



Preliminary Studies on Electrolyte and Electrode Designs for Lithium-Oxygen Batteries and Their Electrochemical Performance

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Abstract

Lithium-oxygen batteries exhibit high charge-discharge capacity and are promising for energy storage applications, such as electrical vehicles. The electrodes and electrolytes in these batteries play an important role on battery life and performance. In this work, the effects of electrolyte composition and electrode design on battery performance were investigated. When MnO₂ on nickel foam was used as air electrode, LiTFSI in tetraglyme electrolyte had a stable cycle life of six cycles (120 h) and a battery capacity of 2000 mAh/g-catalyst, both outperformed those of LiPF₆ in EC/DEC (which had cycle life of three cycles and electric capacity of 1800 mAh/g-catalyst). Spraying Pt on PTFE-containing carbon cloth as electrode was a promising approach to enhance battery life. Sixteen cycles (320 h) and a capacity of 2000 mAh/g-catalyst were obtained for the battery consisting catalyst on PTFE-coated carbon cloth. The coulombic efficiency was almost 100% in these cycles and the energy efficiency ranged from 64 to 77.

Keywords

Aprotic electrolytes, Battery cycling test, Electrochemical impedance spectroscopy, Lithium air battery

Introduction

As technology improves, the need for energy supply rises simultaneously. In addition to establish energy generation systems, the implementation for energy storage devices plays as equally important role as well. The primary advantage of lithium-air battery lies in its extremely high energy capacity. Using lithium metal as anode and oxygen (which can be obtained from ambient air), the maximum energy density can reach up to 11,586 Wh/kg, one order of magnitude higher than that of lithium ion

battery [1]. Therefore, lithium-air battery is considered as “ultimate battery” [2]. In this research, aprotic configuration [3] of lithium-oxygen battery is investigated. The effects of electrode, electrolyte and associated operating parameters are studied and their impacts on battery performance of resulting coin cells are evaluated.

Experimental

Air electrode preparation

Two kinds of air cathodes were made for compari-

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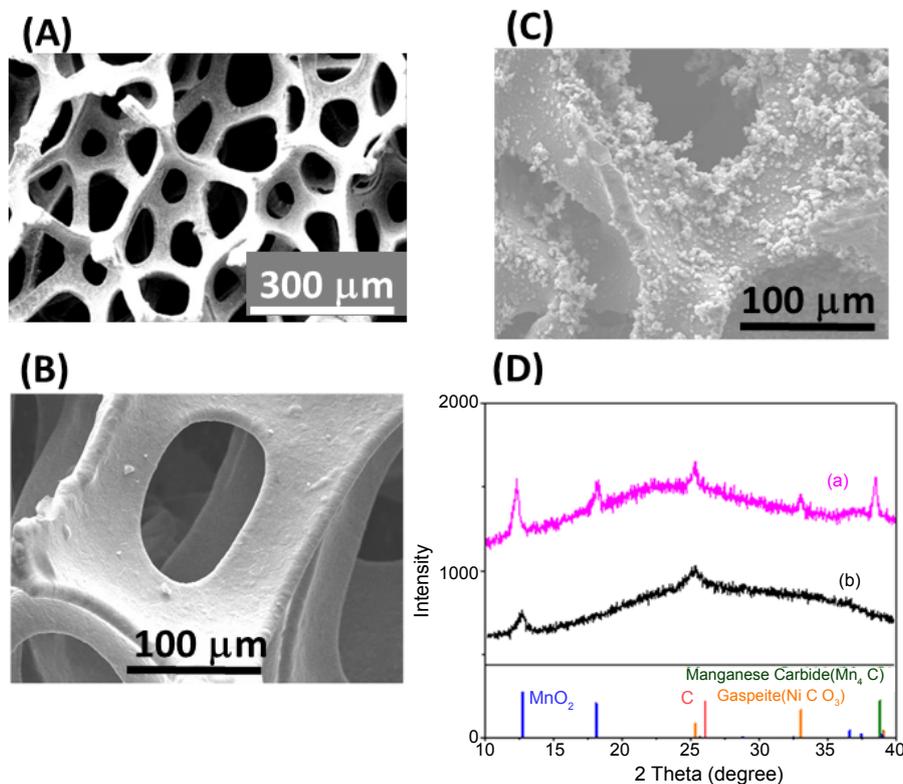


Figure 1: Scanning electron microscopy image of nickel form before MnO_2 loading A,B) After MnO_2 loading; C) and X-ray diffraction patterns; D) of MnO_2 -loaded (a) Onto nickel foam and (b) Onto carbon paper.

