

Electrochemical Performances of Lithium-air Cell with Carbon Materials

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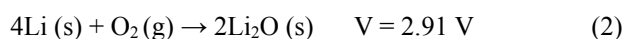
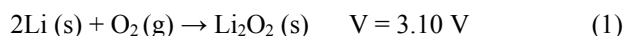
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This study investigates the requirements of lithium-air cathodes, which directly influence discharge capacity. The cathodes of Li-air cell are made by using five different carbon materials, such as Ketjen black EC600JD, Super P, Ketjen black EC300JD, Denka black, and Ensaco 250G. The Ketjen black EC600JD provides discharge capacity of 2600 mAh/g per carbon weight, while that of Ensaco 250G shows only 579 mAh/g. To figure out the differences of discharge capacity from carbon materials, their surface area and pore volume are analyzed. These are found out to be the critical factors in determining discharge capacity. Furthermore, carbon loading on Ni foam and amounts of electrolyte are significant factors that affect discharge capacity. In order to investigate catalyst effect, electrolytic manganese dioxide (EMD) is incorporated and delivered 4307 mAh/g per carbon weight. This infers that EMD facilitates to break O₂ interactions and leads to enhance discharge capacity.

Key Words: Li-air battery, Air electrode, Cathode requirements

Introduction

Lithium-air battery has been considered as a novel promising candidate after first proposal by Abraham *et al.*¹ in 1996. The lithium-air battery goes through two oxygen reduction reactions:



The current density, partial pressure of O₂, and electrolyte composition may be the key factors to determine the ratio of the two processes.^{2,3} Based on the reactions of oxygen reduction, lithium-air battery has one of the largest theoretical energy densities and specific capacities in electrochemical system.⁴ Nevertheless, the applications of lithium-air battery in the power tools and electric vehicles are still premature due to lack of real discharge capacity and reversibility. To overcome the drawbacks of lithium-air battery, considerable researches have been focused on improving the discharge capacity and rechargeability. Read *et al.*⁵ achieved high discharge capacity of 2825 mAh/g by sustaining high oxygen diffusion in electrolyte. Debart *et al.*⁶ reported cathode capacity of approximately 3000 mAh/g using a high surface area of Mn-based catalyst. However, there are a few reports regarding the requirements of cathode, in spite of their key role in high capacity lithium-air battery.

Therefore, the main focus of this study is the requirements of cathode, which could influence the discharge capacity of lithium-air battery. Ketjen black EC600JD, Super P, Ketjen black EC300JD, Denka black, and Ensaco 250G are used as carbon materials to fabricate the air cathode. To figure out the

differences in discharge capacities among various air cathodes, surface area and pore volume of each carbon material are investigated. The various types of carbon loading on the nickel foam and amount of electrolyte are applied to the Li-air cell to investigate each influence on discharge capacity. Electrolytic manganese dioxide (EMD) is incorporated to understand the role of catalyst.

Experimental

For Li-air cathode fabrication, 0.4 g of carbon materials, such as Ketjen black EC600JD, Super P, Ketjen black EC300JD, Denka black, and Ensaco 250G, were mixed with a mixture of 0.16 g of polyvinylidene fluoride (PVDF) and 9.8 g of N-methyl pyrrolidone (NMP). The Ace Homogenizer (Nihonseiki Kaisha LTD, Japan) was used for the excellent blending of the NMP/PVDF/Carbon slurry for 30 min. The circular disks (1.962 cm²) were obtained from the sheets of high-porosity nickel foam and submerged into the NMP/PVDF/Carbon slurry. The nickel foam was sonicated for 2 min to facilitate the slurry penetration into the Ni foam structure. The cathodes were held in a vacuum oven at 80 °C for 24 h. After drying, approximately 5.8 mg of each carbon material was loaded on the Ni foam. In case of Ketjen black EC600JD, the cathodes with different carbon loadings on the Ni foam were prepared by the same procedure except incorporating carbon material in the range of 0.1 - 0.9 mg in mixture of NMP and PVDF. Electrolytic manganese dioxide (EMD) was added in the NMP/PVDF/Carbon slurry for the catalyst test.

