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Discharge Characteristic of Fluorinated Graphene-like Graphite as a Cathode of Lithium Primary Battery

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ABSTRACT

Graphene-like graphite prepared by heating graphite oxide under vacuum at 800 °C was fluorinated by elemental fluorine in the presence of HF at room temperature. The interlayer spacing of the resulting material was 0.639 nm and it showed C_xF type characteristics. The fluorine content of it (x = 1.7) was higher than that obtained from natural graphite (x = 2.3). The discharge capacity of it as a cathode of lithium primary battery reached 940 mAh g⁻¹ at a low current density, which was 50% larger than the theoretical capacity based on the 100% discharge of fluorine.

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Keywords : Lithium Primary Battery, Graphene-like Graphite, Fluorination

1. Introduction

Graphite fluoride, $(CF)_n$ (or CF_r) which is prepared by the reaction of graphite with elemental fluorine at high temperatures (~600 °C) shows a high energy density as the cathode of lithium primary battery. Matsushita Electric Co. (The company name has been changed to Panasonic Corporation) firstly commercialized Li/ $(CF)_n$ batteries in 1975. The theoretical capacity of this material is 865 mAh g⁻¹, according to the discharge reaction of $(CF)_n + nLi^+ +$ $ne^- \rightarrow nC + nLiF.^{1,2}$ Recent studies on such fluorinated carbon materials focus on improving rate performance or increasing the energy density as reviewed in the literature.³ For these purposes, the reduction of particle size, the use of nanocarbon precursors and fluorination at lower temperatures, etc. have been employed.^{4–15} Early studies by Nakajima et al. revealed that smaller crystalline size of $(CF)_n$ along the *c*-axis and higher surface area can decrease the overpotential of the discharge reaction. By using the thermal decomposition products of covalent-type graphite intercalation compounds such as oxidized graphite or $(C_2F)_n$, they have succeeded to reduce overpotential up to 0.6 V.4,5 Ball milling of graphite fluorides can improve their rate performance.^{6,7} Surface modification such as carbon coating⁸ or addition of SiO₂⁹ also improved the utilization of active material and rate performance. The use of nanocarbons such as carbon nanotubes, graphene, etc. as precursors can increase the surface area and accordingly improves the rate performance of the resulting $(CF)_n$.^{10–15}

On the other hand, Rangasamy et al. reported that it is possible to enhance the theoretical limit of Li-(CF)_n batteries to use LiP_3S_4 as a bifunctional solid electrolyte.¹⁶ They succeeded to increase the capacity to 1200 mAh g⁻¹ which is 38% larger than the theoretical one and concluded that LiF formed according to the above discharge reaction catalyzed an electrochemical activity of LiP_3S_4 that offered additional capacity around 2 V. Ahmad et al. also reported up to 40% of extra discharge capacity for carbon nanodiscs fluorinated by elemental fluorine or TbF₄, when appropriate electrolyte solution was used.¹⁷ They have shown that it is related to the LiF covering the surface of carbon nanodiscs regenerated as the result of discharge of $(CF)_n$ and the formation of Li_2F^+ , based on the ⁷Li and ¹⁹F NMR data. They suggested that the morphology, shape and stacking of graphene layers are important to achieve such an extra capacity. More recently, they have shown that carbon nanotubes fluorinated at lower temperatures (~350 °C) show a high energy density of 2565 Wh kg⁻¹, though the fluorine content was lower (F/C = 0.37) than the other cases.

The other ways to increase the energy density is to increase the discharge potential.¹⁸ It is possible to obtain fluorine-intercalated graphite which is usually denoted as C_xF and obtained by the reaction of graphitic materials with elemental fluorine below 100 °C in the presence of catalysts or the other strong fluorinating reagents.^{19–22} The discharge voltage of this material (~3.2 V vs. Li⁺/Li) is higher than that of (CF)_n (~2.4 V vs. Li⁺/Li) because of the lower C-F binding energy. By using IF₅ as one of the fluorinating reagents, high discharge voltage and rate performance with a discharge capacity of 650 mAh g⁻¹ were obtained.^{19,20} Nakajima et al., have also succeeded to obtain C_xF with *x* reaching 1.2 by using metal fluoride catalysts such as KAgF₄.^{21,22} The obtained fluorides delivered a high discharge capacity of 600 mAh g⁻¹. In these cases, the energy density of the fluorinated carbons at lower temperatures reached 2000 Wh kg⁻¹.

