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More sustainable electricity generation in hot and dry fuel cells with a novel hybrid membrane of Nafion/nano-silica/hydroxyl ionic liquid

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ABSTRACT

A new hybrid proton exchange membrane (PEM) has been prepared from hydroxyl functionalized imidazolium ionic liquid (IL-OH), Nafion and nano-SiO₂. The IL-OH, with a hydroxyl group that acts as both a proton acceptor and donor, forms strong hydrogen bonds with both Nafion and nano-SiO₂, resulting in an effective hydrogen bond network in the ternary membrane. Such an anhydrous hydrogen-bond network, which is unknown previously, endows the PEMs with higher proton conductivity, greater thermal stability and surprisingly a more robust mechanical performance than PEMs consisting of conventional ionic liquids. The resulting PEMs have a tensile strength that is more than twice as strong as recast Nafion and an anhydrous ionic conductivity of $\sim 55 \text{ mS cm}^{-1}$ at temperatures above 160 °C, with a proton transfer number of ~ 0.9 . A laboratory assembled H₂-O₂ fuel cell employing this new PEM delivered a power density of 340 and 420 mW cm⁻² at 160 and 180 °C, respectively.

1. Introduction

Fossil energy sources including oil, coal and natural gas form the foundation of our modern civilization. Unfortunately, fossil energy sources are unsustainable, and the fast increase in fossil energy consumption in recent years has resulted in a steady growth of carbon dioxide concentration in the atmosphere [1]. Clean and renewable energy sources have therefore attracted a large number of research and commercial investments in the past few decades to be converted to electricity and then combined to the traditional grid for power supply. On the other hand, most renewable energy sources such as wind and sunlight are intermittent, and their exploitation at large scales requests new technologies for energy storage and conversion. Polymer electrolyte membrane fuel cells (PEMFCs) have long been regarded as one of the most promising devices for clean electricity generation from fuels, in both stationary and mobile applications [2]. The major fuels for PEMFCs are hydrogen and small molecular alcohols, *e.g.* methanol and ethanol. In line with the trend of utilisation of renewable energy sources, hydrogen can be produced by biomethanol reforming or

water electrolysis utilising solar or wind electricity. Therefore, hydrogen is effectively an ideal clean energy carrier for the storage of renewable energy sources and then converted to electricity through fuel cells [2,3].

Currently, most of PEMFCs rely on the Nafion electrolyte in the form of a thin membrane which needs water for proton conduction. These PEMFCs can work at low temperatures but not at temperatures above 90 °C when the Nafion membrane becomes dehydrated and no longer conduct protons effectively. The Nafion fuel cells are the most mature PEMFCs. They can deliver high power density and have long working life, but need noble Pt catalyst to overcome the slow kinetics of electrode reactions and for anti-acid corrosion. Alkaline PEMFCs are being developed for the hope of replacing the Pt by some non-precious metal catalysts, but the alkaline devices suffer from degradation and carbonation in air [4]. The other main problems of the low temperature PEMFCs include CO poisoning of the electrode catalysts, and the complexity of water and heat managements. It has been theoretically and experimentally demonstrated that PEMFCs operating at intermediate temperatures (150 ~ 300 °C) are instrumental in overcoming these obstacles of low temperature PEMFCs [5-10].

Developing intermediate-temperature fuel cells (FCs) relies largely on the availability and effectiveness of anhydrous polymer electrolyte membranes (PEMs) that are stable at temperatures above 150 °C. Potential candidates include inorganic acids that possess intrinsic high proton conductivities at 140 °C and above [11-21]. H₃PO₄ doped polybenzimidazole and a number of other polymer membranes are promising for intermediate-temperature PEMFCs due to their high conductivity and considerable mechanical strength [12-15]. Single H₂-O₂ cells comprised of these H₃PO₄ doped polymer membranes are capable of delivering power densities of 100 ~ 600 mW cm⁻² at 160 ~ 200 °C [12-15]. Despite these promising initial results, ongoing long-term tests of stacks of such FCs revealed leakage and dehydration of the H₃PO₄ doped membranes, resulting in fast degradation of the FC performance [16-18]. Solid acids that exhibit high proton conductivity (1 ~

10 mS cm⁻¹) above their super-protonic phase transition temperatures (for example, CsHSO₄, 140 °C and CsH₂PO₄, 230 °C) were tested for FCs as well [19,20]. Unfortunately, in addition to undergoing noticeable decomposition and/or redox reactions, solid acids seem to be ill suited for forming membranes in FCs [19-21].

Alternatively, the proton conduction in Nafion and other sulfonated polymers can be sustained at temperatures above 150 °C by blending these polymers with non-volatile, thermally stable ionic liquids (ILs) that were reported to have anhydrous ionic conductivities exceeding 10⁻² S cm⁻¹ [22-40]. However, up until now, the validation of sulfonated polymer/IL PEMs in H₂-O₂ FCs has been disappointing. The assembled FCs either failed at the beginning or performed poorly [27-34]. These were ascribed to, in most cases, the poor mechanical strength of the sulfonated polymer/IL blend or composite. As reported, mixing conventional ILs with a polymer, particularly at high concentrations to achieve sufficiently high conductivity, usually deteriorates the mechanical strength of the polymer membrane significantly, and the resultant PEMs were often too weak to endure the FC operations [27, 29, 35-40]. On the other hand, the proton transfer numbers (t_H) of these PEMs could be too low. Considering the fact that ILs are intrinsically conductive, the question is whether the conductivity of a composite membrane of sulfonated polymer and IL is due to proton transfer or the intrinsic conductivity of the ILs [19]. The reported t_H values of sulfonated polymer/IL membrane were about 0.5~0.6, much lower than that of the water-swollen Nafion ($t_H = 1$) [26, 27]. Such a low proton transfer number could lead to serious mass transfer polarization in the FCs, particularly when discharging at high current densities.

