The study on fuel-cell performance by using alkylimidazole ionic liquid as electrolytes for fuel cell

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Abstract. Ionic liquids are widely used in the field of electrochemistry because of its low melting point, wide electrochemical window and outstanding electrical conductivity. Ionic liquids are used as fuel-cell electrolytes in order to optimize the overall performance of fuel cells. Four ionic liquids have been investigated, such as 1-methylimidazolium hydrogen sulfate [Hmim]HSO₄, 1-n-butyl-3-methylimidazolium bromide [Bmim]Br, 1-n-butyl-3-methylimidazolium trifluoroacetate [Bmim]CF₃COO, 1-n-butyl-3-methylimidazolium hydrogen sulfate [Bmim] HSO₄. At the same time, fuel cell shells made of PTFE and stainless steel were designed and processed. The anode and cathode electrode materials were prepared; then the above ionic liquids were used as the fuel-cell electrolyte in turn, The performance of the fuel cell was measured by voltammetry using hydrogen as a fuel and air as an oxygen source.

1. Introduction

Ionic liquids, a range of such green solvents, are organic salts with melting points below or equal to room temperature, also known as room temperature ionic liquids. The interest in ionic liquids begins with a new class of ionic liquids based on alkyl-substituted imidazolium and pyridinium cations with chloride or chloroaluminate anions[1]. Since then, ionic liquids have been widely used, especially as electrolytes for batteries. Ionic liquids are thermally stable over a wide temperature range, in particular, some ionic liquids can maintain their liquid state at temperatures up to 200°C[2]. Therefore, ionic liquids have been used as environmentally friendly solvents in a variety of reactions and are suitable for a range of organic reactions[3-5].

In the 1970s, ionic liquids were used in electrochemical research[6]. Due to its non-volatile, non-flammability, high thermal and electrochemical stability and outstanding ionic conductivity, it can also be widely used in the fields of batteries[7,8], electrochemical sensors[9,10], metal electrodeposition, electric double-layer capacitor[11] and electrical organic synthesis. Most ionic liquids are composed of heterocyclic organic cations, such as 1-alkyl-3-methylimidazolium, n-alkylpyridinium, tetraalkyl ammonium or tetraalkyl phosphonium cations, and various anions such as hexafluorophosphate [PF₆⁻]; tetrafluoroborate [BF₄⁻]; trifluoromethylsulfonate [CF₃SO₂⁻]; bis[(trifluoromethyl)sulfonyl] amide [(CF₃SO₂)₂N⁺]; thiocyanate[SCN⁻]; trifluoroethanoate [CF₃CO₂⁻]; acetate [CH₃CO₂⁻]; nitrate and halide [12]. Because ionic liquids are composed entirely of ions, they can be combined to meet the desired properties for a specific application[13,14].
Fuel cells is a new type of energy conversion device that directly converts chemical energy into electrical energy[15-17]. It is not limited by the carnot cycle, and it is environmentally friendly, directly efficient and clean. Different from the traditional battery, it is an electrochemical reactor that the active material (fuel and oxidant) is not stored inside the battery, but is provided by an external energy storage device. Based on the nature of the polymer electrolyte in the fuel cell, fuel cells can be separated into five categories: Alkaline Fuel Cell (AFC), Molten Carbonate Fuel Cell (MCFC), Proton Exchange Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC) and Solid Oxide Fuel Cell (SOFC). The choice of these fuel cells will depend on the technological applications, whether they be for automotive vehicles, spacecrafts, large power units, power systems for portable electronic devices, etc. It is, however, worth noting that the development of new electrolytic materials that can operate at room temperature with high power density and high overall efficiency. It remains a major challenge that can be used in commercially available fuel cells.

In this work, four ionic liquids, 1-methylimidazolium hydrogen sulfate [Hmim]HSO₄, 1-n-butyl-3-methylimidazolium bromide [Bmim]Br, 1-n-butyl-3-methylimidazolium trifluoroacetate [Bmim] CF₃COO, 1-n-butyl-3-methylimidazolium hydrogen sulfate [Bmim]HSO₄, were prepared. The structure of the synthetic ionic liquid was characterized by infrared spectrometer, and the conductivity of the product is tested by the conductivity meter. The fuel cell shells made of PTFE and stainless steel, anode and cathode materials were assembled into a fuel cell with the synthetic ionic liquid electrolyte, then different ionic liquids are sequentially used as electrolytes of the fuel cell, and hydrogen fuel is used to investigate fuel cell performance.

