

Comparative Investigation of Organic Solution and Ionic Liquid as Electrolyte under Lithium-Air Battery

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Received: 22 May 2013 / Accepted: 18 September 2013 / Published: 15 November 2013

In this study, we compared the performance and cycle life of lithium-air battery with organic solution and ionic liquid as electrolyte, respectively. The electrochemical performance of the electrolyte was examined using Tafel curves, cyclic voltammetry, and the constant current discharge tests. The results indicated that the first discharge specific capacity of the lithium-air battery with ionic liquid electrolyte was 1160 mAh g⁻¹, which was higher than that of the battery with organic solution (1030 mAh g⁻¹). The lithium-air battery with ionic liquid electrolyte showed good rechargeability, indicating that it is a more suitable electrolyte for this type of battery.

Keywords: Lithium-air battery; Electrolyte; Organic solution; Ionic liquid

1. INTRODUCTION

The lithium-air battery with high theoretical special energy (11,140 Wh kg⁻¹ excluding oxygen weight and 5,200 Wh kg⁻¹ including oxygen weight) is obtaining strong interest as a potential energy conversion system [1-7]. The battery usually consists of lithium metal negative electrode, electrolyte, and porous carbon positive electrode. The electrolyte of lithium-air battery is divided into aqueous [8] and non-aqueous [9-12] electrolytes. The non-aqueous electrolytes are mainly composed of two types, namely, organic [13] and ionic liquid [14] electrolytes. The commonly used organic solvents of organic electrolytes comprise carbonic esters, ethers, and alkanes, and their impacts on water absorbability, volatile rate, viscosity, ionic conductivity, oxygen solubility, and diffusion rate, among others, which are related to the performance of lithium-air battery, are relatively large [15-19]. However, solvent volatilization is a problem of organic electrolytes, especially for a semi-opened

system that constantly has oxygen as an active substance. On the other hand, the reduction of battery capacity caused by the volatilization of the electrolyte in the working process, can be prevented by high thermal stability of the ionic liquid. Moreover, the reaction of water from the air to the metal lithium can be remitted by preparing a hydrophobic ionic liquid [20], according to the design of anion and cation. However, conductivity of the lithium ion is relatively low due to the relatively high viscosity of the ionic liquid, and the solubility and diffusion coefficient of oxygen therein are lower than that of the organic electrolyte [21, 22]. The electrolyte not only needs to conduct lithium ions; it also needs to effectively protect the lithium tablet from secondary reaction because oxygen will be constantly infused into the positive electrode of the lithium-air battery as an active substance. The electrolyte that performs well shall partially dissolve lithium oxide, which is a discharge product, to improve the high-rate discharge performance of the battery and the stability of cycle operation.

The further researches have been concentrated on the reaction mechanism [23], the choice and treatment of carbon sources, the determination of catalysts and electrolytes [24, 25] and so on. In this work, we investigated the performances of lithium-air batteries with organic solution and ionic liquid electrolytes by the Tafel curves, the cyclic voltammetry and the constant current discharge tests, respectively, in order to find out the suitable electrolyte used in lithium-air battery.

2. EXPERIMENTAL

2.1 Preparation of electrolytes

A commercial electrolyte solution of 1 mol LiPF_6 in a mixture of 1:1:1 (w/w/w) ethylene carbonate (EC)/ ethyl methyl carbonate (EMC)/ dimethyl carbonate (DMC) (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.) acted as the electrolyte.

About 8 mmol of LiPF_6 salt was dissolved in approximately 10 mL of homemade ionic liquid 1-hexyl-3-methylimidazolium hexafluorophate ($[\text{Hmim}]\text{PF}_6$). The reaction mixture was vigorously stirred for 6 h at room temperature. And the ionic liquid electrolyte was prepared by this way.

2.2 Fabrication of batteries

The air electrode was prepared with double-layer structure of gas diffusion layer and catalyst layer. The gas diffusion layer was fabricated by the following method: the carbon paper (GDL35BC carbon paper, Germany SGL Company) was soaked in the Teflon emulsion (5%, DuPont Corporation) for 20 min, and then dries naturally, at last dry the carbon paper at 350 °C for 1 h. The electrolytic manganese dioxide (EMD, battery grade, Xiangtan Electrochemical Scientific Lid.) was used as catalyst and the Teflon emulsion was used as binder. The catalyst layer was prepared by spraying the aqueous solution mixture of super P conductive carbon black (SCM Industrial Chemical Co., Ltd.) /catalyst/binder (the weight ratio 75/15/10) on the gas diffusion layer with spray gun (Meiji Air Compressor Mfg. Co., Ltd.) at the operation temperature of 340 °C and the gas pressure of 2 atm. The gas diffusion layer had been previously treated with the mixture of carbon powder/catalyst/binder

