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Lithium-air batteries using hydrophobic room temperature ionic liquid electrolyte

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Abstract

Lithium-air batteries using hydrophobic ionic liquid consisting of 1-alkyl-3-methyl imidazolium cation and perfluoroalkylsulfonyl imide anion were investigated. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, which has high conductivity and prevents hydrolysis of the lithium anode, showed the best electrolyte performance. The cell worked for 56 days in air, and the cathode carbon materials showed high discharge capacity of 5360 mAh g^{-1}. In addition to hydrophobic ionic liquids for use as electrolytes, various carbon materials for use as high-capacity cathodes were investigated.
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1. Introduction

Metal-air batteries with aqueous electrolyte, such as zinc-air batteries and aluminum-air batteries, have been studied over a long period. The cathodic reaction consists of the catalytic reduction of oxygen, which is not stored in the batteries but is absorbed from the air; thus, metal air batteries are high-capacity batteries. A lithium-air battery with non-aqueous polymer electrolyte was first reported in 1996 [1]. In this battery system, the operating voltage (theoretically 2.9–3.1 V) is higher than that of metal-air batteries using aqueous electrolyte, but the discharge reaction soon stops because insoluble cathodic discharge products, Li$_2$O and Li$_2$O$_2$, are deposited on the surface of the cathode, inhibiting further catalytic oxygen reduction. However, the lithium-air battery is still attractive because its pseudo cathode capacity of 1600 mAh g^{-1} is much larger than that of lithium-metal oxide batteries using non-aqueous electrolyte. In addition, an excellent discharge capacity of 2120 mAh g^{-1} has been observed on conductive carbon with non-aqueous liquid electrolyte [2]. We have also researched carbon materials for use as high-capacity cathodes for lithium-air batteries and have found that the mesopore of the cathode material

influences the discharge capacity [3]. During an earlier study, we found that the capacity of a cell was constrained not only by the specific capacity of the cathode materials, but also by vaporization of the electrolyte and hydrolysis of the anode.

In this paper, we report for the first time on lithium-air batteries using hydrophobic ionic liquid electrolyte. Non-aluminum chloride room temperature ionic liquids, such as EMIBF$_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate) [4], have been studied as non-volatile, non-flammable, and air-stable electrolytes for electrochemical devices such as batteries and capacitors [5,6]. Certain ionic liquids, for example EMITFSI (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide), are almost immiscible in water [7], and such hydrophobicity is appropriate for the electrolytes of lithium-air batteries, which need air but not moisture. We examined the hydrophobicity of some room temperature ionic liquids and studied the discharge behavior of lithium-air cells using these liquids as electrolytes. In addition, we investigated various carbon materials for use as high-capacity cathodes.

2. Experimental

Battery-grade LiTFSI, LiBETI (lithium bis(pentafluoro-ethylsulfonyl)amide), EMIBF$_4$, and an organic electrolyte

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Table 1
Structural parameters and discharge capacity of carbon materials

Carbon	Specific surface area ($m^2\,g^{-1}$)	Pore volume ($ml\,g^{-1}$)	Micropore ($ml\,g^{-1}$)	Mesopore ($ml\,g^{-1}$)	Capacity ($mAh\,g^{-1}$)	
					($I/mA\,cm^{-2}$)	
					0.1	0.5
A	1329	2.014	–	2.014	2220	1500
B	1473	1.922	0.583	1.339	360	290
C	1286	0.808	0.592	0.216	22	–
D	779	0.462	0.360	0.102	17	–

(1 M LiClO$_4$ EC/PC (EC: ethylene carbonate; PC: propylene carbonate; EC:PC = 1:1)) were used as received. EMIDCA (1-ethyl-3-metylimidazolium dicyanamide) was synthesized according to the literature [8]. Five hydrophobic ionic liquids, EMITFSI, EMIBETI, MOITFSI (1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)amide), BMINf (1-butyl-3-methylimidazolium nonafluorobutyl sulfonate) [7], and BMIPF$_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) [9], were synthesized according to standard procedures as follows. Freshly distilled 1-methylimidazole and an excess of bromoethane were stirred in dehydrated acetonitrile and refluxed for 6 h. After the reaction, the acetonitrile was evaporated almost completely, dehydrated ethyl acetate was added, and the resulting precipitate was filtered off and dried in vacuo. The crude product was re-crystallized from dehydrated acetonitrile and ethyl acetate to obtain EMIBr as a white solid. EMIBr and an excess of LiTFSI were stirred in water at 60 °C for 4 h. The resulting hydrophobic liquid was washed with water several times and then dried in vacuo to obtain EMITFSI as a clear liquid.