In this work, we propose to “humidify” the Nafion with a non-volatile, thermally stable (up to 300 °C) hydroxyl functionalized imidazolium ionic liquid (IL-OH) so that proton conduction can still be effective at intermediate temperatures where Nafion itself alone would not work because of the lost of water. In addition, we have investigated the effect of doping the Nafion/IL-OH membrane with nano-SiO₂. Our original purpose was to increase the proton transfer number of the Nafion/IL membrane by forming an anhydrous hydrogen bond network. In the case of water-

humidified Nafion, the high proton conductivity is well attributed to the rapid proton hopping along the hydrogen-bond chains formed between water molecules [41, 42]. However, no previous report has investigated if IL-OH, which can be both the proton acceptor and donor as water molecules, can mimic the role of water to facilitate fast proton transfer in Nafion at intermediate temperatures. Indeed, we will show evidences supporting the formation of a hydrogen-bond network in the Nafion/IL-OH membrane. Moreover, we will demonstrate that the presence of both IL-OH and a hydrophilic nano-SiO₂ additive in Nafion can lead to a synergistic enhancement on the hydrogen-bonding interactions. As expected, our strategy has resulted in high anhydrous proton conductivity with a t_H value close to 1 at temperatures above 150 °C. Further and surprisingly, the anhydrous hydrogen-bond network also endows the Nafion/nano-SiO₂/IL-OH membrane with a significantly greater mechanical strength than those PEMs containing a conventional IL. These improvements eventually lead to new high-performance anhydrous PEMs that can help the FC to work much better than FCs assembled from previously reported polymer/IL membranes under dry working conditions.

2. Experimental Section

Chemicals. The ionic liquids, 1-(3-hydroxypropyl)-3-methylimidazolium tetrafluoroborate (C₃OHmimBF₄, denoted as IL-OH hereinafter) and 1-(butyl)-3-methylimidazolium tetrafluoroborate (BmimBF₄), were synthesized according to previously reported procedures [43, 44]. Nanometer SiO₂ (~ 10 nm in particle sizes, Hangzhou Jubang Chemical Co.) was used as received. The 5 wt.% solution of Nafion ionomer (Dupont Co.) was dried into a powder.

Membrane preparation. The PEMs were prepared using the solution casting method. Typically, 0.3 g Nafion powder and different amounts of IL and nano-SiO₂ were dissolved into 6 g N,N-dimethylformamide (DMF) at 60 °C. After continuously stirring for about 2 h, the solution was casted onto a glass plate allowing for solvent evaporation, subsequently dried at 80 °C in a vacuum oven overnight, and then at 140 °C for 2 h. The thickness of the resulting membrane depended on the total amount of the solution. The membranes are denoted as Nafion/IL-OH(x)/SiO₂(y), in which

x and y indicate weight percentages of the IL-OH and SiO₂, respectively. Similarly, the BmimBF₄ membranes are denoted as Nafion/IL(x)/SiO₂(y). The membranes were kept in a vacuum oven at 160 °C for about 3 days before testing.

Characterization. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Avatar E.S.P.360 spectrometer at room temperature. To avoid the influence of absorbed water from air, the samples were tested immediately after being taken out from the vacuum oven. The thickness of the membrane sample was controlled to be ~ 40 μm for a suitable light transmittance. Liquid samples were measured by applying a thin layer coated on the KBr pellet (13 mm in diameter, 2 mm in thickness). Thermogravimetric analysis (TGA) of the samples were carried out using TGA Q500 V20.2 Build 27 in the temperature range from 120 to 600 °C at a heating rate of 10 °C min⁻¹ under a nitrogen flow of 20 mL min⁻¹. Before the temperature scan, the samples were preheated at 120 °C for 60 min. The strength and strain correlation of the membranes (5 mm × 50 mm stripes) were measured by a universal testing machine (CMT 6503, SANS Test machine Co. Ltd., China) at ambient temperature.

Electrochemical tests: The ionic conductivities of the membranes were measured by AC impedance with the sample (1*1 cm²) sandwiched between two silver sheets.

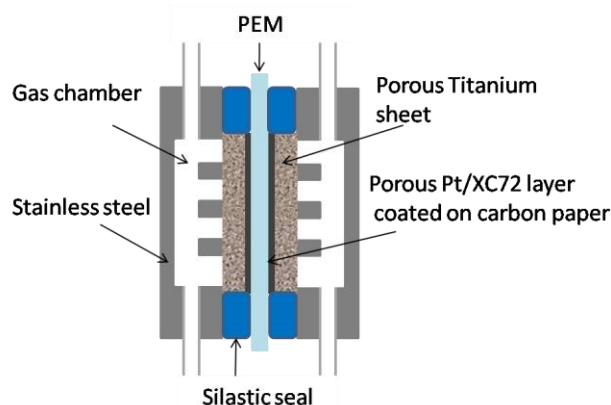


Fig.1. Schematic of the structure and components of the designed electrochemical devices for the hydrogen pump and the H₂-O₂ fuel cell tests.

For the electrochemical cell with gas reactions, the membrane (~100 μm in thickness and 1.15 cm² in area) was sandwiched by two porous carbon-supported platinum electrodes (the apparent Pt

load normalised against the electrode area was 3 mg-Pt cm^{-2}), with each side exposed to a gas chamber through a porous titanium sheet (Fig. 1). This cell can serve as an electrochemical hydrogen pump (EHP) for t_H measurements when both gas chambers are filled with H_2 gas. For FC tests, both dry H_2 and O_2 gases were fed at 1 atmosphere and a flow rate of 120 mL min^{-1} . For polarization curve measurement, the cell voltage was collected after the system became stable (in about 30s) at a given current density.