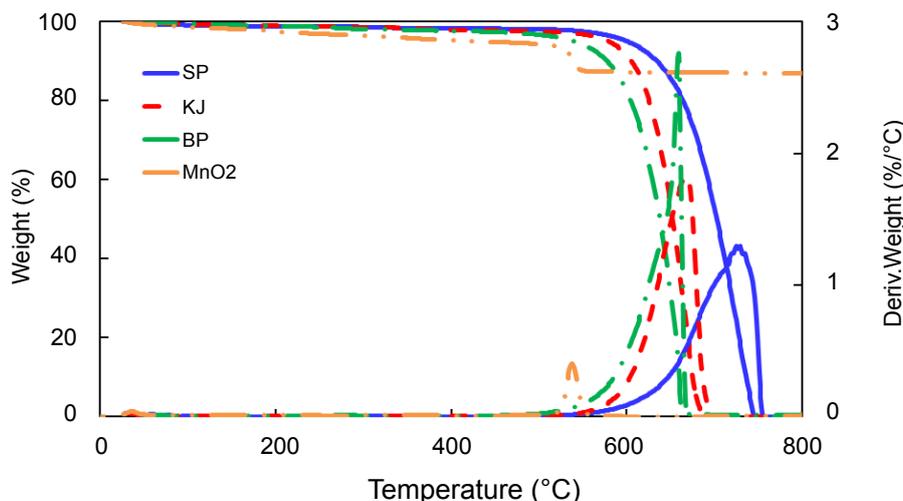


Figure 2: Thermal gravimetric analyses on carbon materials and MnO_2 catalyst.

son. The first cathode was made on nickel foam (Gelon LIB Co., Ltd), with pore size of 150-290 μm (Figure 1A and Figure 1B). The nickel foam was placed in a catalytic ink - a mixture of carbon black, $\gamma\text{-MnO}_2$ catalyst (Tosoh Corp.), PVDF binder ($\gamma\text{-MnO}_2$ + carbon black: PVDF = 9:1 (w/w), $\gamma\text{-MnO}_2$: carbon black = 1:9 (w/w)) in N-methyl-2-pyrrolidinone solvent (from Sigma-Aldrich) - and ultra-sonicated for a few minutes [4]. The foam was then dried at 120 $^\circ\text{C}$ for 24 h, weighed to calculate the amount of catalyst load, and cut into circular shape with 15.8 mm in diameter. The carbon black included Ketjenblack EC-

Table 1: Physical properties of carbon spheres.

Type	Ash (%)	Pour density (kg/m^3)	Surface area (m^2/g)	Particle size (nm)
SP	0.05	160	62	40
BP	1	144	1475	15
KJ	0.1	100-120	1270-1400	34
VX-72		264	254	30

600JD (KJ), Super P (SP), and Black Pearls[®] 2000 (BP). These carbon materials were thermally stable up to 500 $^\circ\text{C}$ (Figure 2). Some physical properties of the conductive carbons are shown in Table 1.

