



A novel air electrode design: A key to high rate capability and long life span



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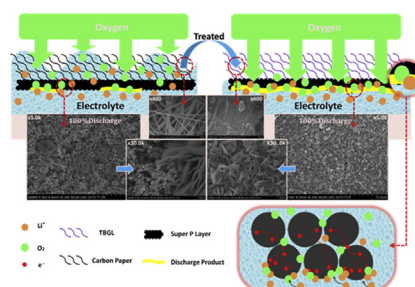
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HIGHLIGHTS

- A novel TBGL was designed on the basis of the nature of electrolyte.
- The oxygen concentration along the thickness of the air electrode was calculated.
- Electrochemical reaction mechanisms for the DMSO-based electrolyte were investigated.
- We demonstrated a long-life Li-O₂ battery with high power and energy densities.
- A brand new view was opened up to greatly boost the electrochemical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

As an appealing storage system for electric vehicle application, the lithium-oxygen battery could theoretically provide ultrahigh energy density; however, its attractive implementation is overshadowed by unsatisfactory electrochemical characteristics of the poor rate capability and the short span life. Here, we put forward one kind of effective strategy to ameliorate these deficiencies. By embedding a novel air electrode, the utilization level of the electrochemically available active sites is effectively increased and meanwhile the mass transfer of oxygen is signally improved. The evaporation speed of the solvent is greatly slowed down to some degree. We demonstrate that a super P-based lithium-O₂ battery could be operated over stable 50 cycles at the current density of 3000 mA g_{Carbon}⁻¹ (equivalent to 2.4 mA cm⁻²), corresponding to a discharge time of about 20 min to 1000 mAh g_{Carbon}⁻¹. Based on the weight of the super P and the resultant Li₂O₂, the specific power density could reach 4040 W kg⁻¹; even so, a substantial specific energy density of 1350 Wh kg⁻¹ still could be achieved.

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1. Introduction

In the past decades, the vast majority of the research work has been performed to upgrade the energy and power densities of the conventional lithium-ion battery; however, it is still far less able to satisfy the increasing stringent demands for electrification transportation and super energy storage system. Based upon the overwhelming storage superiority, a rechargeable lithium-oxygen

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battery has stirred a revived interest and attention [1–5]. But so far now, the discharge specific capacity and the cycling stability achieved come in well short of expectation. In the face of its practical applications in the future, there are formidable challenges to be overcome, for example, the reactivity of aprotic electrolyte towards superoxide anion free radical (O_2^-) or oxygen [6,7], the poor rate capability, the short calendar life [1,8–10] and the low round-trip efficiency. Most recently, strategies targeted to develop a truly rechargeable Li-O₂ battery with outstanding rate capability and long cycle life have mainly been focused on exploration of the electrolyte formula, design of the air electrode and optimization of the operating parameters [1,2,11–15].

Pioneer work has suggested that the reversibility of the lithium-oxygen battery and the nature of the reduction deposits largely depend on the electrolyte formula, especially the composition of solvent [16]. The electrochemical performances are chiefly determined by the oxygen solubility in electrolyte and the oxygen diffusion velocity through the whole air electrode, especially at high current densities [15]. It is clear that for the high-performance, rechargeable lithium-oxygen batteries, screening for solvent is quite demanding. Consequently, the exploitation of the solvent available for the truly rechargeable nonaqueous Li-O₂ battery is always an elusive puzzle. The powerful nucleophilicity of superoxide (O_2^-), which is a primary intermediate in the Li-O₂ battery, or/and the superoxide-mediated oxidation of the hydroperoxides derived in the aprotic solvent are regarded as the first thing to be addressed [6,7,11,12]. Organic carbonates and esters could be easily decomposed at O-alkyl or carbonyl carbon via a nucleophilic attack from the superoxide anion radical (O_2^-). Most of ether- and amide-based electrolytes, which were once believed to be the stable candidates, were prone to autoxidation under oxygen atmosphere. Furthermore, ethers did not support the reversible formation/decomposition of the desired Li₂O₂ and their stabilities were gradually deteriorated upon cycling [11,16]. This or that deficiency

has severely undermined the boost of the electrochemical performance of Li-O₂ battery. Recently, an aprotic dimethyl sulfoxide (DMSO) was much concerned and considered as a promising solvent for Li-O₂ cell, owing to its satisfactory stability against the superoxide radical [17]. However, the relatively lower oxygen solubility and the comparatively higher viscosity are at a disadvantage from the perspective of the electrochemical kinetics. Therefore, it becomes more meaningful to take effective measures to make up its deficiencies.

