Surface Properties and Electrochemical Performance of Carbon Materials for Air Electrodes of Lithium-Air Batteries

Masahiko HAYASHI,* Hironobu MINOWA, Masaya TAKAHASHI, and Takahisa SHODAI

NTT Energy and Environment Systems Laboratories, Nippon Telegraph and Telephone Corporation (3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan)

Received November 19, 2009 ; Accepted January 15, 2010

The electrochemical properties of air electrodes for lithium-air batteries using various kinds of carbon materials were investigated in an organic electrolyte of 1 mol l⁻¹ LiPF₆/PC. High-surface-area carbons such as Ketjen Black EC600JD exhibited large discharge capacities of more than 700 mAh g⁻¹, which were roughly proportional to the surface areas. The high-performance carbons had very similar pore distributions. Moreover, pore distribution measurements revealed that carbons with larger numbers of mesopores delivered larger discharge capacities.

Key Words : Lithium-Air Batteries, Air Electrode, Carbon, Mesopore

1 Introduction

Secondary batteries are urgently needed to increase the energy densities for next-generation type electronic tools and electric vehicles. Metal-air batteries can exhibit high energy densities that exceed those of the widely used lithium ion batteries owing to the use of the oxygen in the air as the positive active material. Thus far, research has mainly focused on aluminum, iron and zinc as the negative active materials for these kinds of batteries, which are used as primary, secondary or mechanical-charging batteries.¹⁻⁴⁾ Recently, new attempts have been made to develop lithium-air secondary batteries using lithium metal as the negative active material in a non-aqueous electrolyte.⁵⁻¹⁶⁾ Lithium-air batteries are promising candidates as high-energy-density batteries because the use of negative lithium metal provides a rather high voltage of 3 V class and a longer discharge time than conventional air batteries. However, there are many problems to overcome as regards the discharge property, especially the high-rate discharge,^{6,9)} and the cycle performance.^{5,6,9,10,13,15)} These problems are generally considered to result from certain properties of the carbon material and the electrocatalyst used for the air electrodes. Specifically, the discharge product, LiO_x (Li₂O and Li₂O₂), of the lithium-air batteries is deposited and decomposed on the carbons and the electrocatalyst incorporated in the air electrodes. Therefore, it is important to choose suitable electrode materials to improve the battery performance.

We have examined the electrochemical properties of various kinds of carbon materials for lithium-air batteries, and each carbon had very different electrochemical properties with respect to the discharge capacity. This may originate in such surface properties as the pore distribution and the wettability of the carbons. In this study, we investigate the relationship between the discharge properties of the lithium-air batteries and the physical properties of the carbons used for the air electrodes.

2 Experimental

Air electrodes using various carbon materials were prepared by the following procedure. The carbon powder was mixed with PTFE powder at a weight ratio of 8 : 2. The mixture was then rolled into a 0.5 mm thick sheet and cut into 16 mm diameter pellets, which were then pressed on a Ti mesh. The lithium-air cell was composed of an air electrode, a lithium metal sheet (0.6 mm thick) and 1 mol l⁻¹ LiPF₆/PC (propylene carbonate) as a positive electrode, a negative electrode and an electrolyte solution, respectively. A propylene membrane (Celgard3501, Celgard, LLC.) was used as a separator. The cell was constructed by stacking the air electrode, the separator immersed in the electrolyte solution and the lithium sheet in series. One side of the air electrode was exposed to dry air. The discharge tests were carried out under a galvanostatic condition at a cut-off voltage of 2.0 V. All the electrochemical tests were carried out in dry air with a dew point of less than -50 °C. Table 1 shows the specific surface areas of the carbon materials used in this study and the 1st discharge capacities of lithium-air cells employing the carbons. The discharge capacities were normalized by the weight of the carbon in the air electrode. Below, the names of the carbon materials are expressed using the abbreviations given in Table 1.