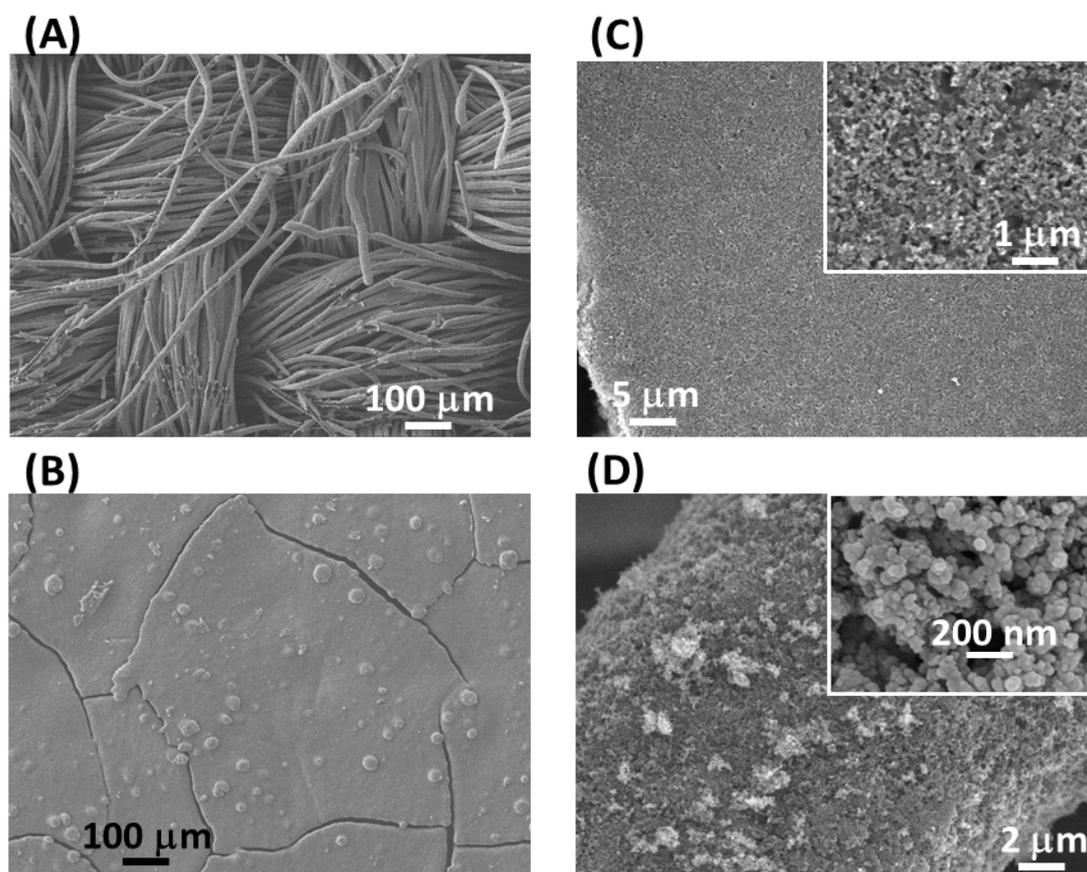


Figure 3: Scanning electron microscopy images of carbon cloth A) With PTFE coated layer; B) PTFE layer loaded with Pt catalyst; C) Carbon fiber loaded with Pt catalyst (D); D) Illustrate the morphologies of electrode configuration type III and type II, respectively, explained in Section III, D.

The other cathode was based on PTFE-coated carbon cloth, with pore size of 20 μm (Figure 3A). A catalyst ink was prepared by mixing Pt/C (40% Pt, Johnson Matthey, carbon support of Vulcan[®] XC-72), Nafion binder solution (D520, Chemours Co.), and water/isopropyl alcohol (from Sigma-Aldrich) solution. Then, the ink was sprayed evenly onto the PTFE layer of the carbon cloth (Cetech Co., Ltd.). The catalyst-loaded carbon cloth was dried at 100 $^{\circ}\text{C}$ for 2 hours, weighed, and cut into circular shape. The resulting catalyst loading was 0.5 mg/cm^2 .

Electrolyte preparation

One electrolyte was 1 M of Lithium Hexafluorophosphate (LiPF_6) in ethylene carbonate and diethyl carbonate mixture (EC/DEC, 50:50 v/v). The other electrolyte was 1M solution of lithium bis(trifluoromethane) sulfonamide (LiTFSI , from Sigma-Aldrich) in tetraethylene glycol dimethyl ether (tetraglyme, from Sigma-Aldrich) solvent. These electrolyte solutions were prepared in an Mbraun glove box to avoid contact with moisture and oxygen. The chemicals are at least of reagent grade.

Battery assembly and test

A glass fiber filter (with thickness of 0.42 mm, pore size of 290 μm) was used as the separator and soaked in

an electrolyte solution for 24 h. The air cathode, electrolyte (3 drops), glass fiber filter, lithium foil (0.2 mm thick, Alpha Aesar), and spring leaf were loaded in order into a CR2032 coin cell compartment (Figure 4). After the battery was sealed, pure oxygen (> 99.5%) at a flow rate of 50 mL/min was circulated to the coin cell to activate the battery for 8 h and during cycling analyses. The battery was tested for cycling charge/discharge condition between 2 and 4.5 V at 0.1 mA current. The charge or discharge period lasted for 10 h with 5 minutes of intermission, unless the voltage limit was reached. The discharge voltage and specific energy capacity were calculated to demonstrate the electrochemical performance of the battery. Figure 5 shows the reproducibility of the battery capacity at a function of cycle times.

Results and Discussion

Discharge current effect

In order to establish a protocol for battery evaluation, electrical current of 0.1 mA and 0.05 mA were used to compare the battery performance with Ni foam electrode. Figure 1 indicates the MnO_2 catalyst was successfully loaded onto the metal foam (Figure 1C); with higher efficiency than on carbon paper (Figure 1D). Figure 6

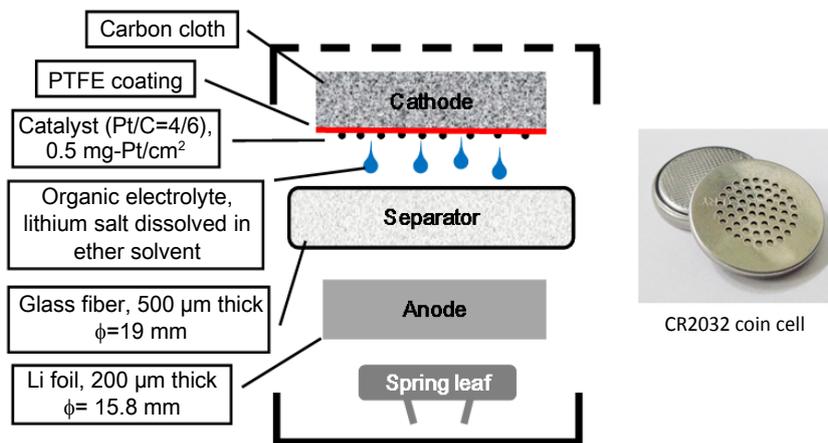


Figure 4: Illustration of lithium-air battery assembly and photo of resulting coin cell.

