



Short communication

## Novel composite polymer electrolyte for lithium air batteries

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### ABSTRACT

Hydrophobic ionic liquid–silica–PVdF–HFP polymer composite electrolyte is synthesized and employed in lithium air batteries for the first time. Discharge performance of lithium air battery using this composite electrolyte membrane in ambient atmosphere shows a higher capacity of  $2800 \text{ mAh g}^{-1}$  of carbon in the absence of  $\text{O}_2$  catalyst, whereas, the cell with pure ionic liquid as electrolyte delivers much lower discharge capacity of  $1500 \text{ mAh g}^{-1}$ . When catalyzed by  $\alpha\text{-MnO}_2$ , the initial discharge capacity of the cell with composite electrolyte can be extended to  $4080 \text{ mAh g}^{-1}$  of carbon, which can be calculated as  $2040 \text{ mAh g}^{-1}$  associated with the total mass of the cathode. The flat discharge plateau and large discharge capacity indicate that the hydrophobic ionic liquid–silica–PVdF–HFP polymer composite electrolyte membrane can effectively protect lithium from moisture invasion.

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### 1. Introduction

Lithium air (oxygen) battery as a novel battery system has huge theoretical specific energy of  $11,140 \text{ Wh kg}^{-1}$  excluding  $\text{O}_2$ , which provides energy density an order of magnitude larger than conventional batteries. Besides, oxygen as an active material from the environment is essentially unlimited. Lithium oxygen non-aqueous battery firstly reported by Jiang and Abraham, had an operating voltage of  $2.4 \text{ V}$  and specific energy density of  $250\text{--}350 \text{ Wh kg}^{-1}$  [1]. By utilizing cobalt phthalocyanine as catalyst, reasonable columbic efficiency upon cycling was achieved. P.G. Bruce's group demonstrated that proper oxygen catalyst could facilitate the electrochemical reaction of  $\text{Li}^+$  react with  $\text{O}_2$  to form  $\text{Li}_2\text{O}_2$  which is reversible, and as a result, lithium air battery could have adequate cycling life [2–4]. Because of its huge application potential, recently many groups are devoting to working on lithium air battery [5–9]. However, many obstacles must be overcome in order to achieve long operating life and large discharge capacity. The issues at least include the volatility and hydrophilic properties of common organic electrolyte; the efficiency and selectivity of catalyst for oxygen reduction, and moreover, the corrosion of lithium by crossover  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the case of its operation in ambient atmosphere.

In case of operation in ambient atmosphere, seeking proper electrolyte is vital to have reasonable performance for lithium air battery because of electrolyte evaporation and lithium corrosion. Hydrophobic ionic liquids were firstly reported by Kuboki et al. as

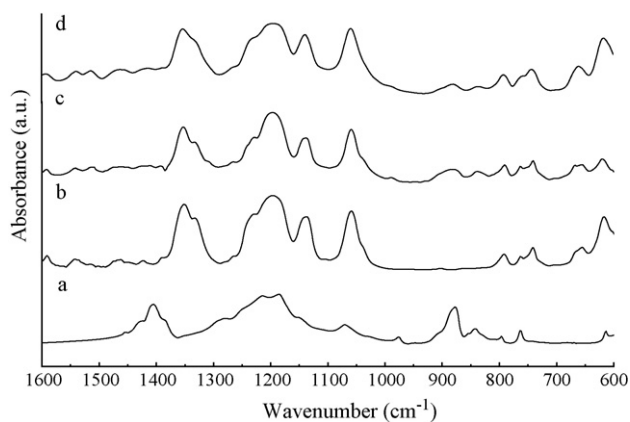
a promising candidate waterproof electrolyte for lithium air battery due to its hydrophobicity and negligible vapor pressure [10]. The cell with cobalt phthalocyanine as oxygen catalyst showed a huge discharge capacity of  $5360 \text{ mAh g}^{-1}$  of carbon at a discharge current density of  $0.01 \text{ mA cm}^{-2}$ . However, even hydrophobic ionic liquid absorb trace amount of water in air, and unsuitable for long time operation. Furthermore, cobalt phthalocyanine catalyst is too expensive as an oxygen reduction catalyst for large scale production. In this paper, hydrophobic ionic liquid–silica–PVdF–HFP polymer composite electrolyte as a moisture barrier to improve the ambient operating life of lithium air battery was investigated.

