Enhancing Effect of Carbon Surface in the Non-Aqueous Li-O₂ Battery Cathode

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ABSTRACT

Influence of carbon surface on the discharge voltage of non-aqueous Li-O₂ battery was investigated. The discharge voltage definitely decreased with the graphitization of as-prepared carbon in spite of almost the same chemical information of carbon surface. Graphitization of carbon led to the dramatic morphological change from granular-type to angulated-type, and as a consequence, the number of defect part toward basal part was decreased. The defect parts of the carbon surface were suggested to promote the Li⁺ containing oxygen reduction reaction (Li⁺-ORR) related with the discharge voltage. Cyclic voltammetry indicated that the ORR potential in the Li⁺ containing media was positively shifted on the edge oriented carbon model plane, compared with those of the graphitized ones. It was, thus, concluded that the carbon surface including defects activated the Li⁺-ORR process on a cathode, resulting in the increase of discharge voltage.

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1. Introduction

Li-air battery is a highly attractive rechargeable cell type for vehicle and stationary applications in terms of high gravimetric and volumetric energy densities beyond lithium ion batteries. The Li-air rechargeable batteries are characterized by the following one-way cathode reactions. The discharge reaction is consisted of a reduction of oxygen gas through an electrolyte on a catalyzed carbon and the subsequent chemical reaction of its reductant with lithium ion. The charge reaction is a direct decomposition of lithium compounds such as Li₂O_x (x = 1, 2) and LiOH to produce oxygen gas. To date, there have been many reports about the cathode reaction mechanisms of the non-aqueous Li-air batteries.^{1–16} Although many carbonate based electrolytes were widely used, it was concluded that lithium alkylcarbonates (RCOOLi, R = alkyl group) as well as Li₂CO₃ were deposited on a discharged cathode due to a decomposition of the electrolyte solvent by O₂ radical species (one electron reductants) as an intermediate. As a result, a high charging voltage over 4 V was needed to decompose the carbonate species and then CO₂ gas was mostly generated during charging.^{4–8} On the other hand, in the ether or ionic liquid based systems, it was observed that Li₂O₂ was mainly detected as a discharge product and then O₂ gas mostly evolved during charging.^{9–14} Selection of electrolyte solvents with high radical stability was suggested to produce the expected reversible reaction on a cathode with a reasonable charge voltage.^{13–15} Although a possibility of a side reaction of Li₂O₂ with carbon during charging has been very recently reported,¹⁶ it is obvious that the electrolyte solvent is a significant key to realize the desirable reaction.

Li-air battery performances greatly depend on the activities of carbon and catalyst for O₂ reduction, Li₂O₂ storage, and Li₂O₂ decomposition. Among them, the O₂ reduction reaction (ORR) process is very important to increase a discharge voltage and to further improve an energy efficiency of the battery. Catalyst has

been loaded on a carbon to enhance the ORR activity.¹² Very recently, Shao-Horn et al. have pointed out that the ORR activity associated with Li⁺ in an ether based media can be explained in term of the O₂ adsorption energy onto a support.¹⁷ Palladium was reported to be a good candidate to enhance the discharge voltage in both model and practical electrodes. On the other hand, it is commonly known in the fuel cell fields that carbon itself has the ORR capability. We have very recently reported that the O₂ molecule was strongly adsorbed at the defect part on a carbon basal plane, and then the magnitude of its adsorption energy was much higher than that of the basal part, which was performed by first principles calculations.¹⁸ As a result, we discovered that the carbon defect was also a good candidate to improve the ORR activity with Li⁺, resulting in an increase of discharge voltage.

In this paper, different types of carbon surfaces were tested in the ionic liquid based Li-air cell, and then the effect of the carbon surface on the initial discharge voltage was examined. First, the increase of discharge voltage was confirmed by using practical carbon electrodes with different surface properties. Then, the cyclic voltammetry was carried out using model electrodes in the electrolyte media with and without Li salt. The voltage increase will be explained from viewpoints of the edge structures of carbon as well as the ORR behaviors.