These previous studies indicate that one of the ways to increase the energy density of fluorinated carbon materials would be using nanocarbons as a precursor and to fluorinate them at lower temperatures. In such a case, both extra-capacity and increase in the discharge voltage are expected. We have recently found that carbon materials obtained by the thermal decomposition of graphite oxide possess a unique structure and, show high capacity and rate performance as an anode of lithium ion battery.²³ Since the morphology and layered structure of the resulting materials were similar to those of graphite but the electrochemical behaviors are rather close to those of graphene, we call these materials as graphene-like graphite (hereafter abbreviated as GLG). The interlayer spacing, morphology and stacking regularity of carbon

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layers of GLG are similar to those of graphite, however, it contains oxygen atoms and nanopores with the size of 1–5 nm within the graphene layers. The structural model of GLG is shown in Fig. S1. Therefore, it shows high capacity and rate performance as those of graphene, though the coulombic efficiency during the 1st cycle is relatively higher because of its lower surface area. In the course of these studies, we also found that the layer separation energy of GLG was smaller than that of graphite,²⁴ which means that its reactivity to form intercalation compounds could be different from that of graphite even in the case of the intercalation of anions. It is expected that highly fluorinated materials are obtained at lower temperatures and they may show an extra-capacity when used as the cathode of lithium battery. Therefore, in this study, we have fluorinated GLG at room temperature and the cathode properties of the resulting material in lithium primary battery were investigated.

2. Experimental

Natural graphite powder (Z-5F, Ito graphite, average particle size, $5 \,\mu$ m) was oxidized in fuming HNO₃ by KClO₃, based on the Brodie's method and graphite oxide was obtained. It was heated at 800 °C under vacuum for 5 h. The temperature increasing rate was 0.1 °C min⁻¹ between 170 and 250 °C in order to avoid exfoliation of graphite oxide, otherwise 1 °C min⁻¹. The obtained GLG was reacted with F₂ gas in the presence of liquid HF for 80 h at room temperature. During reaction, the pressure was kept at 2 atm by adding appropriate amounts of F₂ gas intermittently. For comparison, a C_xF sample was also prepared from graphite powder (Z-5F) by fluorinating it under the same condition. The obtained samples were analyzed by SEM (JEOL, JSM-6010 PLUS/LV), X-ray diffraction (Rint-2100, Rigaku, CuK α radiation), FT-IR (KBr method, Nicolet iS50, Thermo Fisher Scientific) and XPS (PHI-5000, UlvacPhi) measurements.

The electrochemical performance of the fluorinated GLG and C_xF samples as a cathode of lithium primary battery was investigated in 1 mol dm⁻³ LiPF₆-EC+DMC (1:1) (Tomiyama Pure Chemical Industry, LTD) using Li metal as reference and counter electrodes. Acetylene black (AB) and PTFE as conducting additive and binder, respectively, were added to prepare working electrodes with a weight ratio of fluorinated carbon:AB:PTFE of 10:10:2. The discharge measurements were performed by a constant current method at 5.1–550 mA g⁻¹ at room temperature.

3. Results and Discussion

The composition of the resulting yellowish-brown material was determined based on the elemental analysis of carbon (48 wt%) and fluorine (44 wt%), and C1.7FO0.22 was obtained. Here, oxygen content was calculated by subtracting those of carbon and fluorine from 100 wt%. The theoretical capacity of it is calculated to be 624 and $899 \,\mathrm{mAh}\,\mathrm{g}^{-1}$, when only fluorine and both fluorine and oxygen are available for discharge reaction, respectively. SEM observation of fluorinated GLG indicated that its morphology is almost identical to that of the pristine GLG as shown in Fig. S2. On the other hand, the composition of the black C_rF sample prepared graphite (Z-5F) was C2.3F. The larger fluorine content in fluorinated GLG indicates the higher reactivity of it. Figure 1 shows the X-ray diffraction pattern of GLG after fluorination, together with that of C2.3F. In the case of C_{2.3}F, the diffraction peak observed at 26.5° (d = 0.336 nm) for the pristine graphite disappeared and a new peak was observed at 15.1° (d = 0.587 nm). On the other hand, the diffraction peak observed at 26.1° (d = 0.341 nm) for the pristine GLG disappeared and a new peak was observed at $2\theta = 13.9^{\circ}$ (d = 0.639 nm) after fluorination as expected from a higher fluorine content. This interlayer spacing was almost the same or slightly smaller than those reported for C_xF samples with similar fluorine contents which were



Figure 1. X-ray diffraction patterns of fluorinated GLG (red) and $C_{2,3}F$ (black).



Figure 2. IR spectra of fluorinated GLG (red) and C_{2.3}F (black).

prepared using K₂NiF₆ or KAgF₄ (d = 0.63-0.68 nm).²¹ The 100 peak of fluorinated GLG was observed at $2\theta = 42.6^{\circ}$ (d = 0.212 nm) which was slightly higher than that of C_{2.3}F ($2\theta = 42.0^{\circ}$ (d = 0.215 nm)), however, the relative intensity of this peak versus 001 peak was much smaller than that of (CF)_n reported previously.