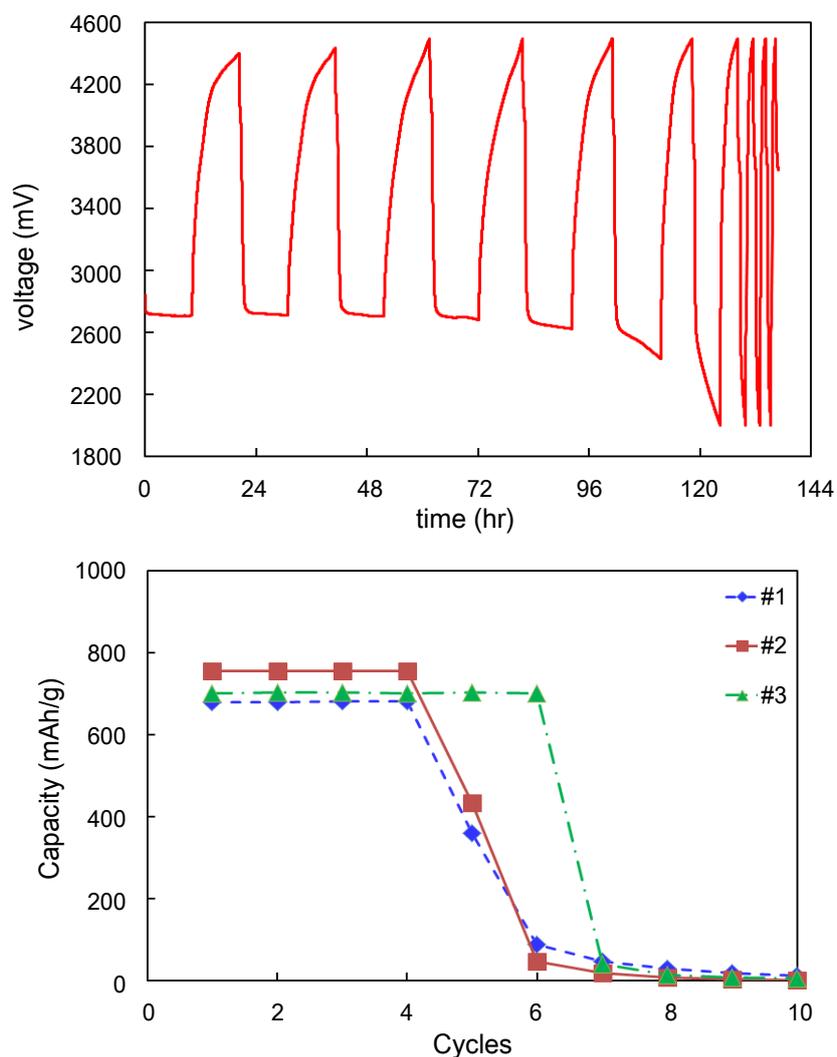


Figure 5: Lithium-oxygen discharge/charge voltage profile (top) and battery capacity during discharge/charge cycles for triplicate samples (bottom), based on nickel foam loaded with BP:MnO₂:HCS (8:1:1) and electrolyte of 1M LiTFSI (tetraglyme). The notations #1, #2, and #3 represent data from the triplicate coin cells at three different dates.

shows the battery capacity at various cycles at these currents. Under a current of 0.1 mA, the battery had electric capacity of about 1800 mAh/g-catalyst, twice of that of 0.05 mA. This is expected because the coin cells were al-

lowed to discharge for the same 10-h period. The battery capacity would be proportional to the current as long as the voltage was within the 2-4.5 V limits. However, the battery capacity under 0.1 mA significantly decreased af-

