12-Silicotungstic Acid Doped Phosphoric Acid Imbedded Polybenzimidazole for Enhanced Protonic Conductivity for High Temperature Fuel Cell Applications

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12-Silicotungstic acid, a heteropoly acid (HPA) - was incorporated into phosphoric acid (PA) doped polybenzimidazole (PBI) membrane that exhibited strong mechanical stability, excellent proton conductivity, and can be used for high temperature proton exchange membrane fuel cells (PEMFCs). At 160 °C, an electrochemical impedance spectroscopy (EIS) fitting of the fuel cells data showed the membrane electrode assemblies (MEAs) made of PBI/20%HPA/PA had three times lower ohmic resistance (0.057 ± 0.002 Ohm·cm²) as compared to the control reference of PBI/PA (0.160 Ohm·cm²). In addition, the ohmic resistance of the composite MEA remained unchanged while the charge transfer resistance decreased after 313 hours conditioning. Fourier transform infrared spectroscopy (FTIR), magic angle spinning - nuclear magnetic resonance (MAS-NMR), and thermogravimetric analysis (TGA) showed 12-silicotungstic acid inhibits water from escaping the membrane at elevated temperatures and adds more acid sites, providing additional paths for proton transport. Scanning electron microscope (SEM), transmission electron microscopy (TEM), and small angle X-ray scattering (SAXS) were used to confirm the structure and morphology of PBI/20%HPA/PA membrane prior making the MEAs. Fuel cell polarization curves indicated MEAs made of PBI/20%HPA/PA produced shallower IR slopes compared to MEAs made of PBI/PA, especially, when the hydrogen fuel was humidified.

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Fuel cell technologies have the potential to reduce our dependence on fossil fuels and to reduce associated emissions of pollutants as the global population continues to grow. Polymer electrolyte membrane fuel cells (PEMFCs) have the advantage of being fully scalable for stationary power generation than other types of fuel cells. PEMFCs have outstanding power density, rapid start-up, and high efficiency.1 In addition, the operation of PEMFCs is straightforward and does not generate any additional pollutants. Despite several advantages, current PEMFCs are not yet widely used or commercialized, because they remain too expensive, do not have enough durability, and require very pure hydrogen as a fuel.2 At the moment, PEMFCs generally operate below 100 °C due to the need to fully humidify commonly used perfluorosulfonic acid electrolytes such as Nafion. At low operating temperatures, a small concentration of CO or SO2 impurities in the fuel could poison the catalysts and lower the fuel cell performance. Therefore, current PEMFCs require high purity hydrogen that can only be cost-effectively produced from natural gas at this time. Furthermore, the humidification of fuel and oxidant in low temperature PEMFCs requires a complicated humidification system. These technical challenges can be addressed by increasing operating temperatures above 120 °C.

High temperature operation is a promising way to improve PEMFC performance; it has been shown that higher operating temperatures would increase chemical kinetics at the anode and dramatically enhance the electrode tolerance to fuel impurities, which allows for the use of lower-cost hydrogen.3 In addition, fuel cell operation above 120 °C can tolerate up to 1% CO and 10 ppm SO2. Operating at elevated temperatures would also provide easier water and thermal management.4 One approach in designing a high temperature electrolyte membrane for PEMFCs is acid doping into aromatic polymer materials that have high thermal stability. The polymer is typically chosen to contain basic sites that serve as proton acceptors, forming an ion-pair after doping with an inorganic acid.5 This type of acid doped, based backbone is favorable to proton transport. One of the most promising acid-base membranes, developed by Litt, Savinell, and Wainright, is based on polybenzimidazole (PBI) doped with phosphoric acid.6 PBI is a class of aromatic heterocyclic polymers containing benzimidazole groups in the backbone, which is mostly available in the form of poly 2,2′-m-(phenylene)-5,5′-bibenzimidazole (m-PBI), where the phenylene ring is meta-coordinated. Since the introduction of acid doped PBI in 1995, several studies have been performed concerning PBI synthesis, membrane casting, thermal and chemical characterizations, and fuel cell applications. In most cases, the proton conductivity and thermal/chemical stability results are very encouraging, making PBI membrane a promising candidate for use in the high temperature fuel cell environment.1,7,8 PBI contains imide groups that can be easily doped with many different acids, particularly phosphoric acid.9 Although the proton conductivity of pure PBI is low, doping with phosphoric acid results in a significant increase in its proton conductivity. Phosphoric acid is amphoteric (i.e. it contains both proton donors and proton acceptors), forming dynamic hydrogen bond networks inside PBI membranes. As a result, phosphoric acid-doped PBI is highly proton conductive, because its protons can freely migrate along the hydrogen bond networks. In addition, phosphoric acid has high thermal stability and low vapor pressure at elevated temperatures; therefore, it forms a doped membrane with excellent thermal and mechanical stability upon casting. Phosphoric acid-doped PBI also has the benefits of almost zero water electro-osmotic drag and excellent oxidative stability.

One unique and particularly important feature of phosphoric acid-doped PBI is that, upon casting, the resulting electrolyte membrane has very high proton conductivity at temperatures above 120 °C, especially in the presence of low humidity (below 10% RH). The minimum water concentration is required, not to act as a vehicle to transport protons, but to prevent the phosphoric acid from forming the anhydride at temperatures above 100 °C.10 Instead, the proton transport in acid-base membranes occurs mainly through a Grothuss mechanism, where the proton transfer occurs through the hopping of protons between two molecules via rearrangement of their hydrogen bonds. This mechanism is the primary means for proton conductivity at temperatures above 120 °C, and results in zero electro-osmotic drag coefficient of water in phosphoric acid-doped PBI.
During PA doping, the active sites of the imidazole rings interact and hydrogen bond with PA, preferably occupying two moles PA per PBI unit. As the doping continues, the number of PA molecules surpasses the basic sites of the imidazole and forms free acid in the polymer membrane. At this stage, the proton migration occurs mainly along the free acid and its anion or water, depending on the water content. In general, high acid doping levels increase the membrane conductivity. However, excess of PA in the polymer matrix may affect the mechanical properties of the polymer, especially at high operating temperature conditions. Therefore, an appropriate PA doping level should be considered to balance both conductivity and mechanical strength.