The specific surface area of the carbon was evaluated with a BET analyzer system (Nova 2200, Quantachrome Instruments) using N₂ as an adsorptive medium. The wettability of the air electrodes was evaluated by measuring the contact angle of the electrodes (C : PTFE = 8 : 2 in weight) with respect to one droplet of 1 mol l⁻¹ LiPF₆/PC by using a contact angle meter (SIimage mini, Excimer Inc.). The pore distribution of the carbon was measured using mercury intrusion porosimetry with an Auto Pore III9420 (Micromeritics Instrument Corp.).

Table 1 Specific surface areas and contact angles of the carbon materials used in this study and the 1st discharge capacities of lithium-air cells using the carbons.

Carbon	Abbr.	Manufacturer	Surface area ^{a)} (m ² g ⁻¹)	Discharge capacity ^{b)} (mAh g ⁻¹)	Contact angle ^{c)} (deg)
<u>Carbon black</u>					
Denka Black	DB	Denki Kagaku Kogyo	68	443	50.8
Super S	SS	MMM Carbon	33	39	85.8
Vulcan XC-72	VX	Cabot Corp.	250	110	42.6
KB EC300J	K3	Ketjen Black Int. Co.	800	177	20.8
KB EC600JD	K6	Ketjen Black Int. Co.	1270	977	41
Super P	SP	TIMCAL Ltd.	36	207	86.4
ENSACO 350G	E3	TIMCAL Ltd.	770	898	44
Printex XE2	P2	Evonik Degussa GmbH	910	793	33
Printex XE2-B	P2B	Evonik Degussa GmbH	1000	973	36
<u>Alkaline-activated carbon</u>					
Maxsorb 1470	M1	Kansai Coke and Chemicals	1470	20	119
Maxsorb 2400	M2	Kansai Coke and Chemicals	2400	208	92.2
Maxsorb 3100	M3	Kansai Coke and Chemicals	3100	761	85
<u>Graphite</u>					
MCMB	MC	Osaka Gas Co., Ltd.	2	20	112
HSAG300	H3	TIMCAL Ltd.	280	145	54

^{a)} measured by BET method.

^{b)} measured at 0.1 mA cm² with cut-off voltage of 2.0 V.

^{c)} values with respect to 1 mol l⁻¹ LiPF₆/PC.

3 Results and Discussion

Figure 1 shows the correlation between the specific surface areas of the carbon materials and the 1st discharge capacities of lithium-air cells using the carbons. Of the carbon materials tested, carbons such as K6, P2B, E3, P2 and M3 with high surface areas of more than about 800 m² g⁻¹ exhibited large discharge capacities of more than 700 mAh g⁻¹. As regards carbon black and graphite, the discharge capacities were roughly proportional to the surface areas of the carbons. The activated carbons showed a similar tendency, even though their dependence was different from that of the other carbons. The Maxsorb series had higher surface areas because of the increasing porousness in the grain induced by the alkaline-activated treatment using KOH of micrometer-sized carbons as the starting material. As a result, the Maxsorb series are composed of micrometer-sized grains despite having very large surface areas of more than 1,000 m² g⁻¹. Generally, carbon black has nano-sized grains, and graphites have large well-crystallized grains, which result in very low surface areas. Exceptionally, graphite H3 has a comparatively large area of 280 m² g⁻¹. As described above, the Maxsorb series have unique characteristics in that they have a rather high surface area despite their large grains. This clearly different grain size affects the conductivity of the electrode and the way oxygen diffuses inside the electrode. Therefore, the activated carbons are considered to be dependent on the surface area, unlike the other carbons, as shown in Fig. 1. These results indicate that the surface areas of the carbons, which reflect the number of LiOx deposition reaction sites, have a great influence on the discharge properties of the cells.

