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Kinetics and Thermodynamics of Hydrogen Oxidation and Oxygen Reduction in Hydrophobic Room-Temperature Ionic Liquids

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Abstract

In this study 1-dodecyl-3-methylimidazolium (C₁₂mim) bis(pentafluoroethylsulfonfyl)imide (BETI) and 1-dodecylimidazolium (C₁₂im) BETI hydrophobic room-temperature ionic liquids (RTILs) were synthesized and used as proton-conducting electrolytes in a nonhumidified feed gas electrochemical cell. The ionic conductivities of C₁₂mimBETI and C₁₂imBETI were similar and increased linearly with an increase in temperature from 20 to 130°C. However, when used in the electrochemical system the protic water-equilibrated C₁₂imBETI had a larger maximum current and power density compared to the aprotic water-equilibrated C₁₂mimBETI. The effect of water content on the reaction rates and thermodynamics of these hydrophobic RTILs was also examined. The efficiency of the C₁₂mimBETI increased upon removal of water while that of the C₁₂imBETI decreased in efficiency when water was removed. The water structure in these RTILs was examined using attenuated total internal reflection Fourier transform IR spectroscopy and depended on the chemical structure of the cation. These studies give further insight into the possible mechanism of proton transport in these RTIL systems.

An increase in global energy demand coupled with the escalating costs of petroleum-based energy has prompted a growing interest in developing alternatives to fossil fuels. Proton exchange membrane hydrogen fuel cells (PEM-HFCs) are among the most attractive sources of alternative power due to their high output power density. Current drawbacks preventing the wide scale adoption of PEM-HFCs include the high cost of the Nafion membrane used in these devices and the low operating temperatures (< 80°C). A low operating temperature is necessary to keep the Nafion membrane hydrated. At higher temperatures the water in the Nafion membrane evaporates and the membrane loses its ability to conduct protons. In addition, the low operating temperature requires ultrapure hydrogen gas to be supplied to the anode in order to prevent poisoning of the platinum catalyst. These limitations add to the overall cost of Nafion-based PEM-HFCs. To increase the operating temperature of a PEM-HFC, Nafion membranes containing imidazolium salts,^{1,2} silica,³ poly(tetrafluoroethylene),⁴ zirconium phosphate,⁵ and sulfated zirconia⁵ have been explored in addition to alternative polymer membranes.^{1,2,6-12} The membranes that incorporate imidazole- or imidazolium-based room-temperature ionic liquids (RTILs) are an attractive subset of these membranes, as they are conductive at temperatures of 100°C or higher using dry gases.^{1,2,8,10,11} At these high temperatures the carbon monoxide poisoning of the platinum catalyst is reduced due to the thermal instability of the Pt–CO surface products,¹³ allowing lower grade hydrogen fuel sources to be used.

Cost could further be reduced if a supplementary polymer membrane, or a liquid membrane cell, could be developed eliminating the need for the Nafion altogether. It was first reported in 2003 that Brønsted acid-base type RTILs are suitable electrolytes for fuel cells.^{14,15} Since this discovery RTILs have been an area of increased study for use in PEM-HFCs.^{1,10,11,14-22} Significant work in the area of the reduction of oxygen^{19,23-29} and oxidation of hydrogen³⁰⁻³² has been studied in a variety of RTILs. Much of this work has been done in aprotic, water-free RTILs.^{23,24,26-29} In these RTIL systems the reversible one-electron reduction reaction of oxygen to form superoxide is observed.^{23,24,26-29} While these studies give insight into possible reactions that may occur when RTILs are used as electrolytes in HFC, they do not include water or a proton source. Detailed work by Evans et al. explored the oxygen reduction reaction in *N*-methyl-*N*-butylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMSI) in the absence and presence of catechol, which acts as a proton source. In the presence of protons superoxide is unstable and hydrogen peroxide is most likely formed.²⁴ The instability of superoxide was also observed in the weakly acidic RTIL tris(*n*-hexyl)tetradecylphosphonium BMSI.²⁴ Superoxide is unstable in RTILs when water is added to the electrochemical system.^{26,27} Other studies exploring the oxygen reduction reaction in RTIL systems when protons are present suggest that oxygen is reduced to form water.^{14,19}

Advantages of using RTILs in HFCs include their stability at high temperatures, negligible vapor pressures, high conductivities, and large electrochemical stabilities. The conductivity of RTILs increases with temperature.^{1,2,14,16,17,20} An increase in conductivity may lead to an increase in efficiency of the HFC due to protons being supplied to the cathode at a faster rate. However, when RTILs are used in combination with either Nafion or alternative proton-conducting membranes, their overall conductivity decreases compared to the neat RTIL.^{1,2,11} In addition, it has been shown that the conductivity of these RTIL-saturated membranes is also orders of magnitude smaller than the conductivity of hydrated Nafion membranes.^{1,2,10,11} Many papers report the conductivity of the RTIL-impregnated membranes outside of working fuel cells^{1,2,10,11} and relatively few report any results in a working H₂/O₂ fuel cell.^{10,11}

Neat RTILs and RTIL mixtures have also been studied for use as fuel cell electrolytes without the use of a polymer membrane.¹⁴⁻²² The hydrophilic non-Brønsted acid-base RTIL 1-butyl-3-methylimidazolium tetrafluoroborate is a useful electrolyte in fuel cells at room temperature and atmospheric pressure.¹⁸ However, the efficiency drops significantly upon the addition of water.¹⁸ This is a major drawback because water is a by-product of the reaction. Other RTILs based on imidazolium and protic ammonium cations with a variety of anions have also been studied for use as fuel cell electrolytes at temperatures above 100°C and nonhumidifying conditions.^{14-17,19,20} Noda et al. reported that by adding an excess mole fraction of imidazole in an imidazolium bis(trifluoromethanesulfonyl)imide ionic liquid, conductivities of up to 80 mS cm⁻¹ at 120°C can be obtained¹⁴ which are comparable to the conductivity of Nafion 112 under 95% relative humidity at 45°C.³³ However, imidazolium poisons the Pt catalyst.^{5,34} When imidazolium becomes deprotonated it is capable of forming a polymetric imidazolium film on Pt surfaces.³⁴ This polymetric film formation can be prevented by simply replacing imidazole with 1-methylimidazole. The methyl group on the imidazole ring is capable of breaking the hydrogen bonding extended network between the imidazole rings.³⁴ Disrupting the extended imidazole network on the Pt catalyst allows the H₂ and O₂ gases to come in direct contact with the Pt where oxidation and reduction reactions can readily occur.

The purpose of this work is to study the electrode kinetics and thermodynamics of the reactions that occur in an HFC, namely, hydrogen oxidation and oxygen reduction, in two synthesized hydrophobic imidazolium-based RTILs. The RTILs synthesized and studied in

this paper consist of the aprotic 1-dodecyl-3-methylimidazolium ($C_{12}mim$) or its protic derivative 1-dodecylimidazolium ($C_{12}im$) cation coupled with bis(pentafluoroethylsulfonyl)imide (BETI) as the anion. The structures of these RTILs can be found in Fig. 1. To prevent the poisoning of the Pt electrode with imidazolium the RTIL cation contains an alkyl chain attached to at least one nitrogen.³⁴ This prevents the possibility of a polymer-like membrane forming at the electrode interface that could potentially interfere with the electrochemical measurements.^{1,2} The RTILs were studied under both water-equilibrated and ambient conditions to see if there is any affect on the efficiency of the reactions with a decrease in water content. The water-equilibrated and ambient RTILs were chosen to represent the two extremes of water content in a functional HFC utilizing these materials. Water is a byproduct of the reduction reaction and over time water will build up in the electrochemical cell saturating the RTIL. The ambient condition was examined because this is the least amount of water that the RTIL can contain at room temperature under normal atmospheric conditions.