2. Experimental

2.1 Detail investigation of carbon surface

Carbon nanospheres (CNS, Tokai Carbon) prepared under various heat-treatment conditions were used for the following electrochemical testing of practical electrodes. Their edge structure was carefully observed by field emission transmission electron microscope (FE-TEM, FEI, TECNAI G²). X-ray diffraction, Raman spectroscopy and nitrogen absorption measurement for the CNS powders were carried out to obtain the physical properties of

Figure 1. TEM images of the CNS powders prepared by the following condition; (a–b) as-prepared, (c–d) heat treatment at 1100°C, (e–f) heat treatment at 2600°C.

graphitization degree (d_{002}), relative intensity of defect part toward basal part (I_D/I_G) and porosity, respectively. Detail analytical methods were described in our recent report.¹⁸ Furthermore, all the chemical information of the carbon surface was quantitatively estimated based on the rule of JIS1417K. The CNS powders were fully soaked in the boiled water for a fixed time, and then their supernatant solutions were evaluated by a pH meter.

2.2 Electrochemical testing of practical electrodes

Our custom-made Li–O₂ cells were fabricated as described in the previous papers.^{4,13,14,18} Air cathode sheets were prepared by mixing and pressing above-mentioned CNS powders with PTFE binder. Battery grade *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)amide (PP13TFSA, Kanto Chemical) and lithium bis(trifluoromethanesulfonyl)amide (LiTFSA, Kishida Chemical) were selected as an electrolyte solvent and salt. The concentration of the electrolyte was 0.32 mol/kg. H₂O content in the electrolyte solution kept less than 50 ppm by Karl-Fischer measurement. The cells were just discharged at the constant current density of 0.02 mA/cm² after holding for 3 h at 60°C.

2.3 Electrochemical testing of model electrodes

Electrochemical reversibility of O₂ radical species on various carbon surfaces was examined by cyclic voltammetry with a potentio/galvanostat (Solartron, 12608W) system as described in our paper.¹³ Three kinds of working electrodes made by BAS Inc. were used; one was the commonly used glassy carbon electrode, while the others were the pyrolytic graphite electrodes with edge and

Figure 2. First discharge curves of the Li–O₂ cells consisting of various CNS powders. Lines (a), (b), and (c) denote the data of as-prepared CNS, heat-treated CNS at 1100°C, and heat-treated CNS at 2600°C, respectively. Current density was 0.02 mA/cm² and the applied temperature was 60°C.

basal oriented planes. Here, the edge oriented plane is distinguished from basal oriented plane by controlling the direction of carbon end plane for the exposed electrode surface. Nickel ribbon was used as a counter electrode. Reference electrode consisted of a silver wire immersed in the acetonitrile solution with both 0.1 M tetrabutylammonium perchlorate and 0.01 M silver nitrate, which was separated from bulk solution with porous vycor glass. Potential of Ag/Ag⁺ as the reference electrode in the pure PP13TFSA media was +0.05 V vs. ferrocene/ferrocium. Pure PP13TFSA ionic liquid and 0.32 mol/kg LiTFSA-PP13TFSA mixed solution were selected as an electrolyte. Oxygen gas (99.9% in purity) was dissolved in the electrolyte by bubbling through a glass ball filter for 30 min under 1 atm at room temperature. Scan rate was 100 mV/s and the applied temperature was 25°C.

3. Results and Discussion

3.1 Physical properties of CNS powders

Figure 1 shows the TEM images of three kinds of CNS powders. As-prepared CNS powder is shown in the images (a–b), while the heat-treated CNS powders at 1100 and 2600°C are described in the images (c–d) and (e–f), respectively. All samples had a diameter of around 100–200 nm and were strung together like beads. Higher magnification images as in (b), (d), and (f) represented the edge structure of carbon led to the dramatic morphological change from granular-type to angulated-type. The samples (b) and (d) exhibited a granular morphology in which many distorted graphene layers were stacked. On the other hand, a well-developed and angulated texture specific to a graphitized carbon was observed in the sample (f) because the heat treatment of 2600°C promoted the graphitization of as-prepared CNS powder. The I_D/I_G ratios and pH values of the CNS powders drawn in the pictures (a), (c), and (e) will be discussed later.

