

Study on the Effect of Carbon Pore Distribution on the Performance of Air Electrode of Lithium-Air Battery Based on Electrochemical Model

Ma Hanxue

Dalian University of Technology, Liaoning Dalian 116024, China

ABSTRACT. *The microstructure of carbon has an important influence on the performance of air electrode of lithium-air battery. In my thesis, relevant experiments were carried out by establishing electrochemical model. What's more, the effect of carbon pore distribution of electrochemical model on the performance of air electrode of lithium-air battery was analyzed in detail in order to improve the quality of lithium-air battery in China.*

KEYWORDS: *Electrochemical model, Pore distribution, Lithium-air battery, Porous carbon-air electrode*

1. Introduction

Compared with other types of batteries, the theoretical specific energy of lithium-air battery is much higher than that of mainstream lithium-ion battery, but in the process of practical application, due to the influence of carbon-air electrode, electrolyte and other reasons, lithium-air battery cannot be popularized in a short time. In order to deeply understand the action mechanism of lithium-air battery and the different relationship between microstructure parameters and discharge performance of carbon materials, in this paper, the effect of carbon microstructure on the electrical performance of air electrode is analyzed by experimental test.

2. Establishment of Electrochemical Model

2.1 Research Object

The purpose of this study is to study the effect of carbon pore distribution on the performance of air electrode of lithium-air battery. It is assumed that the negative electrode of Li_2O_2 , battery will be oxidized to Li^+ and integrated into electrolyte in a short time when the product is in discharge state. The electrons then flow into the

cathode through the circuit, where O_2 is at the positive pole, and Li_2O_2 is formed under the influence of the catalyst and deposited in the gap of the porous cathode. The reaction of the electrode is as follows:

- (1) Negative electrode: $Li \rightarrow Li^+ + e^-$;
- (2) Positive electrode: $Li^+ + 1/2 O_2 + e^- \rightarrow 1/2 Li_2 O_2$;
- (3) Total reaction: $Li + 1/2 O_2 \rightarrow 1/2 Li_2 O_2$

2.2 One-Dimensional Electrochemical Model

2.2.1 Preparation of Porous Carbon-Air Electrode

The raw materials used in this paper are D800, acetylene black, conductive carbon black of Hebei Jipeng Chemical Industry, super P of Shanmitt Company and self-made conductive carbon black. The electrolyte is 1 mol/L $LiPF_6$, vinyl carbonate (EC): diethyl carbonate (DEC=1:1) lithium battery electrolyte.

2.2.2 Geometric Model

What is shown in figure 1 is the geometric state of the one-dimensional model of lithium-air battery, which is completely immersed in organic electrolyte. The whole model is composed of diaphragm and porous electrode, in which the boundary of lithium metal negative electrode.

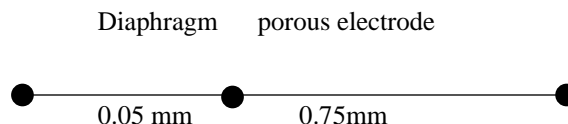


Fig.1 One-Dimensional Geometric Model of Lithium-Air Battery

2.2.3 Model Hypothesis

In order to improve the practicability and reliability of the model, the process simplification can be adopted in the process of model design and the following assumptions can be made: (1) Li_2O_2 is the product of lithium battery discharge, and the product is unique and will only be in the position of porous cathode. (2) The electrolyte of lithium battery itself is a mixed substance in a container full of binary electrolytes, and this turbid mixture is a single salt organic matter; (3) The diffusion of Li^+ can refer to the relevant contents of concentrated solution electrolytes, and the resulting multiphase electrolytes only appear in the position of porous cathode; (4) The oxygen content of the solvent is stable and saturated for a long time. (5) The convection will occur in the material produced at the two poles of the lithium battery, and the effect of its transmission can be ignored.

2.3 Construction of One-Dimensional Electrochemical Model

If the lithium battery is in a state of discharge, the porous carbon electrode will provide a reaction site for the electrochemical reduction of oxygen. In other words, during the discharge of the lithium battery, the oxygen content outside the battery will begin to increase and react with Li^+ near the porous electrode to form a new mixture Li_2O_2 and spread rapidly according to Fick's law.

3. Effect of Carbon Pore Distribution on Air Electrode Performance of Lithium-Air Battery Based on Electrochemical Model

3.1 Experimental Content

3.1.1 Preparation of Porous Carbon-Air Electrode

The air electrode is prepared by slurry scraping method. In the process of preparation, carbon and PVCD are prepared according to the mass ratio at 4:1 to obtain the electrode paste, and then the slurry is uniformly coated on the foamed nickel substrate and dried in an oven at 130 °C for 24 hours to obtain the air electrode sheet.

