Optimizing Main Materials for a Lithium-Air Battery of High Cycle Life

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In memory of Luigi Aloisio Galvani and Alessandro Giuseppe Antonio Anastasio Volta, two great originators of the battery. Dedicated to K. M. Abraham and Peter G. Bruce for their outstanding contributions to lithium-air (oxygen) battery on the 30th anniversary of Shenzhen University and on the 3rd anniversary of the establishment of Shenzhen Key Laboratory of New Lithium-Ion Battery and Mesoporous Materials in Shenzhen, China

By optimizing the main materials in lithium-air batteries, namely sulfolane as electrolyte solvent, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as electrolyte salt, carbon paper as current collector, and Li_2O_2–C hybrids as positive electrode materials, a performance of 800 cycles with a specific capacity of 1000 mAh g^{-1} (based on the total mass of positive electrode materials) and an average energy efficiency of 74.72% has been achieved in this work and for the first time reported in the field of lithium-air battery. Sulfolane-based electrolyte and carbon paper current collector play the most critical role in building such a lithium-air battery of high cycle life. The findings described here are expected to benefit the pursuit of green, sustainable, and high-performance lithium-air batteries.

1. Introduction

Building better batteries contributes to a sustainable energy future as these devices can power an increasingly diverse range of applications (from vehicles to electronics) and store sustainable energy such as wind and solar power.[1,2] Among the "better batteries", lithium-air battery has captured exceptional scientific interest in recent years because of its extremely high specific energy, which is 8 or 28× (including or excluding the oxygen mass) higher than that of today's lithium-ion battery and is crucial for the applications in electric vehicles and energy storage.[3–7] However, progress in utilizing lithium-air batteries is largely hampered due to the fact that they typically display an insufficient cycle life of 100 cycles or so.[8–13] According to the Battery 500 Project by IBM,[5] an electric vehicle battery designed for a general lifetime of ≈300 000 miles and supporting a target range of 500 mile per charge should have a cycle life of at least 600 cycles. Here we describe the rational design and fabrication of a lithium-air battery with substantially long cycle life. We show that, through optimizing the battery formula including solvents, salts, current collector and positive electrode materials, the batteries exhibit high cycle life, namely 800 cycles with a specific capacity of 1000 mAh g^{-1} (based on the mass of whole positive electrode materials) and an average energy efficiency of 74.72%.

A lithium-air battery makes use of a metal-air battery chemistry that involves the oxidation of lithium at the negative electrode and reduction of oxygen at the positive electrode to produce current during discharge (redox reaction is reversible during charge). In contrast to conventional lithium-ion batteries that store an oxidizer internally, lithium-air batteries absorb oxygen from surrounding atmosphere during its discharge and thereby are more compact and light. Typically, the theoretical energy density of lithium-air batteries can reach an extremely high value of 11 140 Wh kg^{-1} excluding the oxygen mass,[3] which far surpasses that of most other types of batteries and is comparable to that of traditional gasoline powered engines.[5] The main parts of a battery are positive electrode, electrolyte and negative electrode. As for lithium-air batteries, the negative electrode is lithium metal and the active material of positive electrode is oxygen during discharge, both of the two electrodes are fixed in terms of active materials. Therefore, the next and critical problem that we have to solve most urgently is electrolyte. Meanwhile, current collector and cathode materials should also be carefully designed and optimized. In consideration of the above critical problems and principles, we constructed a lithium-air battery that contained an electrolyte composed of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in sulfolane and a lithium peroxide/carbon (Li_2O_2–C) cathode based on a carbon paper current collector.

