



Short communication

## Ionic liquids in proton exchange membrane fuel cells: Efficient systems for energy generation

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### ARTICLE INFO

#### Article history:

Received 2 March 2010

Received in revised form 9 April 2010

Accepted 12 April 2010

Available online 24 April 2010

#### Keywords:

Ionic liquid

Proton exchange membrane fuel cell

1-Butyl-3-methylimidazolium chloride

1-Butyl-3-methylimidazolium

tetrafluoroborate

### ABSTRACT

Proton exchange membrane fuel cells (PEMFCs) are used in portable devices to generate electrical energy; however, the efficiency of the PEMFC is currently only 40%. This study demonstrates that the efficiency of a PEMFC can be increased to 61% when 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF<sub>4</sub>) ionic liquid (IL) is used together with the membrane electrode assembly (MEA). The results for ionic liquids (ILs) 1-butyl-3-methylimidazolium chloride (BMI.Cl) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF<sub>4</sub>) in aqueous solutions are better than those obtained with pure water. The current and the power densities with IL are at least 50 times higher than those obtained for the PEMFC wetted with pure water. This increase in PEMFC performance can greatly facilitate the use of renewable energy sources.

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### 1. Introduction

Fuel cells (FC) are devices that convert chemical energy into electrical energy through oxidoreduction reactions [1]. Due to increasing concerns about environmental changes and particularly with respect to global warming, fuel cells have been extensively promoted as alternatives for clean power production because these devices lack the pollutant by-products and produce only electricity, heat and water. Fuel cells can be used to provide power not only for a large variety of equipment such as portable electronic units but also for vehicles and industrial units [2].

Among the many types of fuel cells, usually classified by the electrolyte used, e.g., molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs) and proton exchange membrane fuel cells (PEMFCs), the latter have become the most popular for automotive applications [3–6].

Fuel cells can be fuelled with hydrogen, which undergoes oxidation at the anode, and oxygen, which is reduced at the cathode. This hydrogen is preferentially produced by the electrolysis of water due to the high purity of the resulting product, which is a key factor in extending the useful life of the electrodes in a fuel cell [7–10]. The PEMFC is the system commonly employed in portable units due to

its compact construction regarding the fuel cell stack. The PEMFC contains a membrane electrode assembly (MEA) and two separating plates. The MEA consists of two catalyst layers and two gas diffusion layers [11,12]. The electrolyte material most often used is Nafion polymer, which allows for ionic conduction. The efficiency of a PEMFC is about 40% [13], and this value can be increased with the addition of new materials to the electrolyte. Thus, ionic liquids (ILs) can facilitate the proton conductivity inside a PEMFC [14–16].

The properties of ionic liquids, particularly their characteristics as good electrolytes, are well known [17]. Several systematic studies on the use of ionic liquids in fuel cells have been reported and promising results described [18–20]. An efficiency of 67% was achieved using ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF<sub>4</sub>) as electrolytes in an alkaline fuel cell in a previous work [21].

In this study, the performance of a commercial PEMFC using an MEA impregnated with water, which is the standard procedure, was compared to others with MEAs impregnated with ionic liquid/water mixtures in an attempt to obtain efficiency enhancements arising from improved ion transport in the polymer.

### 2. Experimental

The ionic liquids were synthesised using previously described procedures [22–25]. The purity of the ILs was checked by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy and electrochemical methods, i.e., cyclic voltammetry.

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The solutions tested in the PEMFC were prepared by dissolving 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF<sub>4</sub>) or 1-n-butyl-3-methylimidazolium chloride (BMI.Cl), at distinct concentrations, in ultrapure water (2 μS cm<sup>-1</sup>). The concentration of the solutions was varied between 0 and 1.2 mol L<sup>-1</sup>. These solutions were homogeneously impregnated into the polymeric membrane electrode assembly (MEA) by immersion of the membrane in the solution for 2 min. The MEA consisted of an ion-exchange membrane, anode and cathode electrodes and gas diffusion layers; the experiments were performed in a commercial fuel cell from Electrocell (model FC25-1GH). The active area of the membrane was 25 cm<sup>2</sup>.