All electrochemical tests were carried out on the Autolab potentiostat (PGSTAT 128N) in a glove box filled with argon and integrated with a program-controlled furnace. The temperature was kept stable for 2 h before testing.

3. Results and discussion

3.1. Hydrogen bonding interactions in the Nafion/IL-OH/SiO₂ hybrid membranes

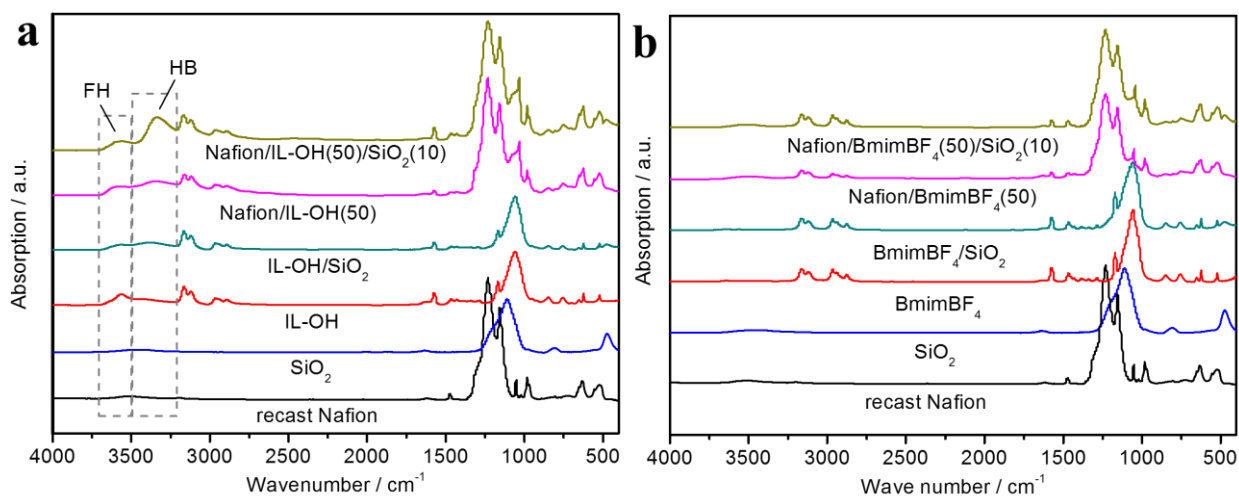


Fig. 1. FTIR spectra of different samples with varying compositions of Nafion, ionic liquid and SiO_2 as indicated. (a) Nafion/IL-OH/SiO₂. (b) Nafion/BmimBF₄/SiO₂. FH and HB refer to the stretching vibrations of free hydroxyls and hydrogen-bonds, respectively.

FTIR was used to examine the hydrogen-bond interactions in different Nafion/IL-OH/SiO₂ ternary membranes [45]. Typical FTIR spectra are shown in Fig. 2a, where the intensity of the strongest absorption peak of each sample had been normalized by reference to the respective absorption peak in Nafion/IL-OH(50)/SiO₂(10). For example, in the case of recast Nafion, the

strongest absorption peak locates at ca. 1230 cm^{-1} . Thus, after normalization, the absorption peaks at ca. 1230 cm^{-1} of both the recast Nafion and Nafion/IL-OH(50)/SiO₂(10) membranes were the same in intensity. With the exception of the IR absorption between $3200 \sim 3700\text{ cm}^{-1}$, the FTIR spectrum of the ternary membranes between 4000 and 400 cm^{-1} featured mostly a superposition of the respective spectra of IL-OH, Nafion and SiO₂.

There are basically two absorption peaks between $3200 \sim 3700\text{ cm}^{-1}$. The peak centered at ca. 3570 cm^{-1} corresponds to the stretching vibration of free hydroxyls (FHs), and the other at ca. 3400 cm^{-1} can be assigned to the stretching vibration of hydrogen bonds. Hydrogen bonds may have formed between the -C-OH group of IL-OH, the -S-OH of sulfonic acid group of Nafion, and the -Si-O or -Si-OH group of nano-SiO₂. The influence of absorbed water in the sample, if any, should be negligible considering the absence of the absorption peak at ca. 1630 cm^{-1} (bending vibration of the -OH group in water) [46,47]. The hydrogen bond peak cannot be attributed to the N atoms on the imidazole ring or the tetrafluoroborate ions of IL-OH, because when IL-OH was replaced by a non-hydroxyl IL, e.g. BmimBF₄, no such absorption was observed (Fig. 2b). These results are strong evidences for our assertion that IL-OH plays a curical role in the formation of anhydrous hydrogen bonds in the binary or ternary membrane.

The portion of the FTIR spectra between $3200 \sim 3700\text{ cm}^{-1}$ in Fig. 2a is then enlarged in Fig. 3a in order to investigate the spectra in greater detail. Pure IL-OH shows two characteristic absorption bands at 3570 and 3420 cm^{-1} that arise from the free hydroxyls and the intermolecular hydrogen bonds, respectively [45]. The spectra of dry Nafion present absorption bands corresponding to free hydroxyls and hydrogen bonds as well [48], but the absorptions are much weaker than those of IL-OH. The FTIR spectra of nano-SiO₂ is composed of a weak and broad absorption peak centered at 3430 cm^{-1} , which can be ascribed to hydroxyl groups bonded on the silica surface [49]. With the exception of Nafion/nano-SiO₂, the binary samples (Nafion/IL-OH and IL-OH/SiO₂) show strong IR absorption peaks that correspond to hydrogen bonds.

