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The use of mixed carbon materials with improved oxygen transport in a lithium-air battery

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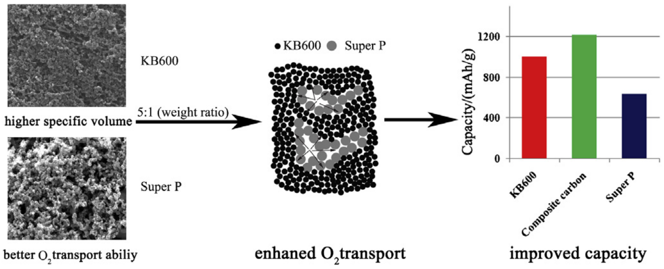
HIGHLIGHTS

- Super P exhibits better use of electrode space than KB600.
- Moderate wettability and hardly blocked pores promote gas transfer for Super P.
- Due to facilitated oxygen transfer, the capacity of mixed carbon is improved.

GRAPHICAL ABSTRACT



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ABSTRACT

Two commercial carbon blacks, Ketjen black EC600JD (KB600) and Super P with quite different porosity parameters, are used for the cathode of a lithium-air battery. With high specific pore volume, KB600 shows a higher weight specific capacity. However, Super P exhibits a super high volume specific capacity, about 7 times higher than that of KB600, ascribed to its higher proportion of pores with suitable size for the deposition of solid products. The effects of O_2 partial pressure and discharge rate on the specific capacity are investigated, combined with characterizations of contact angle and the structure of the electrodes. It is demonstrated that the Super P electrode possesses better O_2 transport that improves the use of the whole electrode volume, and the special mechanism of O_2 diffusion in the Super P electrode is proposed. By mixing KB600 with Super P with a weight ratio of 5:1, an electrode is obtained that exhibits increased O_2 transport. The weight specific capacity is 1219 mAh g^{-1}, about 1.2 times higher than that of KB600.

1. Introduction

The non-aqueous lithium-air/oxygen battery has been attracting more and more interests ascribed to its potential applications as energy conversion systems for various equipments, such as mobile devices, high attitude aircrafts and electric vehicles. Using lithium and oxygen as active materials for anode and cathode respectively, the battery exhibits a super high energy density, about 11,000 kWh kg^{-1}, or 5.5 kWh kg^{-1} if the oxygen is taken into account. However, to be commercialized, there are many obstacles to overcome, such as low rate discharge performance, low charge–discharge energy efficiency and poor cycle life [1,2]. Especially, the detailed charge–discharge reaction process is still unclear, and much work has to be done to make it operate as a rechargeable battery [3–6]. Thus, it might be an achievable target to use it as a primary battery with a super high capacity in the near future.

Same as other metal-air batteries, the oxygen reduction reaction (ORR) of a lithium-air battery takes place in the cathode, which is

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also named as the "air breathing electrode" because the oxygen could be directly obtained from air. Such reaction should occur on the solid–liquid interface formed by the electrode material and the electrolyte so that the charge transfer process involving the electron and the Li^+ can be facilitated. More surface area of the electrode material covered by the electrolyte will provide more interface for the ORR reaction. However, different from traditional metal-air batteries using aqueous electrolyte, the reduced oxygen is combined with Li^+ to form the solid lithium oxide, and the product is insoluble in the organic electrolyte. Therefore, the solid–liquid interface is responsible for both the electrochemical reaction and the deposition of the solid product. As the reaction goes on, the lithium oxides gradually accumulate in the pores of the electrode material, and the discharge process will terminate when the pores are completely filled.

The above analysis implies that the capacity is determined by the available surface for the deposition and the pore volume for the storage of solid products. Large surface area and pore volume are definitely desirable [7], but the pores size distribution (PSD) of the electrode material also plays an important role [8]. At the beginning of the discharge, the micropores and some of the mesopores with smaller size than that of the lithium oxide particles would be easily blocked, and will not be further accessed by either oxygen or Li^+, making them unavailable; in contrast, for the pores with too large size, the growing lithium oxide layer with low conductivity will make the polarization of the electrochemical reaction higher and thus, the discharge process would end before the whole pore volume is occupied. Therefore, the mesopores with appropriate size, e.g. tens of nm, is favorable to obtain a high use, and the synthesis of various carbon materials with a high proportion of mesopores is important for the lithium-air battery [9,10].