The hydrophobicity of the ionic liquid was studied by observing the change of water content under high-humidity conditions. The sample (500 μl) was set in a glass tube (φ10 mm), and the tube was stored in a temperature and humidity chamber (20 °C, 90% RH). The water content was determined based on the change in weight.

For the cathode carbon materials, conducting carbons (A and B) and activated carbons (C and D) with large surface area were used. The structural parameters, surface area, and pore volume were examined by nitrogen absorption at −196 °C. The surface area was estimated using the BET method. The mesopore and micropore volumes were respectively determined using the DH and MP methods.

The performance of the carbon materials as cathodes was evaluated as follows. The carbon materials were made into sheets (100–150 μm in thickness) with PTFE (3–10 wt.%). Carbon A was also made into sheets with cobalt phthalocyanine (CoPc; 3 wt.%) and PTFE (10 wt.%). The carbon sheets were dried in vacuo at 150 °C for at least 12 h before use. To examine the cathode in a dry condition, a lithium sheet on a nickel mesh collector, a glass filter including electrolyte, a cathode carbon sheet on a SUS mesh collector, and a glass filter for use as a gas diffusion membrane were stacked and put into a polypropylene case with air holes above the cathode.

The unit was set in a 500 ml separable flask and standard gas was flow into the flask for 30 min before discharge. The standard gas consisted of dry oxygen (20%) and nitrogen (80%). The flask was closed during discharge. To test the cathode in air, a lithium sheet, a glass filter including electrolyte, a cathode carbon sheet (φ20 mm) on a SUS mesh collector, a glass filter, and a PTFE membrane were stacked in a 2330 coin-type cell. The tab on the air holes was removed at least 30 min before discharge.

3. Results and discussion

3.1. Performance of carbon materials

The structural parameters and discharge capacities (1 M LiClO$_4$ EC/PC, standard gas) of the carbon materials with large surface areas are shown in Table 1, and the discharge curves of the cells are shown in Fig. 1. In the lithium-air battery system, lithium oxides, which are not dissolved in the electrolyte, are formed on the cathode surfaces and prevent further oxygen reduction. Therefore, carbon materials with larger surface areas are more appropriate as cathode materials. As long as the same carbon species is used, the discharge capacity of each cell is proportional to the weight of the carbon in the cathode. The activated carbons C and D showed only a low capacity even at the low discharge rate of 0.1 mA cm^{-2}, partially because of their low conductivities. The conducting carbons A and B showed significantly larger capacities than the activated carbons. The capacity trends
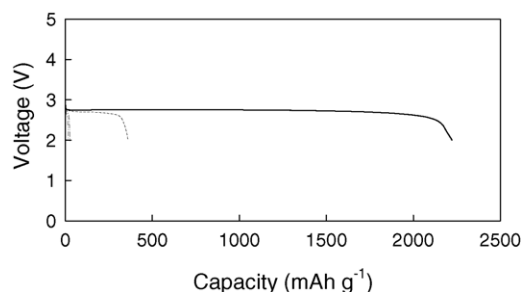
Fig. 1. Discharge curves of the Li-air cell using carbon materials with large surface areas. (—): carbon A; (- - -): carbon B; (—·—·—): carbon C; (—··—··—): carbon D; (electrolyte: 1 M LiClO$_4$-EC/PC; I: 0.1 mAh g^{-1}; condition: standard gas).

seem to be unrelated to the surface area measured by the BET method, as can be seen in the literature [2]. The effective structural parameter that could explain the differences in the capacities of the conducting carbons was not the surface area but the macropore volume. Though the trends of the discharge capacities of carbon materials with large surface areas could be explained by the macropore volumes, it has also been reported that a conducting carbon (Super P; M.M.M. Carbon) with a small surface area of $62 \, cm^2 \, g^{-1}$ has a large discharge capacity [2]. Therefore, the primary factor governing discharge capacity needs further consideration.