The gases supplied to the PEMFC system were hydrogen (99.999% purity, purchased from Air Liquide) and compressed air humidified at room temperature by bubbling through water. These gases were fed to the PEMFC at 2 psig and a flow of 35 sccm using an MKS Instruments flow controller, model MKS Type 250, and a pressure controller, model MKS Type 247.

The performance of the PEMFC was evaluated by discharge experiments. The measurements were realised with an Autolab potentiostat model PGSTAT30. Prior to the discharge experiments, the fuel cell was activated by imposing a convenient current profile. In this work, each activation period was 5 min, and the potentials used for sequence activation were 0.6, 0.0, 0.4 and 0.0 V, respectively, using the chronopotentiometry galvanostatic method. The same activation sequence was repeated twice to ensure a clean electrode surface.

After activation, the discharge procedure (linear sweep voltammetry method) followed a decrease in the potential, characteristic of the use of the fuel cell to provide electrical power to an external device. The discharge was performed at a rate of 1 mV s<sup>-1</sup>.

All experiments were repeated at last three times to certify the reproducibility of the results.

The microscopy images were obtained with a Digital Blue QX5 microscope.

### 3. Results and discussion

Ionic liquids have been previously demonstrated to be excellent electrolytes in liquid contact fuel cells. Given the unequivocal enhancement of fuel cell performance using ionic liquid electrolytes, this innovation has demonstrated a low technological impact to date because solid systems are preferred for practical applications, mostly in mobile uses, like cars. As a natural evolution of this procedure, imidazolium-based electrolytes such as BMI.Cl and the ionic liquid BMI.BF<sub>4</sub> were tested as impregnation agents, dissolved in water and used to wet the classic MEA. This procedure should enhance the proton conductivity of the MEA and was expected to enhance the performance of the PEMFC.

Fig. 1 shows the discharge profile, i.e., dependence of the cell potential and power density on the current, when the MEA was wetted with pure water, BMI.Cl and BMI.BF<sub>4</sub> aqueous solutions. All experiments described herein were performed at room temperature.

The PEMFC system with pure water, shown in Fig. 1a, expanded for clarity in the inset, showed a maximum current density value of 0.11 mA cm<sup>-2</sup>. This current is relatively low due to the operation of the fuel cell at room temperature. This value would be expected to reach ~0.65 A cm<sup>-2</sup> at 353 K [26], but the goal of this work was to use classic fuel cells at room temperature.

Our previous work using liquid contact fuel cells with only BMI.BF<sub>4</sub> ionic liquid solutions as electrolytes revealed current densities around 3.0 mA cm<sup>-2</sup> and power densities of ~1.75 mW cm<sup>-2</sup> [27] at room temperature, values that encouraged the use of these solutions for wetting the membrane.

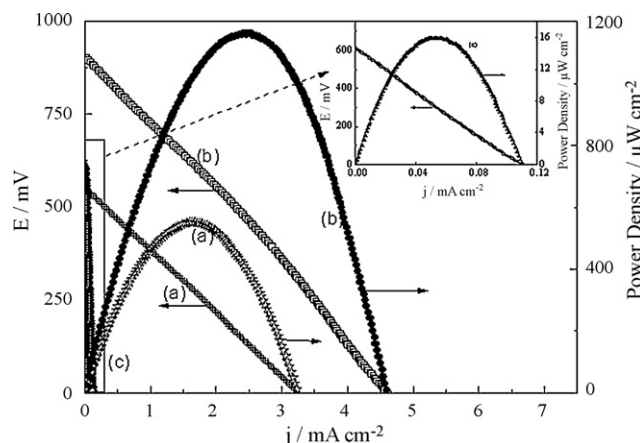


Fig. 1. PEMFC performance using (a) water, (b) BMI.Cl aqueous solution (0.10 mol L<sup>-1</sup>) and (c) BMI.BF<sub>4</sub> aqueous solution (0.17 mol L<sup>-1</sup>).