before spraying in order to reduce the contact resistance, the air electrode prepared was then dry overnight at 60 °C. The carbon loading of the air electrode was 6 mg cm⁻². Disks 13.7 mm diameter, 0.2 mm thick were cut from the lithium ribbon (China Energy Lithium Co., Ltd.) for use as the negative electrode. Disks 10 mm diameter were cut from the air electrode above for use as the positive electrode. A 0.8 mol L⁻¹ organic solution or ionic liquid acted as the electrolytes. Disks 20 mm diameter were cut from polypropylene microporous membrane Celgard 2400 for use as the separator.

The fixture shown in Figure 1. The batteries were constructed in an argon atmosphere glove box. The stainless steel on the bottom of the fixture was just as the current collector of the negative electrode, the foam nickel was used as the current collector of the positive electrode, two pieces of separator were sandwiched between a lithium metal and air electrode, a stainless steel spring was used at the top of the fixture to make sure the contact between the internal circuit and the external circuit is good, the batteries was standing for 3 h before testing.



Figure 1. Structure of the lithium-air battery.

2.3 Electrochemical measurements

Electrochemical study of the electrolyte was conducted in a standard three-electrode cell at CHI 660D electrochemical working station (CH Instruments Inc, Austin, TX). The glassy carbon disk covered the Super P/MnO₂/Nafion (1:1:1) was used as working electrode. A piece of platinum foil of 1 cm² served as the counter electrode and a Ag/AgCl (2.94 V vs. Li/Li⁺) electrode was used as the reference electrode. Cyclic voltammetry was recorded in a 0.8 mol L⁻¹ electrolyte from -2.5 to 2.0 V at a scan rate of 1, 5, 10, 50, 100, 500 mV s⁻¹. And a Tafel test was recorded in a 0.8 mol L⁻¹ electrolyte from -2.5 to 2.0 V at a scan rate of 10 mV s⁻¹. All the electrochemical measurements were carried out at 25 °C.

2.4 Battery tests

The cells were tested in a LAND cyler (Wuhan Land Electronic Co. Ltd.) with a lower voltage limit of 2.0 V and an upper limit of 4.5 V vs Li⁺/Li at different current densities accordingly. All experiments were carried out in dry and pure oxygen, with the battery operating at a constant current density of 0.02 mA cm⁻².

3. RESULTS AND DISCUSSION

3.1 Conductivity of electrolyte

The organic solution and the ionic liquid electrolytes have better thermal stability and electrochemical window. Ion conductivity under room temperature was above the order of magnitude of 10⁻³ S cm⁻¹. Figure 2 shows the correlation between the conductivity and temperature of the organic solution and the ionic liquid electrolytes, wherein the conductivity of the electrolyte increased linearly with temperature. The conductivity of the organic solution was 4.5 mS cm⁻¹ at room temperature, which is higher than that of ionic liquid (4.2 mS cm⁻¹). The conductivity of the lithium ion was relatively low because of the relatively high viscosity of the ionic liquid.

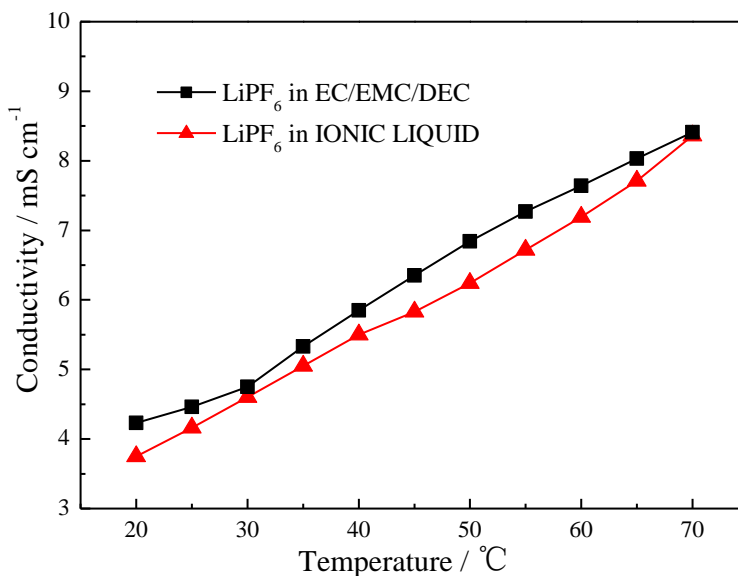


Figure 2. Correlation between the conductivity and temperature of the organic solution and ionic liquid electrolytes.