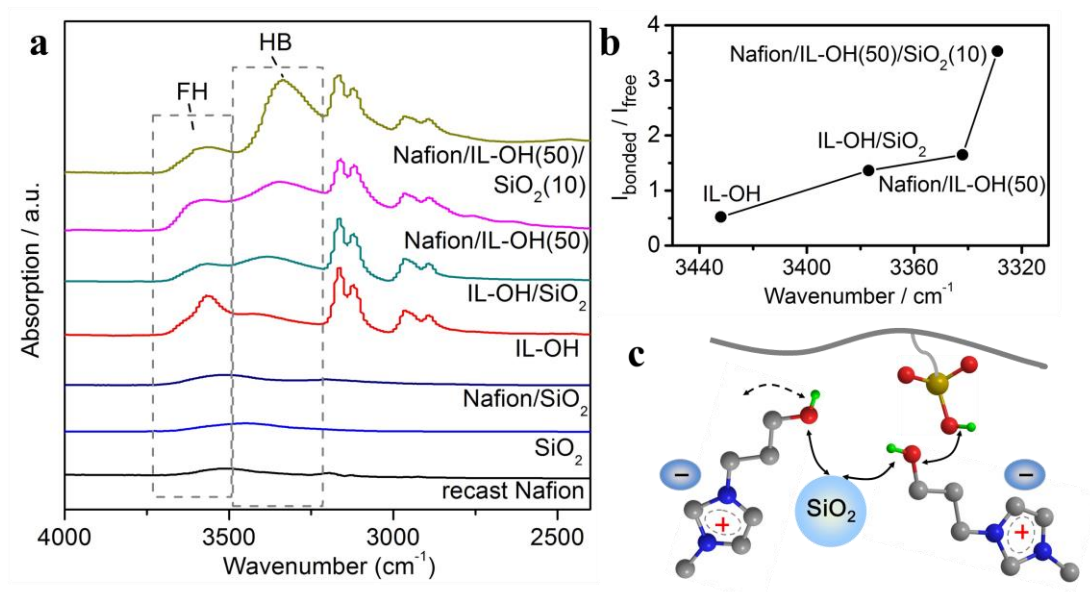


Fig. 3. (a) The enlarged view of FTIR absorptions of the free hydroxyls (FH) and hydrogen-bonds (HB) in Fig. 1a. (b) The peak intensity ratio of the HB (I_{HB}) to FH (I_{FH}) against the peak position of the HB in (a). (c) A schematic illustration of the hydrogen-bonding interactions in the ternary membranes.

Apparently, the stronger is the hydrogen bonding interaction, the larger is the IR absorption peak of the hydrogen bonds, and the more red shift is the hydrogen bond absorption band [45]. To investigate the hydrogen bonding interactions in different membranes, Fig. 3b plots the peak intensity ratio of the hydrogen bond absorption to the respective free hydroxyl absorption against the peak position of the hydrogen bond. Pure IL-OH showed a ratio of about 0.5, which increased to about 1.5 upon mixing with Nafion or SiO₂ alone, and then sharply increased to about 3.5 in the Nafion/IL-OH (50)/SiO₂ (10) ternary membrane. These observations, along with the red shift of the absorption peak from about 3430 to 3330 cm^{-1} , suggest that strong hydrogen bonds have formed between most of the -OH groups in the ternary membranes [45], leading to a highly interconnected hydrogen-bond network in the membrane. Nafion and SiO₂ that display weak hydrogen bonding interactions may be cross-linked by IL-OH through hydrogen bonds as schematically illustrated in Fig. 3c.

3.2. Mechanical and thermal stabilities

The anhydrous hydrogen-bond network has led to an unexpected enhancement in the mechanical performance of the PEMs. The strength and strain of different membranes with and without a hydrogen-bond network were tested and are compared in Fig. 5. The recast Nafion has a tensile strength of ~ 9 MPa [35, 50, 51]. The influence of conventional ILs on the mechanical performance of Nafion and other sulfonated polymers were previously reported. It has been generally observed that the higher the IL content in the sulfonated polymer/IL composite, the higher the anhydrous ionic conductivity of the PEM. However, incorporating ILs at high concentrations usually resulted in poor mechanical performance, and the tensile strengths of the reported sulfonated polymer/IL membranes with considerable conductivities were merely about 10 MPa or lower [26, 29, 35-40].

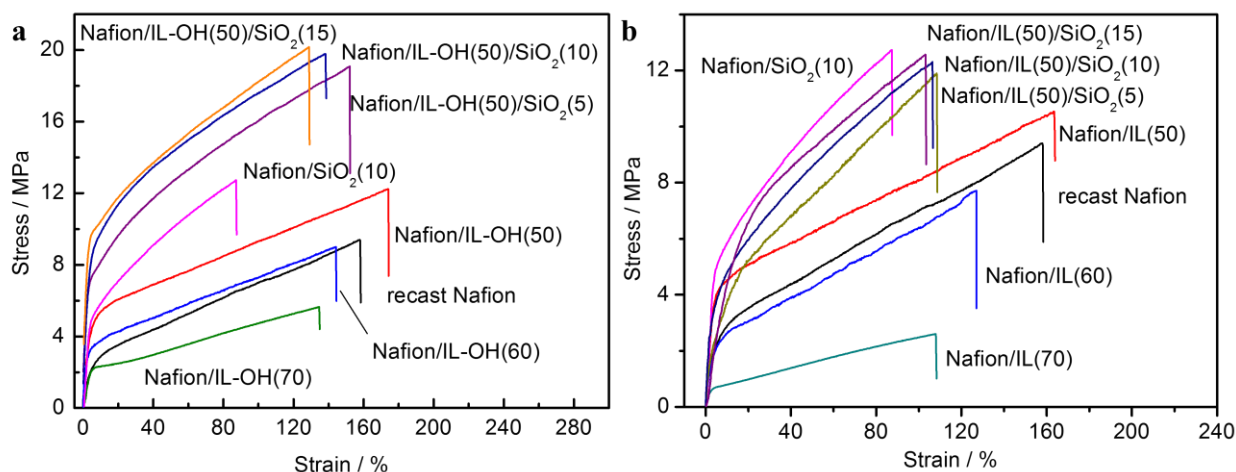


Fig. 4. Stress-strain curves of different samples with varying compositions of Nafion, IL-OH, BmimBF₄ and SiO₂ as indicated. (a) Nafion/IL(BmimBF₄)/SiO₂. (b) Nafion/IL-OH/SiO₂.