The discharge behavior of the coin-type cell with carbon A/CoPc and organic electrolyte is shown in Fig. 2. In the dry condition in the standard gas, the carbon cathode showed a large capacity of $2220 \, mAh \, g^{-1}$ at the discharge rate of $0.1 \, mA \, cm^{-2}$, and a slightly greater capacity of $2440 \, mAh \, g^{-1}$ at the lower discharge rate of $0.01 \, mA \, cm^{-2}$ (Fig. 2a). In air also, a large capacity of $2430 \, mAh \, g^{-1}$ was observed at the discharge rate of $0.1 \, mA \, cm^{-2}$, but, in contrast, an inferior capacity of $940 \, mAh \, g^{-1}$ was observed at the lower discharge rate of $0.01 \, mA \, cm^{-2}$ (Fig. 2b). After discharge in air, the surface of the lithium was hydrolyzed into LiOH. The corrosion was conspicuous at the lower discharge rate in air, but this was not observed for discharge in the standard gas. After discharge in air at the rate of $0.01 \, mA \, cm^{-2}$, the separator of the cell was dried almost completely. Vaporization of the electrolyte was insignificant at the higher discharge rate, which corresponds to a short test time (note that if there is vaporization, it is mainly of the PC in the electrolyte). The decrease of electrolyte was also insignificant in the test in the standard gas even at the discharge rate of $0.01 \, mA \, cm^{-2}$, which corresponds to a long test time. Note that the test in the standard gas was carried out in a closed flask, which probably prevented vaporization of the
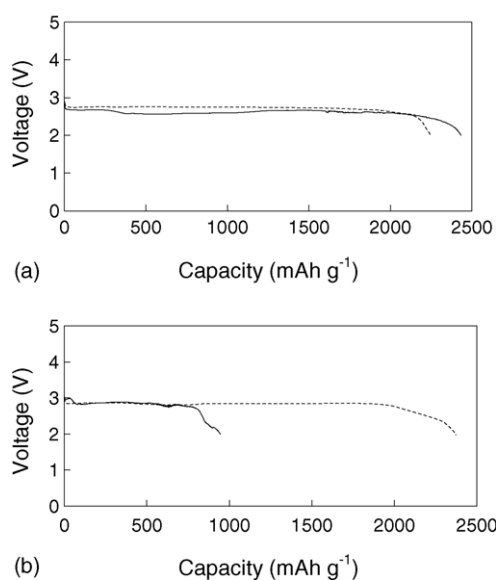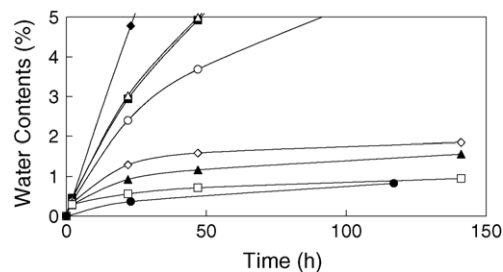

Fig. 3. Water contents of ionic liquids in high humidity condition ($20 \, °C$, 90%RH), (●): EMIBETI, (□): OMITFSI, (▲): EMITFSI, (◇): BMINf, (○): BMIPF$_6$, (△): EMITf, (■): EMIBF$_4$, (◆): EMIDCA.

electrolyte. These results suggest that the discharge capacity of the lithium-air battery with organic electrolyte is restricted by hydrolysis of the anode and vaporization of the electrolyte.

The X-ray diffraction patterns of the carbon cathode after discharge in air showed broad and weak peaks corresponding to Li_2CO_3, but no obvious peaks of lithium oxides (Li_xO_2). These results indicate that the oxygen reduction product reacted further with CO_2 to form Li_2CO_3 in air.

3.2. Performance of ionic liquids

The changes in the water contents of the ionic liquids in the temperature and humidity chamber ($20 \, °C$, 90% RH) are shown in Fig. 3. BMIPF$_6$, EMITFSI, EMIBETI, and MOITFSI were particularly immiscible with moisture, and the water contents after 100 h were 1.7, 1.4, 0.8, and 0.7 wt.%, respectively. The stability of the highly hydrophobic ionic liquids with lithium in dry argon was in the order BMIPF$_6$ « EMITFSI < EMIBETI, MOITFSI. In this stability test, instabilities were easily recognized as changes in the color of the ionic liquid and the surface of the lithium within several days. The potential windows of the ionic liquids with imidazolium cation are not large, so the ionic liquids slowly decomposed. However, in the presence of LiTFSI or LiBETI, EMITFSI, EMIBETI and MOITFSI were found to be stable with the lithium for several months. That probably caused from formation of protective layer on lithium such as LiF. It is known that the PF$_6$ anion is easily decomposed in moisture; thus, ionic liquids with the perfluoroalkyl sulfonyl amide anion are considered desirable electrolytes for lithium-air batteries.
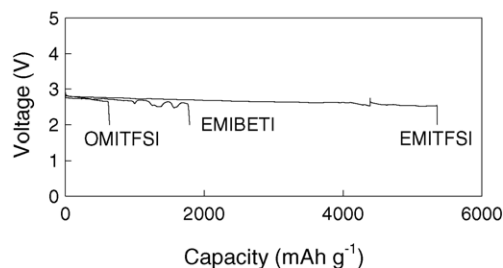

(a)

(b)

Fig. 2. Discharge curves of the Li-air cell in standard gas and air. a: I: $0.1 \, mA \, cm^{-2}$; b: I: $0.01 \, mA \, cm^{-2}$; (- - -): standard gas; (—): air.