3.2 Electrochemical behaviors of practical electrodes with different carbon surface

Figure 2 shows the first discharge curves of the Li–O₂ cells consisting of various CNS powders. Lines (a), (b), and (c) denote the data of the as-prepared CNS, heat-treated CNS at 1100°C, and heat-treated CNS at 2600°C, respectively. Discharge capacity was normalized by the total weight of cathode. Almost the same discharge capacities of about 40 mAh/g were obtained in three cells,

whereas the discharge voltages were clearly different. The voltages increased in the order of heat-treated CNS at 2600°C, heat-treated CNS at 1100°C, and as-prepared CNS. The cell (c) including the heat-treated CNS at 2600°C showed a steep voltage drop at the initial discharge. As can be seen in the TEM images, the surface structures of the CNS powders will affect the discharge voltage. Here, the difference in the cell performances was quantitatively discussed using the physical properties of the CNS powders. According to our previous reports, the discharge capacity strongly depended on the specific surface area and pore volume of original carbon powder even in the ionic liquid system.¹⁸ In this experiment, three kinds of CNS powders had almost the same BET surface area of around 15 m²/g and pore volume of about 0.07 cc/g by BJH analyses, which led to almost the same discharge capacities. From structural points of view, the as-prepared CNS and heat-treated CNS at 1100°C possessed almost the same d_{002} values of 3.56 angstrom, while their I_D/I_G values slightly different. The I_D/I_G values of the as-prepared CNS and heat-treated CNS at 1100°C were around 0.858 and 0.823, respectively. By heat treatment of as-prepared CNS at 1100°C, the small structural change corresponding to the slight decrease of the I_D/I_G value will occur and the surface of heat-treated CNS will be reordered. As a consequence, higher disorder of as-prepared CNS is considered to produce higher discharge voltage as shown in Fig. 2(a). On the contrary, the heat-treated CNS at 2600°C was very different in property. Comparably low values of 3.40 angstrom in d_{002} and 0.17 in I_D/I_G were obtained in the heat-treated CNS at 2600°C, which was similar to the graphite with a well-developed structure. In our preliminary study, it was observed that the graphitized carbon mostly brought about the steep drop at the beginning of discharge and the lowest voltage plateau as shown in Fig. 2(c). Thus, the graphitized structure of the heat-treated CNS at 2600°C is suggested to cause the lowest discharge voltage of all the samples. Furthermore, from chemical viewpoint, it was found that all of the CNS powders had almost the same pH values of around 6.5, indicating that all the carbon surfaces were composed of similar chemical compositions. This means that the discharge voltage demonstrated in this experiment is not enhanced by the surface functional group of carbon. It was, therefore, summarized that the surface edge structure of the CNS powder remarkably influenced the discharge voltage of Li-O₂ cell.

3.3 Electrochemical behaviors of model electrodes with different carbon surface

Combined with the O₂ reduction process, the phenomena of voltage increase was continuously discussed. Figure 3 shows the cyclic voltammograms of (a) pure PP13TFSA system and (b) PP13TFSA-LiTFSA mixed system with a concentration of 0.32 mol/kg. Lines (a-1) and (b-1) represent the voltammograms with glassy carbon electrode. Results of pyrolytic graphite electrodes with edge and basal oriented planes are drawn in the thick lines (a-2, b-2) and thin lines (a-3, b-3), respectively. In the pure PP13TFSA system (a), a pair of cathodic and anodic peaks was observed at around -1.2 V, which is corresponding to the O₂ redox reaction via one electron reaction process.^{12,13,17,19} Although the diffusion limiting process below -1.5 V was a little different, the O₂ reduction reaction on three kinds of electrodes was found to be started at almost the same potential. Also, the anodic behaviors during O₂ radical oxidation reaction were almost the same, although the anodic current above 1.0 V caused by decomposition of electrolyte at the carbon edges was slightly obtained in the edge oriented pyrolytic electrode. It was, thus, found that the carbon surface did not notably affect the O₂ redox process in the pure PP13TFSA system. On the other hand, a clear difference was confirmed in the PP13TFSA-LiTFSA mixed system (b). In all the carbon surfaces, a cathodic current peak was obtained at around -1.2 V and then two anodic peaks were observed above 0 V. The