2. Experimental

2.1. Preparation of ionic Liquids

[Hmim]HSO₄: it was synthesized by direct synthesis. A certain amount of 1-methylimidazole was added in a three-necked flask, which was placed in an ice water bath under magnetic stirring. The temperature in the flask was maintained at 0 to 5℃, then the concentrated sulfuric acid diluted with water was slowly added dropwise with a dropping funnel, wherein the molar ratio of concentrated sulfuric acid to 1-methylimidazole was 1:1. the temperature is slowly raised to room temperature and stirring is continued for a while. After the reaction is completed, the water is distilled off at a suitable temperature by a rotary evaporator, and [Hmim]HSO₄ is obtained.

[Bmim]Br: in a 250 mL three-necked flask, a certain amount of n-bromobutane was added dropwise with a constant pressure dropping funnel to a solution of 1-methylimidazole in a certain volume of 1,1,1-trichloroethane as solvent, wherein the molar ratio of n-bromobutane to 1-methylimidazole was 1:1, under magnetic stirring. When the addition of n-bromobutane was completed, the solution will become turbid, the dropping funnel is removed, and a spherical reflux condenser replaced it, heat and reflux to continue the reaction. After completion of the reaction, resulting viscous liquid was distilled off at a suitable temperature using a rotary evaporator to eliminate 1,1,1-trichloroethane and [Bmim]Br is obtained.

[Bmim]CF₃OO: a certain amount of [Bmim]Br was added in a 250 mL three-necked flask, which was cooled under stirring for a period of time, then the amount of the trifluoroacetic acid was added dropwise with a constant pressure dropping funnel. When the addition of trifluoroacetic acid was completed, the temperature is slowly raised to room temperature and the reaction is continued for a while under stirring. After completion of the reaction, [Bmim]CF₃COO is obtained.

[Bmim]HSO₄: in a 250 mL three-necked flask, a certain amount of concentrated sulfuric acid was added dropwise with a constant pressure dropping funnel to a solution of [Bmim]Br in a certain volume of dichloroethane as solvent, wherein the molar ratio of concentrated sulfuric acid to [Bmim]Br was 1:1, and which was placed in an ice water bath under magnetic stirring. The temperature is slowly raised to room temperature and stirring is continued for a while. After completion of the reaction, resulting viscous liquid was distilled off at a suitable temperature using a rotary evaporator to eliminate Dichloroethane and [Bmim]HSO₄ is obtained.
2.2. IR spectra characterization and conductance measurement of ionic liquids

Ionic liquids can be characterized by means of its spectroscopy, physics and electrochemical methods. The general spectroscopy features are infrared (IR) and nuclear magnetic (NMR). The products can be confirmed by IR and NMR spectroscopy. The characterization of the physical method is generally based on the comparison of the data of conductivity, dielectric constant, viscosity and other known data to estimate whether the product is correct. The electrochemical method is cyclic voltammetry to study the electrochemical activity, determine the electrochemical potential window.

The imidazole ring, alkyl and anion in the synthetic ionic liquids were characterized by IR spectra, and the infrared absorption spectrum was measured by a Nicolet iS5 Fourier transform infrared spectrum analyzer (Thermo Fisher Scientific Co., Ltd.), and the wave number was measured from 400 cm\(^{-1}\) to 3800 cm\(^{-1}\). The conductivity of the synthetic ionic liquids was tested by using a DDS-11A digital conductivity meter (Shanghai Lei Magnetic Company Instrument Factory) at 30 °C.

2.3. Fuel cells performance evaluation

The structure parameters of fuel-cell electrode are shown in Table 1.

| Electrode | Current collector | Thickness / mm | Electrode composition (mass ratio) |
|-----------|-------------------|-----------------|-----------------------------------|
| Anode     | stainless steel grid with 60 mesh | 0.5 | Pt:Pd:C:PTFE=1:1:5:6 |
| Cathode   | stainless steel grid with 60 mesh | 0.5 | Ag2:PTFE:=6:1 |

The assembled fuel cell and resistance box (ZX74E, Shanghai Zhengyang Instrument Factory) were connected with wires, then different ionic liquid electrolyte was injected into it. At room temperature of 20 °C, the hydrogen was connected to the gas chamber of anode, and the atmosphere (at a pressure of 101.325 kPa) was connected to the gas chamber of cathode. The open circuit voltage of the fuel cell was measured when the wire is disconnected, then the resistance box was adjusted, the load circuit was changed, and a digital multimeter (VICTOR Model 88D, Shenzhen Hualun Kangsheng Technology Co., Ltd.) was used to record the voltage and current in the circuit, the power density of the fuel cell was calculated, and performance curve of the fuel cell is drawn.