In this study, we found that Nafion/BmimBF₄(60) showed both lower tensile strength (~ 7 Mpa) and poorer strain than those of recast Nafion (Fig. 4a). When the BmimBF₄ content increased to 70%, the tensile strength significantly decreased to about 2.5 MPa. However, the Nafion/IL-OH membranes with the same IL-OH contents as their Nafion/BmimBF₄ counterparts performed much better mechanically than the counterparts. The tensile strengths of Nafion/IL-OH(60) and Nafion/IL-OH(70) were about 9 and 5.5 MPa respectively (Fig. 4b), both are significantly greater than those of Nafion/BmimBF₄ membranes. The higher mechanical performance of the Nafion/IL-

OH membranes can be attributed to the hydrogen bonding interaction between Nafion and IL-OH. The binary PEMs with 50% BmimBF₄ or IL-OH, showed better tensile strength and strain than recast Nafion, particularly the IL-OH PEM membrane.

On the other hand, similar to previously reported observations, doping nano-SiO₂ alone into Nafion enhances the tensile strength but deteriorates the strain [51, 52], and the Nafion/SiO₂(10) membrane showed a tensile strength of about 12.5 MPa. However, further doping with 50% IL-OH or BmimBF₄ altered the mechanical performance of the ternary PEMs in starkly differing manners. While the addition of 50% BmimBF₄ decreased the tensile strength of Nafion/SiO₂(10) slightly, the Nafion/IL-OH(50)/SiO₂(10) demonstrated a tensile strength as high as about 20 MPa, more than twice that of recast Nafion, without deterioration to the strain. Similar results were observed when comparing Nafion/IL-OH(50)/SiO₂(15) and Nafion/IL-OH(50)/SiO₂(5) with Nafion/BmimBF₄(50)/SiO₂(15) and Nafion/BmimBF₄(50)/SiO₂(5) respectively. These consistent results confirm that the interactions between Nano-SiO₂ and IL-OH synergistically enhanced the mechanical performance of the ternary PEM. Again, these enhancements can be well interpreted by the hydrogen bonds cross-linking between Nafion, IL-OH and nano-SiO₂. As shown in Fig. 5, the Nafion/IL-OH/SiO₂ ternary membranes are free-standing, transparent, flexible, and strong enough for the FC assembling.

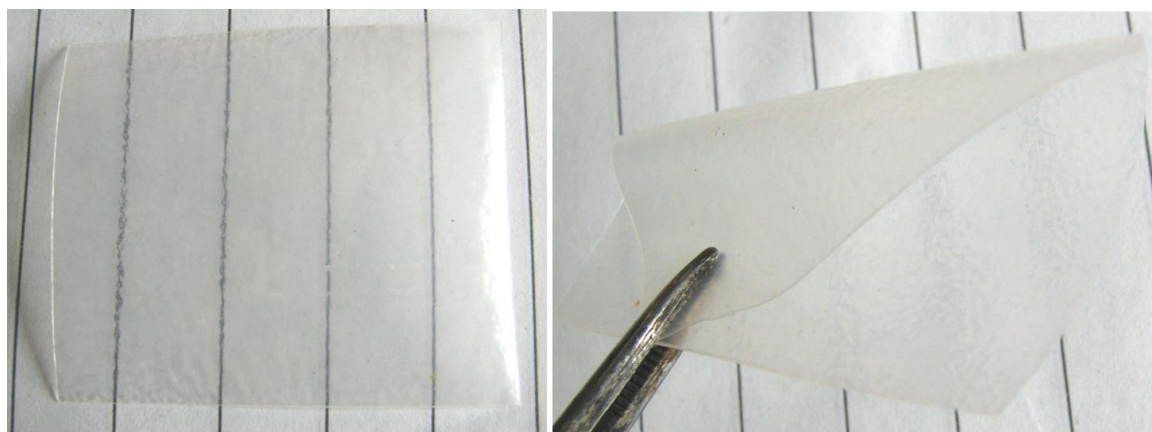


Fig. 5. Digital images of a typical Nafion/IL-OH(50)/SiO₂(10) membrane.

Thermogravimetric analysis (TGA) indicated that, after vacuum drying, all the cast membranes were thermally stable up to 300 °C (Fig. 6) [51, 53, 54]. Incorporation of IL-OH into Nafion is obviously beneficial to the thermal stability, which could be further enhanced by the addition of Nano-SiO₂. If the 5 wt.% weight loss is taken as a reference, the decomposition temperature of Nafion/IL-OH(50)/SiO₂(10) is ca. 405 °C. When compared to the thermal stability of Nafion/BmimBF₄(50)/SiO₂(10), it can be inferred that the hydrogen bonding interactions in the Nafion/IL-OH(50)/SiO₂(10) membrane have contributed to the thermal stability. This is a reasonable account, considering the amount of energy needed to overcome the stable hydrogen bonding network in order for the PEM to deteriorate.