Experimental

Materials

1-bromododecane (98%) and 1-methylimidazole (99%) were purchased from Aldrich. Lithium bis(pentafluoroethylsulfonyl)imide (LiBETI) was purchased from 3M Corporation. 1-dodecylimidazole was purchased from Acros Organics. Hydrochloric acid was purchased from EMD. All chemicals were used as received except 1-methylimidazole, which was distilled before use.

Synthesis

$C_{12}mimBETI$ was synthesized as previously described.³⁵ Briefly, 1-bromododecane was reacted with a slight molar excess of freshly distilled 1-methylimidazole for approximately 4 h at 65°C. The unreacted 1-methylimidazole was removed by distillation. The resulting viscous product was recrystallized in 1,1,1-trichloroethane until white crystals of $C_{12}mimBr$ were obtained. $C_{12}mimBr$ was dissolved in Nanopure water (Barnstead) with a resistivity of at least 18.2 MΩ cm and added to an equimolar aqueous solution of LiBETI. The resulting clear, colorless liquid was washed with copious amounts of Nanopure water to remove any unreacted salts.

$C_{12}imBETI$ was synthesized by dissolving 1-dodecylimidazole in 0.5 M HCl to form $C_{12}im$ chloride. The $C_{12}im$ chloride solution was then added to an equimolar amount of LiBETI, which was also dissolved in 0.5 M HCl. The resulting slightly yellow RTIL was denser than water and settled to the bottom where it was washed with copious amounts of 0.5 M HCl to remove any unreacted salts. Nanopure water was used for all aqueous solutions.

Both $C_{12}mimBETI$ and $C_{12}imBETI$ were dried under vacuum at approximately 65°C for at least 4 h to remove any residual water. The RTILs were then stored under water-equilibrated or ambient conditions. For the water-equilibrated condition the $C_{12}mimBETI$ was stored under Nanopure water and the $C_{12}imBETI$ was stored under 0.5 M HCl. Ambient conditions were achieved by allowing the RTILs to come into equilibrium with atmospheric moisture. All samples were equilibrated at least 14 h before use.

Characterization

The composition of the hydrophobic RTIL $C_{12}imBETI$ synthesized for this work was verified by electrospray mass spectroscopy using a ThermoFinnigan LCQ ion trap mass spectrometer. The RTIL was >98% pure with the only detectable impurity occurring at an $m/$

z^+ of 405.3 which was attributed to the 1-dodecylimidazole starting material containing trace amounts of 1,3-didodecylimidazolium.

The viscosity of the water-equilibrated RTILs was measured using a Zeitfuchs cross-arm viscometer in a silicon oil bath from 20 to 160°C. The Zeitfuchs cross-arm viscometer was left open to the atmosphere to facilitate comparison with the electrochemical experiments. The water content of the water-equilibrated and ambient RTILs was determined using Karl Fischer titration. The Karl Fischer titrant was diluted in anhydrous methanol and standardized with water before use.

ATR-FTIR spectroscopy

Attenuated total internal reflection, Fourier transform IR (ATR-FTIR) was performed on the water-equilibrated and ambient C₁₂mimBETI and C₁₂imBETI RTILs from 3100 to 4000 cm⁻¹ using a Perkin Elmer Spectrum One FTIR spectrometer with an in-compartment horizontal ATR accessory from Pike Technologies. The RTILs were placed in an ATR-FTIR liquid flow cell (~0.5 mL total volume) using a silicon ATR element. Before use, the silicon ATR element was cleaned in piranha solution (3:1 concentrated H₂SO₄/30 % H₂O₂) for 2 h, rinsed with copious amounts of nanopure water, and plasma cleaned (Harrick Scientific) in an Ar⁺ plasma for 2 min. The silicon ATR element and stainless steel flow cell were cleaned in methanol and dried between each sample.

Differential scanning calorimetry

The thermal stability of the RTILs was determined by differential scanning calorimetry (DSC) using a Mettler-Toledo DSC821^e module. Heating curves were obtained at a scan rate of 10°C min⁻¹ from 25 to 500°C for the C₁₂mimBETI and from 25 to 440°C for the C₁₂imBETI. The N₂ carrier gas was flowed at a rate of 10 mL min⁻¹. Pierced aluminum (Al) pans with a volume of 40 µL were used in all experiments. One drop (~9 mg) of each of the RTILs was placed in an open Al crucible pan before adding an Al lid that was crimped to the crucible.

Electrochemical measurements

The ionic conductivity of the RTILs was measured using a standard conductivity probe with a Wien bridge oscillator as the input. The Wien bridge oscillator had a peak-to-peak voltage of 0.8 V at 1 kHz. The standard conductivity probe consisted of two parallel Pt plates with an area of 2 cm² spaced 4 mm apart. The output ac was measured using a Fluke 73 III digital multimeter. Calibration was performed at room temperature by measuring the ac from standard aqueous KCl solutions ranging in concentration from 0.5 to 100 mM. The ionic conductivity of the water-equilibrated RTIL samples was measured from 20 to 130°C. The temperature was controlled by placing a vial of the water-equilibrated RTIL into a silicon oil bath. A mercury thermometer with an accuracy of 1°C was used to measure the temperature of the bath. The electrochemical stability of the water-equilibrated RTILs was measured at room temperature using an EG&G Princeton Applied Research 273 potentiostat. A three-electrode configuration was used which consisted of a 25 µm Pt disk working electrode, Pt wire counter electrode, and an aqueous Ag/AgCl reference electrode. The scan rate was 20 mV s⁻¹. The electrochemical potential windows were determined by scanning the applied potential until a significant current from the oxidation or reduction of the RTILs was observed.

Preparation of electrodes

The Pt electrodes used in the thermodynamic experiments were cleaned daily either by rinsing with a series of organic solvents (benzene, ethanol, and acetone) followed by rinsing

with Nanopure water or held in a natural gas flame for 10–15 s. Each electrode was then electrochemically cleaned as follows: The applied potential was scanned from +1.550 to –0.300 V vs an aqueous Ag/AgCl reference electrode at 100 mV/s in 0.5 M H₂SO₄. One of the Pt wires served as the working electrode and the other as the counter electrode. After cleaning, the surface area of each electrode was determined by the hydrogen adsorption method.^{36,37} The hydrogen absorption curve was obtained by scanning the applied potential from +0.600 to –0.200 V at 25 mV/s in 0.5 M H₂SO₄. The surface area was then calculated using the following equation

$$S_r = \frac{Q_m}{ced_m} \quad [1]$$

where S_r is the surface area, e is the electron charge, d_m is the surface metal atom density (210 $\mu\text{C cm}^{-2}$),³⁷ c is a constant to correct for readily accessible sites (0.84),³⁷ and Q_m is the charge associated with the formation of a hydrogen atom monolayer.^{36,37} Q_m can be calculated by

$$Q_m = \frac{1}{\nu} \int_{(V_0-V_i)/\nu}^{(V_0-V_f)/\nu} IdV - Q_{dl} \quad [2]$$

where ν is the scan rate, I is the current, Q_{dl} is the charge due to the double-layer capacitance, $V_0 - V_f$ is the voltage at which hydrogen desorption begins to occur, and $V_0 - V_i$ is the voltage at which hydrogen adsorption begins to occur.³⁶ An average electrode area was determined by calculating the electrode area from three different scans.

Thermodynamic measurements

Temperature-dependent electrochemical experiments were carried out in a U-shaped glass tube with a volume of about 2 mL (see Fig. 2). Two smooth electrochemically cleaned Pt coiled wires (~2 cm long) were used as the electrodes with an electrochemically determined surface area of approximately 0.8 cm². To eliminate any errors in the measurements that may occur from possible alterations of the electrode surface the current was normalized to the electrode area that was calculated for each specific experiment. The anode was placed over a bubbling stream of H₂ and the cathode was placed over a bubbling stream of O₂. Control experiments were performed by placing both under a bubbling stream of Ar. In all cases the gases were not humidified and were used as received. The distance between the bottoms of the electrodes in the RTIL was approximately 4.5 cm or 0.82 mL. The current–voltage curves were obtained in the galvanostatic mode using the EG&G Princeton Applied Research 273 from low to high current density. The temperature was controlled by placing the U-tube in a silicon oil bath which was heated to the desired temperature. The temperature was recorded using a mercury thermometer with a precision of 1 °C.