### 2. Experimental

Hydrophobic ionic liquid 1,2-dimethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (PMMITFSI) was synthesized by anion exchange reaction. 1,2-Dimethyl-3-propylimidazole bromide (Shanghai Chengjie Regent Company) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich) (molar ratio = 1:1) were mixed together and stirred in distilled water at room temperature for 3 h. Then the obtained product was washed by distilled water repeatedly and extracted with dichloromethane. After drying the compound under vacuum at  $100^\circ\text{C}$  for 24 h to remove solvents, the clear, colorless and inodorous ionic liquid PMMITFSI was obtained. Finally, certain amount of LiTFSI as Li source was added to PMMITFSI to form 1 M LiTFSI–PMMITFSI electrolyte.

For composite polymer electrolyte preparation, PVdF–HFP (Kynar 2801) was dissolved in 1-methyl-2-pyrrolidone (NMP) under stirring, and then the obtained viscous homogeneous solu-

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**Fig. 1.** Infrared spectra of (a) PVdF-HFP; (b) LiTFSI-PMMITFSI; (c) LiTFSI-PMMITFSI-PVdF-HFP polymer electrolyte and (d) LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte.

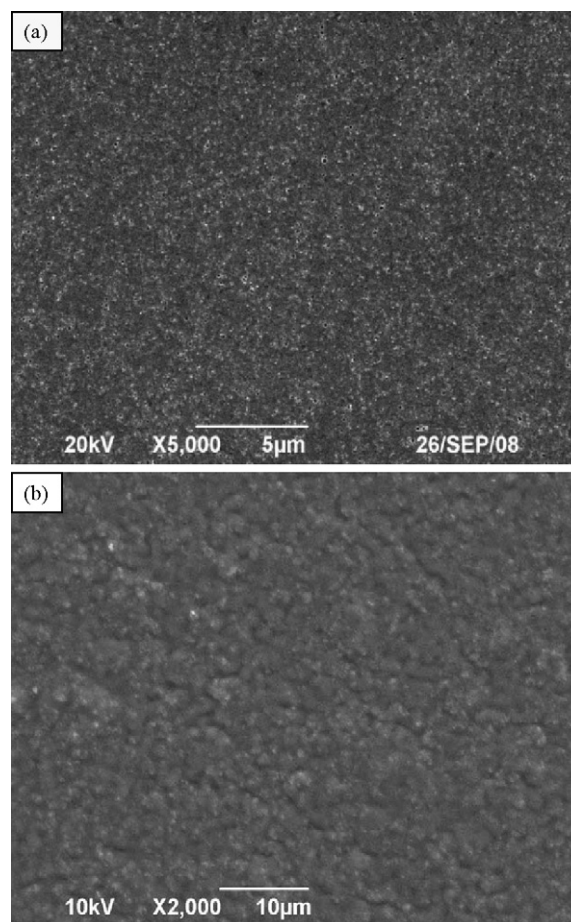
tion was mixed with LiTFSI-PMMITFSI and hydrophobic silica (DM-30, Tokuyama Inc.) with the weight ratio of 27:70:3. The mixture was vigorously stirred and ultrasonically treated to prevent silica lumps formation and uniform dispersion. After degassing, the well mixed solution was casted on a glass substrate with a doctor blade. The polymer composite electrolyte with an average thickness of 100  $\mu\text{m}$  was finally obtained by evaporation of solvent NMP and drying under vacuum at 100  $^{\circ}\text{C}$  for 24 h. For comparison, silica-PVdF-HFP polymer was also prepared in a similar process to that of hydrophobic ionic liquid-silica-PVdF-HFP polymer composite electrolyte except the addition of ionic liquid.

The morphology of the hydrophobic ionic liquid-silica-PVdF-HFP polymer composite electrolyte was observed by scanning electron microscope (JEOL JSM-6390). The interactions of all ingredients in composite electrolyte were recorded by infrared spectra on Varian 3100.