The electrolyte was 1 M of LiPF₆ in an ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution. Lithium metal and Celgard 2500 were used as the counter electrode and separator, respectively. A modified standard

coin cell (2032 type) was produced by making a 0.5 mm radius pinhole at the center of cathode cap and it was applied to examine the discharge capacities of the cathodes. The Li-air cell was assembled in a dry-room having dew point about $-100\text{ }^{\circ}\text{C}$. Before discharging, the cell rested for 2 h to induce good permeation of the electrolyte into the carbon materials. The cell test was performed in a box, which had gas inlet, outlet, and dry air flowing through the box. The Maccor 4000 battery cycler with a 1.5 V cut-off voltage and 0.1 mA/cm^2 current density was used to analyze the discharge capacity. The morphology of the cathodes was examined by field emission scanning electron microscopy (SNE-1500M, SEC). The surface area and pore volume of carbon materials were investigated by Brunauer-Emmett-Teller (BET, ASAP2010).

Results and Discussion

Figure 1 shows the voltage-capacity discharge profiles for Li-air cells using five different carbon materials such as Ketjen black EC600JD, Super P, Ketjen black EC300JD, Denka black, and Ensaco 250G. The discharge plateaus appear from 2.4 to 2.7 V and they show well consensus with previous reports.^{2,7} An extremely large capacity difference is obtained from various carbon sources with Li-air cell. The Ketjen black EC600JD and Ketjen black EC300JD cathodes deliver significantly large capacities which were 2600 and 2150.5 mAh/g, respectively, while discharge capacity of Super P, Denka black, and Ensaco 250G cathodes show only 956.3, 757.3, and 579.9 mAh/g, respectively. All the discharge capacities are achieved at 0.1 mA/cm^2 current density and carbon loadings of all cathodes are approximately 5.8 mg which show the best electrochemical performances. Only the weight of carbon is considered and weights of the Ni foam and PVDF are not included. To clarify the differences of discharge capacities obtained from the five different carbon materials, surface area and pore volume of each carbon material were analyzed by Brunauer-Emmett-Teller (Table 1). While the low surface areas of the Super P, Denka black, and Ensaco 250G result in low discharge capacity, the high surface areas of the Ketjen black EC600JD and Ketjen black EC300JD lead to high discharge capacity. However, the differences in discharge capacity cannot be explained by the surface area of Super P, Denka black, and Ensaco 250G. The pore volume of the three samples can be used to predict the difference of discharge capacity. In fact, Super P, which has a larger pore volume than Denka black and Ensaco 250G shows better electrochemical performance. The surface and pore of carbon may be used as deposition sites of the discharge products, such as Li_2O and Li_2O_2 , in order that carbon material with high surface area and large pore volume can be selected to obtain high discharge capacity.^{3,8}

The correlation between discharge capacity and carbon loading on nickel foam is investigated in the range of 1.2 to 11.6 mg as shown in Figure 2. The Ketjen black EC600JD is used as carbon material. The 5.8 mg carbon loading on the Ni foam demonstrates the best performance in discharge capacity. Nevertheless, when carbon is more or less loaded than 5.8 mg on Ni foam, the discharge capacity drastically decreases. Figure 3 (a), (b), and (c) demonstrate the SEM images of the morpho-

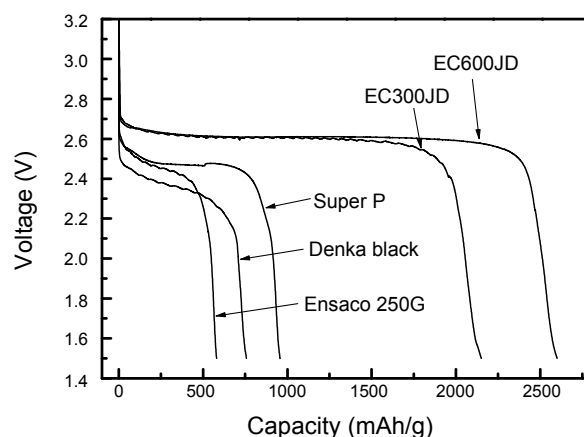


Figure 1. Discharge profiles of Li-air cells with various carbon materials. Carbon loading of all cathodes is approximately 5.8 mg.