Results and Discussion

The thermodynamics of the hydrogen oxidation and oxygen reduction reactions in the C₁₂mimBETI and C₁₂imBETI RTILs were studied simultaneously to gain a better understanding of how these materials would function if used as the electrolyte in an HFC. Because water is a by-product of the oxygen reaction the RTILs will become saturated with water over an extended period of time in a running electrochemical cell. For this reason the physical properties and initial electrochemical studies were conducted under water-equilibrated conditions. Before using the water-equilibrated C₁₂mimBETI and C₁₂imBETI RTILs as electrolytes in the electrochemical cell their thermal stabilities, ionic

conductivities, and electrochemical stabilities were studied. The thermal stability of the electrolyte is essential if they are to be used at high temperatures ($> 80^{\circ}\text{C}$). We need to understand how their conductivities change with temperature. These hydrophobic RTIL materials would have no advantages over conventional electrolytes used in fuel cell (FC) membranes if their conductivity decreases at temperatures above 80°C . If the RTILs are not electrochemically stable at the potentials of the electrochemical half-reactions occurring in the cell they will react and decompose before the oxidation in hydrogen gas or reduction of oxygen gas occurs.

Thermal stability

One of the many advantages of RTILs is that they are conductive liquids without distinguishable vapor pressures; therefore, they eliminate the need for a supplementary solvent and do not evaporate upon heating. This is highly advantageous when using them as the electrolyte in HFCs. As the temperature of the HFC increases above 100°C the only substance that vaporizes is water, leaving the fluid RTIL behind. Current PEM-HFCs containing Nafion rely on H_2O for proton conduction, resulting in reduced performance at temperatures greater than 100°C . However, RTILs remain conductive well beyond 100°C ,¹⁹ and should theoretically remain conductive until they reach their decomposition temperature. DSC was used to determine the thermal decomposition limits of the $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ RTILs. The DSC traces are shown in Fig. 3. Both the water-equilibrated $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ can withstand temperatures over 350°C before they begin to decompose (see Fig. 3). A decomposition temperature of over 300°C is commonly found for other hydrophobic RTILs based on the C_nmim cation.³⁸⁻⁴¹

Electrochemical measurements

In addition to analyzing the thermal stability of these RTILs we investigated how their conductivity changes with an increase in temperature. The ionic conductivities of the water-equilibrated $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ as a function of temperature are shown in Fig. 4. In both cases the ionic conductivity increases linearly as the temperature is increased from 20 to 130°C . For the aprotic $\text{C}_{12}\text{mimBETI}$ the conductivity increased from 0.97 ± 0.09 to $3.06 \pm 0.20 \text{ mS cm}^{-1}$ and for the protic $\text{C}_{12}\text{imBETI}$ RTIL the conductivity increased from 1.21 ± 0.11 to $3.23 \pm 0.21 \text{ mS cm}^{-1}$. To verify that the increase in the ionic conductivity is directly related to an increase in the ionic mobility, the viscosity of the RTILs was measured from 20 to 130°C . Figure 5 shows the $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ ionic conductivities vs the inverse viscosity. The linear relationship between the conductivity and the inverse of the viscosity indicates that these RTILs obey the Nernst–Einstein relationship given by

$$\kappa = \frac{z^2 F^2 D}{RT} \quad [3]$$

where κ is the Debye length, z is the charge of the ion, F is Faraday's constant, R is the molar gas constant, T is the temperature in kelvin, and D is the diffusion coefficient defined by the Stokes–Einstein equation

$$D = \frac{k_B T}{6\pi\eta r} \quad [4]$$

where k_B is the Boltzmann constant, η is the viscosity, and r is the radius of the ion.⁴² A direct measurement of proton conductivity is not feasible because RTILs consist of mobile cations and anions which contribute to the measured conductivity.⁴² Therefore, only total

ionic conductivity was obtained and is presented in Fig. 4 and 5. The ionic conductivities of the RTILs are slightly higher than the ionic conductivity of poly(vinylidene fluoride-*co*-hexafluoropropylene) saturated with 2,3-dimethyl-1-octylimidazolium trifluoromethanesulfonylimide, which is 2.51 mS cm^{-1} at 130°C .¹⁰ However, these ionic conductivities are still orders of magnitude below the proton conductivity of the fully hydrated Nafion membrane ($20\text{--}100 \text{ mS cm}^{-1}$) at temperatures below 80°C .³³

In addition to ion conductivity, we determined the usable potential window of these RTILs to ensure that there will be no electrochemical breakdown of these materials when placed in a working HFC. Figure 6 shows the cyclic voltammograms (CVs) of the water-equilibrated $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$. Before obtaining the CVs, the RTILs were purged with N_2 to remove any dissolved oxygen. Therefore, the anodic limit of the RTILs is determined by the oxidation of the BETI anion and the cathodic limit is determined by the reduction of the imidazolium cation.⁴³ However, the reduction of atmospheric O_2 cannot be entirely eliminated at the cathodic limit because the CVs were recorded under atmospheric conditions. Possibly the potential limits of the RTIL electrochemical stability are determined by the oxidation and reduction in water. However, the reduction of water in RTILs is usually seen as a prominent wave between -0.8 and -1.5 V and the oxidation of water occurs between $+1.4$ and $+1.75 \text{ V}$ vs a Pt quasi-reference electrode.⁴⁴ No oxidation/reduction waves were observed for water in the CVs of the RTILs studied in this paper; see Fig. 6. It is not uncommon for water to remain undetected in the CVs of hydrophobic RTILs.^{43,44} This is the case even for RTILs that contain a significant amount of water such as 1-butyl-3-methylimidazolium trifluoromethylsulfonate, which contains 15,227 ppm water under ambient conditions.⁴⁴

The potential window of the $\text{C}_{12}\text{mimBETI}$ is clearly larger than the $\text{C}_{12}\text{imBETI}$. The cathodic limit of $\text{C}_{12}\text{mimBETI}$ is -1.5 V . Replacing the methyl group on the 3 position of the imidazole ring with a proton increases the cathodic limit by 0.4 to -1.1 V . The CVs of the $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ show anodic limits of 1.9 and 1.7 V , respectively. These numbers agree well with the anodic limit of other $\text{C}_n\text{mimBETI}$ water-equilibrated RTILs studied previously in our laboratory.⁴³ The discrepancy in the anodic limit between the $\text{C}_{12}\text{mimBETI}$ and $\text{C}_{12}\text{imBETI}$ may be due to a difference in the amount of water in each of these RTILs.

The electrochemical window of other $\text{C}_n\text{mimBETI}$ RTILs is dependent on water concentration.^{43,44} The water content, determined by Karl Fischer titration, for the water-equilibrated $\text{C}_{12}\text{mimBETI}$ are 0.28 ± 0.01 ³⁵ and $1.25 \pm 0.10 \text{ M}$ for the water-equilibrated $\text{C}_{12}\text{imBETI}$. These prior studies showed that the electrochemical window decreased with an increase in water content,^{43,44} which is consistent with the BETI oxidizing at a lower potential in the $\text{C}_{12}\text{imBETI}$ compared to the $\text{C}_{12}\text{mimBETI}$.

Even though the $\text{C}_{12}\text{imBETI}$ RTIL has a smaller potential window compared to the $\text{C}_{12}\text{mimBETI}$ its electrochemical stability is sufficient to allow the hydrogen oxidation and oxygen reduction reactions shown below⁴⁵

which makes these RTILs suitable for HFC applications.