In the present case, when using an aqueous solution of BMI.Cl or BMI.BF<sub>4</sub> to wet the MEA instead of pure water, the system became more conducting than with pure water, and the performance was dramatically enhanced, as shown by the results using IL solutions presented in Fig. 1b and c, respectively, for BMI.Cl and BMI.BF<sub>4</sub>.

The performance enhancement obtained using BMI.BF<sub>4</sub> (a) and BMI.Cl (b) when compared with water pure water (c) is dramatic. The PEMFC with the BMI.BF<sub>4</sub> ionic liquid (a) showed the best performance, with a power density 73 times better and a current density 50 times higher than the values obtained for the discharge of the MEA with pure water.

Table 1 shows the characteristic parameters of the FC using water and IL solutions. Using the ionic liquid BMI.Cl, the current density was 1.7 mA cm<sup>-2</sup>, which is 35 times higher than the discharge with water, and the power density was 35 times greater.

The open circuit potential increased from 600 to 900 mV when the electrolyte was changed from H<sub>2</sub>O to BMI.BF<sub>4</sub>. The overall efficiency of the cell,  $\eta$ , changed from 40% (a value usually obtained with classic PEMFC [26]) when the polymer membrane was wetted with pure water to 31% when the membrane was wetted with a 0.17 mol L<sup>-1</sup> aqueous solution of BMI.Cl and 61% when the membrane was wetted with 0.1 mol L<sup>-1</sup> BMI.BF<sub>4</sub>. Here,  $\eta$  was calculated as  $\eta = \varepsilon_i \varepsilon_v \varepsilon_f$ , where  $\varepsilon_i$  is the thermal efficiency,  $\varepsilon_f$  is the Faraday efficiency and the value of the tension efficiency,  $\varepsilon_v$ , for the H<sub>2</sub>/O<sub>2</sub> system is 0.83, obtained from the relation between the cell potential and the reversible potential ( $E_r = 1.229$  V). These results are extremely impressive because the performance enhancement was significant in both aspects: cell potential and current at maximum cell power.

Solution resistance, capacitance, charger transfer resistance and impedance of PEMFC with pure water, BMI.BF<sub>4</sub> and BMI.Cl, determined through electrochemical impedance spectroscopy, do not explain the best performance of PEMFC with BMI.BF<sub>4</sub> system. The higher efficiency observed for PEMFC with BMI.BF<sub>4</sub> when compared with the PEMFC with pure water should be ascribed to the better wettability when IL aqueous solution is used in the membrane.

Table 1

Comparison of results using fuel cells with the MEA wetted with water, 0.17 mol L<sup>-1</sup> BMI.Cl and 0.1 mol L<sup>-1</sup> BMI.BF<sub>4</sub> aqueous solutions.

	H <sub>2</sub> O	BMI.Cl	BMI.BF <sub>4</sub>
E (mV)	300	280	430
E <sub>OCP</sub> (mV)	600	550	900
j (mA cm <sup>-2</sup> )	0.06	1.7	2.5
P (μW cm <sup>-2</sup> )	16	480	1180

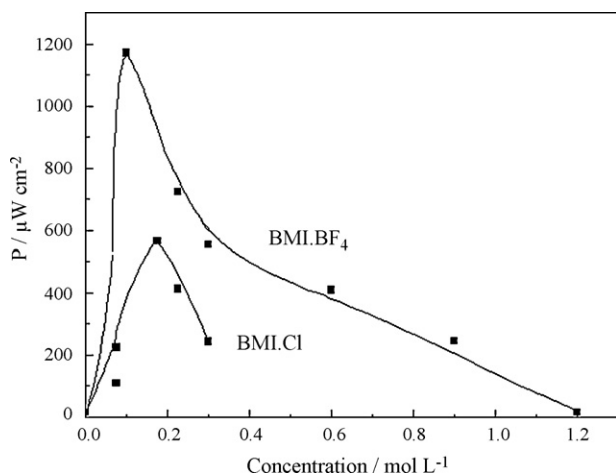


Fig. 2. Effect of the concentration of BMI.BF<sub>4</sub> (a) and BMI.Cl (b) on the power density in a PEMFC at room temperature.