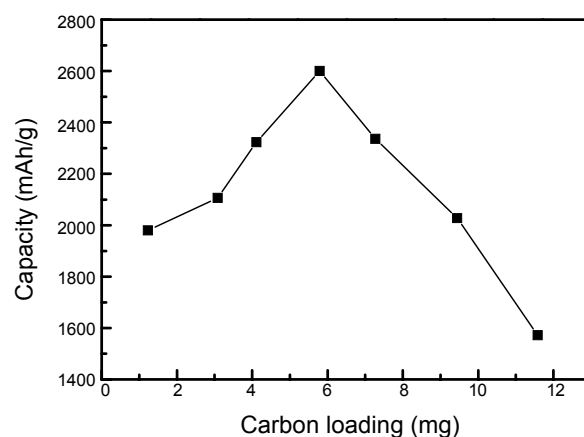


Figure 2. Discharge capacity of Ketjen black EC600JD with various carbon loadings.

Table 1. Comparison of surface area and pore volume of the carbon materials

Carbon material	Surface area (m^2/g)	Pore volume (cm^3/g)
Ketjen black EC600JD	1325	2.47
Super P	62	0.32
Ketjen black EC300JD	890	1.98
Denka black	60	0.23
Ensaco 250G	62	0.18

logy of air cathodes with 1.2, 5.8, and 11.6 mg of carbon loadings. When the carbon loading is smaller than 5.8 mg, the carbon only adheres to Ni foam structure instead of agglomerate itself, which should reduce pore volume for depositing Li_2O and Li_2O_2 . Therefore, the cathodes do not perform enough discharge capacity. On the other hand, having the status of more than 5.8 mg of carbon loaded on the Ni foam closes the opening structure of the foam. This closing is caused by vast amount of carbon, which results in impeding the flow of oxygen. Therefore, the discharge capacity drastically reduces.

As shown in Figure 4, various amounts of electrolyte are incorporated in Li-air cells to analyze the effect of electrolyte

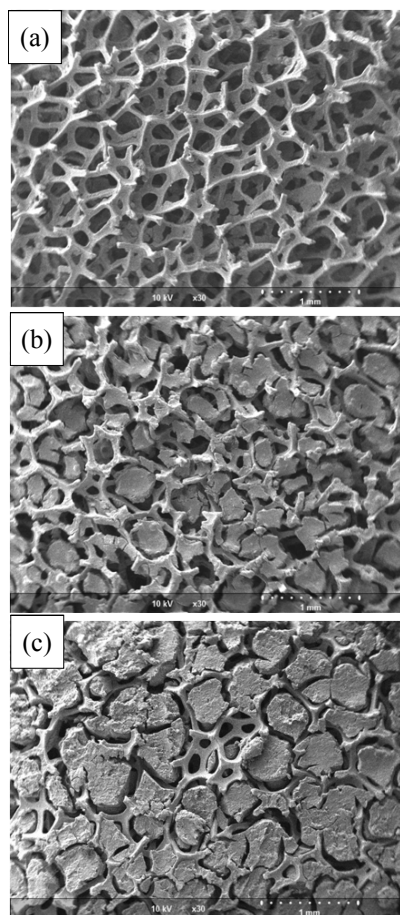


Figure 3. SEM micrographs of air cathodes with various carbon loadings (a) 1.2 mg (b) 5.8 mg and (c) 11.6 mg.

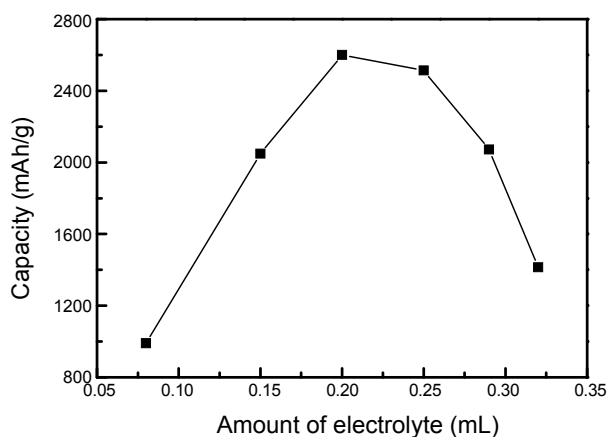


Figure 4. Discharge capacities of Ketjen black EC600JD with different amounts of electrolyte.

