



A dual pore carbon aerogel based air cathode for a highly rechargeable lithium-air battery



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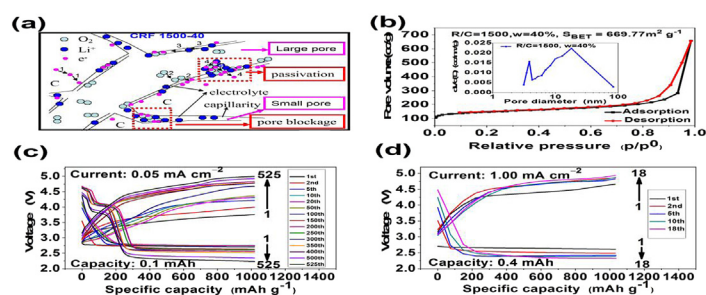
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HIGHLIGHTS

- Carbon aerogel's dual-pore enables mass transport in two separate channels.
- Low carbon loading cathode is favorable for lithium-air batteries' reversibility.
- A current density between 0.10 and 0.20 mA cm⁻² contributes to better cyclability.

GRAPHICAL ABSTRACT



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ABSTRACT

Cathode structure plays a vital role in lithium-air battery for that it can provide space for discharged products accommodation and free path for oxygen, e⁻ and Li⁺ transport. However, pore blockage, cathode passivation and degradation all result in low discharge rates and poor cycling capability. To get rid of these predicaments, a novel highly conductive dual pore carbon aerogel based air cathode is fabricated to construct a lithium-air battery, which exhibits 18 to 525 cycles in the LiTFSI/sulfolane electrolyte at a current density varying from 1.00 mA cm⁻² to 0.05 mA cm⁻², accompanied by a high energy efficiency of 78.32%. We postulate that the essence lies in that the as-prepared air cathode inventively create a suitable tri-phase boundary reaction zone, facilitating oxygen and Li⁺ diffusion in two independent pore channels, thus realizing a relative higher discharge rate capability, lower pore blockage and cathode passivation. Further, pore structure, carbon loading, rate capability, discharge depth and the air's effect are exploited and coordinated, targeting for a high power and reversible lithium-air battery. Such nano-porous carbon aerogel air cathode of novel dual pore structure and material design is expected to be an attractive alternative for lithium-air batteries and other lithium based batteries.

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1. Introduction

Lithium-air battery, with a high energy density of 1000 Wh kg⁻¹ which is 2–4 times higher than that of current state-of-art lithium-ion battery, has attracted unprecedentedly broad attention and is destined to be further developed to address series of problems,

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such as the finite oil resources, deteriorated climate and high fuel prices, and to meet the demand of long distance transport's energy storage in electric vehicle industry [1–3]. A typical non-aqueous rechargeable lithium-air battery involves reversible formation/decomposition of Li_2O_2 via multiple discharge-charge cycles. However, despite such unmatched potential superiority, pore blockage, cathode passivation and degradation all result in low discharge rates and poor cycling stability (about 100 cycles), restricting its practical utilization [2–15].

To build a reversible and long-life span lithium-air battery, cathode design is an indispensable task as well as challenge. Since cathode has function of accommodating discharge products and providing free path for oxygen, e^- and Li^+ transport, the porous structure is a prerequisite and highlighted. What's more, requirements like high conductivity, low cost and ease of fabrication all render carbon one of the most attractive materials for constructing a porous (three-dimensional) electrode. In order to achieve an optimum performance, various carbon sources (with surface defects and functional groups, hydrophobicity/hydrophilicity and oxygen adsorption of the carbon surface et al.), specific surface area, pore volume, pore size distribution and mass density must be all considered and synergistic, at last to get a compromise. Though lots of efforts have been spared in optimizing the cathode structure, pore blockage, cathode passivation and degradation are still encountered [16–26].

Inspired by Zhang et al. [23,27,28], a novel highly conductive nano-porous carbon aerogel comprising of fine dual pore structure was successfully fabricated here to improve the mass transport and to reduce pore blockage and cathode passivation. For such type battery, we postulate that the large pore is apt to facilitate oxygen penetration, and simultaneously yield and store discharged products at its abundant catalytically active carbon surface; while the small pore with little or non-catalytic active center will be filled with highly conductive Li^+ electrolyte due to the coalition of hydrophilic carbon surface and capillary pressure, conducive to Li^+ transfer. By this new approach of cathodes designing, high oxygen-transport properties and degenerative pore blockage will be realized, favorable for the high discharge rate performance and cyclability. Free charges (e^-) will mainly transfer to tri-phase boundary reaction zones where accumulates higher oxygen concentration, through carbon aerogel's highly conductive interconnected 3D network. Meanwhile, electro-active material's high specific surface area can provide more reaction sites for electrochemical reaction and its large pore volume renders large space for discharged products accommodation. Li-oxide precipitation will be eventually filled in the pores which house a catalytic active junction (with an enormous amount of both O_2 and Li^+ , complementary subsystems) [24,25].