The ionic conductivities of hydrophobic ionic liquid-silica-PVdF-HFP polymer composite electrolyte were measured by a.c. impedance on an IM6 frequency analyzer (ZAHNER elektronik) with a stainless steel blocking cell by sweeping the frequency from  $10^6$  to 1 Hz with an amplitude of 5 mV. A symmetric Li/composite electrolyte/Li cell was used to measure the composite electrolyte/Li interface resistance. The resistance of ambient lithium air cell was also measured by a.c. impedance under open-circuit condition over the frequency range from 0.1 to  $10^5$  Hz with an amplitude of 5 mV. All the tests were carried out at room temperature.

According to previous work [11], the best performing  $\text{MnO}_2$  catalyzed air cathode was with the Mn/carbon weight ratio of 1:5. With this ratio, both manganese catalyst and carbon could be efficiently used during the reduction of oxygen. So in this paper, the air electrode was prepared by casting a mixture of Super P carbon,  $\alpha\text{-MnO}_2$  catalyst and PVdF-HFP binder with weight ratio of 5:1:4 onto a foam nickel current collector. In case of the electrode without catalyst, the ratio of Super P carbon to PVdF-HFP was 6:4. Typical loading of the air electrode is 3  $\text{mg cm}^{-2}$ . A swagelok cell with Li metal as anode, air electrode as cathode and composite electrolyte membrane as separator was assembled for electrochemical test. Air electrode was soaked in LiTFSI-PMMITFSI before assembly. An open hole ( $0.4\text{ cm}^2$ ) was placed on cathode side to allow air flow in, and a hydrophobic PTFE membrane was stacked on air vent to repel moisture. For comparison, the cell without composite electrolyte was assembled with pure ionic liquid LiTFSI-PMMITFSI as electrolyte, celgard 2400 as separator with the same cell structure.

The cell was tested in ambient atmosphere at a current density of  $0.02\text{ mA cm}^{-2}$  with cutoff voltage of 2.0 V, and for cycling test,

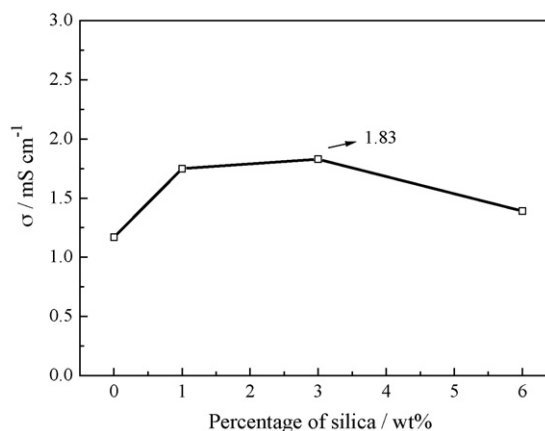


**Fig. 2.** SEM images of (a) silica-PVdF-HFP polymer electrolyte and (b) LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte.

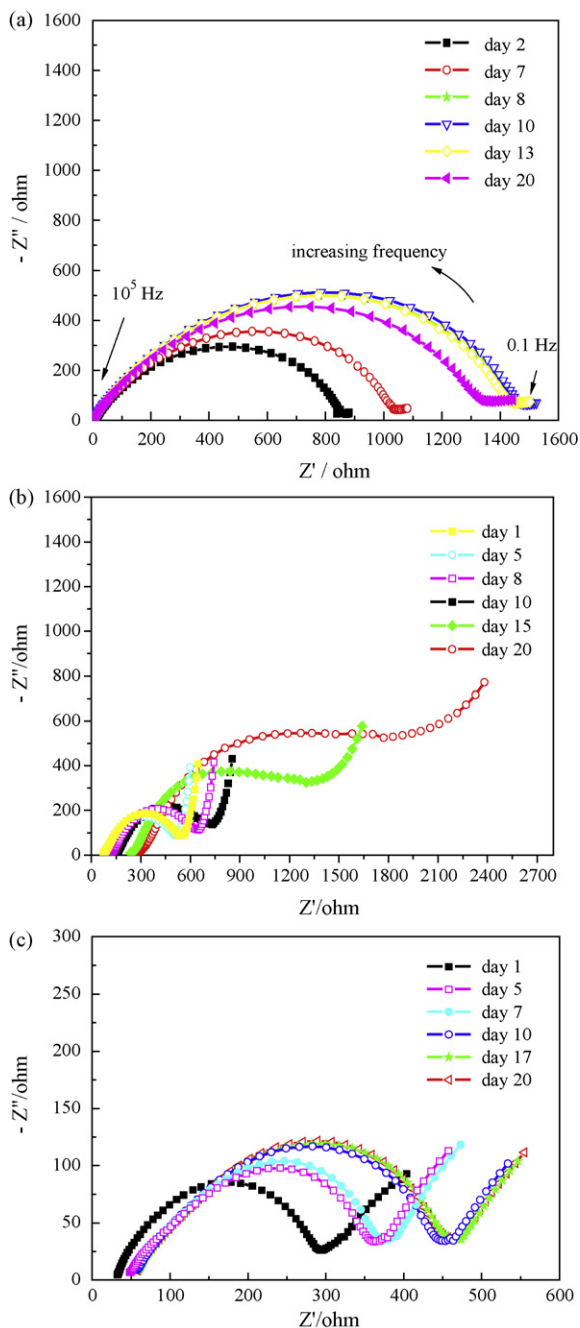
the cell was charged/discharged in oxygen atmosphere between 2.0 and 4.3 V at a current density of  $0.05\text{ mA cm}^{-2}$ .