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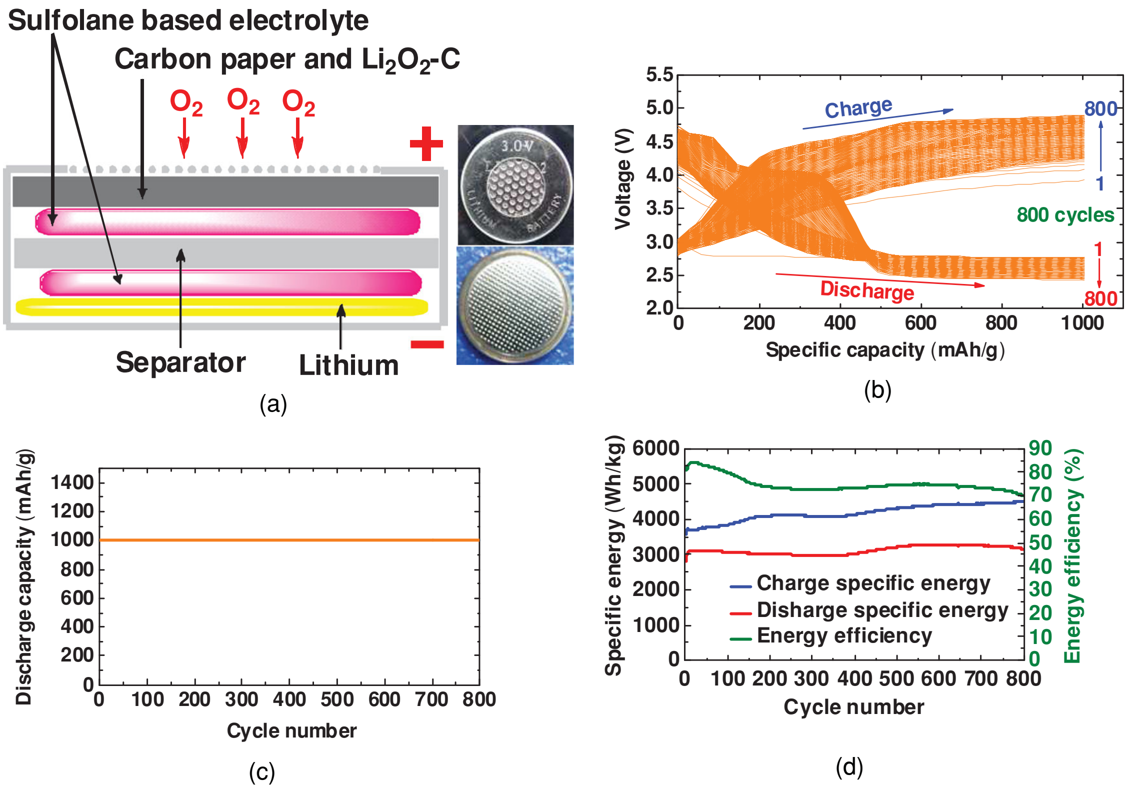

Figure 1. a) Schematic and cycle performance of a lithium-air battery using a LiTFSI-sulfolane electrolyte. b) Specific capacity–voltage. c) Specific capacity-cycle number. d) Specific energy and efficiency-cycle number. The battery was tested at 0.5 A m^{-2}. The composition of the carbon cathode is Ketjen black (KB) carbon: Li_2O_2: teflon polytetrafluoroethylene (PTFE) = 7.2: 1.8: 1 (m/m). It shows that the battery can perform 800 cycles between 2.44 V and 4.90 V while remains a relatively high average energy efficiency of 74.72%.

2. Results and Discussion

The battery ran 600 cycles between 2.54 V and 4.81 V while remained a relatively high average energy efficiency of 75.32% and can perform 800 cycles or more with a specific capacity of 1000 mAh g^{-1} based on the total mass of cathode material (**Figure 1**). We managed to make it through a series of designs and experiments including electrolyte (solvent and salt), current collector and positive electrode materials.

First, through summarizing the arduous exploration of electrolyte in the area of lithium-air battery and based on the electrochemical properties of different electrolyte solvents, we analyzed the suitability of sulfones in lithium-air battery previously.[14] Sulfolane (tetramethylene sulfone) was proved experimentally to be a suitable electrolyte solvent for lithium-air battery.[15–17] The physicochemical properties and structure of sulfolane (Table S1 and Figure S1, Supporting Information) can explain its suitability in lithium-air battery. Its relative permittivity (ε_υ) is 43.4 at 30 °C and close to that of propylene carbonate (PC).[18,19] The molecular structure of sulfolane combines the most-used electrolyte solvents in lithium-ion battery (Figure S1, Supporting Information), namely it has the five-membered ring structure of cyclic carbonates (ethylene carbonate and propylene carbonate) and the chalcogen function group of both cyclic carbonates and straight-chain carbonates (diethyl carbonate, dimethyl carbonate, and ethyl methyl carbonate).[16] Sulfolane's physical and electrochemical properties, coupled with its unique structure, make it possibly be used in lithium based batteries.

Second, to choose a suitable electrolyte salt, we tested the cycle performance of lithium-air batteries that consisted of the identical Ketjen black (KB) carbon cathodes. Each battery contained a sulfolane based electrolyte (Figure S2–S4, Supporting Information) that comprised one of the four different salts respectively, namely LiTFSI, lithium hexafluorophosphate ($LiPF_6$), lithium bis(oxalate)borate (LiBOB), and lithium tetrafluoroborate ($LiBF_4$). The results show that, among the four salts, LiTFSI is the most suitable salt for sulfolane based lithium-air batteries in terms of cycle performance including specific capacity, specific energy, energy efficiency, and discharge/charge voltage.