The oxygen reduction reaction shown in Eq. 6 is not the only possible reduction reaction that can occur in aprotic RTILs. In 1-alkyl-2-methylimidazolium RTILs the reduction of oxygen is a one-electron process which produces superoxide.^{23,26} Superoxide is stable in the RTILs unless protons or water are present in which the two-electron irreversible process shown below is expected^{26,27}

Therefore, the formation of hydrogen peroxide in the 1-alkyl-3-methylimidazolium RTILs is also possible.

Galvanic cell electrochemical experiments

The favorable properties of these RTILs, such as thermal stability above 350°C, increasing ionic conductivity with temperature, and large electrochemical stability, make them good candidates as electrolytes in HFCs. To further explore their potential use in HFCs the oxidation of hydrogen and reduction of oxygen in these RTILs was studied simultaneously at a wide range of temperatures. The hydrophobic RTILs were placed in an electrochemical cell which consisted of a glass U-tube with a smooth Pt wire electrode on each side; see Fig. 2. One electrode was placed in a bubbling stream of O₂ (cathode) and the other was placed in a bubbling stream of H₂ (anode). The gases were kept at atmospheric pressure. No external humidification or additional polymer membrane was used. The external current was controlled using a galvanostat and scanned from low to high current density.

Current–voltage and power density data were collected for the water-equilibrated C₁₂mimBETI from 30 to 120°C and are shown in Fig. 7a and b, respectively. Even though DSC results (Fig. 3) show that these RTILs are thermally stable beyond 350°C, the current–voltage experiments were only performed up to 120°C because the C₁₂mimBETI begins to irreversibly discolor when heated to 140°C for over 90 min when placed in the electrochemical cell resulting in a decrease in efficiency. Reasons for the discoloration are unknown at this time, but it most likely results from oxidation or reduction from a side reaction occurring in the RTIL. The work by Katayama et al. shows that imidazolium cations may react with superoxide, leading to degregation of the RTIL.²⁷ If oxygen is reduced to superoxide in this electrochemical system the discoloration observed may be a consequence of this reaction. Nafion discolors after prolonged exposure to oxygen at temperatures >80°C.⁴⁶ The current–voltage and power density data for the C₁₂imBETI are shown in Fig. 7c and d from 20 to 160°C. The C₁₂imBETI showed no discoloration or decrease in efficiency at these higher temperatures.

The current–voltage curves for the C₁₂mimBETI and C₁₂imBETI, Fig. 7a and c, respectively, show a linear decrease with an increase in current density. This is consistent with ohmic losses in the system.⁴⁷ The ohmic loss is likely due to the high resistivity of the RTILs. Upon heating the cell, the slope of the curve begins to become less steep, which coincides with the hydrophobic RTILs becoming less viscous, and less resistive, at higher temperatures. In the C₁₂mimBETI current–voltage curves (Fig. 7a) at 80°C and above a region with a steeper slope appears at current densities less than 2 μA cm^{−2}. This second region of loss is due to activation losses in the system from the oxygen reduction reaction.⁴⁷ Current–voltage curves reported by Sekhon et al. for an HFC containing a membrane composed of the polymer poly(vinylidene fluoride-co-hexafluoropropylene) doped with the RTIL 2,3-dimethyl-1-octylimidazolium trifluoromethanesulfonylimide +0.5 M bis(trifluoromethanesulfonyl)imide also show that ohmic loss is the predominate loss occurring at 100°C.¹⁰

The current–voltage curves were used to determine the open-circuit potentials (OCPs) of the C₁₂mimBETI and C₁₂imBETI electrochemical cells and are reported in Table I. The OCP for the water-equilibrated C₁₂mimBETI varies from 309 ± 173 to 363 ± 127 mV. This is low compared to the standard redox potential of oxygen being reduced to form water at 25°C of 1.23 V vs a normal hydrogen electrode.⁴⁵ The OCP is also low compared to the standard redox potential of oxygen to form hydrogen peroxide of 0.695 V under standard conditions.⁴⁵ The OCP of the water-equilibrated C₁₂imBETI (Table I) is also less than the theoretical values of 1.23 and 0.695 V⁴⁵ and decreases from 532 ± 68 mV at 20°C to 382 ± 16 mV as the temperature is increased to 160°C. RTIL-based fuel cells have an OCP ranging from 400 mV¹⁰ to over 1.0 V.¹⁷ Measured OCP can be lower than the theoretical value if the electrode surface is contaminated.⁴⁸ Contamination of the Pt electrodes due to the C₁₂mimBETI or C₁₂imBETI is unlikely because 1-methylimi-dazolium cations do not poison Pt electrodes.³⁴ Other possibilities for the low OCP include water in the RTILs¹⁸ or a sluggish O₂ reduction reaction at the cathode.²⁰ Results from de Souza et al. showed that upon addition of 20% deionized water to 1-butyl-3-methylimidazolium tetrafluoroborate the OCP dropped from 1.0 V to ~ 630 mV in an alkaline FC.¹⁸ The basic character of the water in the RTIL, and the possibility of water solvating the individual ions preventing direct contact between them, was postulated to cause this decrease in the OCP.¹⁸ Because the C₁₂imBETI has a higher OCP and contains more water than the C₁₂mimBETI RTIL it is unlikely that solvation of the ions by water molecules is responsible for the low OCP. Therefore, the low OCP is most likely due to a sluggish O₂ reduction reaction in the RTILs.²⁰

As the temperature increases, the maximum current density, and therefore the maximum power density, also increases (see Fig. 7). The maximum current densities, current densities at maximum power, and maximum power output for the water-equilibrated C₁₂mimBETI and C₁₂imBETI are all tabulated in Table I. The maximum current density of the water-equilibrated C₁₂mimBETI is 6.84 ± 3.13 μA cm⁻² and for the water-equilibrated C₁₂imBETI is 24.23 ± 3.71 μA cm⁻² at 120°C (Table I). Their maximum power densities were calculated to be 0.42 ± 0.18 and 2.18 ± 0.50 μW cm⁻² for C₁₂mimBETI and C₁₂imBETI, respectively. It is apparent from these results that the oxidation of hydrogen and reduction of oxygen are much more efficient in the protic C₁₂imBETI compared to the C₁₂mimBETI. It is possible the C₁₂imBETI may show an increase in efficiency due to differences in viscosity between the RTILs; however, Fig. 8 shows that the viscosities of the two RTILs are similar at every temperature studied. Another possible explanation for the increased efficiency seen in the protic C₁₂imBETI is that the protonated cation is capable of serving as a Brønsted acid (pK_a of 1-methylimidazole is 7.2⁴⁹) that initiates the reduction reaction at the cathode as shown below

or for hydrogen peroxide formation

The C₁₂im⁺ cation acts as a proton source that can be replenished by the generation of H⁺ at the anode. A similar mechanism using imidazolium as the proton source was postulated by Noda et al. for imidazolium bis(trifluoromethanesulfonyl)imide ionic liquids.¹⁴ Having a proton donor present will increase the rate of reaction by decreasing the time it takes for protons to reach the anode. However, proton transport due to water cannot be ruled out because the RTILs contain a measurable amount of water and water may be continuously

generated in the electrochemical cell. The aprotic $C_{12}mim$ cation has no donor protons or proton acceptor sites; therefore it is not able to actively serve in proton conduction and water must be the primary transporter of protons.