Although the use of phosphoric acid in PBI introduces proton conductivity, the phosphoric acid still dissolves in the presence of liquid water and does not enhance the oxygen reduction reaction at the cathode. Long-term operation of phosphoric acid doped PBI membranes often loses proton conductivity due to acid leaching. The free phosphoric acid also degrades and embrittles the polymer. As a consequence, the membrane is degraded at elevated temperatures, has poor mechanical properties, and has a narrow operational temperature range. To solve these technical problems, one of the solutions is to add inorganic fillers into the polymer to improve its mechanical properties. However, the inorganic fillers may interfere with the proton conducting pathway, and therefore, lower the membrane proton conductivity. Adding inorganic proton donors, such as heteropolyacids (HPAs), into the polymer matrix can improve both mechanical and thermal properties while increasing the proton conductivity of the polymer electrolyte. HPAs have shown high thermal stability and proton conductivity. However, the inorganic fillers may interfere with the proton mobility of the polymer.

Several groups have attempted to incorporate HPAs into a PBI matrix as inorganic-organic composites by a variety of methods; however, none of these methods are simple or have been shown to be effective. Numerous efforts ended up losing most HPA content as the membranes were soaked in water post-casting because HPAs are highly soluble in aqueous solutions. To stabilize HPAs inside a PBI matrix as inorganic-organic composites by a variety of methods; however, none of these methods are simple or have been shown to be effective. Numerous efforts ended up losing most HPA content as the membranes were soaked in water post-casting because HPAs are highly soluble in aqueous solutions. To stabilize HPAs inside a PBI matrix, SiO2 was used as a support to entrap HPAs, making HPAs/SiO2 insoluble in water; however, the presence of a non-conductive SiO2 support decreases the proton conductivity of the composite membrane, reaching only 0.0012 S cm⁻¹ at 160 °C. The second challenge of adding HPAs into a PBI matrix is to find a compatible medium to mix HPAs and PBI polymer homogeneously. N,N-dimethylacetamide (DMAc) seems to be a good solvent, but the acidic versus basic nature of HPAs and PBI, respectively, causes precipitation of the polymer from the solution containing HPAs. HPAs can be neutralized with NaOH. The resulting sodium salts are easier to disperse in PBI; however, the salt is not readily soluble in DMAc. As a result, the process of mixing HPAs in PBI becomes extremely difficult. The loss of acidic sites due to neutralization decreases proton conductivity, while the formation of sodium phosphate after phosphoric acid-doping decreases the fuel cell potential and increases the ohmic resistance, mainly due to cross-over issues. Even successful addition of HPAs in PBI only obtained a maximum of 0.058 S cm⁻¹ at 200 °C and at 5% RH. Similarly, Cs⁺ substituted HPAs prepared by ball milling of CsH2SO4 and HPAs were incorporated into a PBI/DMAc solution. However, the presence of Cs⁺ substituted HPAs prevented phosphoric acid absorption, causing a low doping level of less than 3 moles of acid per PBI unit, and hence, the conductivity of the resulting membranes only reached 0.0172 S cm⁻¹ at 160 °C. In addition, Cs⁺ substituted HPAs also decreased fuel cell potential and increased ohmic resistance.

We have found a successful method to incorporate 12-silicotungstic acid into PBI and then dope the cast membrane with phosphoric acid, resulting in a highly proton conductive membrane which can potentially be used for high temperature PEMFCs applications. The method is relatively straightforward, and effectively keeps most of the HPA in the polymer matrix after doping with phosphoric acid. After extensive analyses of the best performing membrane, we have found the addition of this hygroscopic HPA indeed increases the water retention and improves the membrane thermal stability. Through FTIR, MAS-NMR, TGA, SAXS, SEM, TEM, and EIS, we have found 12-silicotungstic acid not only inhibits water from escaping the membrane at elevated temperatures, but also adds more acid sites, consequently, providing additional paths for proton transport. Phosphoric acid-doped PBI membranes at different doping levels of 12-silicotungstic acid are evaluated in detail and compared to the non-HPA-added membrane in real fuel cell conditions. The proton transport as well as water retention will be discussed in order to understand the functions of HPA in enhancing the membrane proton conductivity.

**Experimental**

**Synthesis of PBI.**—PBI was synthesized and provided by Danish Power Systems by a procedure that can be found in the literature. In short, the polymer was prepared by reacting 3,3′-diaminobenzidine tetrahydrochloride and isophthalic acid with a molar ratio of 1:1 using polyphosphoric acid as a solvent. The synthesis was completely optimized to obtain a high molecular weight PBI approximately 54 kDa with inherent viscosity of 0.98 dL g⁻¹. The polymer is soluble in DMAC and can be cast to form a membrane which has excellent oxidative stability, high acid doping, good proton conductivity, and strong mechanical strength.