On the other hand, since the reaction takes place at the solid–liquid interface as mentioned above, O_2 should be dissolved in the electrolyte and diffuses to the interface to participate in the reaction. Therefore, the solubility and the diffusion rate of O_2 would have significant impacts on the reaction [11,12]. It is confirmed that an appropriate choice of the electrolyte and increasing the O_2 partial pressure are effective strategies to improve the solubility and can achieve increased O_2 transport in the electrode [13]. Meanwhile, intelligent designs of the pore architecture and the electrode structure could also promote the transport [14,15]. For example, Williford and Zhang [16] proposed an interconnected dual-pore structured electrode, where pores with high ORR activity allow for the deposition of products, and the other pores with low or no activity will remain open for the O_2 access. Another feasible solution is to modify the configuration of the electrode with supporting materials [17,18], such as Ni foam and carbon cloth, which can form open and interconnected three-dimensional (3D) channels; by this means, the active materials, such as carbon blacks (CBs), carbon nanofibers, are supported on the framework of supporting materials, so that an efficient O_2 transport as well as a high Li^+ migration rate can be obtained, which is favorable for the high capacity and rate discharge performance.

It is now clear that a better use of the pores of electrode materials requires appropriate PSDs, and for a better use of the whole electrode volume, efficient O_2 transport is necessary. Normally, commercial Ketjen black EC600JD (KB600) [19,20] is used as the cathode material ascribed to its high specific volume, in order to obtain a high discharge capacity. Super P [21–23], whose specific volume and surface area are both quite low, has also been used, and can produce a relatively high performance. In order to better understand the factors influencing the use of the electrode volume and achieve an optimal battery performance, we herein studied both KB600 and Super P as the cathode materials with different porosity parameters, by carrying out systematic pores structure characterizations combined with discharge tests at different conditions. We also proposed an O_2 transport mechanism in the electrodes fabricated using different CBs. Finally, with the understanding on the unique property of Super P in the O_2 transport, we fabricated a novel composite cathode comprising KB600 and Super P with a selected ratio, and examined its feasibility in improving the discharge capacity.

2. Experimental

2.1. Materials and characterizations

Commercial CBs, KB600 (AkzoNobel) and Super P (TIMCAL) were purchased and directly used for cathode preparations without further treatments. The analysis of nitrogen adsorption–desorption isotherms was carried out to measure the porosity of the CBs by an ASAP 2420 adsorption analyzer (Micromeritics). The Brunauer–Emmett–Teller (BET) method was used for the surface area measurement. The Barrett–Joyner–Halenda (BJH) adsorptions–desorption was used for the pore analysis. The total pore volume was calculated from the adsorbed volume of nitrogen at $P/P_0 = 0.99$ (saturation pressure). PSDs were obtained by the BJH method from the desorption branches of the isotherms. All the results were related to the pores between 1.7 nm and 300 nm.

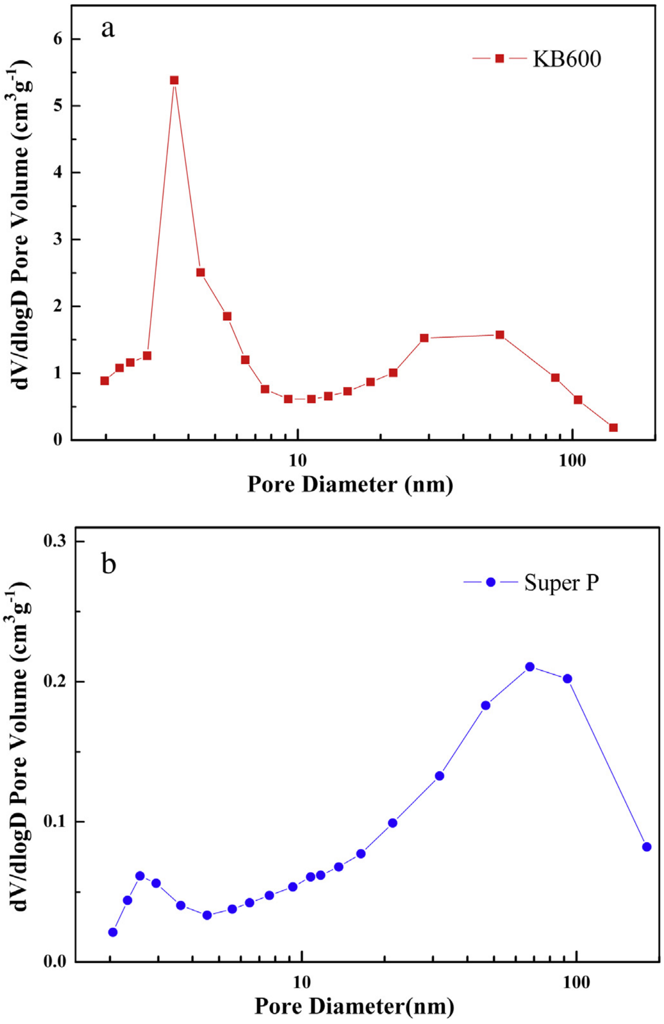

Fig. 1. PSDs of the CBs (a) KB600 [25], (b) Super P.