**Influence of Morphology of Highly Ordered Mesoporous Carbon Replica on Electrochemical Properties of Air Electrodes with Pt-Ru Electrocatalyst/Carbon Replica Support in Nonaqueous Electrolyte Solution**

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**ABSTRACT**

Electrochemical properties of lithium air battery (LAB) cells incorporating highly ordered mesoporous carbon replica (CR) support materials were examined in nonaqueous electrolyte solution of 1 mol/l LiTFSI/TEGDME. The CR support was prepared with pore sizes of 10, 40, and 100 nm. The cycle properties of the LAB cells with the CR support was improved by using Pt-Ru electrocatalyst. As a result, the LAB cells with Pt-Ru electrocatalyst/CR (pore size: 10 nm) exhibited the highest performance of the first discharge capacity of 1000 mAh/g and capacity retention of about 50% at 10th cycle. Moreover, different growth behavior of the discharge product was observed as a consequence of the pore size of the CR support.

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1. Introduction

Lithium air batteries (LAB) are promising as high-energy-density storage system beyond lithium ion batteries because they have the highest theoretical energy density of 3861 Wh/kg among the currently-proposed secondary batteries.1–4 A LAB is composed of lithium metal and oxygen supplied from air as a negative and a positive active material, respectively, with a nonaqueous solution as an electrolyte. This combination of active materials such as oxygen and lithium lead to high energy density (large discharge capacity and high battery voltage). However, LABs reported so far have problems to be overcome with their electrochemical properties, such as cycle property and rate property, and thus LABs need further improvement in order to put them into practical use.

The ideal discharge product, Li2O2, of a LAB without by-product such as Li2CO3 is deposited on the air (positive) electrode. Therefore, it is very important to control the morphology of discharge product for the sake of improving the cycle properties. In many reports, carbon black particles such as Ketjen Black EC600JD (KB), with nano-sized and unarranged shapes have been used as carbon support materials for air electrodes.5–8 As a result, non-uniform and micrometer-order discharge product Li2O2 deposits on the air electrode. The discharge product was hardly reversibly deposited and decomposed in the discharge and charge process, respectively, due to the poor contact between the carbon and insulating Li2O2. Various morphologies of the discharge product for LAB have been reported, for example, particle-shape morphology,9–13 where the product covers the support particles; film-shape morphology,14–16 where the product grows in the planar direction; spiky needle or rod-shape morphology,17,22–24 where the product grows in linear shape; and toroid-shape morphology,22,25 where the product grows in a circular pattern. Whether there is a correlation between these shapes and the experimental conditions, such battery components and discharge/charge test, was difficult to explain. It is very important to clarify such correlation by using the electrode materials with highly ordered structure as typical support for LAB.

Previously we investigated CMK-3 and carbon replica (CR) materials for air electrode.18–21 These carbons consist of a carbon matrix arranged with regularly patterned mesopores.22–30 The CMK-3, which was synthesized by using rod-shaped silica SBA-15 coating a carbon source as the template, has stacks of hollow rod-shaped pores with about 2–3 nm. On the other hand, the CR, which was synthesized using silica nano-spheres (SNs) coating a carbon source, has close cubic packing of sphere-shaped pores with a diameter of about 10 nm. LAB cells with these carbons should show large capacity and better cycle performance because the shape of discharge product is changed by controlling the pore structure. The CR has a high specific surface area and large total pore volume, whose values were found to be an order of magnitude larger than those for CMK-3. In our previous report,31 a LAB cell incorporating Pt-Ru/KB electrocatalyst shows discharge capacities of more than 800 mAh/g for over 8 cycles in tetraethylene glycol dimethyl ether (TEGDME) based electrolyte solution. The Pt-Ru electrocatalyst could be supported with particle size of 1–3 nm on the CMK3 or the CR. As a result, the LAB cell incorporating CR support showed much higher capacity (1000 mAh/g) than the cell with CMK-3 (103 mAh/g). The first coulombic efficiency of the cell with Pt-Ru/CR was improved from 62 to 100% by loading Pt-Ru electrocatalyst. However, the electrochemical properties of CR support have not been examined yet with respect to the CR pore size.

In this study, our purpose was to control the morphology of discharge product, Li2O2, deposited on the air electrode and improve the reversibility of electrochemical deposition/decomposition of Li2O2 when the Pt-Ru-loaded CR with various pore sizes is used as
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the support material. Thus, we investigated the cell properties of the Pt-Ru-loaded CR with pore sizes ranging from 10 to 100 nm and consequently ascertained correlation between the cell properties and growth behavior of the discharge product through detailed observation of its morphological features.