Figure 2 shows the pore distributions of the carbon

Fig. 1 Correlation between specific surface areas of carbon materials and 1st discharge capacities of lithium-air cells using the carbons.

materials measured using mercury intrusion porosimetry. High-performance carbons with discharge properties of more than 700 mAh g⁻¹ are indicated in bold face in this figure. K3 has the largest total pore volume, however this carbon has a small capacity of about 200 mAh g⁻¹. This result indicates that carbons with a large total pore volume do not necessarily exhibit large discharge capacities. Furthermore, with the exception of M3, the high-performance carbons (K6, P2B, E3 and P2) have similar pore distributions. This result suggests that the LiO_x deposition (discharge) reaction proceeds via a similar mechanism on these electrodes. It is noteworthy that there are larger numbers of fine pores of less than 0.1

Fig. 2 Pore distributions of carbon materials measured by mercury intrusion porosimetry. (a) DB, SS, VX, K3, K6, SP, E3, MC, H3, (b) P2, P2B, M1, M2, M3.

μm in the high-performance carbons such as K6, P2B and M3 than in the other carbons. M2 and M3 exhibit discharge capacities of 208 and 761 mAh g^{-1} , respectively, whereas M1 shows a very small discharge capacity of 20 mAh g^{-1} as shown in Table 1. This may be because M2 and M3 have more fine pores than M1. On the basis of the above results, the pore distribution of carbon is considered to be an important property as regards preparing superior air electrodes.

The volumes corresponding to mesopores and macropores were calculated from the pore distributions as shown in Fig. 2. Here mesopores and macropores are defined as pores with diameters (D) of $3 \leq D < 50 \text{ nm}$ and $50 \text{ nm} \leq D \leq 200 \mu\text{m}$, respectively. Figure 3 shows the correlation between the pore volumes corresponding to mesopores and macropores in the carbon materials and the 1st discharge capacities. The mesopore volumes correlate roughly with the discharge capacities. In particular, K6, which has the largest discharge capacity, has the largest volume of mesopores. This indicates the importance of the pore distribution in relation to the discharge property. In contrast, the macropore volume has no clear dependence on capacity. From these results, the reaction mechanism in an air electrode should involve the carbon mesopores as the active site. It was also confirmed that the carbons with a larger number of mesopores tended to have a higher surface area. Considering the correlations with the discharge capacity, the air cells exhibit superior discharge properties when high-surface-area carbons containing nano-sized pores such as mesopores are used as the electrode materials.

The contact angles of the air electrodes using various kinds of carbons with respect to 1 mol l^{-1} LiPF_6/PC are listed in Table 1. The electrodes with the lower angles can make contact more easily with the electrolyte solution. High-performance carbons such as K6, P2B and E3 have comparatively low angles. This result indicates that the discharge reaction could proceed because the solution was in good contact with the electrode.

Fig. 3 Correlation between volumes of mesopores ($3 \text{ nm} \leq D < 50 \text{ nm}$) and macropores ($50 \text{ nm} \leq D$) of carbon materials, and 1st discharge capacities.

However, K3, which has a rather low angle of 20.8° , exhibits a smaller discharge capacity despite its high surface area of $800 \text{ m}^2 \text{ g}^{-1}$. This rather good wettability may prevent the diffusion of oxygen in the electrode. By contrast, DB with a rather high angle of 50.8° exhibits a comparatively large discharge capacity despite its low surface area of $68 \text{ m}^2 \text{ g}^{-1}$. This unexpectedly large discharge capacity of DB appeared to be induced by the high wettability. These results suggest that the high-performance electrode required the moderate wettability. On the other hand, the contact angles of the Maxsorb series decrease as the surface areas increase. Such an increase in the wettability seemed to be caused by the introduction of surface functional groups such as OH^- on the carbon by the alkaline-activated treatment. However, even the contact angle of M3, the highest-performance carbon of the series, exhibited a higher value than the carbon blacks, which indicates unfavorable contact with the solution. The large

capacity of the M3 seemed to result from the rather high surface area of more than 3000 m² g⁻¹. As stated above, air electrodes with high wettability do not always exhibit good discharge performance.