quantity. The discharge capacity is drastically increased until 0.2 mL of electrolyte has been added. However, there is a steep diminish in capacity as the amount of electrolyte increases by over 0.25 mL. It is evident that capacity of the cells directly depends on the status of electrolyte filling; insufficient electrolyte facilitates the gas diffusion into the cathode, which may

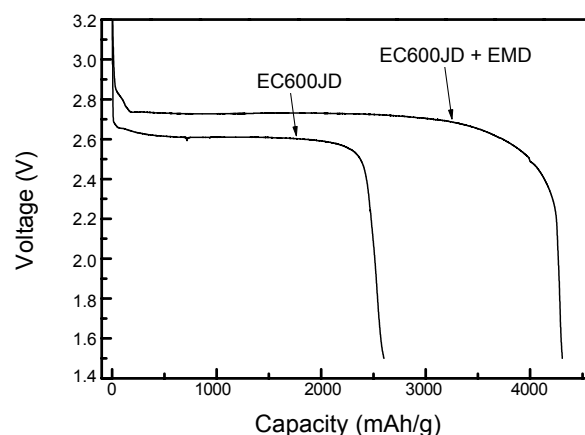


Figure 5. Discharge profiles of Ketjen black EC600JD cathode containing EMD as catalyst and Ketjen black EC600JD cathode.

lead to depositing surplus discharge products, such as Li_2O and Li_2O_2 , on the cathode.⁹ Eventually, the excess of discharge products, which are not soluble in electrolyte, impede the oxygen intake into the cathode and thus, ends cell life. On the other hand, surfeit electrolyte gives rise to full wet of the carbon material, which prohibits the oxygen transfer into the carbon due to poor oxygen solubility and low oxygen diffusion in the electrolyte.¹⁰ The best case for status of electrolyte is when the air cathode is wetted by electrolyte with remaining sufficient pore volume. The result reveals that amount of the electrolyte filled in Li-air cell is one of the significant factors in determining discharge capacity.

Figure 5 shows the discharge profile of Ketjen black EC600JD air cathode containing EMD as a catalyst compared with that of bare Ketjen black EC600JD air cathode. The former cathode delivers 4307 mAh/g and discharge plateau is at 2.73 V, while the bare Ketjen black EC600JD cathode provides 2600 mAh/g and discharge plateau is at 2.61 V. Except incorporating catalyst, the electrochemical test of two cathodes is performed under completely the same conditions of carbon loading and current density. This result suggests that catalyst assists to break Li-O interaction of Li_2O_2 or Li_2O ,⁷ which facilitate to keep air intake into cathode. In addition, the discharge plateau increases by 0.12 V after incorporating EMD, which indicates polarization of the cell decreases. As a result, discharge capacity of the cathode containing catalyst increases by 65% compared with that of the bare cathode.

Conclusions

The electrochemical properties of the air cathode are governed by a number of factors. In addition to the correlation between discharge capacity, surface area and pore volume of carbon, the electrolyte-filling, carbon loading on Ni foam, and catalyst are investigated. The following points are worth to be noted: (1) A carbon of high surface area associated with large pore volume is beneficial to achieve high discharge capacity. This is because surface and pore of carbon is used as a site of discharge products such as Li_2O and Li_2O_2 . (2) A proper carbon loading on nickel foam is important in determining discharge

capacity because enough pore volume and open structure of nickel foam are required to acquire the high discharge capacity. (3) Adequate amount of electrolyte-filling is required to deliver high discharge capacity. The cell that contains insufficient electrolyte and surplus electrolyte hinder further oxygen intake due to excessively deposited Li_2O and Li_2O_2 on cathode and full wet of the carbon material, respectively. (4) The catalyst facilitates to break Li-O interaction of Li_2O and Li_2O_2 and diminishes polarization resulted in the high discharge capacity.

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