2. Experimental

2.1 Synthesis of highly ordered mesoporous carbon, CR, and air-electrode material, Pt-Ru-loaded CR

The CR was synthesized using the parent SNSs as a template as reported elsewhere.32 L-arginine (Kanto Chemical Co., 0.174 g, 98%) and tetraethyl orthosilicate (TEOS) (10.45 g) as a base catalyst and a silica source, respectively, were mixed in distilled water. The mixture had been stored still at 70°C for 24 h and then it was dried at 100°C. Size tuning (100–10 nm) of the SNSs was conducted by the seed regrowth method as described elsewhere.40 Mixture of the initial SNSs (a diameter of approx. 10 nm) before drying was added into the solution containing an appropriate amount of arginine. Then, an appropriate amount of TEOS was added into the solution. The mixture was stirred at 70°C followed by drying at 100°C. The powders obtained thus were heated for 10 h at 550°C under air to obtain the larger size of SNSs (diameters of approx. 40 and 100 nm). The SNSs were carbonized by heat-treatment at 800°C for 3 h in Ar. Then, the carbonized powder was soaked in 20-wt% HF aqueous solution to remove the silica template. Finally, CR powder was obtained after washing it with distilled water and ethanol. The CR synthesized from SNSs of 10, 40 and 100 nm in diameter are hereafter denoted as CR10, CR40, and CR100. Pt-Ru-loaded CR was prepared by the formic acid reduction method.41 The powder was dispersed in formic acid solution by sonication, and then a mixed aqueous solution (Pt:Ru = 10:90) of H$_2$PtCl$_6$6H$_2$O (Kanto Chemical Co.) and RuCl$_3$ (Furuya Metal Co., Ltd.) was dropped into the CR/formic acid dispersion solution. The solution was then stirred for 12 h and the mixed powder of Pt-Ru and CR was collected by filtration followed by drying. Then, Pt-Ru/CR was obtained by heat-treating the resultant mixture at 300°C for 12 h in Ar. Pt-Ru/CR was prepared in the ratio of 80 to 10 by weight.

2.2 Characterization of CR and Pt-Ru/CR

The specific surface area of CR powder was determined by BET measurement equipment (BEL JAPAN INC., BELSORP-mini) with nitrogen gas as adsorptive medium. The CR pore distribution was analyzed by the BJH method. The crystalline phases of the CR and Pt-Ru/CR were identified with a powder X-ray diffractometer (XRD) (Rigaku Corp., Ultima-IV) using CuK$_\alpha$ radiation. The bonding structures of as-prepared CR and Pt-Ru/CR were characterized with Raman spectroscopy equipment (JASCO Corp., NRS-5100).

The morphology of the CR and Pt-Ru/CR samples and the dispersion state of Pt-Ru were observed with a scanning electron microscope, SEM (JEOL Ltd., JEM-2100F) and by scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) (JEOL Ltd., JEM-2100F). The atomic ratio of Pt/Ru loaded into the CR was analyzed by the STEM-EDS method. To analyze the morphology of discharge products by SEM observation, the LAB cells were opened after discharge in dry air with a dew point of less than −60°C, and air electrodes were washed with dimethyl carbonate and dried at 100°C in the dry air.

2.3 Electrochemical measurements of LAB cells with CR and Pt-Ru/CR

The air electrodes were prepared by coating a titanium mesh (100 mesh, Nilaco Corp.) with the mixture of CR or Pt-Ru/CR and PVdF (Kureha Battery Materials Japan Co.) in N-methylpyrrolidone solvent (Tomiyama Pure Chemicals Industries Ltd.), and drying the coated mesh at 100°C. The composition of an air electrode with a diameter of 5 mm was CR:PVDf = 90:10, or CR:Pt-Ru:PVdF = 80:10:10 in weight. The LAB cell (ECC-Air, EL-Cell GmbH) was constructed, incorporating the air electrode with CR or Pt-Ru/CR, an electrolyte solution (1-mol/1 lithium bis(trifluoromethanesulfonyl)amide [LiTFSI]/TEGDME (Tomiyama Pure Chemicals Industries Ltd.), a glass separator, and Li metal sheets (600-µm thickness, 17-mm diameter) (Honjo Metal Co., Ltd.). Electrochemical measurements were carried out using an automatic galvanostatic charge-discharge system (Hokuto Denko Corp., HJ1001SD8) at a constant current density of 0.1 mA/cm$^2$ in the voltage range between 2.0 and 4.2 V in dry air with a dew point of less than −60°C. These discharge/charge steps were set at the limited capacity of 1000 mAh/g. The discharge/charge capacities were normalized by the weight of the CR, Pt-Ru electrocatalyst, and PVdF in the air electrodes.