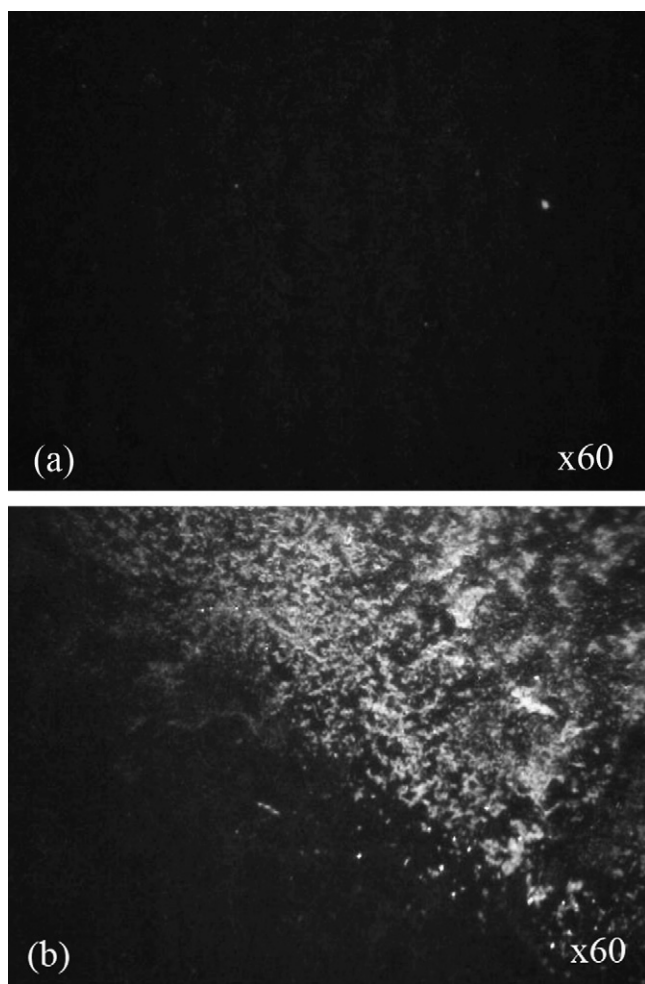


Fig. 3. Microscopy images of (a) MEA without use and (b) MEA with BMI.BF<sub>4</sub> after use in the PEMFC.

The results described above correspond to the use of IL concentrations of 0.17 mol L<sup>-1</sup> for BMI.Cl and 0.1 mol L<sup>-1</sup> for BMI.BF<sub>4</sub>, which correlate to the maxima of the curves, showing the dependence of the power density on concentration, as depicted in Fig. 2.

It is worth noting that the power density increased significantly, even for low amounts of added IL, reached a maximum and then decreased smoothly with an increasing concentration, as expected for weak electrolytes, which are dissociated at low concentrations.

Together, these results support the conclusion that the improved performance of these IL-wetted fuel cells (IL-PEMFC) can be attributed to the formation of an IL layer on the surface of the MEA, as suggested by the microscopy images shown in Fig. 3. This layer, which is intrinsically highly conductive, gives rise to the measured high power density and efficiency.

#### 4. Conclusions

The use of IL aqueous solutions for wetting the MEA used in fuel cells yielded an impressive performance enhancement. Compared with the classic PEMFC, which uses only water on the polymeric membrane, the IL-PEMFC, using BMI.BF<sub>4</sub> IL aqueous solutions, enhanced the current density 50-fold, the power density 73-fold and increased the efficiency by 21%. This increase in the performance of the IL-PEMFC have high technological impact.

#### Acknowledgments

CNPq, Electricas Cachoeira Dourada S/A, Capes and FAPERGS are acknowledged for their contributions.

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