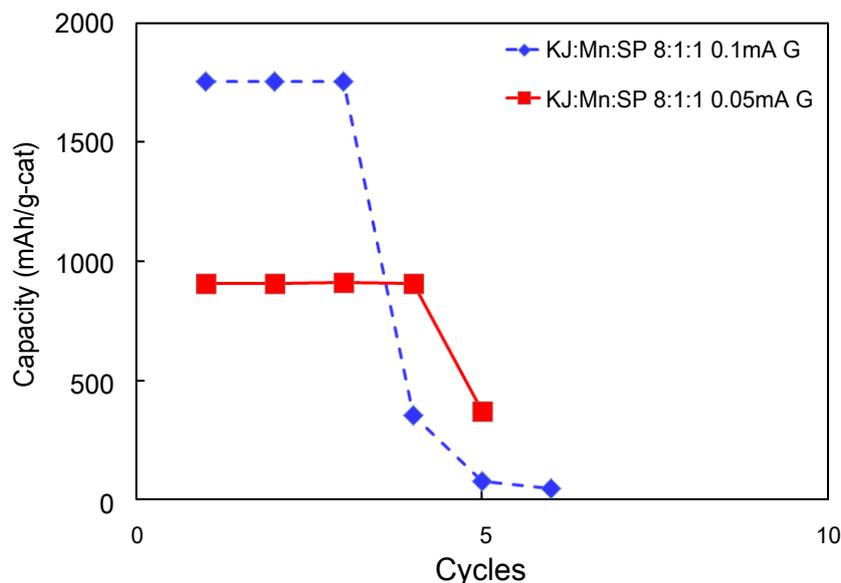


Figure 6: Effect of electrical current on battery capacity at various cycle times using Ni-form based gas electrode and KJ carbon spheres.

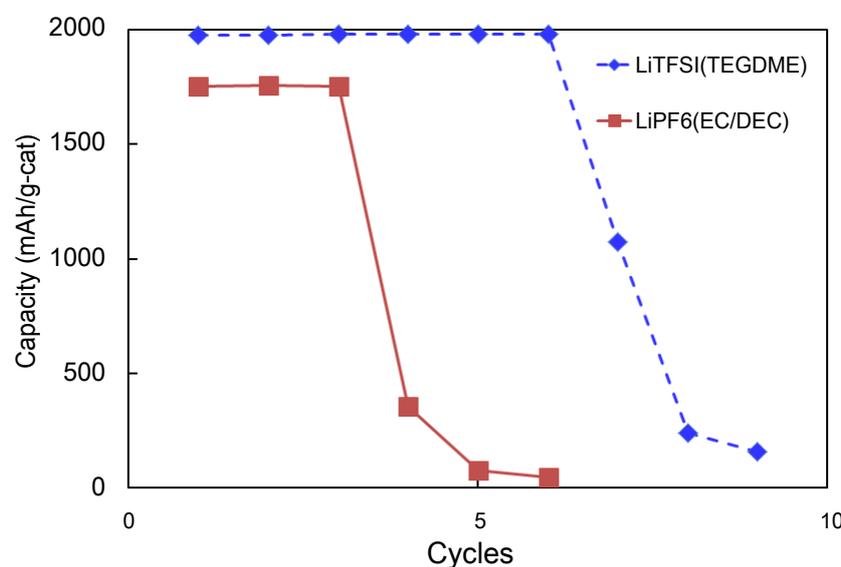


Figure 7: Effect of electrolyte on battery capacity at various cycle times using Ni-form based gas electrode and KJ carbon spheres.

ter the third cycle, and the fourth cycle had electric capacity of less than 100 mAh/g-catalyst. On the other hand, the battery life was longer (4 cycles) at the lower current and the capacity decay was less severe than the higher current. At the current of 0.05 mA, the capacity was 900 mAh/g-catalyst, and decreased to 400 mAh/g-catalyst in the fifth cycle. Using lower current density has two impacts: The battery would be discharged at a higher voltage (near open-circuit voltage) due to less voltage drop of ohmic loss. A lower current may result in smaller oxide deposit at the air electrode than a higher current, thus easier for reversible reaction to occur and to decompose these deposits upon charge. Overall, considering the fast charge/discharge rate requirement and capacity advantage, the 0.1 mA was adopted in the following tests.

Electrolytes effect

Two kinds of electrolytes were tested in this experiment: 1M LiPF₆ (EC/DEC) and 1M LiTFSI (tetraglyme). EC/DEC has higher conductivity than tetraglyme (2.6 vs. 1.5 μS/cm at 25 °C) and lower viscosity (1.4 vs. 4.6 mPa·s at 20 °C). However, the battery with 1M LiTFSI in tetraglyme had a stable cycle life of six cycles (120 h) and a battery capacity of 2000 mAh/g-catalyst, both outperformed those of 1M LiPF₆ in EC/DEC (which had cycle life of three cycles and electric capacity of 1800 mAh/g-catalyst), as shown in Figure 7. The better performance of the tetraglyme solvent than the EC/DEC carbonate solvent is associated with the chemical inertia of the ether groups [5], which is resistant to decomposition