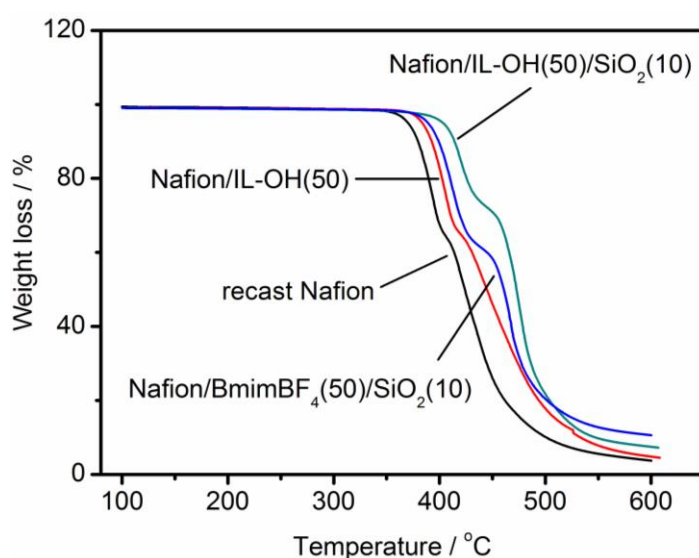


Fig. 6. TGA curves of different cast membranes as indicated.

3.3. Anhydrous Proton conductivity

The Nafion/IL-OH(50)/SiO₂(10) membrane was selected for further electrochemical characterization due to its high mechanical and thermal stabilities. As shown in Fig. 7, the anhydrous conductivities were measured by AC impedance over an 80 to 190 °C temperature range. While the pure recast Nafion showed a conductivity lower than 10^{-4} S cm⁻¹, the conductivity of the Nafion/IL-OH(50)/SiO₂(10) was fairly larger than 10 mS cm⁻¹, which increased with temperature conforming to the Arrhenius law. The conductivity reached about 39 and 54 mS cm⁻¹ at 160 and

190 °C respectively, which are among the highest values reported for an anhydrous polymer/IL membrane (2~30 mS cm⁻¹) [22-40].

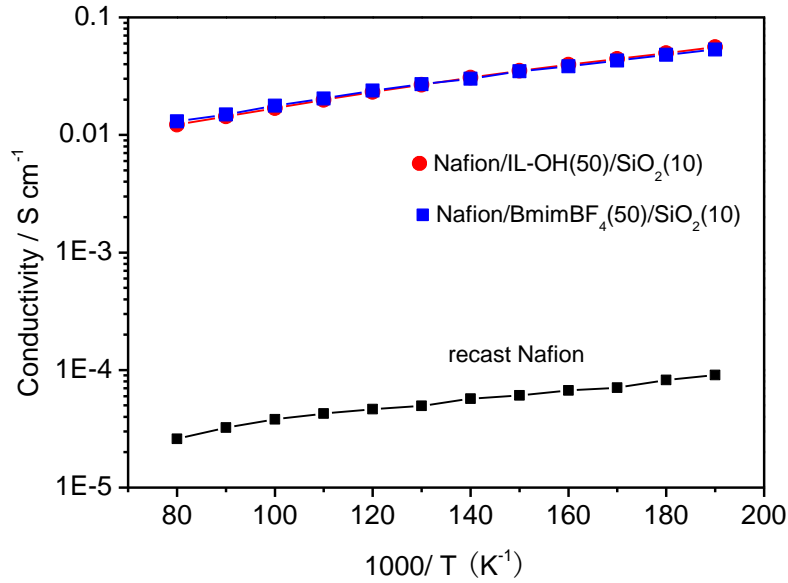


Fig. 7. Temperature-dependent anhydrous ionic conductivities of the recast Nafion, the Nafion/IL-OH(50)/SiO₂(10) and the Nafion/BmimBF₄(50)/SiO₂(10).

The Nafion/BmimBF₄(50)/SiO₂(10), however, showed almost the same conductivities as those of Nafion/IL-OH(50)/SiO₂(10). This can be attributed to the fact that AC ionic conductivity (σ_{AC}) could include the contributions from not only protons (σ_H), but also the cations (σ_c) and anions (σ_a) of an ionic liquid [22, 26, 27]. Even non-proton conducting polymers such as PVDF, when mixed with ILs, can exhibit ionic conductivities, but the t_H value would be zero [44]. There is,

$$\sigma_{AC} = \sigma_H + \sigma_c + \sigma_a \quad (1)$$

Since pure IL-OH shows a conductivity much lower than that of BmimBF₄ due to its higher viscosity [55], it is speculated that Nafion/IL-OH(50)/SiO₂(10) should possess a higher proton conductivity (σ_H) than that of Nafion/BmimBF₄(50)/SiO₂(10). To verify this, the proton transfer number t_H was calculated by Equation (2)

$$t_H = \sigma_H / \sigma_{AC} = R_{AC} / R_H \quad (2)$$

where R_H and R_{AC} are the proton and total ionic resistance respectively. Equation (1) and (2) are generally applicable to polymer based membranes containing ILs.

The σ_H was estimated by EHP tests conducted with both the cathodic and anodic chambers filled with 1 atm dry H_2 . Figure 8a shows the steady-state polarization curves at 160 °C. The linear relationships can be used to calculate the total direct current resistances of the EHP (R_{DC}), which were 0.278 Ω and 0.347 Ω for the EHP with Nafion/IL-OH(50)/SiO₂(10) and Nafion/BmimBF₄(50)/SiO₂(10), respectively. Note that R_{DC} is comprised of proton conduction resistance (R_H), charge transfer resistance on both electrodes ($2R_{CT}$), and gas diffusion resistance (R_D),