3. Results and Discussion

Figure 1 shows XRD patterns of powder samples of CR and Pt-Ru-loaded CR. Broad peaks at around 23 and 44 deg were confirmed in all the XRD patterns. These peaks correspond to typical patterns of carbon black.32 There was no significant difference between CR and Pt-Ru-loaded CR samples. These results indicated that the crystallographic structures of CR samples are similar to conventional carbon black with a low degree of graphitization. There are no peaks corresponding to Pt, Ru, or Pt-Ru alloy in any of the patterns of the Pt-Ru-loaded CR samples. These results suggest that the electrocatalyst should be nanometer-sized particles.

Figure 2 shows the pore size distributions for CR10, CR40, and CR100. The BJH plot of CR10 exhibits a sharp peak only near 10 nm, which is similar to our previous result.32 The CR40 has a sharp peak at 33 nm and a broad peak around 5 nm, which indicates that it has large pores of 35-nm diameter and small pores of less than 10 nm in the large pores. On the other hand, CR100 has a peak near 100 nm and a flat distribution of less than 15 nm. This indicates that the CR100 sample has large pore of 100 nm in diameter and small pores in the large pores. As mentioned above, the three CR samples have main pores size of approximately 10, 40, and 100 nm, even though there were broad distributions of smaller pore sizes than expected, especially for CR40 and CR100. The pore size is consistent with the following TEM observation, and these results are in good agreement with previous ones.33,34 The specific surface area and total pore volume of the CR samples obtained from the analysis by the BET method are shown in Table 1, together with the peak pore sizes indicated in Fig. 2 as references. Both the specific surface
areas and total pore volumes decreased as the pore size increased as a whole tendency, even though there were an imperfect linear relationship on the pore size of CR. Such an imperfect relationship could be due to inhomogeneous pore size distributions of CR40 and CR100. For example, CR40 and CR100 contain certain amounts of fine pores of less than 10 nm, which were smaller than main pore sizes of 40 nm and 100 nm, as shown in Fig. 2. As a result, the CR10 sample had the finest and most porous structure with a rather high surface area of about 1000 m²/g. The well-known KB support has physical properties of BET surface area: 1270 m²/g, pore volume: 1.2 cm³/g. The CR10 sample would be effective as the support material for the air electrode in nonaqueous solution.

Table 1. Physical properties of CR10, CR40 and CR100.

|          | CR10 | CR40 | CR100 |
|----------|------|------|-------|
| Peak pore size (nm)a | 11   | 35   | <15, 110 |
| BET Specific surface area (m²/g) | 993  | 693  | 550  |
| Total pore volume (cm³/g) | 2.0  | 2.6  | 2.6   |

a: See Fig. 2.

Figure 3. Raman spectrum of as-prepared CR10 and Pt-Ru/CR10.

Figure 4. SEM images of CR and Pt-Ru/CR samples. All scale bars: 100 nm.
are imperfect circles, particularly in the CR40 and CR100 samples. Smaller pores of less than 10 nm are seen in the main pores of 40 and 100 nm for the CR40 and CR100 samples, respectively. Morphological properties of the CR samples agreed with the features obtained from the BJH plots as shown in Fig. 2. Besides, as can be seen in these images, there were no significant structural changes between CR and Pt-Ru-loaded CR. The results in Figs. 2, 3 and 4 indicate that neither crystallographic nor morphological changes occurred by loading the Pt-Ru electrocatalyst into the CR support. The thickness of the carbon layer between the main pores and the particle size of Pt-Ru electrocatalyst could be difficult to confirm, because it was less than 10 nm. The mesoporous structure of the CR support would prevent particle growth and agglomeration of Pt-Ru electrocatalyst in it.