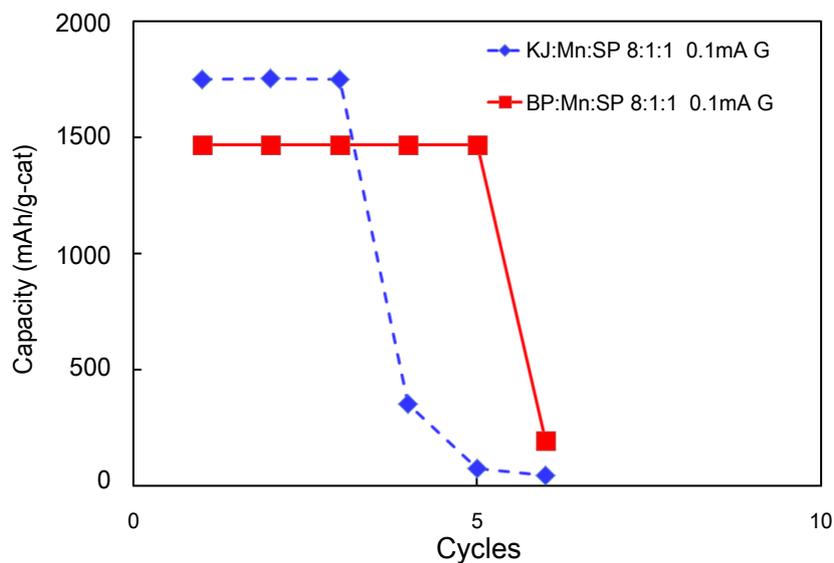


Figure 8: Effect of carbon sphere on battery capacity at various cycle times using Ni-form based gas electrode.

by the oxygen radical anion ($O_2^{\cdot-}$) [6,7] resulted from the oxygen reduction process to the formation of lithium peroxide (Li_2O_2). On the contrary, the carbonate based EC/DEC is prone to decomposition in the Li-oxygen battery [8]. The tetraglyme seems more stable than the conventional carbonate solutions from this study. The tetraglyme stability during long-term operation is currently under investigation. In addition, tetraglyme has a higher boiling point (276 °C) than ethylene carbonate (244 °C) and diethyl carbonate (126 °C). The tetraglyme did not evaporate nor dry out easily during the cycling test. Overall, the 1M LiTFSI (tetraglyme) had a higher capacity and more stable than 1M LiPF₆ (EC/DEC) in the battery test.

Effect of carbon sphere in electrode

Two kinds of carbon spheres (KJ and BP) were both mixed with SP, MnO₂ catalyst, and loaded to nickel foam, and were tested for battery performance. The ash contents, pour densities, surface areas, and particle sizes of these carbon materials are summarized in Table 1. Basically KJ had larger particles than BP, and less ash content.

The KJ-containing battery had a capacity of 1800 mAh/g-catalyst, higher than that of the BP's (1500 mAh/g-catalyst), as shown in Figure 8. However, BP-containing battery could last for five cycles whereas KJ could only sustain for three cycles, indicating that even though KJ has higher electric capacity, BP is more suitable for longer duration usage. The reason is hypothesized that BP has greater surface area than KJ, according to Table 1. Therefore, BP can contain more Li₂O₂, the solid product of batteries with aprotic systems.

Electrode design based on carbon cloth electrode

In order to enhance the contact area of catalysts and provide high porous yet small channel for accommodat-

ing lithium products, carbon cloth was selected as porous support for air electrode. The pore size of the carbon cloth was 25 μm, much smaller than that of nickel foam (150-290 μm). The carbon cloth can be coated with PTFE to serve as a barrier layer to reduce solvent evaporation. There were three configurations of air electrode under this investigation: Only PTFE-coated carbon cloth (type I), catalyst-loaded carbon cloth (type II), and catalyst-loaded, PTFE-coated carbon cloth (type III).

Figure 9 shows the discharge and charge voltage at elapsed times, as well as the corresponding battery capacity values on type II and type III electrodes. These results clearly demonstrate the advantage of incorporation of the PTFE layer: Lower over-potential at charge cycles, longer lifetime (16 vs. 7 cycles). The battery capacities were at 2000 mAh/g-catalyst. The PTFE may prevent solvent from drying (leading to longer cycle life, 300 vs. 150 h) and prohibit excess lithium oxide product formation. The latter is parallel to the lowered charge voltage for the MPL-containing cells in the first half life period (i.e., in the first 50% of the total life time). The PTFE coating (Figure 2) might significantly reduce the lithium ion flux due to its hydrophobic nature. Therefore smaller oxide precipitate size was formed, requiring lower energy to decompose at charge cycle. It is clear that this PTFE-containing cell had a charge voltage less than 4 V in the first 140 h, whereas the counterpart's charge voltage exceeded 4 V after 60 h (Figure 9).