Hyodo et al. examined the oxygen reduction properties of various kinds of carbon materials in 9 mol l⁻¹ NaOH aqueous solutions.¹⁷⁾ They reported that there were clear correlations between the electrode performance and such physical properties as the surface areas and the pore distributions of the carbons. This is very similar to the results we obtained in a nonaqueous electrolyte solution. These results suggest that factors such as surface area and pore size are very important as regards improving the properties of air electrodes used in aqueous or nonaqueous solutions. Furthermore, it is now important to investigate the electrochemical properties of the carbons in the charging process to realize practical lithium-air secondary batteries.

4 Conclusion

Electrochemical tests were performed on air electrodes using various kinds of carbon materials in 1 mol l⁻¹ LiPF₆/PC. The discharge capacities of lithium-air cells showed a rough correlation with the surface areas of the carbon materials used for the air electrodes. As a result, carbons with high surface areas such as K6, P2 and P2B exhibited large discharge capacities. The capacities were found to be in proportion to the surface areas of the carbon, and so the discharge product was deposited on the carbon surface. Nano-sized pores such as mesopores on the carbons seemed to function as active sites during the discharge process based on the results of the pore distributions. Moreover, the suitable wettability of the air electrodes resulted in large discharge capacities.

Acknowledgements

We are grateful to Mr. Yosuke Nozaki of NTT Energy and Environment Systems Laboratories for helpful guidance and discussions. We also thank Mr. Shoji Oriuchi of

NTT Facilities Research Institute Inc. for his assistance with the experiments.

References

- 1) N. Miura, M. Hayashi, T. Hyodo, and N. Yamazoe, *Mater. Sci. Forum*, **315-317**, 562 (1999).
- 2) H. Arai, S. Müller, and O. Haas, *J. Electrochem. Soc.*, **147**, 3584 (2000).
- 3) J. Goldstein, I. Brown, and B. Koretz, *J. Power Sources*, **80**, 171 (1999).
- 4) B. T. Hang, H. Hayashi, S. Yoon, S. Okada, and J. Yamaki, *J. Power Sources*, **178**, 393 (2008).
- 5) K. M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, **143**, 1 (1996).
- 6) J. Read, *J. Electrochem. Soc.*, **149**, A1190 (2002).
- 7) A. Doble, C. Morein, and K. M. Abraham, *208th Meeting of the Electrochemical Society*, Abst. 823 (2005).
- 8) T. Kuboki, T. Okuyama, T. Ohsaki, and N. Takami, *J. Power Sources*, **146**, 766 (2005).
- 9) T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, and P. G. Bruce, *J. Am. Chem. Soc.*, **128**, 1390 (2006).
- 10) A. Debart, J. Bao, G. Armstrong, and P. G. Bruce, *J. Power Sources*, **174**, 1177 (2007).
- 11) T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, and N. Sammes, *J. Electrochem. Soc.*, **155**, A965 (2008).
- 12) S. N. Mohamed, N. A. Johari, A. M. M. Ali, M. K. Harun, and M. Z. A. Yahya, *J. Power Sources*, **183**, 351 (2008).
- 13) T. Hirai, T. Sakaki, and Y. Uno, *215th Meeting of the Electrochemical Society*, Abst. 239 (2009).
- 14) S. D. Beattie, D. M. Manolescu, and S. L. Blair, *J. Electrochem. Soc.*, **156**, A44 (2009).
- 15) A. K. Thapa, K. Saimen, H. Matsumoto, and T. Ishihara, *76th Annual Meeting of the Electrochemical Society of Japan*, p. 383 (2009) [in Japanese].
- 16) Y. Wang, and H. Zhou, *76th Annual Meeting of the Electrochemical Society of Japan*, p. 381 (2009) [in Japanese].
- 17) T. Hyodo, Y. Shimizu, N. Miura, and N. Yamazoe, *Denki Kagaku (Electrochemistry)*, **62**, 158 (1994) [in Japanese].