The current and power densities of these RTILs are extremely low when compared to HFC membranes utilizing RTILs as the electrolyte.^{10,11,14,15} Recent work in the area of the oxidation of hydrogen in 1-alkyl-3-methylimidazolium BMSI RTILs under vacuum was found to stabilize the strong acid hydrogen bis(trifluoromethylsulfonyl)imide (HBMSI).^{30,32} This may pose a problem when using imide RTILs as electrolytes in HFCs if no water is present, resulting in low current and power densities. However, when water is present in the system, stabilization of HBMSI should not be possible due to the higher pK_a of water ($pK_a=14.0$)⁵⁰ compared to HBMSI ($pK_a = 1.7$).⁵¹ The low current and power densities measured using these RTILs may simply be because these experiments were carried out on smooth Pt electrodes instead of the more common carbon/Pt or platinized Pt electrodes, and were conducted under atmospheric pressure. Using either a sputtered Pt electrode^{52,53} or using H_2 and O_2 gases above atmospheric pressure should increase their efficiency.⁵⁴⁻⁵⁶ Although the current densities of the electrochemical cells studied are quite low, and orders of magnitude below that of RTIL HFC systems, they are higher than those reported by Parthasarathy et al. for the oxygen reduction at a smooth Pt microelectrode/Nafion membrane 175 μm thick (Nafion 117) interface under 5 atm of O_2 .⁴⁶

To determine if the reactions that took place in the electrochemical cell were indeed due to the transfer of protons from the anode to the cathode, argon gas was used in place of hydrogen and oxygen. The temperatures of the electrochemical cells were 120°C for the $C_{12}mimBETI$ RTIL and 140°C for the $C_{12}imBETI$ RTIL. The OCPs for the argon experiments are reported in Table II. Regardless of the RTIL used the OCP was near zero and the electrochemical cell failed to produce any power.

It is important for voltage output to remain stable as the electrochemical cell operates under a constant load to ensure stable power output. To confirm that these RTILs are capable of functioning over an extended period of time, the potential of the water-equilibrated $C_{12}mimBETI$ electrochemical cell was measured as a function of time while run at a current density of 3.1 $\mu A\ cm^{-2}$ at 120°C. The potential of the water-equilibrated $C_{12}imBETI$ electrochemical cell was measured as a function of time at a current density of 20.1 $\mu A\ cm^{-2}$ at 140°C. These current densities were chosen because this is where the RTIL electrochemical cells produce the most power. The time vs potential curves for these RTILs are shown in Fig. 9a and b, respectively. The measured voltage of the $C_{12}mimBETI$ continues to decrease for 16.7 min until it reaches 0 mV. However, the water-equilibrated $C_{12}imBETI$ electrochemical cell was run for more than 4 h (Fig. 9b) with little change in voltage with time. As a result, this RTIL functions ideally in that, as long as reactant fuel is supplied, the cell will continue to produce constant power. One possible explanation why the $C_{12}imBETI$ voltage is stable over extended periods of time is that it contains a higher percentage of water. Therefore, protons are more easily supplied to the cathode. If the diffusion of protons through the solution is slow compared to the rate of reaction, they become depleted and the electrochemical cell stops functioning,⁵⁷ as shown in Fig. 9a.

To investigate if the amount of water in the RTILs affects the efficiency of the $C_{12}mimBETI$ and $C_{12}imBETI$ electrochemical cells these RTILs were dried under vacuum for ~4 h at 65°C and placed under ambient conditions for at least 24 h. Karl Fischer titration experiments revealed that the ambient $C_{12}mimBETI$ contains 2.8 ± 0.2 mM of water compared to 280 ± 10 mM³⁵ under water-equilibrated conditions, and the ambient $C_{12}imBETI$ contains 537.0 ± 18.32 mM of water compared to 1250 ± 103 mM under water-equilibrated conditions. If bulk water is the proton conductor the efficiency of both the

C₁₂mimBETI and C₁₂imBETI should decrease with a decrease in water content. A decrease in the efficiency of the protic C₁₂imBETI electrochemical cell was observed when the concentration of water decreased. The OCP for the ambient C₁₂imBETI dropped from 492 ± 73 to 336 ± 15 mV at 40°C and from 382 ± 16 to 221 ± 35 mV at 160°C (see Table III). The C₁₂imBETI ambient system also showed a decrease in the maximum current density, current density at maximum power, and power output compared to the water-equilibrated system. The power output and current density for the ambient C₁₂imBETI system do not initially increase with temperature, but rather decrease from 40 to 100°C before starting to increase. The fact that when water is depleted from C₁₂imBETI the electrochemical cell loses efficiency suggests that bulk water conducts protons through the RTIL.

Contrary to the C₁₂imBETI system, which is adversely affected upon removal of water, the efficiency of the C₁₂mimBETI improved when water was removed. The OCP of the ambient C₁₂mimBETI RTIL increased to between 654 and 770 mV (see Table III). The current density, current density at maximum power, and power output also significantly increased with a decrease in water at all temperatures studied; see Table III. Clearly, the water content must have an effect on the efficiency of these electrochemical cells.

In traditional PEMs, such as Nafion, the current measured is directly related to proton conductivity. The protons are conducted through these membranes by water.^{58,59} Two mechanisms have been proposed for proton conduction, a hopping mechanism and direct diffusion of the hydronium ion, H₃O⁺.^{58,59} In the hopping mechanism, a proton moves through water by transferring, or hopping, from one water molecule to a neighboring water molecule. The efficiency of this mechanism depends on the proximity of water molecules to each other, which is affected by the concentration and structure of water in the system.⁵⁹ If neighboring water molecules are not close enough to transfer protons, the hopping mechanism ceases. The other mechanism involves the direct translation of the hydronium, which is limited by diffusion of H₃O⁺. Because both of these mechanisms are thought to occur in fully hydrated Nafion membranes, the measured proton conductivity is an average of these two mechanisms.⁵⁸ Because the RTILs examined here also contain water, similar methods of proton conduction may occur.

Examination of the data in Tables I and III suggests that the water content has an effect on the current, and therefore proton conduction, in the C₁₂mimBETI and C₁₂imBETI RTILs. To investigate the role water content has on proton conduction in the C₁₂mimBETI and C₁₂imBETI RTILs, the measured current densities were corrected for changes in water content and the diffusion coefficient of the hydronium ion. Assuming that water is responsible for proton conduction in the C₁₂mimBETI and C₁₂imBETI RTILs, the concentration of bulk water (*C*) and the diffusivity of the hydronium ion (*D*) will affect the measured current in the RTILs. Consequently, the maximum current densities of the protic C₁₂imBETI and aprotic C₁₂mimBETI RTILs were corrected for changes in *D* and *C*, using the steady-state equation for the limiting current (*i_l*) for a well-mixed system⁶⁰

$$i_l = \frac{nFA_eCD}{\delta} \quad [10]$$

where *n* is the number of electrons in the reaction, *F* is the Faraday constant, *A_e* is the area of the electrode, and *δ* is the thickness of the diffusion layer. The maximum current densities of the C₁₂mimBETI and C₁₂imBETI RTILs were corrected for changes in the electrode area (*A_e*) by dividing the measured currents by the calculated electrode area (~ 0.8 cm²). Details of the method used to determine *A_e* can be found in the Experimental section. The maximum current density of the RTILs was divided by the initial water content obtained from the Karl

Fischer titration data to correct for any changes due to variances in water content between the samples. Changes in water content as a function of temperature could not be measured in these systems using Karl Fischer titration. The Karl Fischer titrant contains methanol, which has a boiling point of 64.6°C, precluding its use at elevated temperatures.⁵⁰ Changes due to water content upon heating are discussed in more detail below. The water generated by the electrochemical reaction was assumed to be negligible because it would take over 16 days with a current density of 55.27 $\mu\text{A cm}^{-2}$ (the maximum current density obtained in these experiments) for the water content of the C₁₂imBETI and C₁₂mimBETI electrochemical cells to increase by 0.02 and 0.07%, respectively. The Stokes–Einstein equation, Eq. 4, relates D to the hydrodynamic radius (η) of the hydronium ion and the inverse viscosity (ν) of the system as a function of temperature. However, the hydrodynamic radius (r) for the hydronium ion in these systems is unknown. Therefore, the relative change in D between the different RTILs as a function of temperature was corrected for by multiplying the maximum current density by the measured viscosity. The approximation of using the inverse measured viscosities to represent changes in D vs temperature is valid because only a comparison between the maximum current densities is desired.