### 3. Results and discussion

Infrared spectroscopy was firstly performed to characterize the composite electrolyte and study the interactions between ionic liquid, hydrophobic silica and PVdF-HFP polymer matrix. Fig. 1a–d shows the FTIR spectra of PVdF-HFP, LiTFSI-PMMITFSI electrolyte, LiTFSI-PMMITFSI-PVdF-HFP polymer electrolyte and

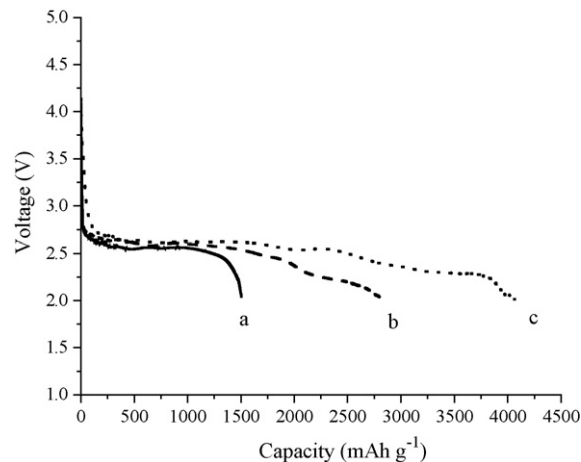


**Fig. 3.** Dependence of ionic conductivity of the composite electrolyte with silica content.



**Fig. 4.** Nyquist impedance plots of cells with different electrolyte. (a) Symmetric Li/composite electrolyte/Li cell; (b) lithium air cell by using pure LiTFSI-PMMITFSI as electrolyte and (c) lithium air cell by utilizing LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite as electrolyte.

LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte, respectively. The peaks at  $741$ ,  $763$  and  $792\text{ cm}^{-1}$  in Fig. 1b are fingerprints of TFSI ion of 1 M LiTFSI-PMMITFSI corresponding to the sensitivity of the formation of ion pair. It can be seen from Fig. 1b–d, the intensity and frequency of these peaks remained unchanged which means the interaction between all types of components has negligible effect on the state of ionic liquid electrolyte. Compared Fig. 1c and d with Fig. 1a, it can be seen that the  $\text{CF}_2$  stretching band at  $1185\text{ cm}^{-1}$  becomes border which indicating higher level of amorphous state of PVdF-HFP. The disappearance of the peak at  $1405\text{ cm}^{-1}$  corresponding to scissoring vibration of the vinyl