As another crucial component, a typical porous air electrode mainly consists of a collector (metal grid, metal foam, carbon paper and etc.) and a porous electrode material layer with or without catalyst, as illustrated in Fig. 1. As a vital arena, where Li-O₂ heterogeneous reactions happen and the discharge products are hosted, the porosity and tortuosity of the air electrode will have a significant impact on the electrochemical characteristics of Li-O₂ batteries [2,3,18,19]. Thus, the choice and microstructure design of the air electrode materials come into a paramount important issue. Until now, various carbonaceous materials [8,18–23] (for example, super P, carbon nanofiber, graphene, ketjen black), conductive polymer (polypyrrole [24]) and precious metal (Au [8]) have been investigated as electrode materials aiming to realize the higher discharge capacity and rate capability. In some cases, the transition metal oxide and metal (or alloy) catalysts [16,23,25–31] (Pt, Au, MnO₂ and MnCo₂O₄) were exploited to improve the electrochemical properties. The round-trip hysteresis was greatly reduced, however the undesired decompositions/side reactions were often promoted simultaneously [32,33]. Admittedly, the performance level of Li-O₂ cell has gotten a great promotion via quantitatively increasing the solid–liquid interfaces and the storage volumes, provided by the vesicular structure of the air electrode materials themselves or/and the air electrode itself [19]. Unfortunately, these underlying active sites seems not be fully utilized because of the inaccessibility of oxygen.

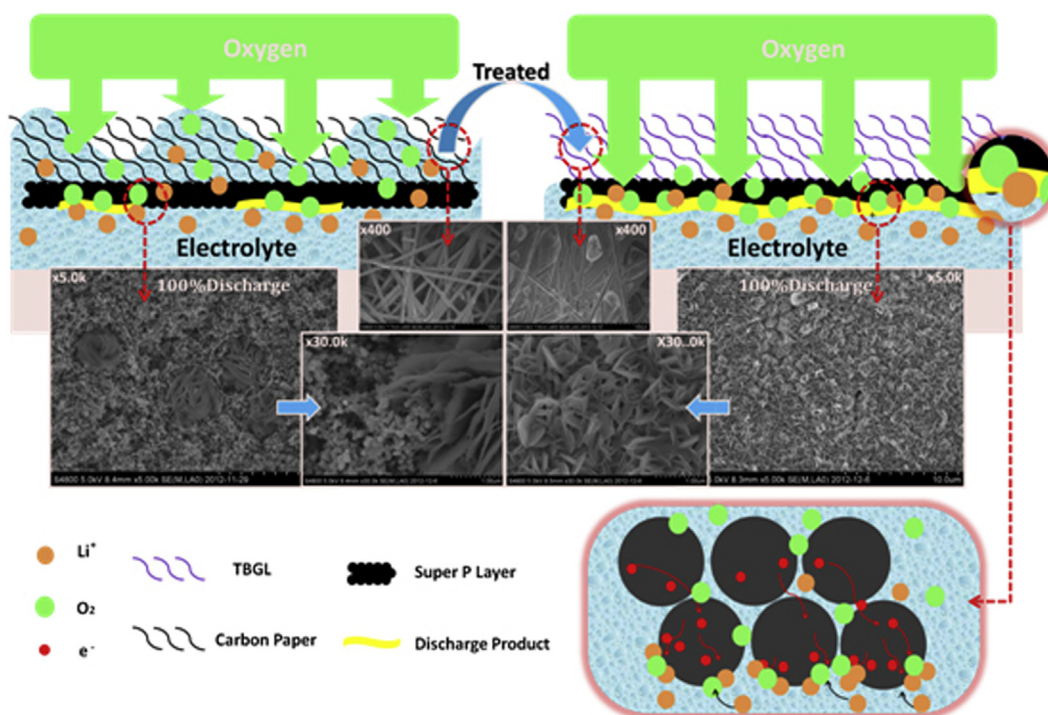


Fig. 1. Schematic diagram of the air electrode configuration. The conventional flooded air electrode on the left and our novel one on the right. Inset: FESEM images for carbon paper and TBGL; and surface morphologies for these two kinds of air electrodes after full discharge.

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