A plot of the corrected maximum current densities vs temperature is shown in Fig. 10. Correcting the maximum current densities for changes in viscosity, and therefore changes in the diffusivity of the hydronium ion (Eq. 4), as a function of temperature reveals a nearly constant current value for each RTIL. Because the water content correction in the RTILs was only used to scale the data, and did not vary with temperature, this nearly constant current value vs temperature suggests that the change in diffusivity is the predominate factor affecting the changes in current as a function of temperature. A constant current density as a function of temperature is most noticeable in the ambient C₁₂mimBETI which is the driest of the RTILs explored. The low water content in this RTIL (2.8 ± 0.2 mM at room temperature) minimizes any errors in the correction associated with the approximation that water content does not change as a function of temperature. Slight digressions from a constant current density in the water-equilibrated and ambient C₁₂imBETI RTILs and the water-equilibrated C₁₂mimBETI RTIL as a function of temperature may be due to the loss of water in these materials at elevated temperatures ($> 80^\circ\text{C}$).

Figure 10 also shows that the corrected maximum current densities of the water-equilibrated C₁₂mimBETI and C₁₂imBETI RTILs and ambient C₁₂imBETI RTIL agree very well across all temperatures studied. The similarity in the maximum current densities for these RTILs after correcting for water content supports the idea that water is responsible for proton conduction through the RTILs. The small differences that do exist between the corrected maximum current densities, especially for the ambient C₁₂imBETI above 100°C, may be due to the water content changing as a function of temperature. The largest and most prominent effect of water content on the maximum current density of the electrochemical cells is observed for C₁₂mimBETI. Under ambient conditions the corrected maximum current densities of the C₁₂mimBETI are the highest of the RTILs studied. Clearly, a decrease in water content in these RTILs increases the efficiency of the electrochemical cell, possibly due to changes in water structure. It has been shown previously in our laboratory the water structure in ambient 1-alkyl-3-methylimidazolium BETI RTILs is more structured than under water-equilibrated conditions.⁶¹ This increased structure may provide a more ordered network of water molecules to transport protons through the RTIL. The water structure and its possible role in proton conduction in these RTILs are discussed in more detail below.

Water structure in the RTILs

The data presented in Table III and Fig. 10 clearly shows that the amount of water in the system is affecting the electrochemical efficiency of hydrogen oxidation and oxygen

reduction in these RTILs. For example, the C₁₂imBETI lost efficiency and the C₁₂mimBETI gains efficiency with a decrease in water content. To gain a better understanding of why the depletion of water in the two RTILs shows conflicting trends, the water structure in these two RTILs was studied using ATR-FTIR.

ATR-FTIR spectra were collected from 3100 to 4000 cm⁻¹ under both ambient and water-equilibrated conditions for the two RTILs and the spectra are shown in Fig. 11 and 12. There are two prominent peaks at 3120 and 3155 cm⁻¹ which are from the H-C-C-H vibrations in the imidazolium ring of the cation.^{61,62} The peaks in the region from about 3200 to 3650 cm⁻¹ are O-H vibrations from water.^{63,64} It is clear from these spectra that the water molecules are interacting with these two RTILs very differently. The water-equilibrated C₁₂imBETI spectra (Fig. 11a) shows two clear water peaks at 3259 and 3578 cm⁻¹ with a shoulder between the two at 3423 cm⁻¹. The peak at 3259 cm⁻¹ is assigned to water that is highly ordered or “icelike” in structure with the hydrogens bonded to neighboring molecules with equal strength, the shoulder at 3423 cm⁻¹ is assigned to liquidlike water, and the peak at 3578 cm⁻¹ is a combination of the O-H...N and free O-H stretches of water molecules singly and doubly bound to the BETI anions at 3563 and 3642 cm⁻¹, respectively.^{61,63-65} Contrary to the water-equilibrated C₁₂imBETI which shows a significant amount of liquidlike water, the ambient C₁₂imBETI ATR-FTIR spectrum (Fig. 11b) shows only the highly ordered icelike water peak at 3259 cm⁻¹. This increase in water structure in the ambient C₁₂imBETI leads to a decrease in the efficiency of the electrochemical cell. Research by Pines and Huppert observed that proton conduction in ice ranges from 3.5×10^{-6} to 13.0×10^{-6} cm² s⁻¹ compared to that of super-cooled water at the same temperature with a proton conductivity of $(4.1 \pm 0.1) \times 10^{-5}$ cm² s⁻¹.⁶⁶ The decrease in proton conduction observed in ice is consistent with the decrease in the electrochemical cells efficiency observed for the ambient C₁₂imBETI, which also shows a significant icelike water structure, as determined from the IR spectrum (Fig. 11b).

The ATR-FTIR spectrum of the C₁₂mimBETI is very different from the C₁₂imBETI RTIL due to the aprotic cation. The water-equilibrated C₁₂mimBETI spectra (Fig. 12a) show two small water peaks at 3563 and 3642 cm⁻¹ with a shoulder to the left of the 3563 cm⁻¹ peak at 3489 cm⁻¹. The peaks at 3563 and 3642 cm⁻¹ correspond to the O-H...N and free O-H stretches of water molecules singly and doubly bound to the BETI anions,^{61,63} and the peak at 3489 cm⁻¹ has previously been assigned to liquidlike water that is not bound to the RTIL anion or cation.^{61,64} In the ambient C₁₂mimBETI spectra (Fig. 12b) the shoulder at 3489 cm⁻¹ disappears and the intensity of the 3563 and 3642 cm⁻¹ peaks decrease. The disappearance of the “waterlike” peak at 3489 cm⁻¹ suggests that all the water molecules are hydrogen bound to the BETI anion. Unlike the ambient C₁₂mimBETI, where all of the water resides in an icelike state, all of the water in the ambient C₁₂mimBETI is associated with the anion of the RTIL. Based on the evidence presented in this paper a different mechanism that conducts protons more efficiently must occur when the water molecules are only associated with the BETI anion. Figures 10 and 12 show that even small amounts of liquidlike water in the C₁₂mimBETI electrochemical cells hinder the electrochemical cells efficiency. Further research is needed to fully understand why this type of water structure is more efficient than liquid water in transporting protons.

Electrode kinetics and thermodynamics

To gain a better understanding of how these C₁₂mimBETI and C₁₂imBETI electrochemical cells compare to proton-conducting polymer membranes such as Nafion, their reaction rates and activation energies, E_a , were calculated from the current-density data. Using the following equation, the reaction rate of the overall electrochemical reaction was calculated from the current density at maximum power (see Tables I and III)

$$\text{net rate} = \frac{i}{nFA_e} \quad [11]$$

where i is the current, n is the number of electrons in the reaction, F is Faraday's constant ($96,485 \text{ C mol}^{-1}$), and A_e is the area of the electrode ($\sim 0.8 \text{ cm}^2$).⁴⁵ To calculate the net rate of the reaction $n = 4$ was used because four electrons are needed to balance the overall chemical reaction for the production of water. The production of water was used instead of the production of hydrogen peroxide ($n = 2$) because this gives a lower limit for the net reaction rate. The current density at maximum power was chosen instead of the highest current density because this is where the electrochemical cell is the most efficient. Arrhenius plots were constructed from 30 to 120°C for the C₁₂mimBETI, from 20 to 160°C for the water-equilibrated C₁₂imBETI, and from 30 to 160°C for the ambient C₁₂imBETI electrochemical cells and are shown in Fig. 13. Using the Arrhenius equation

$$\ln(k) = \frac{-E_a}{RT} + \ln(A) \quad [12]$$

where k is the rate of reaction, E_a is the activation energy, R is the molar gas constant ($8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature in kelvin, and A is the pre-exponential factor. E_a was calculated for the various RTILs and the results are tabulated in Table IV.