3. Results and discussion

3.1. Determination of synthetic ionic liquids and measurement of electrical conductivity

IR detection was performed on the four synthetic ionic liquids, and then the data obtained by IR detection was compared with the relevant data in the reference. It is determined that the ionic liquid synthesized by the experiment is the desired product. Table 2 shows the infrared spectrum data, and Figure 1 shows IR spectra of the synthetic ionic liquids.

It can be observed in Figure 1 that 3096 and 3041 cm\(^{-1}\) are the absorption peaks of the unsaturated alkyl C-H stretching vibration, 2914 cm\(^{-1}\) is the side chain alkyl C-H stretching vibration absorption peak, and 1805 cm\(^{-1}\) is the C=O asymmetric stretching vibration, 1605 cm\(^{-1}\) is the C=N stretching vibration absorption peak, 1566 and 1494 cm\(^{-1}\) are the vibration of the imidazole ring skeleton, 1420 cm\(^{-1}\) is the C-C deformation vibration, and 1112 cm\(^{-1}\) is the HSO\(_4^-\) - ʋ(S-O). It is proved that the synthetic product is [Hmim]HSO\(_4\).
3184 and 3124 cm$^{-1}$ are the unsaturated alkyl C-H stretching vibration absorption peak, 2885 cm$^{-1}$ is the side chain alkyl C-H stretching vibration absorption peak, 1605 cm$^{-1}$ is C=N stretching vibration absorption peak, 1540 and 1492 cm$^{-1}$ are imidazole ring skeleton vibration, 1436 cm$^{-1}$ is C-C deformation vibration, 707 and 798 cm$^{-1}$ are C-H stretching vibration absorption peaks in long-chain CH$_2$, 585 cm$^{-1}$ is the stretching vibration absorption peak of C-Br. The analysis proves that the synthetic product is [Bmim]Br.

| Group characteristic absorption peak | Wave number (cm$^{-1}$) |
|-------------------------------------|-------------------------|
| O-H stretching vibration            | 4000–3200               |
| Unsaturated alkyl C-H stretching vibration | 3200–3000            |
| Side chain alkyl saturation C-H stretching vibration | 2960–2853          |
| C=O asymmetric shrinkage vibration | About 1800              |
| C=N                                | 1608–1600               |
| Imidazole ring skeleton vibration  | 1576, 1468              |
| C-C deformation vibration          | 1460                    |
| C-F vibration                      | 1180                    |
| HSO$_4^-$-ʋ (S-O)                   | 1220–1040               |
| C-H stretching vibration in long chain CH$_2$ | 744               |
| C-Br stretching vibration          | 600–500                 |

**Table 2.** IR spectra datas in the reference

![IR spectra of [Hmim]HSO$_4$, [Bmim]Br, [Bmim]CF$_3$COO and [Bmim]HSO$_4$]

2985 cm$^{-1}$ is the unsaturated alkyl C-H stretching vibration absorption peak, 2944 and 2889 cm$^{-1}$ are the side chain alkyl C-H stretching vibration absorption peak, 1843 cm$^{-1}$ is C=O asymmetric stretching vibration, 1605 cm$^{-1}$ is C=N stretching vibration absorption peak, 1533 and 1497 cm$^{-1}$ are imidazole ring skeleton vibration, 1436 cm$^{-1}$ is C-C deformation vibration, 726 cm$^{-1}$ is the C-H stretching vibration absorption peak in long-chain CH$_2$; 1092 cm$^{-1}$ is the C-F vibration absorption peak. The analysis result proves that the synthetic product is [Bmim]CF$_3$COO.
2922 cm$^{-1}$ is the unsaturated alkyl C-H stretching vibration absorption peak, 2890 cm$^{-1}$ is the side chain alkyl C-H stretching vibration absorption peak, 1805 cm$^{-1}$ is C=O asymmetric stretching vibration, 1600 cm$^{-1}$ is C=N stretching vibration absorption peak, 1525 and 1436 cm$^{-1}$ are imidazole ring skeleton vibration, 1405 cm$^{-1}$ is C-C deformation vibration, and 1095 cm$^{-1}$ is the HSO$_4$- $\nu$(S-O), 787 cm$^{-1}$ is the C-H stretching vibration absorption peak in long-chain CH$_2$. It is proved that the synthetic product is [Bmim]HSO$_4$.

