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Improving the performance of proton exchange membrane fuel cells

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Incorporation of an ionic liquid into sulfonated poly(ether ether ketone) polymer membranes increases their thermal stability and power density.

An energy crisis is being faced because of the depletion of natural resources and increasing environmental problems.[1] Indeed, energy was picked as the top priority in a list of humanity's ten problems for the next 50 years.[2] In this context, there is growing interest in new materials and devices for power generation, especially research into fuel cells. Fuel cells operate similarly to conventional batteries, other than their requirement for a continuous fuel supply. For example, the proton exchange membrane fuel cell (PEMFC) transforms chemical energy liberated during the electrochemical reaction of hydrogen and oxygen into water, electricity, and thermal energy. Regarded as future energy conversion devices, PEMFCs are especially attractive because of their ability to operate at low temperatures with a high power density, high efficiency, and relatively low emission.[3,4] The most commonly used polymer membrane in PEMFCs is Nafion, but this has limitations, such as the need for permanent gas humidification to assure high proton conductivity, the low proton conductivity at temperatures above 100°C, and high manufacturing costs.[5–7]

In recent years, some studies[8,9] have suggested sulfonated poly(ether ether ketone), SPEEK, as a promising polymer membrane candidate to replace Nafion. It is known that the incorporation of aprotic ionic liquid in the polymer may increase ionic mobility and facilitate the transport of protons inside the membrane. Ionic liquids are compounds that consist exclusively of ionic species—generally an organic cation and an inorganic or organic anion—which are liquid at temperatures below 100°C. This class of fluids have interesting properties, such as negligible volatility, good thermal stability, high ionic conductivity, and a wide electrochemical potential window. These properties mean that there is a growing interest in testing ionic liquids as a protonic charge carrier in proton exchange membranes, which could allow PEMFCs to operate at low humidity and at temperatures above 80°C. To attempt to improve PEMFCs, the thermal stability and conductivity of polymer membranes with incorporated ionic liquid has thus been studied.[10–12]

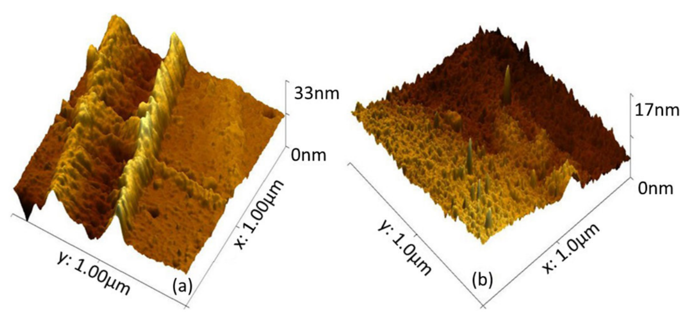

Figure 1. *Atomic force microscope images of (a) a sulfonated poly(ether ether ketone)—SPEEK—membrane, and (b) a modified SPEEK membrane (SPEEK/BMI^{+}). This membrane incorporates the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF$_4$). Immersion in the ionic liquid reduced the membrane's surface roughness.*

We have evaluated the physical and chemical properties of SPEEK membranes, with a 65% degree of sulfonation, that we modified with the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF$_4$).[13] We fabricated the modified membrane (SPEEK/BMI^{+}) by immersing the SPEEK membrane in a solution of 5mmol BMI.BF$_4$ in 50mL of ultrapure water, at room temperature for 2min. After immersion, we washed the membranes with deionized water to remove any residual ionic liquid and prevent its physical adsorption on the membrane surface.[14]

Atomic force microscopy images of the SPEEK and SPEEK/BMI^{+} membranes are shown in Figure 1. We observe that the average surface roughness of the pristine SPEEK membrane was reduced from 3.84 to 2.76nm after contact with the ionic liquid solution. We also used electrochemical impedance spectroscopy to determine the ionic conductivity as a function of temperature (25–100°C). Our results showed

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that the conductivity of the SPEEK membrane increases with increasing temperature and reached $8.91\mu Scm^{-1}$ at 100°C. The modified SPEEK/BMI^+ membrane has a similar behavior to that of Nafion membranes modified with imidazole cations,[7] which reach a conductivity of $1.02 mScm^{-1}$ at 100°C.

The performance of these two membranes in a PEMFC is illustrated in Figure 2. The open-circuit potential (OCP) value of the SPEEK/BMI^+ membrane is 0.909V, which is higher than the OCP value of pristine SPEEK (0.690V). The OCP of the pristine membrane was probably reduced because of fuel crossing the electrolyte membrane. It has also previously been observed that SPEEK-based membrane electrode assemblies (MEAs) are not stable at high temperatures, and that they may even be punctured above 90°C,[9] suggesting that the SPEEK membrane is unsuitable for such fuel cell conditions.