TEM observation was carried out to investigate the correlation between morphological properties of the CR sample and dispersion state of the Pt-Ru electrocatalyst on it. This information would be helpful in discussing the growth mechanism of the discharge product on the CR sample. Figure 5 shows bright-field (BF) images and high-angle annular dark-field (HAADF) images of Pt-Ru/CR10 obtained from the TEM analysis. The pores are indicated by dotted circles to understand their sizes in CR10. The CR10 sample has a highly ordered mesoporous structure with a main pore size of about 10 nm as shown in the BF images of Fig. 5(a). The thin carbon framework between the pores is found to be about 3-nm thick. The dispersion state of Pt-Ru particles on the CR10 support were confirmed by the HAADF images shown in Fig. 5(b). The brightness intensity in an HAADF image is proportional to the squared atomic number and is also affected by film density. Therefore, the bright and dark areas in Fig. 5(b) correspond to the Pt-Ru phase and CR, respectively. The Pt-Ru particles are dispersed over the whole area of the CR as seen in the left low-magnification HAADF image of Fig. 5(b). With higher magnification (right image), the particle size of Pt-Ru was estimated to be less than 5 nm, and comparatively larger numbers of Pt-Ru particles were supported on the surface of the thin carbon layer between the main pores of about 10 nm than inside the main pores. As a whole, the Pt-Ru particles were homogeneously supported over the CR sample even though their dispersion was not low as expected. Figure 6 shows BF and HAADF images of Pt-Ru/CR100. The pores are indicated by dotted circles to understand the pore sizes of CR100. The CR100 sample has highly ordered mesoporous structure with main pore size of about 100 nm as shown in the BF images. Smaller pores of less than 10 nm are also confirmed to be in the main 100-nm pores. The thin carbon framework between the pores is found to be about 2-nm thick, which is almost the same as the CR10 thickness. These results are consistent with the pore distributions shown in Fig. 2.

Figure 5. BF and HAADF images at the same observation site in TEM analysis of Pt-Ru/CR10. Left side: low magnification. Right side: high magnification.

Figure 6. BF and HAADF images at the same observation site in TEM analysis of Pt-Ru/CR100. From left to right, lower to higher magnification.
The Pt-Ru particles were homogeneously supported over the CR100 as shown in the HAADF images. The Pt-Ru particles might be easily dispersed on the CR100 compared those on the CR10 due to its larger pore size. The Pt-Ru particle size of less than 10 nm is similar to that of the CR10 as shown in the HAADF images of Fig. 5 and Fig. 6. These results suggest that Pt-Ru particle size is determined not by the physical properties of the carbon support but by the way the electrocatalyst is supported such as by the formic acid reduction method for Pt-Ru electrocatalyst.

Figure 7 shows Pt/Ru ratio obtained from STEM-EDS analysis results of Pt-Ru/CR10 and Pt-Ru/CR100 to determine the atomic ratio of Pt-Ru phase. By averaging the ratio at three point shown in Fig. 7(a), the Pt/Ru ratio for Pt-Ru/CR10 was calculated to be 10:90, which is the desired one. On the other hand, the Pt/Ru ratio for Pt-Ru/CR100 was calculated to be 6:94, which is slightly different from the desired one. However, this analysis technique usually has rather high error because elemental information about a material is collected at deeper sites. Therefore, the Pt/Ru ratio for Pt-Ru/CR100 could actually be closer to the desired ratio. As a result, the formic acid reduction method was effective for preparing highly dispersed nanometer-sized Pt-Ru particles supported on the CR.

Figures 8 and 9 show the first discharge-charge curves and the cycle properties of LAB cells incorporating the CR samples with/without Pt-Ru electrocatalyst under the condition of limited discharge/charge capacity of 1000 mAh/g and a voltage range between the 2.0 and 4.2 V, respectively. With the Pt-Ru-unloaded CR, the cells with CR10 and CR40 exhibited the first discharge capacity of 1000 mAh/g, and the cell with CR100 exhibited the capacity of about 950 mAh/g. All the cells with unloaded CR exhibited rather large irreversible capacities due to their small charge capacities. The charge capacities increased as the CR pore size decreased, even though the charge capacities were less than 1000 mAh/g. On the other hand, with the Pt-Ru-loaded CR, the discharge properties of the cell were very similar to those for the unloaded CR. The cells with Pt-Ru-loaded CR exhibited larger charge capacities and lower charge voltages than the unloaded CR samples. These results indicate that the charge properties were improved by employing the Pt-Ru electrocatalyst. As shown in Fig. 9, the cells with Pt-Ru-unloaded CR10, CR40, and CR100 show discharge capacity of only 100 mAh/g at the 5th cycle. On the other hand, the cycle properties were improved by loading Pt-Ru electrocatalyst into the CR samples. Among the CR samples, the cell with Pt-Ru/CR10 showed the most stable cycle properties, though the discharge capacity gradually decreased: 550 mAh/g at the 10th cycle. Consequently, the Pt-Ru/CR10 had the highest electrochemical performance among the CR samples tested. These properties are likely to result from the porous features of the surface areas and pore volumes of the CR samples in a similar manner to that in a previous report. The finest porosity of the CR10 support leads to improvement of discharge/charge properties as a result of the formation of a large number of reaction sites for oxygen reduction/evolution, though a gradual decrease in discharge capacities was seen in all the CR samples.