3.1.2 Performance Test of Porous Carbon Air Electrode

Take out the Li piece in the box and confirm whether the diaphragm is complete, then put the air electrode into the mold according to the corresponding order, add 4:1 electrolyte and assemble into an air simulation battery. Put the assembled battery into the charge and discharge testing instrument to detect its charge and discharge. By using the charge-discharge tester, the density of the discharge current can be measured as 0.2 mA/cm², and the cut-off voltage is 3V. It is worth noting that the whole process of the experiment is in a constant temperature and pure oxygen environment (26°C).

3.1.3 Measurement of Pore Distribution and Air Electrode Morphology of Carbon

Using the Quadrs Subtype specific surface-pore analysis equipment of Karl Zeiss brand in Germany, nitrogen was used as adsorption gas, and the relevant microscopic parameters of carbon were obtained by DAD. The discharge process of the battery was observed by Huadsi-F520 high precision scanning microscope, and the working voltage was 30 kV.

4. Results and Discussion

Figure 2 shows the discharge curve of the air electrode made of carbon materials with different microscopic angular structure parameters. It can be seen from the diagram that the specific capacity of the curve CB5 is the largest, that of CB3 and

CB4 is less than that of CB5, and that of CB1 and CB2 is the smallest. Figure 3 shows the pore distribution curves of several carbon materials by means of nitrogen adsorption. From the content of figure 3, we can see that there is a high similarity between CB1 and CB2, and the distribution of holes is mainly concentrated between the micropores and the mesoporous range of 3~7nm. CB3, CB4 and CB5 are obviously different from CB1 and CB2 in pore size distribution, and the first three are larger than the latter two. The pore size of CB3 is distributed in the region of 5~9nm, and that of CB4 is distributed in 15~35nm. From the position change in the figure, we can see that CB5 has the curve characteristics of CB3 and CB4, and is more stable in proportion. The micro-parameter structure and discharge specific capacity of five different types of carbon can be obtained from the data changes of figure 2 and figure 3.

According to the above content, the pore model of carbon was constructed, and the deposition and growth process of discharge products in the carbon channel were simulated by electrochemical method. The pore inside the carbon is composed of macro pores, mesopores and micro pores, while macropores and mesopores are the main body of the whole pore, and micropores are the branches attached to the pore structure. These three different types of holes will produce adsorption force due to internal scattered force, and the phenomenon of "micropore filling" will occur, resulting in the adsorption of oxygen atoms in micropores and some small pores, resulting in the formation of sediments. In the process of discharge, the oxygen concentration in the main channel area increases rapidly, resulting in a large number of deposition blockage. Due to the blockage of discharge products, oxygen transport becomes more difficult, resulting in less and less space for reaction on the surface of porous carbon-air electrodes, and the contact between reactants becomes more sufficient in such an environment. The reaction rate and carbon pore utilization have been significantly improved, and the discharge performance of the air electrode has become better.

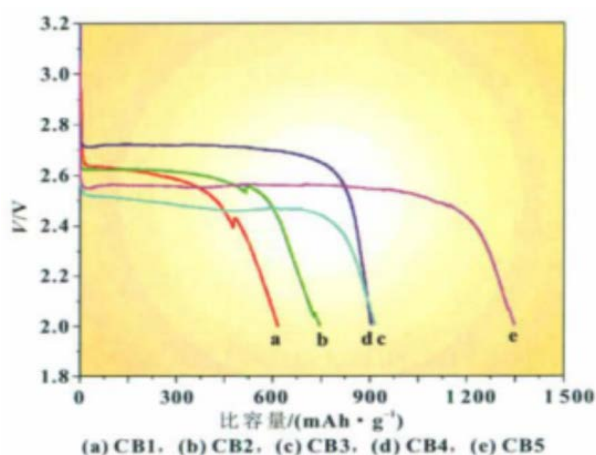


Fig.2 Specific Capacity

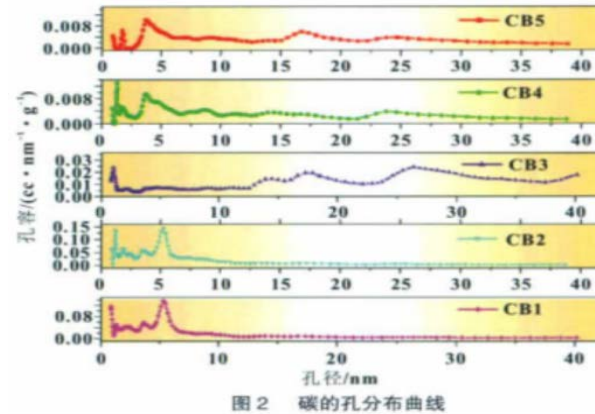


图2 碳的孔分布曲线

Fig.3 Carbon Pore Distribution Curve

5. Conclusion

According to figure 1 above, it can be seen that CB1 and CB2 are similar, but their specific capacity is the lowest, and CB3 and CB4 are less than CB5; In figure 2, the pore distribution of CB1 and CB2 is similar, concentrated in the mesoporous range of micropores and 4~8nm, and less in the large mesoporous range.

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