$$R_{DC} = R_H + 2R_{CT} + R_D \quad (3)$$

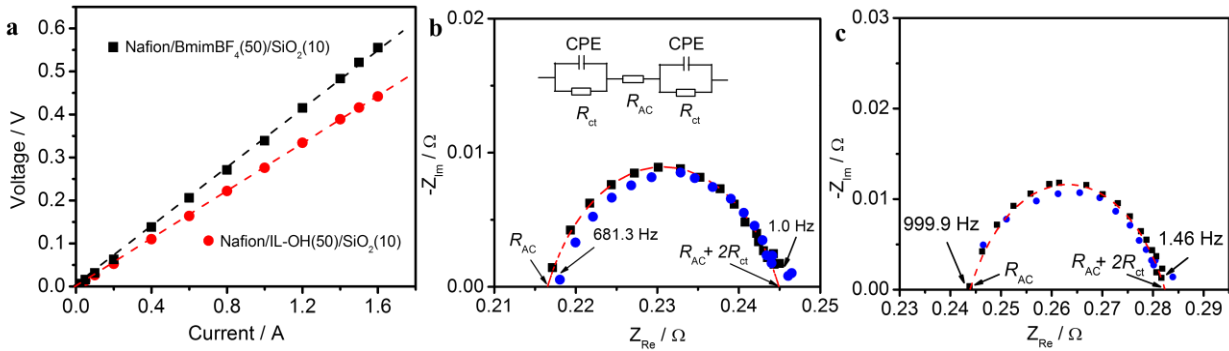


Fig. 8. The electrochemical hydrogen pumps (EHP) tests at 160 °C under 1 atm dry H_2 . (a) Steady-state polarization curves of EHP with different PEMs. Electrochemical impedance spectra of the EHP without (dark squares) and with (blue circles) a bias current of 200 mA with (b) Nafion/IL-OH(50)/SiO₂(10) and (c) Nafion/BmimBF₄(50)/SiO₂(10). The dash line is a result of the curve fitting according to the inserted equivalent circuit.

At the same time, AC impedance analysis was performed to distinguish between these resistances. As shown in Figure 8b and 8c, R_{AC} and $2R_{CT}$ can be directly read on the plot. R_{AC} and R_{CT} did not vary regardless whether a bias current of 200 mA cm⁻² was applied, which indicates that R_D is negligible and R_H can be calculated using Equation (3). The t_H values of the Nafion/IL-OH(50)/SiO₂(10) and Nafion/BmimBF₄(50)/SiO₂(10) membranes at 160 °C were calculated to be about 0.87 and 0.79, respectively, and they increased to 0.9 and 0.82 at 180 °C. It can then be

concluded that there is an anhydrous hydrogen-bond network in the Nafion/IL-OH(50)/SiO₂(10) membrane, this network can facilitate much faster proton conduction.

In addition, it is worth noting that R_{CT} of the H₂/H⁺ couple in the Nafion/IL-OH(50)/SiO₂(10) cell was as low as $\sim 0.015 \Omega \text{ cm}^{-2}$ (Fig. 8b) which is smaller than that of the Nafion/BmimBF₄(50)/SiO₂(10) cell ($\sim 0.02 \Omega \text{ cm}^{-2}$, Fig. 8c), suggesting that the hydroxyl functionalized IL is also better suited for the proton transfer reaction at the electrode/IL membrane interface. This should be very conducive to the high power operation of the H₂-O₂ fuel cells.

3.4. H₂/O₂ single cell tests

Test of the membrane in the single H₂-O₂ cell was carried out at temperatures between 140 and 180 °C. When it was fed with dry H₂ and O₂ gas at 1 atm, the fuel cell with the Nafion/IL-OH(50)/SiO₂(10) membrane reached an open circuit voltage of about 1 V. The polarization curves at 160 °C and 180 °C are shown in Fig. 9a. The performance of the fuel cell was improved with increasing the working temperature. At 160 and 180 °C, the maximum power densities were about 340 and 420 mW cm⁻², respectively. These performances are comparable to the present intermediate-temperature FCs with H₃PO₄ doped PEMs [12-15].

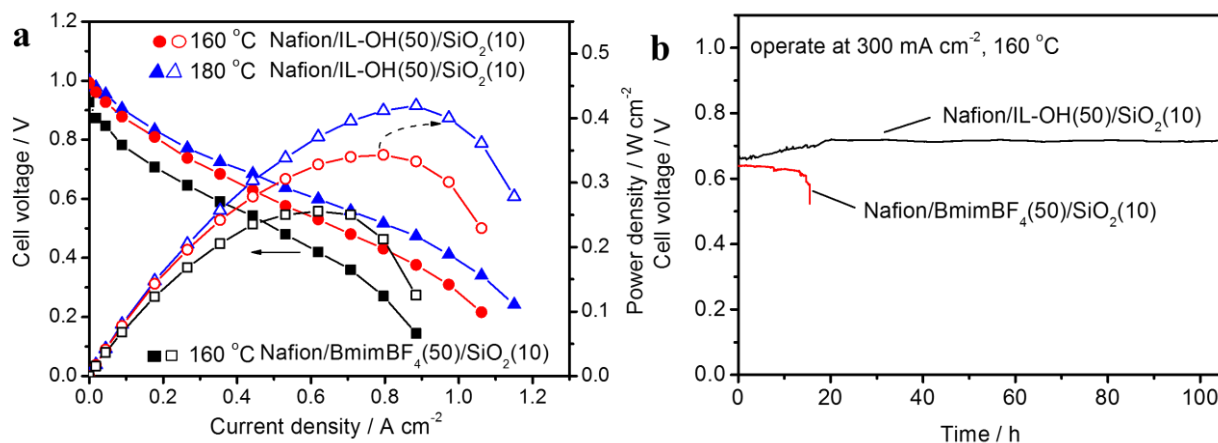


Fig. 9. (a) Polarization curves of the H₂-O₂ fuel cell with different PEMs at varying temperatures as indicated. (b) Cell voltage change as a function of time by operating the fuel cell at a constant current density of 0.3 A cm⁻² and 160 °C. Dry H₂ and O₂ were fed into the fuel cell at 1 atm and a gas flow rate of 120 mL min⁻¹ in these tests.