Electrochemical behavior, including degradation of discharge performance, was examined to understand the oxygen reduction reaction on the air electrode. For this purpose, SEM observation of
air electrodes at various depths of discharge was carried out to obtain information about the growth behavior of the discharge product. Here, the discharge product was identified as Li2O2 with a low degree of crystallization when the CR samples were used as the support material for air electrode of LAB cells, as reported elsewhere.32 Figure 10 shows SEM images of air electrodes with CR10 and Pt-Ru/CR10 before discharge and after discharge of 100, 500, and 1000 mAh/g. At first, the discharge products grew along the circular carbon framework of CR10, and the circles became smaller from SEM images of CR10 and Pt-Ru/CR10 at 100 mAh/g. It was impossible for the discharge product to deposit within the 10-nm pores even in the case of small discharge capacity of 100 mAh/g. At 500 mAh/g, the discharge products on CR10 and Pt-Ru/CR10 grew perpendicular to the electrode, and then the surface became wavy without effects of the circle shape of CR10. At 1000 mAh/g, the discharge product of both electrodes grew parallel to the electrode, and the products densely covered the electrode surface, which led to a decrease in the surface roughness. Comparing the two images at 1000 mAh/g for CR10 and Pt-Ru/CR10 were not confirmed in Fig. 11, even though the circles became smaller as a result of the deposition of the discharge product at the end of discharge for CR100 and Pt-Ru/CR100. At the depth of discharge, the discharge product layers have low density with a porous structure, because dense deposition did not occur on the CR10 and Pt-Ru/CR100. Therefore, the discharged air electrodes with CR100 and Pt-Ru/CR100 might have low conductivity and exhibit poor charge properties due to difficulty in decomposing the discharge product. The results in Figs. 10 and 11 suggest that the pore size of CR has a significant effect on the growth behavior of the discharge product and that CR10 with smaller pore size can maintain a porous structure and high conductivity and thus provide better cycle properties. The growth behavior shown in Figs. 10 and 11 has never been reported, and the CR pore size was confirmed to correlate with geometric properties such as the growth of discharge product. There was no clear difference in the growth mechanism with and without Pt-Ru electrocatalyst. The catalytic activities of Pt-Ru had some effects on not the geometric properties but on the electrocatalytic mechanism involved catalytic adsorption of oxygen and decomposition of the discharge product. Finally, the growth mechanism with respect to depth direction in the pore was not precisely investigated in this study. Such knowledge should lead to a better understanding of discharge/charge reaction on CR or Pt-Ru/CR. We will report the growth mechanism analyzed in three dimensions in our forthcoming paper.

From the results of this study, we can conclude that the growth mechanism of discharge product can be controlled by the geometric features of CR, such as its ordered and mesoporous structure, even
though an electrocatalyst such as Pt-Ru has to be loaded to reduce overpotentials for oxygen reduction/evolution. There was a clear decrease in discharge capacities, such as retention of about 50% at the 10th cycle for Pt-Ru/CR10, which had the highest activity in this study. It is necessary to improve the electrochemical properties by clarifying changes in geometric and electrochemical properties during discharge/charge cycles.

4. Conclusion

Highly ordered mesoporous carbons with various pore sizes were examined as support material for air electrodes in LABs. The CR with pore size of 10, 40, and 100 nm materials were prepared in a regular manner with almost homogeneous pores. Moreover, nanometer-sized Pt-Ru electrocatalyst could be supported on the CR materials with a high-dispersion state. Among the LAB cells with these CR and Pt-Ru-loaded CR samples, the cell with Pt-Ru-loaded CR10 exhibited the highest performance of the first discharge capacity of 1000 mAh/g and capacity retention of about 50% at the 10th cycle. Furthermore, the growth mechanism of the discharge product on the air electrode had a clear effect on the morphological features of the CR. For example, the discharge products were densely deposited at the 10th cycle. It is necessary to improve the electrochemical properties for oxygen reduction though an electrocatalyst such as Pt-Ru has to be loaded to reduce overpotentials for oxygen reduction/evolution.

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