Figure 2 shows the IR spectrum of fluorinated GLG, together with that of $C_{2.3}F$. The absorption peak due to C-F stretching vibration appeared at 1144 cm⁻¹, which was higher than that of $C_{2.3}F$ (1121 cm⁻¹). In addition, absorption peaks at 1256 and 1520–1540 cm⁻¹, ascribed to C=C bonds²⁵ and clearly observed for $C_{2.3}F$, were very weak. This means that most of double bonds of carbon atoms are cleaved to bound to fluorine atoms as expected from high fluorine content of it. In addition, the absence of the peak at 1256 cm⁻¹ which is observed for C_xF containing HF molecules indicates that fluorinated GLG did not contain them.

Figure 3 shows the XPS data of pristine GLG and fluorinated GLG. Two peaks at 286.2 and 288.8 eV with a shoulder at 290.2 eV were observed for fluorinated GLG in C1s region. These two peaks are ascribed to the carbon atoms unbound and bound to fluorine atoms, which were commonly observed for $C_{2.8}F^{26}$. The lower binding energy than that observed for $(CF)_n$ is due to the weakening of covalency by hyperconjugation between the C-F group and the adjacent sp² carbons in nonsaturated C_xF.²⁵ This type of C-F bond was previously called semi-ionic bond. The shoulder at 290.2 eV suggests that fluorinated GLG partly contains a covalent C-F bond like $(CF)_n$. Only one peak at 687.4 eV which was almost the same as that for C_xF was observed in F1s region. This binding energy is also much lower than that observed for $(CF)_n$ (690 eV). The characteristic feature of fluorinated GLG was that the peak at 534.4 eV was strongly observed in O1s region. We have already reported that GLG contains C-O-C within its carbon layers.²³ This result indicates



Figure 3. XPS of fluorinated GLG (red), together with that of pristine GLG (black).



Figure 4. Discharge curves of fluorinated GLG at various current densities.

that oxygen atoms remains in the fluorinated GLG. The slight shift from the peak at 533.4 eV observed for pristine GLG could be due to the introduction of C-F bonding adjacent to the C-O-C. These results indicate that fluorination of GLG by elemental fluorine and HF at room temperature gives a highly fluorinated C_x F-type material without adding any additional catalysts such as inorganic metal fluorides.

Figure 4 shows the discharge curves of fluorinated GLG in a lithium primary battery at various current densities. With decreasing the current density, the cell voltage and capacity increased to 3.2 V and 610 mAh g^{-1} at 110 mA g^{-1} , respectively, as reported for C_xF samples in the previous literatures.^{19–22} At a lower current density of 5.1 mA g^{-1} , the cell voltage became higher and interestingly another plateau at 2.7 V appeared. The capacity increased to 940 mAh g⁻¹ and slightly larger than the value estimated by assuming that oxygen is also available for discharge reaction (899 mAh g⁻¹). The energy density of fluorinated GLG reached 2581 Wh kg⁻¹. It was much higher than those reported for typical (CF)_n⁶ and almost comparable



Figure 5. Discharge curve of $C_{2,3}F$ (black) at 5.1 mA/g, together with that of fluorinated GLG (red) shown in Fig. 4.

to that reported for carbon nanotube fluorinated at higher temperatures. $^{\rm 5}$

Figure 5 shows the discharge curve of $C_{2.3}F$ at 5.1 mA g⁻¹, together with that of fluorinated GLG shown in Fig. 4 for comparison. A plateau was observed at 3.3 V for C_{2.3}F, which was almost the same as that observed for fluorinated GLG. However, the discharge capacity was only 531 mAh g^{-1} . This value was still smaller than the calculated one (574 mAh g^{-1}) and no additional capacity was achieved as reported in the previously studies.^{21,22} At the plateau of 3.3 V, a similar discharge reaction to that of $(CF)_n$ occurs, namely, $C_xF + Li^+ + e^- \rightarrow xC + LiF$. Therefore, it is suggested that at the plateau of 2.7 V or lower cell voltages, oxygen was also discharged and/or the resulting carbon/LiF composite can accept additional lithium ions as was the case of fluorinated carbon nanodisc.¹⁷ Since no capacity was observed at such cell voltage regions for the pristine GLG when it was used as an anode of lithium ion battery,^{23,24} the introduction of fluorine atoms into it could result in the activation of oxygen. In the latter case, since the particle size of fluorinated GLG was much larger than that of carbon nanodisc

as shown in Fig. S2, nanopores in GLG and/or oxygen atoms introduced within GLG layers might be responsible for the additional capacity. Further investigation of the discharge products should be needed in order to clarify the origin of the additional capacity, which will be reported in the near future.

In conclusion, fluorination of GLG by elemental fluorine in the presence of liquid HF at room temperature provided C_x F-type material with a very high fluorine content of x = 1.7. The discharge capacity of fluorinated GLG reached 940 mAh g⁻¹ at a low current density which was 50% higher than the theoretical value based on the 100% discharge of fluorine, while this additional discharge capacity was not observed for $C_{2.3}$ F obtained from graphite powder.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-64068.

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