Figure 3. Cyclic voltammograms of O₂ redox species in the (a) pure PP13TFSA system and (b) PP13TFSA-LiTFSA mixed system with a concentration of 0.32 mol/kg. Lines (a-1) and (b-1) represent the voltammograms with glassy carbon electrode. Results of pyrolytic graphite electrodes with edge and basal oriented planes were drawn in the thick lines (a-2, b-2) and thin lines (a-3, b-3), respectively. Scan rate was 100 mV/s and the applied temperature was 25°C.

cathodic peak is attributed to the O₂ reduction reaction associated with lithium ion, and the anodic peaks are derived from the decomposition reaction of its cathode deposits. Although the detailed assignment of two anodic peaks is not clear yet, three hypotheses as follows are considered. First is the decomposition due to two cathodic products such as Li₂O₂ and Li₂O formed by a multiple O₂ reduction process. Second is the two step decomposition of Li₂O₂ via LiO₂ intermediate. Last is the decomposition due to two cathodic species that is solid product and dissolved species. Compared with the ORR behaviors on three kinds of cathode surfaces, the starting potential of cathodic current was positively shifted only at the edge oriented pyrolytic electrode as drawn in Fig. 3(b-2). A largest cathodic current was observed at the edge oriented electrode, and furthermore, the basal oriented electrode exhibited higher current than the glassy carbon electrode. Since the basal oriented electrode possesses some terraces of basal plane and their defect parts and boundaries, a comparably high current is presumed to be observed at the basal oriented plane rather than smoothly-polished glassy carbon electrode. Giorgio et al. have examined the redox reaction of O₂ radical species in an ionic liquid with and without Li⁺ supporting salt using the typical glassy carbon working electrode.²⁰ It was observed that the addition of Li⁺ in the media caused a notable distortion of voltammogram derived from O₂

radical redox reaction, making the reaction processes electrochemically irreversible. Compared with the published results, our reversibility of the redox reaction in the Li^+ containing media seemed to be high. The difference would be derived from the purity and kind of ionic liquids. According to our knowledge, it was found that comparably reversible redox reactions occurred in the Li^+ containing system, and then the difference of carbon surface structure in the redox reaction, in particular ORR process, was clearly distinguished. Moreover, in our recent report, it was confirmed by first principles calculations that the O_2 molecule was strongly adsorbed on the defect part of carbon plane rather than on the basal part.¹⁸ Such difference is suggested to induce the positive potential shift during the ORR process. It was, therefore, concluded that in the Li^+ containing system, the ORR process was activated at the carbon surface including defects and terraces, resulting in the increase of discharge voltage as shown in the Fig. 2.

4. Conclusions

We demonstrated that the discharge voltage of ionic liquid based $\text{Li}-\text{O}_2$ battery was enhanced by the surface edge structure of carbon used in a cathode, which is closely related with the relative ratio of defect and basal parts, and was not improved by the porosity, graphitization degree, and chemical information of carbon. On the defect parts of the carbon surface, O_2 molecule were strongly adsorbed, and then the Li^+ containing oxygen reduction reaction (Li^+ -ORR) was promoted, resulting in an increase of discharge voltage. The increase of discharge voltage will be sometimes linked with the chemical information of carbon powder, in particular surface functional groups, although their difference was not observed in this experiment. On the other hand, the surface functional group might induce the chemical reaction with a discharge product, Li_2O_2 . Detailed investigation of carbon surfaces and structures which will influence the battery performances will have to be performed.

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