**Composite membrane preparation.**—A solution of 10 wt% of PBI was prepared by sonicating the PBI solid in DMAC that contains 3 wt% LiCl at 60 °C for 4 h, followed by stirring and heating at 80 °C for 3 days to produce a homogeneous PBI/DMAC solution. In a separate container, a solution of 5 wt% of silicotungstic acid (HPA) was dissolved in DMAC by gently stirring at room temperature. The two solutions were then mixed in the right proportions and stirred at room temperature for at least 8 h to obtain 5%, 10%, 15%, 20%, 30%, and 40% HPA in PBI. All casting solutions, including a 0% HPA as the control, were diluted to the final 5 wt% concentration of PBI in DMAC. The solution was then poured onto a glass plate and cast using a DCX Plus DC Motor Control doctor blade, setting at 20 mil, at initially 20%, and then 80%, of its maximum speed to produce a uniform thin film of 20–50 μm. The cast film was then covered with a wire mesh on top and dried in an oven at 120 °C for 24 h. To remove the film after drying, the glass plate was briefly steamed for 5 seconds above a boiling water bath and carefully peeled off the membrane using a sharp razor blade. The membrane was immediately placed in an oven at 120 °C for at least 2 hours before doping with 85 wt% concentrated phosphoric acid. The doping procedure was kept the same for all membranes. First, the dried membrane was immersed in warm phosphoric acid solution at 40 °C for 1 hour. Then, the acid solution was allowed to cool to ambient temperature, and the membrane was slowly soaked in phosphoric acid for 7 days to form a dense composite membrane ready to make MEA for fuel cell testing.

In order to calculate the doping level of PA in the membranes, three samples of 4 × 4 cm² of un-doped membranes were pre-weighted, followed by impregnation in 85% phosphoric acid solution for 7 days. The doped membranes were completely wiped off any excess PA on the surface and dried at 110 °C under vacuum until no more weight change observed. The weight difference between the doped and undoped membranes were obtained and used to determine the doping level.

**Membrane characterization.**—ATR-FTIR spectroscopy ( Nicolet-Nexus 470 FTIR) with a heated zinc selenide (ZnSe) crystal ATR accessory (Specac, Inc.) was used to study the prepared polymer
membranes. A liquid nitrogen cooled mercury–cadmium–telluride detector was used to improve the measurement accuracy. All spectra were collected with 256 scans and resolution of 4 cm⁻¹. A common background collected at ambient temperature and humidity conditions was subtracted from all spectra. FTIR spectra were collected at 80–160°C at 5% RH. The dry and wet nitrogen gas flowrate was kept constant at 210 scm and was controlled using mass flow controllers (MKS Instrument Inc.). The temperature and RH were controlled using an in-house custom built system for the ATR-FTIR spectroscopy. The IR spectra were smoothed for atmospheric CO₂ suppression and corrected to a common baseline.

'H and 'P solid-state NMR spectroscopy were collected on a Bruker AVANCE III 400 MHz Spectrometer with a 50 kHz B₂ field. A 4 mm MAS probe was used. 'H MAS NMR spectra were collected at 400 MHz, with a 12 kHz spinning speed, and 5 s recycle delay. 'P Cross Polarization and Magic Angle Spinning (CP/MAS) spectra were recorded at 162 MHz, with a 5 kHz spinning speed, 5 s recycle delay, and 3 ms contact time.

SAXS was performed on beamline 12-ID-C at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL, USA. The energy of the X-ray beam was 12 keV with a wavelength of 1 Å. Spectra were collected using a Pilatus 2D detector. A custom built temperature and humidity control setup was used as described in the literature. SAXS spectra were collected during heating and cooling at 30–160°C and 160–80°C, respectively, under anhydrous and 10% RH conditions. Membranes were equilibrated for 20 min before collecting the spectra. Particle size analysis was performed by the maximum entropy method assuming a spheroid particle shape model using the IRENA version 6.64 SAXS package developed in Igor Pro at Argonne National Laboratory.

Environmental Scanning Electron Microscope (ESEM) images were acquired with an FEI Quanta 600i ESEM. An FEI Helios 600i DualBeam SEM/focused ion beam (FIB) instrument was used to lift-out a thin section of a PBI/20%HPA/PA sample for TEM analysis. The FIB procedure was performed using a 30 kV accelerating voltage, modest currents (< 0.77 nA), and zero overlap in the milling patterns as described elsewhere. While some liquid became apparent on the surface during this process, the membrane remained intact. TEM and scanning TEM (STEM) imaging and energy dispersive X-ray spectroscopy (EDX) mapping were performed on an FEI Talos F200X at 200 kV. In order to minimize damage to the specimen during imaging, the electron beam dose was limited by using the smallest possible spot size.

TGA was performed in the temperature range of 30–600°C using a Pyris 1 TGA in argon atmosphere with a scanning rate of 20°C/min. Prior to the analysis, the membrane samples were dried with a Kimwipe to remove excess phosphoric acid on the surface. All membranes were kept in inert atmosphere before TGA measurement. Tensile strength of the membranes was evaluated using an Instron Model 4201 tensile tester. The membranes were cut into rectangular shape with 30 mm in length and 2 mm in width. They were tightly clamped between the jaws at 20 mm apart. All tests were performed with a constant separating speed of 10 mm min⁻¹ in an ambient atmosphere. The tensile strength was calculated from dividing the recorded load by the cross sectional area obtained from the width and the thickness of the sample.