Besides electrolyte, the equally important task is to design efficient positive electrode. Current collector of the positive electrode plays a vital role in the cycle performance of lithium-air battery since it supports the cathode materials and provides a venue for the discharge–charge reactions. In our experiments, we found that carbon paper is more suitable than nickel foam in terms of the cycle performance of the batteries (Figure S5, Supporting Information), so we used carbon paper as current collector in this work.

In addition, discharge product should be fully considered when designing a positive electrode. Li_2O_2 is believed to be the main discharge product during discharge process in lithium-air battery.[3–9,12–15] Meanwhile, Li_2O_2, as a positive electrode material in lithium-air battery, is activated by initially charging the peroxide to oxygen and lithium metal.[20,21] The Li_2O_2 formed on discharging would disappear (be fully charged) after a sufficient charge to decompose all the Li_2O_2 directly and electrochemically according to the reaction $Li_2O_2 \rightarrow O_2 + 2Li^+ + 2e^-$.[20–22] Crystallization of Li_2O_2 (≈700 nm toroids) according to the electrochemical reduction of O_2 is affected by its rate of nucleation/precipitation from LiO_2, low solubility, and interaction with the carbon electrode surface.[23,24] If the formation of Li_2O_2 can be controlled, the charge voltage will be relatively low and side reactions will be suppressed because other oxygen-containing discharge products can only be oxidized at high potential with the parallel formation of CO_2.[25,26] However, sufficient charging of Li_2O_2 and the formation of Li_2O_2 would be limited by the electron transport in Li_2O_2.[27] Li_2O_2 is the discharge product and active material in lithium-air battery, just like $LiFePO_4$ (lithium iron phosphate) in lithium-ion battery, but the electronic conductivity of Li_2O_2 is much lower than that of $LiFePO_4$.[28] The bulk ionic conductivity of Li_2O_2 (10^{-10}–10^{-9} S cm^{-1} at 100 °C) is in the same range as σ_{ion} of $LiFePO_4$ (10^{-11}–10^{-10} S cm^{-1} at 100 °C), but the electronic conductivity of Li_2O_2 (10^{-12}–10^{-11} S cm^{-1} at 100 °C) is much lower than that of $LiFePO_4$ ($2 \cdot 10^{-7}$–$4 \cdot 10^{-6}$ S cm^{-1} at 100 °C).[28] Obviously, the electronic conductivity of $LiFePO_4$ is relatively enough to support electron transfer among electrode materials during discharge and charge processes in lithium-ion batteries, but the electronic conductivity of Li_2O_2 is so low that it can not effectively sustain electron transfer among electrode materials during discharge and charge processes in lithium-air batteries.

Therefore, to optimize the positive electrode and in consideration of the properties and the formation/decomposition of discharge product, we have investigated Li_2O_2–C hybrids (as positive electrode materials) of different proportions (0%, 20%, 40%, 60%, 80% and 100% respectively based on the mass of lithium peroxide accounting for the total mass of lithium peroxide and carbon) systematically in lithium-air battery for the first time. For the different Li_2O_2–C hybrids of the six proportions, the battery with the Li_2O_2–C hybrids of 20% exhibits the highest energy efficiency (Figure S6, Supporting Information).

According to the above designs and experiments including electrolyte (solvent and salt), current collector and positive electrode materials, our battery exhibits satisfactory performance. The schematic and cycle performance of the battery are illustrated in Figure 1.

The average open circuit potential of our batteries with Li_2O_2–C hybrids is 3.0 V. Based on this voltage, the theoretical energy density is 11 655 Wh kg^{-1} excluding the oxygen mass. **Figure 2**a shows that the batteries used Li_2O_2–C hybrids of the four Li_2O_2 proportions (0%, 20%, 40%, and 60%) have lower impedance than that with too much Li_2O_2 (80% or 100%). However, each Ohmic resistance of the batteries with Li_2O_2–C hybrids is below 105 Ω cm^2, which is much lower than that in the previous reports,[10] benefiting the battery's performance. The kinetics of the oxygen electrochemical process in the lithium-air battery was investigated further using cyclic voltammetry (CV). Figure 2b presents the CV response of the cell at a constant scan rate of 0.1 mV s^{-1}. The curves reveal that the potentials of the cathodic and anodic peaks well match the voltage change obtained by cycle performance test (Figure S6b, Supporting Information). The CV result shows that the voltage gap between charge and discharge is relatively large, which limits the improvement of energy efficiency.