3.2 Tafel curve test

Figure 3 shows the Tafel curves of electrolytes at a voltage range of -2.5 to 2 V. A weak polarization area exists in the Tafel curve at negative 100 mV of the equilibrium potential. This finding indicates that a Tafel linear area in the cathodic Tafel slopes of the organic solution and ionic

liquid electrolytes in the Tafel linear area are 120 mV dec^{-1} , according to the calculation formula of Tafel slope $b_c = -\frac{2.3RT}{\alpha nF}$. In the equation, R is the gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T is the absolute temperature, F is the Faraday constant (96485 C mol^{-1}), n is the electronic number gained and lost in the reaction rate controlling step, and α is a mass transfer coefficient of 0.5. The Tafel slope of 120 mV dec^{-1} in the weak polarization area indicates that the electronic number gained and lost in the reaction of the rate-controlling step can be obtained as 1. Thus, the rate-controlling step is $\text{Li}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{LiO}_2$, which is consistent with the discharge process of lithium-air battery.

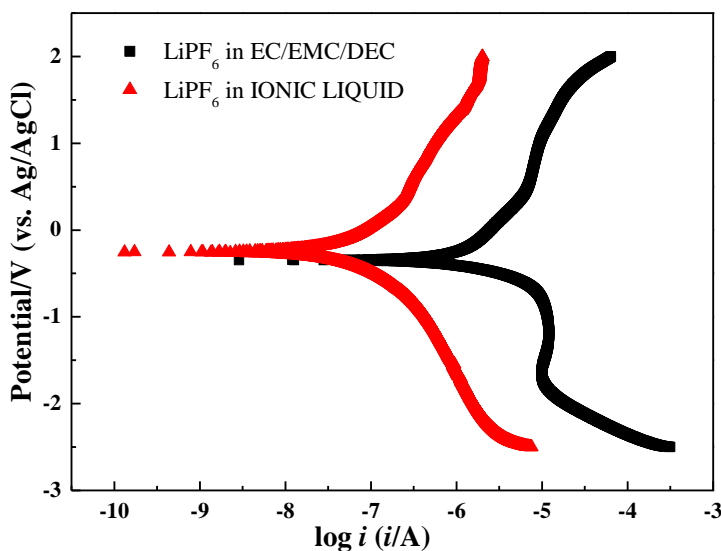


Figure 3. Tafel curves of electrolytes at voltage range of -2.5 to 2 V.

3.3 Cyclic voltammetry test

In the cyclic voltammetry test, the peak current of oxygen reduction and evolution has a linear relationship as the formula $i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} \nu^{1/2} C_0^*$ to the square root of the scanning speed. In the formula, i_p is the peak current, A is the area (approximately 0.07065 cm^2) of the working electrode, n is the number of electrons that reacted, ν is the scanning speed, and D_0 and C_0^* are the diffusion coefficient and solubility of oxygen in the electrolyte, respectively. Figure 4 shows the relation curves of the peak current of oxygen reduction of the electrolyte to the square root of the scanning speed. These relationships show that all peak currents of the oxygen reduction of the electrolyte have relatively good linear relationship to the square root of the scanning speed, indicating that the process of oxygen reduction is controlled by diffusion. Furthermore, the effects of dissolution and diffusion of oxygen and the migration of oxygen ion on the reduction of the ionic liquid electrolyte are relatively large because the solubility and diffusion coefficients of oxygen in non-aqueous electrolyte are small. The solubility and diffusion coefficient of oxygen are lower than that of the organic electrolyte.

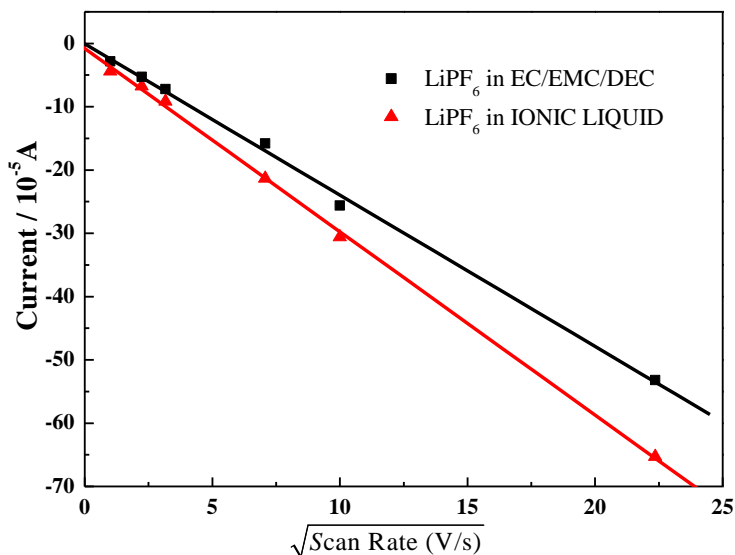


Figure 4. The relation curves of the peak current of oxygen reduction to the square root of the scanning speed.