Proton conductivity measurements.—The in-plane ionic conductivity was measured using a BeckTech (BT-112) insert with 4 platinum electrodes located inside a custom stainless steel ring and assembled into fuel cell hardware (Fuel Cell Technology, Inc.). The measurement was carried out using a Gamry Electrical Impedance Spectrometer (EIS 300). Frequency was swept between 10 MHz to 1 Hz for the EIS experiment as a function of temperature and humidity. The humidity of each sample was controlled by using a Scribner Fuel Cell Test System (Scribner 850e). Humidified nitrogen was fed at 0.1 L/min to one inlet, and was allowed to exit at the opposite outlet. The other inlet and outlet of the hardware were plugged. Nitrogen was flowed and humidified through a sparging bottle with modular gas handling and a gas metering system (Scribner, Inc.). The temperature of the cell and the sparging bottle were adjusted to reach the desired conditions. The collected impedance spectra were fitted to the Randall circuit to find the total resistance of the membrane. The conductivity (mS·cm⁻¹) was calculated from the measured membrane resistance using the following equation:

\[
\sigma = \frac{l}{t \times w \times R}
\]

where l, t, w, R are the distance between two electrodes (4.25 mm), film thickness (30 μm), film width, and the resistance of the membrane, respectively.

Fuel cell testing.—The MEA was prepared and tested at Danish Power Systems. Each MEA used in this study had an active area of 21 cm². Both the anode and the cathode contained 1.56 mg-Pt/cm² that was coated on hydrophobic gas diffusion layers. The membranes were either PBI/PA (control reference) or PBI/20%HPA/PA (inter- ested composite membrane). The MEA was hot-pressed at 1.5 tons at 100°C for 3 minutes before assembly and testing. In this work, hydrogen was used as the fuel, while air was used as the oxidant. The stoichiometric ratios of hydrogen and air were 1.5 and 2.5, respectively. To activate the MEA, the fuel cell was operated at a current density of 0.2 A/cm² for 48 hours. After the activation process, the polarization curve at 160°C was measured. Electrochemical impedance spectroscopy (EIS) was used to study the resistance distribution of fuel cells. The ohmic resistance, charge transfer resistance (mainly at the cathode), and mass transfer resistance of an MEA were estimated by using the method of equivalent circuit fitting.

Results and Discussion

Figure 1 illustrates the polymer matrix structure of PBI/HPA/PA membrane and the physical appearance of our cast membrane. Phosphoric acid (PA) doping level is defined as the mole number of H₃PO₄ per repeat unit of PBI. Since one unit of PBI contains two basic sites, it takes two moles of PA to neutralize each PBI unit. However, the doping level can be much higher than two because additional free acid can still be stored within the polymer matrix after the initial neutralization process. Especially, the presence of HPA in the composite membrane, shown in Figure 1, creates dipole-dipole interactions and hydrogen bonds pulling more phosphoric acid inside the polymer matrix and increasing the PA doping level. Table 1 compares the compositions of polybenzimidazole-based phosphoric acid-doped (PBI/PA) versus polybenzimidazole-based heteropolyacid-added phosphoric acid-doped (PBI/HPA/PA) membranes used in this study. For high molecular weight PBI synthesized at Danish Power Systems, we have found the optimal doping level is around 10–12 moles of H₃PO₄ per repeat unit of PBI, which is about the same level of our PBI/HPA/PA membranes.

Elemental analysis of the membranes was obtained from Huffman Hazen Laboratories by different analytical techniques (detail technical descriptions are available in the supplemental information). The results show about the same compositions as calculated based on the known weight percent of each compound during preparation of the membranes. The addition of LiCl helped to dissolve HPA with PBI solution during membrane preparation, however the presence of chloride can deactivate the catalyst and hurt the fuel cell performance. Fortunately, Table S1 (supplemental information) indicates LiCl salt was completely removed from the membranes after soaking in concentrated phosphoric acid for seven days. More importantly, the membrane still contains the same amount of HPA after the phosphoric acid doping period.

TGA was used to study the effect of HPA on the thermal stability of PBI membranes. TGA was measured in an argon atmosphere, showing two dramatic weight loss ranges with increasing temperature. The first weight loss appears at 40–100°C due to the loss of unbound water. Another weight loss occurs at 130–200°C caused by the loss of...
water from the phosphoric acid and the HPA. Figure 2 shows the TGA patterns of PBI/PA and PBI/20%HPA/PA. As shown for PBI/PA membrane, there is approximately 18% unbound water evaporated below 100°C and 6% water subsequently lost above 130°C due to phosphoric acid dehydration. The corresponding loss of water observed in PBI/20%HPA/PA is about 9% unbound water and 9% dehydrated water that is from both phosphoric acid and HPA.

TGA results indicate free water absorbed in the membrane was reserved more effectively in PBI/20%HPA/PA than in the case of PBI/PA. This may be due to the presence of HPA hydration. The retention of water in the membrane absolutely helps the conductivity of the membrane, since water contributes to the hydrogen network as well as acting as a proton carrier to transport the proton to other proton acceptor sites throughout the membrane. As the temperature reached above 400°C, the polymer chain started to decompose. Figure 2 also indicates that the composite PBI/20%HPA/PA membrane has less thermal degradation than PBI/PA membrane. It is possible that the HPA helps to anchor and hold the polymer chains together providing more support within the polymer matrix.

The Mechanical properties of PBI/PA and PBI/20%HPA/PA systems were compared at room temperature as shown in Figure 3. Although PBI/PA membrane shows more elastic as it elongates more than 250% of its original length, the PBI/20%HPA/PA system has higher tensile strength at break reaching almost 140 MPa. In addition, at any given elongation, the PBI/20%HPA/PA membrane has more tensile strength that is possibly due to the presence of the anchoring HPA in the PBI polymer.

SEM and TEM were used to study the micro-structure and nano-features of the membranes. The SEM images of PBI, PBI/20%HPA, and PBI/20%HPA/PA can be found in the supplemental information (Figure S1). Among these images, the morphology of PBI/20%HPA shows agglomeration of particles which qualitatively determined by EDX as LiCl salt. However, both PBI and PBI/20%HPA/PA show dense structures with similar morphological appearance. The LiCl salt was washed away after impregnating the membrane in phosphoric acid solution for seven days, which agrees with the elemental analyses.