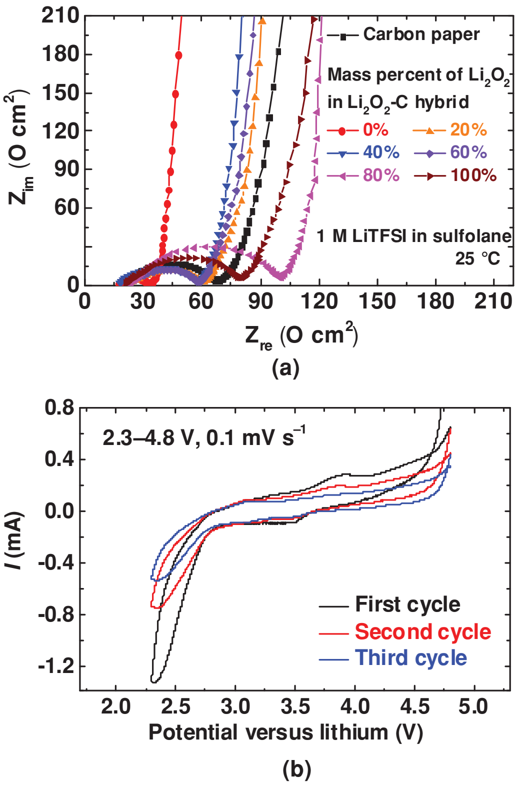

Figure 2. A.C. impedance and CV curves. a) A.C. impedance of a carbon paper based lithium-air battery without coating materials and six lithium-air batteries with Li_2O_2–C hybrids of different mass percent of Li_2O_2 as coating materials. b) CV of the KB carbon based oxygen electrode in a lithium-air battery using a sulfolane-LiTFSI electrolyte. CV result was obtained at a constant scan rate of 0.1 mV s^{-1}.

We used X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) to further confirm the reversibility of the electrochemical process in KB based electrodes which contained sulfolane-LiTFSI electrolyte without adding Li_2O_2. **Figure 3** shows that the discharge product is granular. The superficial layers of separator and positive electrode were linked together during testing, so the discharge product attaches to the separator. As can be seen from Figure 3, the electrode was tested to emerge at least 8 characteristic diffraction peaks of Li_2O_2 (PDF-74–115), demonstrating that Li_2O_2 was produced during discharge. Table S2 (Supporting Information) also shows that the percentage of the oxygen content decreased after charging. The decreases in weight percentage and atomic percent of oxygen atom should be attributed to the electrochemical decomposition of discharge product (Li_2O_2), namely the oxygen evolution reaction during charge.

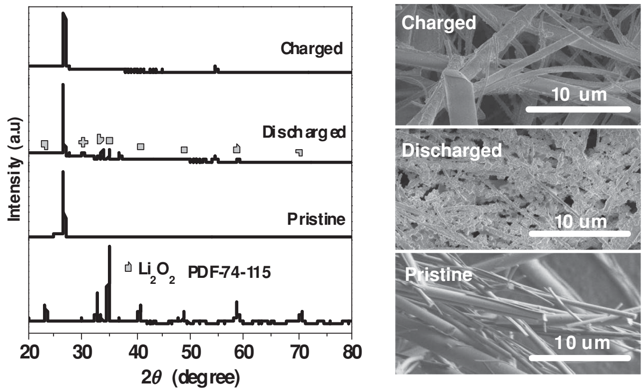

Figure 3. XRD profiles and FE-SEM images of charged, discharged, and pristine electrodes of a lithium-air battery using a sulfolane-LiTFSI electrolyte. The battery is introduced in Figure 2, which contained a sulfolane-LiTFSI electrolyte and a KB based electrode without adding Li_2O_2.

3. Conclusion

From a fundamental perspective, our discovery addresses a key problem of cycle life that dictated the practical application of lithium-air battery, which is mainly benefited from the key designs, namely sulfolane as electrolyte solvent, LiTFSI as electrolyte salt, carbon paper as current collector, and Li_2O_2–C hybrids as positive electrode materials. Although the cycle performance of our constructed lithium-air batteries is very appealing, this lithium-air battery system is not a final solution but should be optimized in terms of discharge/charge rate. From a forward-looking perspective, as we show here that the seriously insufficient cycle life (the biggest obstacle) can be changed and improved to a desired level, optimization of the lithium-air battery system by the peers in this area will make the particularly exciting "next-generation battery" move forward.