It should be pointed out that although anhydrous PEMs consisting of non-hydroxyl ILs have been investigated for many years, their fuel cell tests were often unsatisfactory. Those previously reported fuel cells often showed low open circuit voltages (< 0.9 V) and delivered much low power densities (< 35 mW cm⁻²) at temperature above 150 °C [27-34]. Sometimes, higher power densities, for example 203 mW cm⁻², were reported at temperature < 150 °C, but these cells failed after a short period of operation and did not work at higher temperatures [29]. These phenomena were frequently reported in the literature for PEMs consisting of non-hydroxyl ILs, and ascribed to the poor mechanical strength of the PEMs [27, 29, 30]. Therefore, it can be concluded that fuel cells fabricated with the Nafion/IL-OH(50)/SiO₂(10) PEM outperform fuel cells made from existing polymer/ILs membranes when tested under similar conditions [27-34].

In this work, fuel cells made from Nafion/BmimBF₄(50)/SiO₂(10) PEMs were also tested at 160 °C for comparison, and their performances were indeed inferior (Fig. 9). The open circuit voltage and maximum power density were only about 0.92 V and 250 mW cm⁻², respectively. It showed much larger polarization than the Nafion/IL-OH(50)/SiO₂(10) fuel cell, likely due to the lower proton conductivity and a smaller proton transfer number, as well as unsatisfactory compatibility between the BmimBF₄ ionic liquid and the electrode reactions

The operational stability of the H₂-O₂ cells was initially examined at 160 °C and a constant current density of 0.3 A cm⁻². The cell with a Nafion/BmimBF₄(50)/SiO₂(10) PEM lasted only for several hours (Fig. 9b), which is consistent with previously reported PEMs composed of conventional non-hydroxyl ILs, and can be attributed to the poor mechanical strength of the PEMs [29]. On the contrary, the fuel cell constructed from Nafion/IL-OH(50)/SiO₂(10) showed a promising working stability at 160 °C. As can be seen in Fig. 9b, the initial discharge voltage was about 0.67 V, which increased to 0.72 V in about 20 h and then remained fairly stable over the 100 h observation with a power output of ~ 220 mW cm⁻². Obviously, the data shown in Fig. 9 were obtained without any optimization in the cell design and manufacturing method and, therefore, there should be a large room for improvements in the future.

It is worth mentioning that our test of the single cell FC was carried out using pure O₂ to feed the cathode. Usually, for real application, in the cathodic chamber, O₂ will be from the air which may contain trace amount of H₂O. Further, the fuel cell operation will discharge water into the cathodic chamber as well. Thus there should always be some water vapor in the cathodic chamber in a practical cell. Water in general can improve the proton conductivity of PEMs and addition of water vapor (or humidification of the feeding gases) is often carried out at relatively low temperatures. Our membranes are also stable in moisturized air. However, the operation becomes more difficult and less effective at temperatures higher than 150 °C when the equilibrium water vapor pressure will be higher than 5 atm. This is the reason why researchers are trying to develop anhydrous PEMs that can work properly at intermediate temperatures even in the absence of added water vapor.

In our view, the results and analyses given above may lead to two favorable consequences. First, the high performance PEMs with a relatively long working life will enable the design of high temperature membrane electrodes and consequently fuel cell stacks. Accordingly, the intermediate-temperature electrocatalytic activities of Pt and other non-precious catalysts (such as WC) at the electrode/IL membrane interface can be properly assessed. Second, the findings that the presence of hydroxyl functionalized cations in the Nafion membrane can significantly increase both the anhydrous proton conduction and mechanical strength of Nafion will inspire the investigation of many other high temperature PEMs consisting of various hydroxyl ILs and different sulfonated polymers. Moreover, our findings would be of general interest in developing IL membranes for uses in other energy related areas, for example, the IL membranes for CO₂ separation, where sufficient mechanical strength of the membranes is also a basic requirement for the practical application [56].

4. Conclusions

In summary, anhydrous Nafion/IL-OH/nano-SiO₂ membranes have been prepared and characterized for mechanical strength, thermal stability and proton conduction at intermediate temperatures (≥ 150 °C). Evidence has been provided to support the formation of highly interconnected hydrogen-bond networks in the PEMs, leading to better thermal stabilities, increased

greater mechanical strength, and higher proton conductivities than their counterparts consisting of a non-hydroxyl ionic liquid. It was also found that the hydroxyl functionalized IL is more compatible with the electrode reactions in H₂-O₂ fuel cells. Moreover, the Nafion/IL-OH/nano-SiO₂ membrane performed very well above 140 °C in single-cell H₂-O₂ FCs, thus, making them very promising materials for a number of applications. We believe that the findings reported here can lay the foundation for a new generation of hybrid sulfonated polymer membranes for electrochemical devices that can work at intermediate temperatures.

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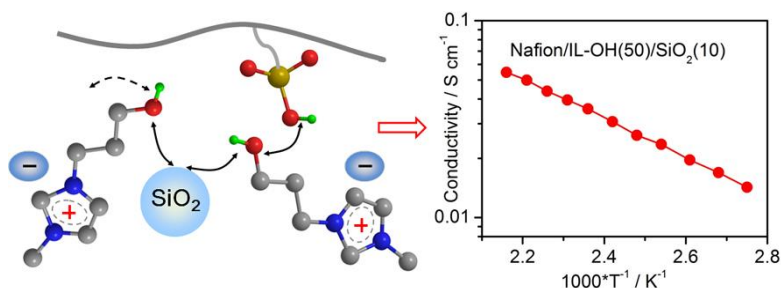
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Table of Contents Graphic and Synopsis



Anhydrous hydrogen-bond network in a Nano-SiO₂ Doped Nafion fused by a hydroxyl functionalized ionic liquid for high-performance intermediate-temperature proton exchanging membranes.