**Table 1. Properties of PBI/PA and PBI/HPA/PA membranes used in this work.**

| Membrane Composition | Membrane (wt%) | HPA (wt%) | PA (wt%) | Water (wt%) | nPA/PBI (molar ratio) | Conductivity at 160°C, 10% RH (S/cm) |
|---------------------|----------------|----------|---------|------------|----------------------|---------------------------------------|
| PBI/PA              | 20.7           | 0.0      | 67.4    | 11.9       | 10.2                 | 0.049                                 |
| PBI/10%HPA/PA       | 19.5           | 1.9      | 66.8    | 11.8       | 10.8                 | 0.094                                 |
| PBI/20%HPA/PA       | 15.7           | 3.1      | 69.0    | 12.2       | 13.8                 | 0.127                                 |

Figure 1. A sketch showing how 12-silicotungstic acid (O in red and W in blue) imbibed inside doped phosphoric acid polybenzimidazole polymer matrix and the physical appearance of a casted PBI/HPA/PA membrane.

Figure 2. TGA curves of PBI/PA in red (below) and PBI/20%HPA/PA in blue (above).

Figure 3. Tensile stress-strain comparison of PBI/PA and PBI/20% HPA/PA systems.
More importantly, the HPA remains in the dense polymer structure as can be seen from EDX spectrum, tungsten map, and TEM images shown in Figure 4 and Figure 5, respectively. The 1.5–2.1 nm particles detected in both Z-contrast and bright field STEM images in Figure 5 are likely from the tungsten species within the HPA clusters given the high amount of observed scattering. These size features are also observed in the SAXS patterns discussed in the following sections.

SAXS is a powerful technique to study the morphology of PBI/PA and PBI/20%HPA/PA membranes under changing environmental conditions, such as temperature and humidity. There are three classification features that are observed in most of our SAXS patterns, except PBI/PA at 10% RH, which does not show any peak identity indicating the sample is most likely amorphous due to polymer swelling. First, the existence of peaks in the high q region indicates our samples contain ordered structures, and the peak position gives the distance between the scattering objects. The second important feature is the middle q region of our SAXS patterns either shows a broad peak as in PBI/HPA/PA or a straight line as in PBI/PA. These features indicate our films contain particles that have different sizes and shapes. Lastly, the slope at low q region can be used to determine the size of the particles as well as the shape of the feature through the power law estimation.

SAXS data can be obtained by using unified and diffraction fitting models (Modeling II of Irena macros). Through these fits, the morphological behavior of PBI/PA and PBI/20%HPA/PA at different temperatures and humidity conditions can be interpreted and clearly visualized from the following sections.

Figure 4. TEM preparation by FIB (top left), EDX map of tungsten element from HPA in the TEM sample (top right), and the EDX mass spectrum showing the W peaks at 0.27 keV, 1.8 keV, and 8.4 keV (bottom).

Figure 5. TEM images of PBI/20%HPA/PA membrane in bright field STEM (a), and Z-contrast image by high angle annular dark field (HAADF) STEM (b).

Figure 6. SAXS patterns of PBI/20%HPA/PA; (a) Under anhydrous condition during heating up (top left) and cooling down (top right); (b) At 10% RH during heating up (bottom left) and cooling down (bottom right). During heating up, the temperature starts at 30°C then increases to 80°C, 100°C, 120°C, 140°C, 160°C, and 180°C. During cooling down, the temperature starts at 180°C then cools to 160°C, 140°C, 120°C, 100°C, and 80°C. Arrows indicate increasing temperature direction corresponding to the rainbow color.
the extracted data. Detail extracted SAXS data can be found in the supplemental information (Tables S2, S3, S4). In summary, under anhydrous condition, PBI/PA contains approximately 1 nm and 20 nm featured domains separated by about 0.9–1.2 nm. These domain sizes and their inter-crystal planes were unchanged during the courts of heating and cooling from 80°C to 180°C and vice versa. However, the fitting parameters, based on Porod’s law which relates the scattering intensity I(q) with the specific surface area of the particles Ss, as following, 22

\[ \lim_{q \to \infty} I(q) \propto S_s \times q^{-6-\delta}, \]

where q is the scattering wavenumber and d is the particles’ dimensionality, show these domains changed their shapes from some unresolvable peaks to more likely lamellar or vesicles.

The morphology of PBI/20%HPA/PA is slightly different under anhydrous conditions. It contains a 1.5 nm featured particle and a 23 nm featured domain. The 1.5 nm particle slightly grew to 2.1 nm upon heating from 80°C to 180°C and remained the same size during cooling. The size of the 23 nm domain, however, remained unchanged throughout heating and cooling. The smaller feature appeared lamellar or vesicular at 180°C whereas the larger feature was an unresolved shape. The diffraction peak at 1.2 nm (inter-crystal planes) belongs to HPA molecules. This distance remained almost unchanged throughout the heating and cooling cycles. It is interesting that the smaller feature, which is most likely HPA clusters, grew with temperature but was irreversible upon cooling back to 80°C.