3.4 Constant current discharging test

Figure 5 shows the constant current discharge curves of lithium-air batteries with organic solution and ionic liquid electrolytes at 0.02 mA cm^{-2} . The first discharge-specific capacity of the lithium-air battery with ionic liquid electrolyte was 1160 mAh g^{-1} , which is higher than that of the battery with an organic solution (1030 mAh g^{-1}). In addition, a long-term operation can reach 740 h for 10 cycles.

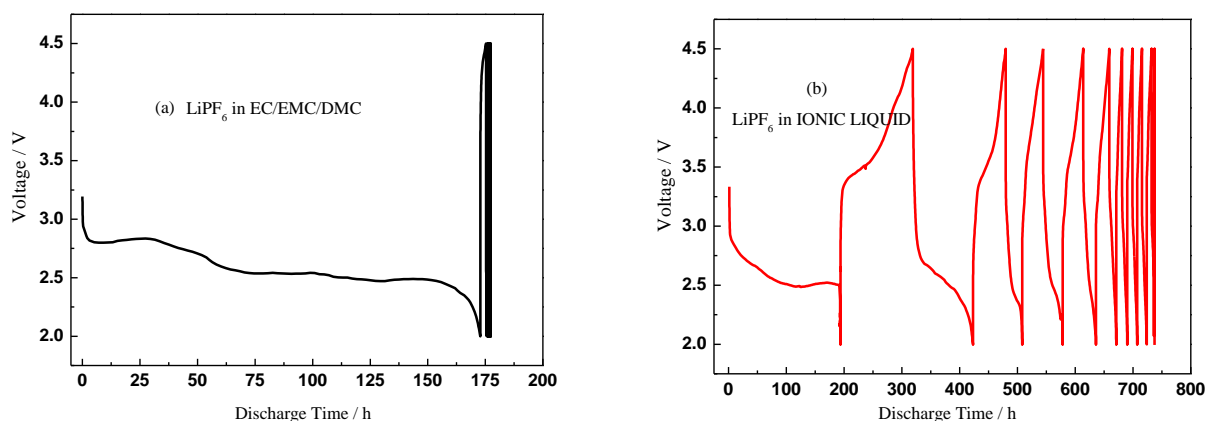


Figure 5. The constant current discharging curves of lithium-air batteries with organic solution and ionic liquid electrolytes at 0.02 mA cm^{-2} .

The lithium-air battery that uses an ionic liquid electrolyte exhibited a relatively excellent discharge performance. The excellent performance of the electrolyte is attributed to the reduction in battery capacity because good thermal stability prevents electrolyte volatilization in the working

process. Unlike common organic electrolytes, the vapor pressure of the ionic liquid electrolyte can be neglected. Hence, the electrolyte can be used in a mild open environment; the effect of humidity and temperature to the discharge process of the battery becomes relatively small. In addition, volatilization and water absorption problems of the electrolyte can be resolved instantly in an oxygen atmosphere. However, the hydrophobic-mixed electrolyte of lithium-ion liquid can be used to prevent a reaction when metal lithium comes in contact with water vapor. These factors prolong the service life of the lithium-air battery with ionic liquid electrolyte.

4. CONCLUSIONS

The use of ionic liquid and organic solution as electrolytes for lithium-air battery was successfully demonstrated in this study. The battery with ionic liquid showed a specific capacity of 1160 mAh g⁻¹ for the first discharge; long-term operation can reach 740 h for 10 cycles. The lithium-air battery with ionic liquid electrolyte showed good capacity and rechargeability, which was higher than that of the battery with organic solution. Therefore, the ionic liquid electrolyte is a more suitable electrolyte for lithium-air batteries.

ACKNOWLEDGMENTS

This work was supported by the National High Technology Research and Development Program of China (863 Program, No. 2011AA11A257), the Natural Science Foundation of China (No. 21206083), and the Excellent Talents of Liaoning Province of China (No. LJQ2011121).

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