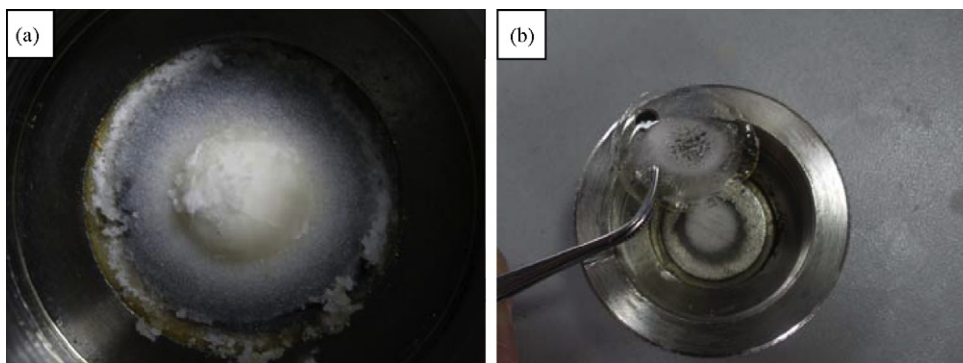
**Fig. 5.** Discharge curves of lithium air batteries with different electrolytes. (a) LiTFSI-PMMITFSI based non-catalyzed lithium air battery (solid), (b) LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte based non-catalyzed lithium air battery (dash) and (c) LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte based  $\alpha\text{-MnO}_2$  catalyzed lithium air battery (dot) in ambient atmosphere at the discharge current density of  $0.02\text{ mA cm}^{-2}$ .

and the decreasing intensities of the bands at  $877$  and  $842\text{ cm}^{-1}$  suggest that certain degree of co-ordination, complexation and ion association exist among the composite electrolyte components of LiTFSI-PMMITFSI, silica and PVdF-HFP [13].

Fig. 2 shows SEM images of silica-PVdF-HFP polymer electrolyte (Fig. 2a) and LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte (Fig. 2b). Both films are homogeneous porous structure with negligible silica aggregation since the average particle size of silica is of 7 nm. The LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte membrane is more compact than silica-PVdF-HFP electrolyte, which helps to repel ambient moisture. Silica DM-30 treated with hexamethyldisilazane was considered extremely hydrophobic [14] and also, it is well known that the addition of silica could stabilize the Li/composite electrolyte interface, increase ionic conductivity and mechanical strength of the film [12,13,15].

The ionic conductivities of the composite electrolytes with various silica contents are presented in Fig. 3. It can be seen, with 3% of silica in the composite electrolyte, it gives the highest ionic conductivity of  $1.83\text{ mS cm}^{-1}$ , which is close to that of ionic liquid electrolyte 1 M LiTFSI-PMMITFSI ( $2.08\text{ mS cm}^{-1}$ ), whereas, the conductivity of LiTFSI-PMMITFSI-PVdF-HFP polymer electrolyte is only  $1.19\text{ mS cm}^{-1}$ . Proper addition of silica could lead to higher amorphous phase of the film which improves the conductivity of the composite electrolyte. The Lewis acid–base interactions between the silica and electrolyte, co-ordination, complexation and ion association behaviors between the polymer matrix, ionic liquid and silica could strength and homogenize the composite electrolyte film [15]. However, higher content of silica filler could result in the aggregation of silica particles and thus reduces the conductivity.

The compatibility of the LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte with lithium metal was investigated by a.c. impedance spectroscopy at open-circuit potential. Typical Nyquist plot for the symmetric cell with time is exhibited in Fig. 4a. The intercepts with the real axis at high frequency is associated with the bulk resistance ( $R_b$ ), and the low frequency which controlled by diffusion process is related to the resistance of the Li/electrolyte interface ( $R_f$ ). The width of the semicircles corresponding to  $R_f$  presents initial increase during first 10 days and after that, the impedance is time insensitive which means

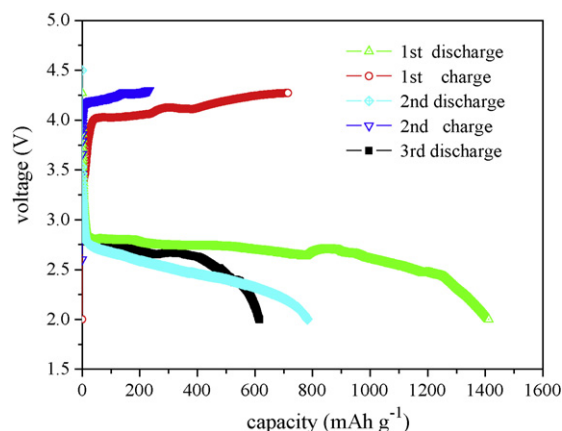


**Fig. 6.** Photographs of lithium anode in lithium air cells after fully discharged with (a) LiTFSI-PMMITFSI electrolyte and (b) LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte.

that the Li/electrolyte interface can be relatively stable during long time test. The impedances of ambient lithium air cells using different electrolytes are also measured. Fig. 4b depicts the resistance of the cell ceaselessly increases due to the poor interface resistance and contamination of water by utilizing only ionic liquid. However, when using composite electrolyte (Fig. 4c), the resistance remains constant after an activation time, which suggests the lithium air battery employing composite electrolyte could have better hydrophobicity, stable resistance, and suitable for operating in ambient atmosphere.