Ionic liquids have good conductivity (up to 10mS/cm), but their conductivity is relatively low compared to aqueous electrolyte solutions with higher concentrations. The reasons are mainly caused by two aspects: one is the accumulation of ions leading to the reduction of charged charge, The other is the large size of ions of the ionic liquid leading to the decrease of mobility. Conductivity of four synthetic ionic liquids was measured at 30°C. The data of conductivity are shown in Table 3.

**Table 3. Conductivity of four synthetic ionic liquids.**

| Ionic liquids | [Hmim]HSO$_4$ | [Bmim]Br | [Bmim]CF$_3$COO | [Bmim]HSO$_4$ |
|---------------|--------------|----------|----------------|--------------|
| Conductivity(mS/cm) | 4.82 | 2.37 | 3.77 | 3.71 |

[Bmim]Br, [Bmim]HSO$_4$, [Hmim]HSO$_4$ and [Bmim]CF$_3$COO ionic liquids were synthesized by direct synthesis or two-step synthesis, and the synthetic ionic liquids were proved to be the target products by the IR spectra. In addition, the conductivity of the synthetic ionic liquid is characterized by the order, [Hmim]HSO$_4$ > [Bmim]CF$_3$COO > [Bmim]HSO$_4$ > [Bmim]Br.

3.2. Hydrogen fuel cell performance

As can be seen in Figure 2, the external voltage in the loop decreases rapidly with the decrease of loop load, and the trend is fast then slow. Figure 3 shows that as the load decreases, the power density increases, and the trend is fast to slow. When the electrolyte is [Bmim]Br, the open circuit voltage is 510 mV and the electric power is up to 0.41 mW/cm$^2$. When the electrolyte is [Bmim]HSO$_4$, the open circuit voltage is 400 mV and the electric power is up to 0.2 mW/cm$^2$; when the electrolyte is [Hmim]HSO$_4$, the open circuit voltage is 330mV and the electric power is up to 0.33 mW/cm$^2$; when the electrolyte is [Bmim] CF$_3$COO, the open circuit voltage is 650 mV and the electric power is up to 0.95 mW/cm$^2$.

[Bmim]Br, [Bmim]HSO$_4$, [Bmim]CF3COO voltage and power density are all dependent on the increase of current density, the corresponding increase is always in accordance with [Bmim]CF$_3$COO > [Bmim]Br > [Bmim]HSO$_4$. When the cations in the ionic liquid are the same, the anions will have a certain impact on its performance. From the strength of the acid corresponding to the anion, the stronger the electronegativity is, the stronger the ability to attract hydrogen ions is, the weaker the ability to release hydrogen ions is, and the weaker the acidity is, so the acid sequence corresponding to the anion is: HSO$_4$ > Br > CF$_3$COO. Thus its performance is negatively correlated with the acidity of anions.
Figure 2. Relationship between current density and voltage

The voltage of [Hmim]HSO₄ and [Bmim]HSO₄ is initially less than [Bmim]HSO₄. With the increase of current density, it becomes that the voltage of [Hmim]HSO₄ is greater than [Bmim]HSO₄, the power density of [Hmim]HSO₄ is always greater than [Bmim]HSO₄. It can be illustrated that the anions of ionic liquids are the same, and the performance of fuel cell is negatively correlated with the cationic carbon chain length.

Figure 3. Relationship between current density and power density
4. Conclusion

[Hmim]HSO₄, [Bmim]Br, [Bmim]CF₃COO and [Bmim]HSO₄ ionic liquids were synthesized by direct synthesis or two-step synthesis, and the ionic liquids synthesized by the experiments were characterized by IR spectra. After comparison with the relevant data in the literature, it is analyzed that the prepared ionic liquid is the desired product; and the conductivity is measured at the same time. The fuel cell shell is designed and manufactured, and the anode and cathode of fuel cell are prepared, and then the fuel cell was assembled together with the four synthetic ionic liquid, respectively. Fuel cell performance tests show that [Bmim]CF₃COO is the most effective ionic liquid electrolyte. The performance of the fuel cell is inversely related to the acidity of the anion in the ionic liquid electrolyte and negatively correlated with the length of the cation.

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