diffusion (see Fig. 1).

Conclusions

PEM were successfully produced from the blends of ABPBI and PSSA by solution casting. Protonation of the membrane has been confirmed by FT-IR study. Formation of homogeneous polymer blends was seen from the SEM and DSC pictures. TGA showed that the onset in the decomposition temperatures of the membranes changes from approximately 160 to 255 °C. WU as well as the proton conductivity of the samples increased with increasing PSSA content. The proton conductivity for the anhydrous membranes, ABPBI:PSSA blend with 1:4 molar ratio, was measured as around 10^{-3} S/cm at high temperatures. After humidification, the sample ABPBI:PSSA (1:2) depicted proton conductivity of 0.02 S/cm at ambient temperature (RH = 50%). The swelling experiment suggested the complexation between ABPBI and PSSA that inhibited dopant exclusion up on swelling in excess water. As a conclusion, ABPBI/PSSA blend membranes can form homogeneous free-standing thin films which have thermomechanical stability and illustrate sufficient proton conductivities under low humidity conditions to be used in PEM-based fuel cells.

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