Using LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte as an electrolyte membrane, the discharge curves of lithium air battery at a current density of  $0.02 \text{ mA cm}^{-2}$  in ambient atmosphere are depicted in Fig. 5 in a comparison with the cell use ionic liquid as electrolyte. The little fluctuation mostly aroused by ambient atmosphere and temperature variation. All cells exhibit a typical plateau around 2.6 V. Without oxygen catalyst, the cell with LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte gives a capacity of  $2800 \text{ mAh g}^{-1}$  of carbon which is much larger than that of the cell with only ionic liquid ( $1500 \text{ mAh g}^{-1}$ ). The stable interface resistance and better waterproof condition contribute to higher capacity. Decomposing the cells after fully discharged, the lithium anode protect by ionic liquid was completely powdered (see Fig. 6a), and for polymer composite electrolyte, with a better waterproof condition, the lithium only suffered little scathe (see Fig. 6b), which is favorable for long time discharge test and deliver larger capacity.

The performance of  $\alpha\text{-MnO}_2$  catalyzed lithium air battery is preliminary investigated and the discharge curve is also displayed in Fig. 5. It can be clearly seen that the initial discharge capacity of  $\alpha\text{-MnO}_2$  catalyzed cell extends to  $4080 \text{ mAh g}^{-1}$  of carbon, and specific capacity associated with the total mass of the cathode (carbon + binder + catalyst) can be calculated as  $2040 \text{ mAh g}^{-1}$ . This observation suggests that the introduction of  $\alpha\text{-MnO}_2$  electrocatalyst can facilitate the oxygen electrode reaction by providing higher oxygen reduction catalytic activity and reducing polarization, thereby brings additional 45% of capacity. Although the cell gave excellent initial discharge capacity, the reversibility is rather poor with the second discharge capacity of only  $50 \text{ mAh g}^{-1}$ . This might be due to the reaction of discharge products  $\text{Li}_2\text{O}_2$  with  $\text{CO}_2$  existing in ambient atmosphere which require further studies. In order to eliminate the effect of the reaction of discharge products  $\text{Li}_2\text{O}_2$  with  $\text{CO}_2$ ,  $\alpha\text{-MnO}_2$  catalyzed cell cycled in pure oxygen atmosphere between 2.0 and 4.3 V at a higher current density of  $0.05 \text{ mA cm}^{-2}$  is shown in Fig. 7. The cell gives first discharge capacity of  $1400 \text{ mAh g}^{-1}$  of carbon, and delivers excitable reversible capacity on subsequent cycles. Further works on optimizing air electrode to improve the energy density, rate capability and cyclability of the cell are still going on.



**Fig. 7.** Charge/discharge curves of LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte based  $\alpha\text{-MnO}_2$  catalyzed lithium air battery in oxygen atmosphere between 2.0 and 4.3 V at a current density of  $0.05 \text{ mA cm}^{-2}$ .

#### 4. Conclusions

Novel hydrophobic LiTFSI-PMMITFSI-silica-PVdF-HFP polymer composite electrolyte was synthesized and employed in lithium air battery. IR spectra and ionic conductivity tests showed that the interaction between all types of components has negligible effect on the state of ionic liquid. The ionic conductivity of the composite electrolyte was  $1.83 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature which is in the same order of ionic liquid electrolyte. The compact structure and stable interface resistance is in favor of long time durability when the cell tested in ambient atmosphere, which may due to that the polymer composite electrolyte membrane can effectively stabilize the interface and diminish lithium corrosion by water and thus gave higher discharge capacity in cases of without and with  $\text{O}_2$  catalyst. The cell also showed reasonable cyclability which means this novel polymer composite electrolyte may provide an opportunity for fabrication of rechargeable lithium air battery for practical application.

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