Now that the PTFE was beneficial for improving lithium-air battery performance, we also compared catalyst effect on the PTFE-coated carbon cloth. The data in Figure 10 indicate that without catalyst, the battery needed more time for activation. After additional 10 h, the battery was able to discharge and charge as other batteries. However, the battery life was shorter, only 7-8 cycles,

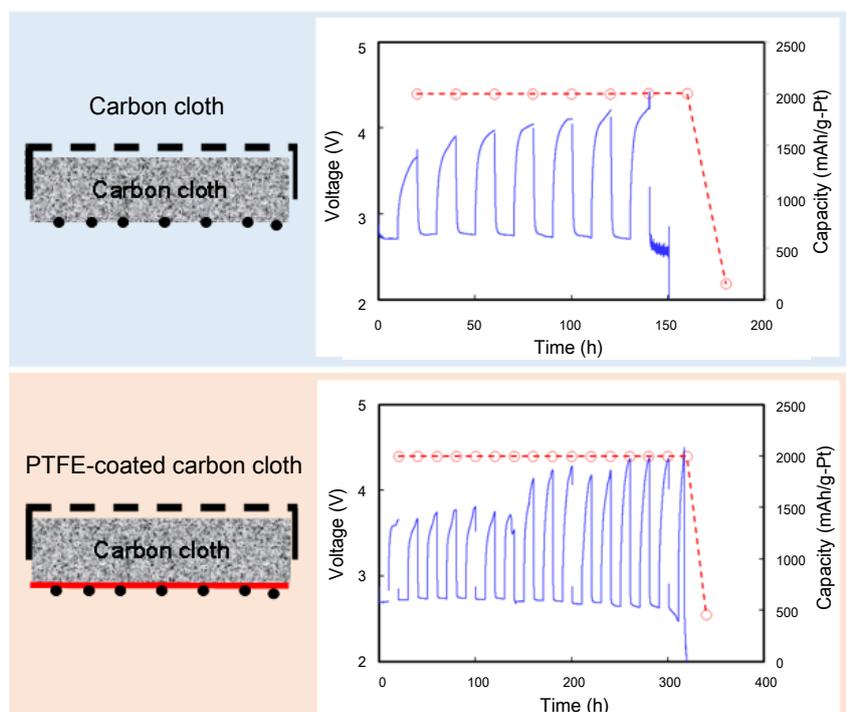


Figure 9: PTFE coating effect on lithium battery cycling performance and capacity values using type II and type III electrodes, with electrolyte of 1M LiTFSI (tetraglyme).

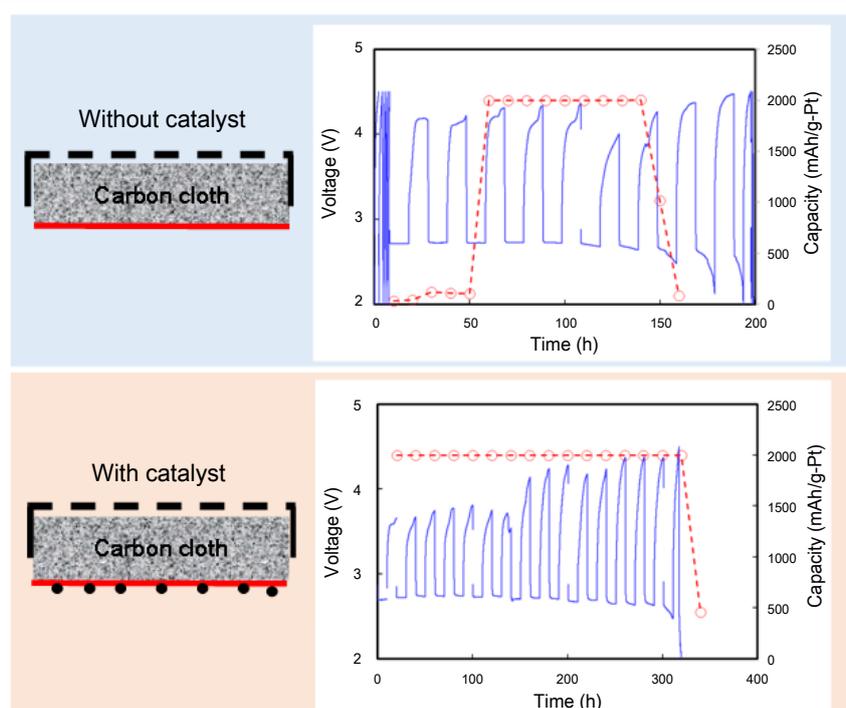


Figure 10: Catalyst effect on lithium battery cycling performance and capacity values using type I and type III electrodes, with electrolyte of 1M LiTFSI (tetraglyme).

due to high discharge and charge over-potentials without catalyst's facilitating oxygen reduction and oxygen evolution reactions [9]. At 9th cycle, the discharge voltage dropped significantly to nearly 2 V. On contrary, the battery with catalyst could operate for longer time (16 cycles, 320 h) at 2000 mAh/g-catalyst. The incorporation of PTFE coating and catalyst greatly improved the battery capacity and cycle life.