At 10% RH, however, the particles in PBI/20%HPA/PA appear a little bit different with slightly larger particle size of 3 nm (maybe due to HPA hydration) and smaller feature domain of 15 nm (maybe due to the polymer chain steric effect). These particle and domain, however, seem to shrink upon heating from 80°C to 180°C to smaller size features. The 3 nm feature is most likely lamellar or vesicle at 80°C but becomes non-resolvable due to variation in shapes after shrinking to 1.8 nm at 180°C. The 15 nm feature, on the other hand, is almost spherical at 80°C but shrinks to 3.4 nm and forms a cylindrical shape at 180°C. The diffraction peak at 1.3 nm (inter-crystal planes) still belongs to HPA, but it is slightly larger than under anhydrous conditions due to swelling of hydrated HPA. This distance is constant with temperatures throughout the heating and cooling cycles. Most of these features seem to be reversible upon cooling back to 80°C. The SAXS fitting results explain why PBI/HPA/PA requires some humidification to boost its proton conductivity. At 10% RH, the HPA clusters seem to dissolve in the polymer matrix forming a more uniform structure which distributes proton conducting sites more homogeneously.

The FTIR bands are highly sensitive to changes in molecular structure, which becomes valuable to understand the acid-base proton exchange reaction between PBI and H3PO4 as well as the dipole-dipole interactions between membrane components. Figure 7 shows the FTIR spectra of a pristine PBI membrane and a PBI/HPA composite membrane. The spectrum of the pure PBI contains all featured bands that were previously assigned. 23 The spectrum of PBI/HPA composite membrane shows some shifts and extra absorptions peaks that have been assigned according to the literature. 24 Table II summarizes these band assignments. Most noticeably, a strong absorption peak at 1628 cm−1 can be attributed to O-H bending of water absorbed on HPA. In addition, four absorption peaks at 963 cm−1, 922 cm−1, 851 cm−1, and 797 cm−1 are attributed to asymmetric W = Oterminal, asymmetric Si-O, symmetric W-Ocorner-W, and asymmetric W-Oedge-W, respectively. 25 Figure 8 shows multiple spectra of PBI/HPA and PBI/20%HPA/PA as the membranes were heated up from 80°C to 160°C at 5% RH. Both membranes’ spectra show absorption bands at 938 cm−1 and 861 cm−1 associated with phosphate modes. The presence of phosphate anions confirms proton conduction in these membranes occurs through a Grothuss mechanism. The band at 938 cm−1 has been assigned to the asymmetric stretch P(OH)1 of the HOPO4− anion, while the 861 cm−1 is attributed to the symmetric stretch P-O of the anion. 26 The presence of H3PO4− anion confirmed the acid-base proton exchange between PBI and H3PO4, which produces an imidazolium cation along the polymer backbone. 27 Since the imidazole group is protonated, the vibrational modes associated with N-H bending and ring stretching shift to higher frequencies. As shown in Figure 8, the broad band appears between 2500–3000 cm−1 has been assigned to N3−H stretching, whereas band at 2250–2500 cm−1 is associated with O-H stretching. 28 In addition, bands as 1628 cm−1, 1581 cm−1, and 1460 cm−1 are from C=N and C=C stretching of the ionized imidazole group on the polymer backbone, although band at 1628 cm−1 can also be contributed by OH bending of free water. These observations confirm the acid-base interaction of phosphoric acid with imidazole group through a protonation reaction. Although ionized imidazole groups do not contribute to the membrane proton conductivity due to its immobilization, they are the substrate holding the anion of diprotinated phosphate (H2PO4−), which creates a hydrogen bond network of excess phosphoric acid within the matrix of the polymer. It is interesting that PBI/PA also has a shoulder band near 1720 cm−1 that belongs to a hydronium ion, which indicates the presence of proton transport contributed by free water in the membrane. 29 As the temperature increased from 80°C to 160°C, it is clearly shown that more water and structural loss occur in the PBI/PA sample, which negatively affects the proton conductivity of the membrane. Both samples, however, showed a shift of asymmetric to symmetric stretch of H2PO4− anion at temperatures above 140°C due to the formation of pyrophosphoric acid.

Solid-state NMR spectroscopy was used to study the conduction mechanism of phosphoric acid doped PBI polymer. While the chemical shifts give information about the chemical environments, the line widths of the signals at different temperatures often provided mobility.

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Table II. FTIR band assignments of PBI/HPA.

| Wave number (cm⁻¹) | Assignment                        |
|-------------------|-----------------------------------|
| 3389 (b)          | Free non-hydrogen bonded N-H stretching |
| 3147 (b)          | Self-associated N-H stretching      |
| 3060 (b)          | Aromatic C-H stretching             |
| 1628 (vs)         | C=C and C=N stretching or water O-H bending |
| 1448 (vs)         | In-plane ring vibration              |
| 1418 (m, sh)      | C-C stretching                      |
| 1298 (m)          | Imidazole ring breathing             |
| 1262 (w)          | In-plane C-H deformation             |
| 1017 (w)          | Benzene ring breathing               |
| 963 (w)           | W-O asymmetric stretching            |
| 922 (m)           | Si-O asymmetric stretching           |
| 851 (w)           | W-O-W symmetric stretching           |
| 797 (s)           | W-O-W asymmetric stretching          |
| 695 (m)           | C-H out of plane bending             |

Note: These band assignments are based on previous publications with abbreviations s (strong), m (medium), w (weak), sh (shoulder), vs (very strong), b (broad), t (terminal), c (corner), and e (edge).
information on the molecular level. During this study, the interaction between PBI and phosphoric acid was characterized by $^1$H MAS and $^{31}$P CP/MAS NMR spectroscopy. CP/MAS NMR technique is used to obtain $^{31}$P spectra in order to enhance signal to noise at a much shorter experimental time.