4. Experimental Section

Instruments and Materials: Agate mortar, precision disc cutter, compact tape casting film coater with dryer, electric precision 4" width rolling press with dual micrometer, argon-filled glove box and argon tank, lithium tablets, electrolytes, Li_2O_2 powder (purchased from Acros, 95% in purity), carbon powder, battery separator, carbon paper, respirator, gloves, calcium oxide, silica gel, sample sack, electronic balance, weighing disk, beaker, corning stirring hot plate, drying oven, alcohol swab, tweezer, hair drier, micropipette, button battery box set, compact hydraulic crimping machine, disassembling machine, temperature and humidity recorder, electrochemical workstation, dual electrical measuring four-probe tester, battery tester, battery testing box, X-ray diffractometer, and scanning electron microscope. Electrolytes are 1 mol L^{-1} (M) LiTFSI, $LiPF_6$, LiBOB, or $LiBF_4$ in sulfolane respectively. Both the contents of deionized water and dissociation acid in electrolyte were controlled to less than 20 ppm. The salts and solvent used in the electrolyte were all battery-grade materials purchased from Shenzhen Capchem Technology Co.Ltd.

Positive Electrode Preparation: Ketjen black (KB) carbon EC600JD (Akzo Nobel Corp, BET surface area of 1400 m^2 g^{-1}, primary particle size of 34 nm) was selected as the conductive additive and was mixed with Li_2O_2 to obtain Li_2O_2–C hybrids. KB carbon was dried at 80 °C for 3 h and with a certain amount (different proportions based on the mass of Li_2O_2 accounting for the total mass Li_2O_2 and KB carbon) of Li_2O_2 powder pestled in a pestle and mortar to make coating materials. Then the obtained Li_2O_2–C mixture was added into normal methylpyrrolidinone (NMP) to be heated and stirred by a corning stirring hot plate. Teflon polytetrafluoroethylene (PTFE) was dropwise added according to need during the heating and stirring to obtain slurry. The slurry was cast onto carbon paper to make positive electrode sheet. Then the sheet was heated at 85 °C for 3 h to remove solvent NMP. Thus, Li_2O_2–C hybrids were finally made and coated on the carbon paper successfully to obtain positive electrode. Electric precision 4" width rolling press with dual micrometer (purchased from MTI Shenzhen Corp.) was used to planish carbon electrode sheet. The thickness of the positive electrode is ≈220 μm. Li_2O_2 is sensitive to water and vapor invasion is harmful to the performance of Li-air battery, the preparation of positive electrodes should be conducted under the circumstance which is as dry as possible to avoid vapor invasion. For example, preparing the positive electrodes when the weather is good and trying to select dry environment for preparation would be corking choices.

Battery Assembly and Testing: Li-air batteries were constructed in an argon-filled glove box (MBraun) in which the oxygen and moisture concentrations were both less than 5 ppm. Type 2032 coin cell kits (purchased from MTI Shenzhen Corp.) with a diameter of 20 mm and a thickness of 3.2 mm were used to assemble these batteries. The positive pan of each coin cell is scattered by 40 apertures with a diameter of 1 mm, these holes can allow oxygen to pass through. A lithium disk (15 mm in diameter and 1 mm thick) was used as the anode. To absorb more electrolyte a Whatman GF/D glass microfiber filter paper (19 mm in diameter) was chosen as the separator. The coin cells were stored in the argon-filled glove box for about 3 h prior to the electrochemical tests. Discharge and charge performance testing was carried out under dry atmospheric circumstance (dried by silica gel and calcium oxide, 25 °C controlled by air-conditioner) using a LAND CT2001A battery tester (Wuhan Jinnuo Electronics Co. Ltd.). The cells were cycled with a preset discharge/charge of 1000 mAh g^{-1} based on the total mass of positive electrode materials. A.C. impedance and CV curves were carried out by a CHI660D electrochemical workstation (Shanghai Chenhua Device Company).

Instrumentation: An energy dispersive X-ray spectrometer (EDX) equipped in a scanning electron microscope (SEM) (Hitachi S-3400N II) was used for identifying the elements in the composite sample of positive electrode. Observations with plane and cross-sectional views of the electrodes were made using a field-emission scanning electronic microscopy (FE-SEM, Hitachi SU-70) at 2 kV and 1 kV. X-ray diffraction (XRD, D8 Advance, Bruker) was utilized to analyze the discharge products in positive electrode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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