The catalyst application on the electrode also reduces the electrical resistance, as shown in the lower charge-transfer impedance (17 vs. 44 Ω , shown in Figure 11) of the catalyst-containing battery. Therefore the power density of this battery was higher (3.7 vs. 3.5 mW/cm²) than that without the catalyst. Based on the battery with type III electrode design (catalyst-loaded, PTFE-coated carbon cloth), the maximum power density was 14.5

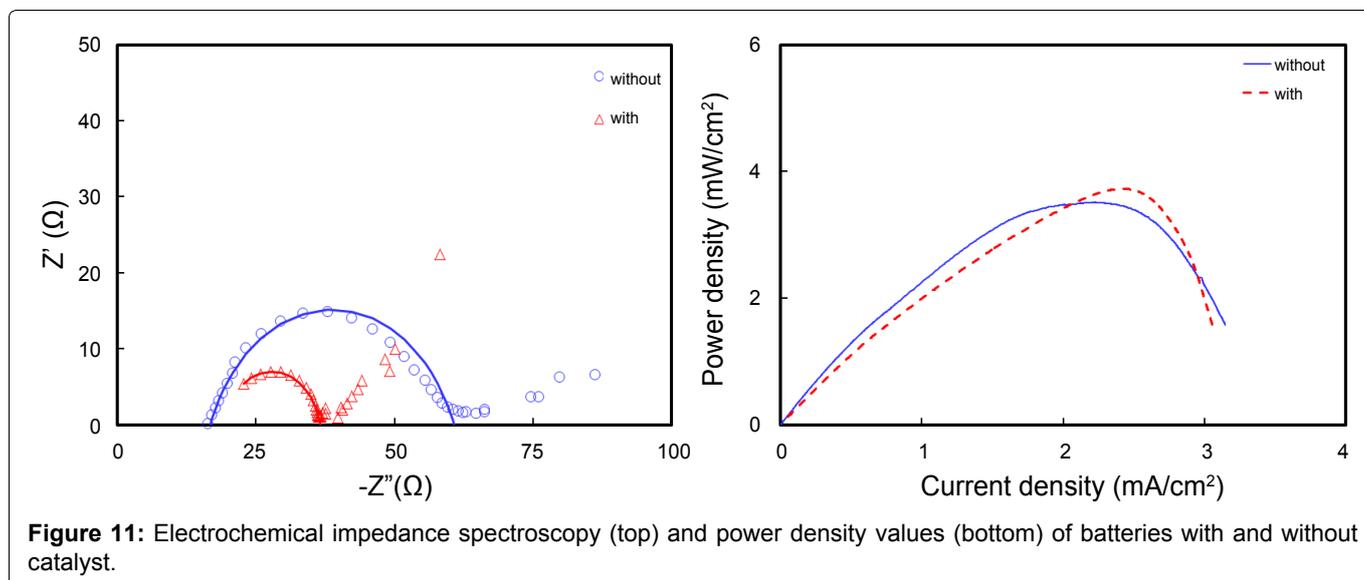


Figure 11: Electrochemical impedance spectroscopy (top) and power density values (bottom) of batteries with and without catalyst.

W/g-catalyst the coulombic efficiency was almost 100% in these cycles and the energy efficiency ranged from 64 to 77%.

Between the nickel foam and carbon cloth electrodes, there was a difference in the choice of binders. The former used PVDF while the later contained Nafion. Cheng and Scott [10] showed that the Nafion binder help catalyst dispersion and the resulting electrode were resistant against catalyst agglomeration. The Nafion also formed robust microstructure, and provided effective three phase reaction zones, which was beneficial for mass transfers during the redox reactions.

Based on the capacity and cycle life data of the coin cells containing air electrodes made of MnO_2 /nickel (shown in Figure 6, Figure 7 and Figure 8) and Pt/carbon cloth (Figure 9 and Figure 10), the cell with carbon cloth loaded with Pt/C provided a longer lifetime (320 vs. 120 h) than that of nickel foam, at comparable capacity (2000 mAh/g-catalyst). The reasons may be due to smaller pore sizes of the carbon materials (to facilitate lithium oxide dissolution upon charge) than that of nickel foam and more effective Pt catalyst than MnO_2 .

Conclusion

In this work, effect of electrolyte composition was evaluated on lithium-oxygen battery using nickel foam electrode. The best electrolyte was LiTFSI (tetraglyme), which resulting in a capacity of 2000 mAh/g-catalyst and six cycles (120 h). The carbon cloth loaded with Pt/C provided a better cathode material than nickel foam: Longer lifetime (320 vs. 120 h) than nickel foam, at comparable capacity (2000 mAh/g-catalyst). The PTFE coating on carbon cloth, high efficient Pt catalyst, and Nafion binder all contribute to the more stable performance and longer lifetime.

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