Figure 9 shows the $^1$H MAS NMR spectra of PBI/PA and PBI/20%HPA/PA at 80°C and 120°C. In both cases, the $^1$H signal resonated at 9 ppm is assigned to free H$_3$PO$_4$ while the one at 8 ppm corresponds to imidazolium -NH sites on the polymer. Due to the constraint of our solid-state NMR spinning rate capability, these peaks are not separated as described in the literature. The linewidths of PBI/20%HPA/PA $^1$H spectra are narrower, which indicates higher mobility of proton motions due to their smaller dipole-dipole interaction. In addition, as temperature increased from 80°C to 120°C, the integral peaks ratio at 9 ppm to 8 ppm were estimated through deconvolution processes and found to increase from 3.38 to 4.88 in PBI/20%HPA/PA, which indicates more free phosphoric acid appeared in the polymer matrix. This means that the proton transfers more dominated through hoping via hydrogen bonding between the free phosphoric acid, its anion, and water molecules. On the other hand, the corresponding integral peaks ratio slightly decreased from 3.18 to 3.13 at 80°C and 120°C, respectively, in PBI/PA. The proton transport between phosphate anion and protonated imidazole on PBI, which is a slower proton conducting route, still plays a major contribution to the total proton conductivity of PBI/PA at higher temperatures.

Figure 10 shows the $^{31}$P CP/MAS NMR spectra of PBI/PA and PBI/20%HPA/PA at 80°C and 120°C. The $^{31}$P chemical shift for phosphoric acid is close to 0 ppm. The other peak appears at $-10$ ppm has been assigned to the dimeric compound pyrophosphoric acid.
temperature increased from 80°C to 120°C, the phosphoric acid peak shifted to 2 ppm and the pyrophosphoric acid peak grew stronger as shown in the PBI/PA/NMR spectrum. This observation indicates more pyrophosphoric acid formation while the rest of free phosphoric acid becomes hydrogen bonded to the imidazole of the backbone, as the temperature rises to 120°C. As a result, it reduces the number of available proton acceptor groups and immobilizes proton vacancies, and therefore, inhibits proton conduction. These changes are not observed in PBI/20%HPA/PA/NMR spectrum. The presence of HPA obviously helps to maintain free acid inside the polymer matrix as well as avoid condensation defects of phosphoric acid.

Figure 11 shows the effects of temperature on proton conductivities of PBI/HPA versus PBI/20%HPA/PA membranes under anhydrous condition and at 5% RH. Under anhydrous conditions, both PBI/PA and composite PBI/20%HPA/PA membranes decline in conductivity as temperatures reach above 120°C. The loss of free water and dehydration of phosphoric acid / HPA both contribute to the suffering of conductivity. However, the composite PBI/20%HPA/PA membrane seems to have a more dramatic effect due to the dehydration of HPA. At 5% RH, however, both the PBI/PA and composite PBI/20%HPA/PA membranes increase in conductivity with increasing temperature as expected. As shown, the temperature/conductivity relationships of both membranes are linearly dependent following the Arrhenius equation with calculated activation energies of 26.3 and 17.5 kJ/mole for PBI/PA and composite PBI/20%HPA/PA, respectively. Besides lowering activation energy, it also clearly shows the conductivity of PBI/20%HPA/PA is about three times higher than PBI/PA throughout the temperature range.

Since PA-doped PBI consists of an extensive hydrogen bond network, its proton conduction occurs mainly through a Grothuss mechanism, in which molecules are reoriented to form hydrogen bonding and allow protons to hop from one site to another through the hydrogen bridge. However, at elevated temperatures, as shown and discussed in FTIR and NMR analyses, PA-doped PBI tends to lose water and dehydrate phosphoric acid more. As a result, proton hopping occurs mainly between the NH sites and the bound phosphate anions. Since the bound anions are immobile, the proton transfer occurring in PA-doped PBI is relatively slow. Moreover, the strong interaction between protons and nitrogen atoms of the imidazole reduces the proton mobility and prohibits its transfer. On the other hand, the existence of HPA in PA doped PBI enhances the presence of free phosphoric acid and preserves water in the polymer matrix, protons now can freely jump along different paths, between free anion/PA, water/PA, or bound anion/NH, by reorientation of anions and transferring of protons. With excess of PA in the membrane, protons migrate more favorable along the anion/PA or water/PA chain, whereas the bound anion/NH only gives a relatively small contribution to the total proton conductivity. In addition, the excess PA helps to draw more water in the membrane, leading to higher conductivity since proton transfer is faster along the water/PA path. Furthermore, higher water concentration lowers the viscosity of the polymer allowing faster mobility and conductivity of the molecules.

Figure 12 shows the correlation of proton conductivity and doping level of the membranes upon adding different amount of HPA. At 160°C and 5% RH condition, addition of up to 20% HPA increased the acid doping level from 10 to 14, but dropped to 12 at higher than 20% HPA addition. The conductivity results are consistent with the doping data showing conductivity maximized at 20% HPA. Previous studies have shown that the conductivity increases with the doping level for a given temperature and RH. The activation energy decreases with increasing doping level due to the higher mobility of protons. In fact, excess phosphoric acid increases the proton conductivity, by both Grothuss and Vehicle mechanisms, by either increasing the probability of proton hopping via hydrogen bonds or the proton diffusion rate due to higher phosphoric concentration in the polymer matrix. It is still unclear why the doping level, and therefore conductivity, decreases when more than 20% HPA is added into the polymer membrane. The more concentrated HPA membrane might spatially squeeze excess phosphoric acid out of the polymer.

Figure 13 shows the relative humidity dependence of proton conductivity for the control PBI/PA membrane versus various compositions of PBI/HPA/PA composite membranes. Conductivity generally increases with relative humidity for all membranes. As reported earlier, an increase in RH leads to higher water content in the membrane, leading to higher mobility and conductivity of protons. The addition of 20% HPA gives the highest conductivity at 160°C and 10% RH reaching 0.127 S+cm⁻¹. This is more than 3 times higher than PBI/PA.
Figure 13. Relative humidity dependence of ionic conductivity of different HPA loading on phosphoric acid doped PBI membrane at 160°C.