Figure 13 clearly shows that the ambient C₁₂imBETI does not follow Arrhenius behavior from 30 to 100°C, but rather decreases from 40 to 80°C before starting to increase. As the temperature increases from 40 to 80°C water is continually being driven off by heat and the dry input gases. The water that does exist in the RTIL is in a highly ordered icelike state, see Fig. 11b. With water in this state it is unable to efficiently conduct protons through the RTIL as shown in Table III. At temperatures above 100°C most of the water has been driven off and enough energy is being provided to the system to increase the mobility of the ions and remaining water, which in turn increases the reaction rate. Because there is a linear correlation from 100 to 160°C this region was used to calculate the E_a of the ambient C₁₂imBETI system.

The overall E_a of the water-equilibrated and ambient C₁₂mimBETI was found to be 16.63 ± 3.04 and $26.65 \pm 1.16 \text{ kJ mol}^{-1}$, respectively, and 25.86 ± 2.26 and $55.23 \pm 7.84 \text{ kJ mol}^{-1}$ for the water-equilibrated and ambient C₁₂imBETI. Comparable activation energies in the ambient C₁₂mimBETI and water-equilibrated C₁₂imBETI systems suggest that the reactions must overcome a similar barrier in each system. The large E_a of the ambient C₁₂imBETI is attributed to the water in this RTIL being in an icelike state. Based on the E_a values alone it would appear that the water-equilibrated C₁₂mimBETI would be the most efficient RTIL to use in an HFC. However, the water-equilibrated C₁₂imBETI electrochemical cell has a higher maximum current density and higher power density than the water-equilibrated C₁₂mimBETI. The water-equilibrated C₁₂imBETI electrochemical cell can operate at higher temperatures and has a stable voltage output over time when a constant load is applied (Fig. 9).

Because one of the most common causes of efficiency loss in PEM-FCs is the cathode overpotential,¹ the reaction rates and activation energies of these RTIL systems were compared to those of the oxygen reduction reaction at the oxide-covered Pt microelectrode/Nafion 117 interface. The oxide-covered Pt microelectrode was used for comparison instead of the oxide-free Pt microelectrode because oxygen-containing species are known to adsorb onto Pt at low current densities.⁶⁷ It has also been observed that an oxide film forms on Pt

electrodes when in contact with 1-alkyl-3-methylimidazolium BMSI RTILs.³⁰ The reaction rates of the oxygen reduction under 5 atm of O₂ pressure at the smooth oxide-covered Pt microelectrode/Nafion 117 interface were calculated using Eq. 11 and the current densities reported by Parthasarathy et al.⁴⁶ For the oxygen reduction reaction $n = 4$ was used because the number of electrons required for the reduction of 1 mole of oxygen to form water is four.⁴⁵ The fastest reaction rate of the Nafion system was measured to be $4.88 \times 10^{-14} \text{ mol cm}^{-2} \text{ s}^{-1}$ at 80°C, which is magnitudes slower than the total reaction rate calculated at 80°C for both the C₁₂mimBETI electrochemical cell (water-equilibrated: $3.31 \times 10^{-12} \pm 0.20 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$; ambient: $1.93 \times 10^{-11} \pm 0.14 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$) and C₁₂imBETI electrochemical cell (water-equilibrated: $9.14 \times 10^{-12} \pm 1.60 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$; ambient: $1.28 \times 10^{-12} \pm 0.15 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$). The higher reaction rates for the RTIL are directly related to the higher current densities measured in these electrochemical systems ($\mu\text{A cm}^{-2}$) compared to those reported by Parthasarathy et al. (nA cm^{-2}).⁴⁶

Similar to the RTILs studied in this paper, with the exception of the ambient C₁₂imBETI, the oxygen reduction reaction at the smooth Pt/Nafion 117 interface increases with temperature from 30 to 80°C.⁴⁶ Using the Arrhenius equation (Eq. 12) Parthasarathy et al. calculated an E_a at an oxide-covered smooth Pt microelectrode/Nafion 117 interface of $73.22 \pm 1.67 \text{ kJ mol}^{-1}$.⁴⁶ This E_a differs from that reported by Zhang et al. of $26.76 \text{ kJ mol}^{-1}$ for the oxide-covered Pt microelectrode/Nafion 117 interface.⁵⁵ This discrepancy may arise from different treatment of the Nafion 117 membrane. Zhang et al. soaked the Nafion membrane for 48 h in 1 M sulfuric acid prior to conducting any experiment. There was no mention of soaking the Nafion membrane in acid before use in the paper by Parthasarathy et al. Table IV shows that the E_a of the overall reaction is much lower in the RTIL systems studied here compared to the oxygen reduction reaction at the Pt/Nafion interface when the Nafion has not been soaked in acid. After the Nafion 117 membrane has been soaked in acid, an E_a similar to those in the RTILs was observed with the exception of the ambient C₁₂imBETI. Therefore, the energy required to initiate the net reaction in these RTILs is similar to the energy required to initiate oxygen reduction at the Pt/Nafion interface in the presence of 1 M sulfuric acid.

Conclusion

The thermal and electrochemical stability, as well as the ionic conductivity, of the water-equilibrated C₁₂mimBETI and C₁₂imBETI were measured and found to be efficient for use in HFCs above 100°C. Their ionic conductivities increase linearly with temperature well beyond 100°C. The electrochemical cells were operated without an additional polymer membrane under nonhumidifying conditions. For both the water-equilibrated C₁₂mimBETI and C₁₂imBETI the current and power density increased with temperature. However, the protic C₁₂imBETI was more thermally stable in the electrochemical cell and able to achieve higher current densities and power densities than its aprotic analog C₁₂mimBETI. Good correlation was found between the maximum current densities for the water-equilibrated RTILs after correcting for changes in viscosity and water content. The effect of water in the RTIL systems was also investigated. The performance of the C₁₂mimBETI increased with a decrease in water content. However, the performance of the ambient C₁₂imBETI drastically decreased compared to the water-equilibrated C₁₂imBETI. The conflicting trend between the ambient C₁₂mimBETI and C₁₂imBETI is attributed to differences in their water structures. The overall E_a of the ambient C₁₂mimBETI and water-equilibrated C₁₂imBETI electrochemical cells are similar to the oxygen reduction reaction in Nafion PEM-HFCs when the Nafion has been soaked in sulfuric acid. This study gives insight into the proton-conducting mechanism that occurs in the hydrophobic imidazolium-based RTILs and shows that they are promising electrolytes for HFCs at temperatures above 100°C under nonhumidifying conditions.

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Figure 1.
Structures of the $C_{12}mim$ and $C_{12}im$ cations and BETI anion used in this study.

Figure 2.
Illustration of the RTIL electrochemical cell.

Figure 3. DSC traces of the water-equilibrated C₁₂mimBETI (—) and C₁₂imBETI (---) acquired at a scan rate of 10°C min⁻¹.

Figure 4. Conductivity of the (●) C₁₂mimBETI and (□) C₁₂imBETI RTILs vs temperature. Lines are linear fits to the data.

Figure 5. Conductivity vs the inverse viscosity from 20 to 130°C for (●) $\text{C}_{12}\text{mimBETI}$ and (□) $\text{C}_{12}\text{imBETI}$. Lines are linear fits to the data.

Figure 6. CVs representing the electrochemical stability of the C₁₂mimBETI (—) and C₁₂imBETI (···) RTILs used in this study collected at a scan rate of 20 mV s⁻¹ vsAg/AgCl reference electrode. A 25 μm Pt disk electrode was used as the working electrode.

Figure 7. Current–voltage curves and current–power density curves for the [(a) and (b)] $\text{C}_{12}\text{mimBETI}$ electrochemical cell from 30 to 120°C and [(c) and (d)] $\text{C}_{12}\text{imBETI}$ electrochemical cell from 20 to 160°C under nonhumidifying conditions and atmospheric pressure at smooth Pt electrodes. H_2 gas was supplied to the anode and O_2 gas was supplied to the cathode.