Thermogravimetric analysis (TGA) curves obtained for the ionic liquid and membrane samples are shown in Figure 3. These results indicate an improvement in the thermal stability of the modified SPEEK/BMI^+ membrane compared with the pristine SPEEK membrane. This increase in thermal stability arises because of the interaction between sulfate groups and 1-butyl-3-methylimidazolium (BMI^+) cations. The increase also allows the membrane to be used in a fuel cell under high-temperature test conditions. The thermal stability and conductivity improvements achieved with the SPEEK-based MEA provide a higher power density of up to $0.13 Wcm^{-2}$.

In summary, we have demonstrated that incorporation of BMI^+ cations into SPEEK membranes leads to increased conductivity and thus an improved performance of a PEMFC operating at 80°C. We have therefore shown that membranes modified with $BMI.BF_4$ are promising for use in PEMFCs operated at temperatures above 80°C. The next stage of our work will be to evaluate the physical and chemical properties of composite SPEEK/zeolite/ionic liquid polymer membranes for use in PEMFC applications. Zeolites have been chosen because they are hydrophilic and have excellent heat resistance. The combination of ionic liquids and zeolites may result in composites with high water retention and increased proton conductivity.

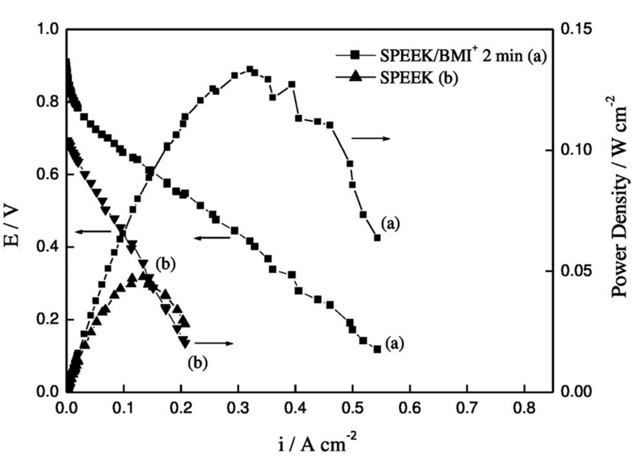

Figure 2. Polarization curves of the (a) SPEEK/BMI^+ and (b) SPEEK membranes. For these measurements both hydrogen and oxygen were pressurized to 2 bar and the fuel cell operating temperature was 80°C. The increased thermal stability and conductivity of the SPEEK.BMI^+ membrane allows better fuel cell operation and a higher power density compared with fuel cells that include the unmodified SPEEK membrane. Left- and right-pointing arrows indicate energy (E) and power density results, respectively. i: Current density.

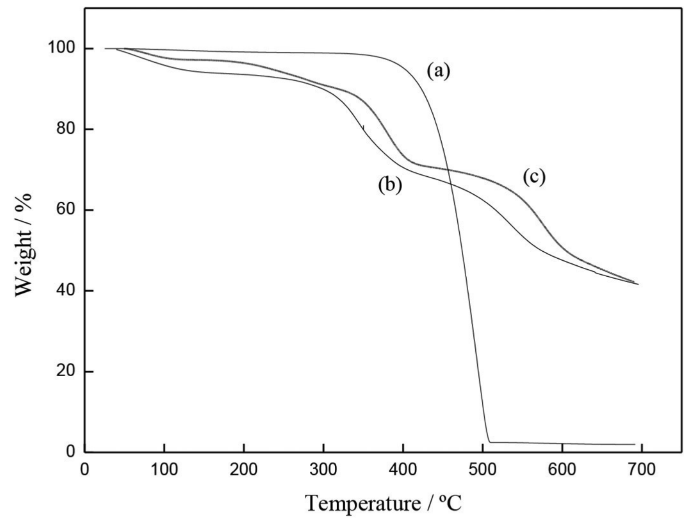

***Figure 3.** Thermogravimetric analysis curves of (a) $BMI.BF_4$, (b) SPEEK, and (c) SPEEK/BMI^+ membranes. The modified membrane exhibits an improved thermal stability compared with the pristine SPEEK membrane.*

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Letícia Guerreiro da Trindade's main focus is the modification, preparation, and characterization of polymer composites. She has experience in the field of conductive polymers for use in proton exchange membrane fuel cells, as well as the synthesis and characterization of ionic liquids.

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