Figure 14. Polarization curves of PEMFCs under dry hydrogen and dry oxygen at 160°C with MEA made of PBI/PA (●) and PBI/20%HPA/PA (▲). MEA active area is 21 cm² with $\lambda_{H_2} = 1.5$ and $\lambda_{oxygen} = 2.5$.

itself, which shows a conductivity of 0.049 S cm⁻¹ at the same conditions.

Figure 14 compares the polarization curves of MEAs made from PBI/20%HPA/PA MEA and PBI/PA MEA, using dry hydrogen and dry oxygen, after 700 hours testing. As can be seen, although the open circuit voltage (OCV) of PBI/20%HPA/PA MEA is lower, which is possibly due to higher fuel cross-over of the composite membranes, the IR slopes of the polarization curve of the composite PBI/20%HPA/PA MEAs (approximately, 0.25 Ohm cm⁻²) is shallower than of the control PBI/PA MEA (0.31 Ohm cm⁻²), clearly indicating the HPA doped membrane has higher conductivity. As shown in Table III in the following impedance study section, although the ohmic resistance of MEA containing PBI/20%HPA/PA is much lower than the control PBI/PA, the cathode and mass transport resistances are not. The higher resistances of the cathode and mass transport may decrease the fuel cell performance and counter affects the membrane ionic conductivity of PBI/20%HPA/PA. One will have to optimize the properties of the electrodes in order to fully exploit the reduced membrane resistance, this is the subject of a future study.

Figure 15 shows the results of the above fuel cells EIS measurements at 160°C using dry hydrogen and dry air. Two MEAs of PBI/20%HPA/PA were used to compare to the control reference MEA (PBI/PA). As stated earlier, both composite membrane MEAs show three times lower ohmic resistance (0.057 ± 0.002 Ohm cm⁻²) compared to the control reference (0.160 Ohm cm⁻²). Table III summarizes the fitting resistances obtained for these three MEAs. To check the membrane durability by ionic conductivity, each MEA was continuously run at a current density of 0.2 A cm⁻² for several days. EIS was then measured at 169 h and 313 h. As shown, the ohmic resistance of our composite PBI/20%HPA/PA MEA was unchanged after 313 hours, while the charge transfer resistance was improved over time. We have not fully understood the fuel cell break in as shown after 313 hours conditioning, and at the moment, several fuel cell parameters have not been optimized yet. Clearly, as stated above, these fuel cell data are preliminary, and a lot of work is ongoing to successfully obtain and truly appreciate the high temperature PEM fuel cells using phosphoric acid doped PBI/HPA as the electrolyte.

### Table III. EIS data provided from equivalent circuit fitting to determine ohmic resistance, cathode resistance, and mass transport resistance.

| MEA                  | Ohmic resistance (Ohm cm⁻²) | Cathode resistance (Ohm cm⁻²) | Mass transport resistance (Ohm cm⁻²) |
|----------------------|----------------------------|-----------------------------|----------------------------------|
| PBI/20% HPA/PA (1)   | 0.05888                    | 0.31185                     | 0.06936                          |
| PBI/20% HPA/PA (2)   | 0.05607                    | 0.20093                     | 0.16733                          |
| PBI/PA               | 0.16025                    | 0.19992                     | 0.13440                          |
Conclusions

Polybenzimidazole-based, heteropolyacid-added, phosphoric acid-doped (PBI/20%HPA/PA) membranes have good proton conductivity, strong mechanical stability, and can potentially be great candidates for use in high temperature PEMFCs. At 160 °C and 10% RH, the conductivity of PBI/20%HPA/PA was 0.127 ± 0.007 S·cm⁻¹, which is approximately three times higher than the current used PBI/PA membrane (0.049 ± 0.005 S·cm⁻¹). It has been found that LiCl helps to dissolve PBI and HPA in DMAC forming a homogenous solution ready for casting. The lithium salt can be completely removed after soaking the membrane in concentrated phosphoric acid (85 wt%) for seven days. Adding HPA to the polymer seems to increase acid doping level; however, it maximizes at approximately 20 wt% of HPA addition. Through FTIR, ¹H / ³¹P MAS NMR, and TGA, we found the addition of HPA helps to increase the proton conductivity of PBI-based phosphoric acid-doped membranes by inhibiting the water from escaping the membrane at elevated temperatures, minimizing the dehydration of phosphoric acid, and adding more acid sites by providing additional paths for proton transport. The tensile stress–strain test shows PBI/20%HPA/PA has better mechanical properties. SAXS data show PBI/20%HPA/PA morphology depends on both temperature and humidity. Under anhydrous conditions, there are 1.5–2.1 nm hydrated HPA clusters that grow irreversibly larger into lamellar or vesicle shape as the temperatures increasing to 180 °C. Under humidified conditions, however, these 3 nm hydrated HPA clusters tend to dissolve uniformly in the membrane, producing a 1.8 nm feature at 180 °C. The results indicate minimum humidity is required to dissolve HPA clusters and boost the composite membrane conductivity. This observation is consistent with the proton conductivity behavior. To verify that these membranes were still viable in a fuel cell, preliminary fuel cell data was collected using an un-optimized single MEA constructed from hydrated PBI/20%HPA/PA membranes that were still viable in a fuel cell, preliminary fuel cell testing the fuel cells. Further thanks goes to the Innovation Fund Denmark, energetnet.dk and the Danish Energy Agency (the EUDP program).

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