Figure 8. Viscosity vs temperature from 20 to 160°C for the C₁₂minBETI (●) and C₁₂imBETI (□).

Figure 9.

Voltage output vs time at maximum power for the RTIL electrochemical cells: (a) water-equilibrated $\text{C}_{12}\text{mimBETI}$ at $3.1 \mu\text{A}$ of applied current and 120°C and (b) $\text{C}_{12}\text{imBETI}$ at $20.1 \mu\text{A}$ of applied current and 140°C .

Figure 10.

Natural log of the maximum current density after being corrected for water content and viscosity (see text) as a function of inverse temperature for (●) water-equilibrated $C_{12}\text{mimBETI}$, (■) water-equilibrated $C_{12}\text{imBETI}$, (○) ambient $C_{12}\text{mimBETI}$, and (□) ambient $C_{12}\text{imBETI}$.

Figure 11.

ATR-FTIR spectra of (a) C₁₂imBETI water-equilibrated and (b) C₁₂imBETI ambient from 3100 to 4000 cm⁻¹. The thin lines are fits to the spectra.

Figure 12.

ATR-FTIR spectra of (a) C₁₂mimBETI water-equilibrated and (b) C₁₂mimBETI ambient from 3100 to 4000 cm⁻¹. The insets are a magnification from 3300 to 4000 cm⁻¹ to more clearly distinguish the water peaks in the C₁₂mimBETI spectra. The thin black lines are fits to the spectra.

Figure 13.

Arrhenius plots for the ($\bullet$) $C_{12}mimBETI$ and ($\square$) $C_{12}imBETI$ electrochemical cells: (a) water-equilibrated and (b) ambient. The reaction rates were calculated from the current at maximum power using Eq. 11 and Tables I and III.

Table I
OCP, maximum current density, current density at maximum power, and the maximum power output of water-equilibrated C₁₂mimBETI and C₁₂imBETI electrochemical cells at the various temperatures studied in this paper

Temp. (°C)	OCP (mV)		Maximum current density ($\mu\text{A cm}^{-2}$)		Current density at maximum power ($\mu\text{A cm}^{-2}$)		Maximum power output ($\mu\text{W cm}^{-2}$)	
	C ₁₂ mim BETI	C ₁₂ im BETI	C ₁₂ mim BETI	C ₁₂ im BETI	C ₁₂ mim BETI	C ₁₂ im BETI	C ₁₂ mim BETI	C ₁₂ im BETI
20	n/a	532 ± 68	n/a	2.28 ± 0.60	n/a	1.18 ± 0.30	n/a	0.33 ± 0.13
30	336 ± 153	n/a	1.44 ± 0.33	n/a	0.71 ± 0.21	n/a	0.10 ± 0.02	n/a
40	309 ± 173	492 ± 73	1.53 ± 0.66	3.12 ± 0.39	0.73 ± 0.35	1.46 ± 0.17	0.09 ± 0.05	0.35 ± 0.07
60	352 ± 154	426 ± 76	1.56 ± 0.27	4.23 ± 1.05	0.72 ± 0.11	2.13 ± 0.57	0.12 ± 0.06	0.40 ± 0.13
80	363 ± 127	384 ± 26	2.77 ± 0.06	7.00 ± 1.39	1.28 ± 0.08	3.53 ± 0.62	0.20 ± 0.07	0.60 ± 0.16
100	331 ± 84	355 ± 27	4.45 ± 1.36	12.26 ± 1.63	2.04 ± 0.54	6.15 ± 0.89	0.29 ± 0.03	0.92 ± 0.19
120	344 ± 62	378 ± 26	6.84 ± 3.13	24.23 ± 3.71	3.07 ± 1.53	13.44 ± 1.40	0.42 ± 0.18	2.18 ± 0.50
140	n/a	360 ± 29	n/a	37.81 ± 12.64	n/a	20.06 ± 5.83	n/a	3.40 ± 0.98
160	n/a	382 ± 16	n/a	55.27 ± 15.64	n/a	29.15 ± 8.15	n/a	5.53 ± 1.90

Table II
OCP, maximum current density, and maximum power output of the water-equilibrated C₁₂mimBETI (120 °C) and C₁₂imBETI (140 °C) RTILs with the cathode and anode in an Ar atmosphere. (Data from Table I is shown for direct comparison.)

	OCP (mV)		Maximum current density ($\mu\text{A cm}^{-2}$)		Maximum power output ($\mu\text{W cm}^{-2}$)	
	C ₁₂ mim BETI	C ₁₂ im BETI	C ₁₂ mim BETI	C ₁₂ im BETI	C ₁₂ mim BETI	C ₁₂ im BETI
O ₂ cathode	344 ± 62	360 ± 29	6.84 ± 3.13	37.81 ± 12.64	0.42 ± 0.18	3.40 ± 0.98
H ₂ anode ^a						
Ar cathode	6 ± 1	1 ± 1	0	0	0	0
Ar anode						

^aFrom Table I.

Table III
 OCP, maximum current density, current density at maximum power, and the maximum power output of ambient C₁₂mmBETI and C₁₂imBETI electrochemical cells at the various temperatures studied in this paper

Temp. (°C)	OCP (mV)		Maximum current density ($\mu\text{A cm}^{-2}$)		Current density at maximum power ($\mu\text{A cm}^{-2}$)		Maximum power output ($\mu\text{W cm}^{-2}$)	
	C ₁₂ mm BETI	C ₁₂ im BETI	C ₁₂ mm BETI	C ₁₂ im BETI	C ₁₂ mm BETI	C ₁₂ im BETI	C ₁₂ mm BETI	C ₁₂ im BETI
30	766 ± 28	327 ± 24	3.26 ± 0.46	1.30 ± 0.03	1.62 ± 0.23	0.67 ± 0.04	0.48 ± 0.02	0.10 ± 0.01
40	770 ± 43	336 ± 15	5.29 ± 1.77	1.89 ± 0.08	2.76 ± 1.09	0.96 ± 0.08	0.90 ± 0.51	0.14 ± 0.02
60	685 ± 52	290 ± 65	9.03 ± 1.24	1.49 ± 0.68	4.61 ± 0.63	0.75 ± 0.41	1.27 ± 0.19	0.10 ± 0.07
80	667 ± 61	193 ± 13	14.17 ± 1.77	1.10 ± 0.20	7.43 ± 0.54	0.49 ± 0.06	1.99 ± 0.11	0.04 ± 0.01
100	654 ± 52	146 ± 46	24.03 ± 3.57	1.22 ± 0.13	11.83 ± 1.41	0.53 ± 0.06	3.36 ± 0.06	0.04 ± 0.01
120	674 ± 49	138 ± 58	40.54 ± 6.30	1.97 ± 0.12	21.09 ± 2.72	0.87 ± 0.17	6.04 ± 0.08	0.05 ± 0.01
140	n/a	192 ± 22	n/a	4.66 ± 0.10	n/a	2.13 ± 0.15	n/a	0.15 ± 0.01
160	n/a	221 ± 35	n/a	11.24 ± 1.45	n/a	6.21 ± 1.66	n/a	0.49 ± 0.07

Table IV
The activation energy (E_a) calculated using the current at maximum power and Eq. 9 and 10 for the RTIL electrochemical cells. The E_a at the oxide-covered smooth Pt microelectrode/Nafion 117 interface is included for comparison

	Activation energy (kJ mol ⁻¹)	
	Water-equilibrated (RTIL)	Ambient (RTIL)
C ₁₂ mimBETI	16.63 ± 3.04	26.65 ± 1.16
C ₁₂ imBETI	25.86 ± 2.26	55.23 ± 7.84
Oxide-covered smooth Pt microelectrode/Nafion	73.22 ± 1.67 ^a	
Oxide-covered smooth Pt microelectrode/Nafion	26.76 ^b	

^aData from Parthasarathy et al.³⁷

^bData from Zhang et al.⁴⁴