1 M LiTFSI/sulfolane was chosen as electrolyte for its relative stability which was previously testified by Zhang and our group et al. [29–36]. For this newly built battery system, when controlling the specific capacity of 1000 mAh g^{-1} , 525 cycles and 112 cycles were obtained at a current density of 0.05 mA cm^{-2} and 0.10 mA cm^{-2} , respectively, which far exceeds that of the previous researches that identically adopted carbon aerogel as air electrode active materials [37–43]. Such impressive cycling behavior can be attributed to the distinctive battery structure which includes both the well modified cathode structure and relatively stable electrolyte, certainly in addition to an oxygen filled environment and the effective control of discharge rates and depth. As compared to common used carbonate, ester, dimethylformamide and ether-based electrolyte [44–49], sulfolane-based electrolyte could endure high overpotential during charge process and thus shows superior antioxidant ability which is bound to obtain a relatively stable $\text{Li}-\text{O}_2$ battery. Following the carefully controlling of the

discharge rates and depth, granular to sheet-shaped or layered lithium peroxides (unlike bulk precipitates) which could undermine the cathode passivation formed during discharge process, and had already been proved to be metallic in certain lattice surface [50–55].

2. Experimental

2.1. Preparation of carbon aerogel and cathode, and cell assembling/disassembling

Carbon aerogel was taken as the cathode active materials here due to its light density, high specific surface area, good conductivity as well as its wide scale of pore size distribution. It was synthesized according to a resorcinol-formaldehyde (R-F) polycondensation and carbonization method previously reported by Richard W. Pekala [37]. After successful preparation, it was mixed with pVdF powder in a molar ratio of 9:1 and stirred in an NMP containing bottle to make appropriate viscous slurry, which was soon deposited on carbon paper to make various air cathodes, where the aerogel coating was applied as a layer on one side of the carbon paper. Here, cathodes with different carbon loading ranging from 0.1 mg to 0.6 mg were obtained. The aerogel loading also can be shown in the unit of mg cm^{-2} , which was in the range of 0.057 mg cm^{-2} to 0.340 mg cm^{-2} . Hereafter, with a whatman GF/D glassy fiber separator and 1 M LiTFSI/sulfolane electrolyte, the lithium-air batteries were assembled in a glove box with moisture and oxygen concentration lower than 0.5 ppm. The schematic diagram of the lithium-air battery model (CR2032) can be seen in Fig. S1. Then the cells were aged for 12 h in an inert atmosphere and exposed to oxygen for more than 30 min prior to electrochemical test. The boundaries were chosen according to both the literature and our previous experimental (see details in the Supporting Information). Intermittently, the batteries of different discharge or charge state were disassembled in the glove box. After DME solution soaking and vacuum drying for another 12 h, the cathode was sealed quickly in a gas-tight device for the subsequent XRD and SEM test.

2.2. Materials characterization and electro-chemical measurements

SEM and TEM tests were exploited to analyze the morphology of the synthesized RF aerogel and carbon aerogel, as well as the discharged/charged products. The TG-DTA test was used to evaluate the RF aerogel's thermal stability and ensure the degassing temperature for the following N_2 absorption/desorption test which aimed at studying the specific surface area, the BJH pore size distribution and pore volume. Here, XRD test was adopted to inquire the discharged and charged products composition and investigate the mechanism of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in lithium-air batteries. The standard electrical four-probe method was utilized to check the cathode and carbon aerogel's electrical conductivity.

With regard to electrochemical measurement, galvanostatic charge/discharge test, CV test and electrochemical impedance analysis were all performed to examine the cycling stability and cycling life, the dynamic process of the inner electrochemical reaction and mechanism, respectively. All the cycling numbers were recorded under the cut off voltage of 5.0 V for charge or above 2.0 V for discharge with fixed specific capacities or capacities. The discharge time is controlled to be 2.3 h simultaneously when the current density surpasses 0.10 mA cm^{-2} , which aims at obtaining a practical use. It's highlighted here that the specific capacity is presented as capacity per gram of carbon, which would be convenient for comparison to previous work, however it probably grossly

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