Fig. 4. Discharge curves of the Li-air cell using hydrophobic ionic liquids. I: $0.01 \, mA \, cm^{-2}$; $20 \, °C$; in air.
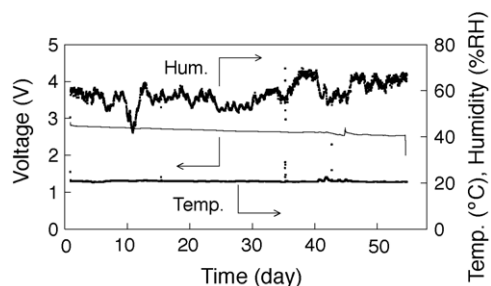
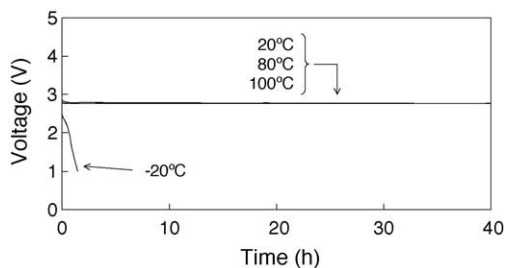Fig. 5. The effect of humidity on discharge profile. Electrolyte: 0.5 M LiTFSI-EMITFSI; I: 0.01 mA cm^{-2}; in air.

Fig. 6. Discharge curves of the Li-air cells at various temperature. Electrolyte: 0.5 M LiBETI-EMIBETI; I: 0.01 mA cm^{-2}; in air.

3.3. Lithium-air cells with hydrophobic ionic liquids

Fig. 4 shows the discharge profiles at the discharge rate of 0.01 mA cm^{-2} in air for coin-type cells with carbon A/CoPc that use hydrophobic ionic liquids with perfluoroalkyl sulfonyl amide that contain 0.5 M Li salts. The ordering of the capacities, which are proportional to the cell lives, did not follow the hydrophobicity trend suggested by the change of water content under the high-humidity condition. The cell using MOITFSI showed a carbon cathode capacity of 640 mAh g^{-1}, and after discharge, foamy ionic liquid leaked through the air holes to prevent oxygen absorption in the cell. The leak was probably caused by the highly viscous MOITFSI, which includes a long alkyl chain, acting as a surfactant and allowing the bubbles generated in the hydrolysis reaction of lithium to stabilize. The cells using EMIBETI and EMITFSI showed larger capacities than those using organic electrolyte, 1790 and 5360 mAh g^{-1}, respectively. The trend was probably because the conductivity and the viscos-

ity of EMIBETI were inferior to EMITFSI. Fig. 5 shows the changes in temperature, humidity, and cell voltage for the EMITFSI cell. The cell worked for 56 days in air, and the humidity and long discharge time did not affect the discharge behavior significantly. The effect of using non-volatile electrolyte appeared notably in discharge test at high temperature. Fig. 6 shows the first 40 h of the discharge profiles of the cell using EMIBETI, that was most stable of the electrolytes studied in the presence of lithium metal, at 20 and 100 °C. The cell could favorably operate at 100 °C, the environment that metal-air cell using aqueous electrolyte could not operate because of the vaporization of water.

4. Conclusions

The discharge capacity of the cathode carbon material is affected by the mesopore volume of carbon. Carbon A showed a particularly high capacity of 2433 mAh g^{-1} in air at the high discharge rate of 0.1 mA cm^{-2}, but the same cell showed a low capacity of 944 mAh g^{-1} in air at the low discharge rate of 0.01 mA cm^{-2} because of electrolyte vaporization and anode hydrolysis. When the hydrophobic ionic liquid electrolyte EMITFSI was used, a particularly high capacity of 5360 mAh g^{-1} was observed because EMITFSI prevented vaporization of the electrolyte and hydrolysis of the anode.

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