Electrochemical oxidation of graphite in aqueous hydrofluoric acid solution at high current densities

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ABSTRACT

Electrochemical oxidation of graphite was performed at high current densities in 47% HF aqueous solution. Cyclic voltammetry indicated that covalent C—F bonding formed above 2.4 V vs Pb/PbF$_2$. The sample obtained at higher current densities than 200 mA cm^{-2} was stage 1 type material with an interlayer spacing of 0.55 nm and it contained a considerable amount of oxygen, together with the covalently bonded fluorine. The discharge profile of this sample as a cathode of lithium primary battery was similar to that of C$_{2.5}$F prepared under F$_2$ gas atmosphere and the capacity reached 550 mAh g^{-1}. This strongly indicated that not only fluorine but also oxygen in this sample was utilized.

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1. Introduction

Graphite intercalation compounds of fluorine (hereafter abbreviated as C$_x$F; x shows the carbon/fluorine ratio) are attracting much attention because of their unique carbon—fluorine bonding, c-axis structure and electrochemical properties, especially for the cathode materials of lithium primary battery with high voltage and energy density [1–4]. In C$_x$F, fluorine atoms are ionically bonded to carbon at lower fluorine contents, however, they are covalently bonded when the fluorine contents increase. Interestingly, when the XPS measurement is performed for these materials, the peak position of the binding energy of F1s electron in C$_x$F with larger fluorine contents locate between those observed for C$_x$F with lower fluorine contents and graphite fluorides. This C—F bond also provides shifted a ^{19}F NMR peak [5]. Therefore, it is usually called as "semi-ionic" or "semi-covalent" C—F bonding, though the bond length of it has been estimated as 0.14 nm [6] which is the same as that of covalent one. The slightly lower C—F bond order in C$_x$F than those in poly(carbon monofluoride) ((CF)$_n$) and poly(dicarbon monofluoride) ((C$_2$F)$_n$) is explained by the hyperconjugation involving the C—C bonds on the carbon sheets and C—F bond [6] and this seems responsible for the change in the F1s binding energy. Reflecting this change in the nature of C—F

bonding depending on the fluorine contents various c-axis repeat distances have been observed.

Concerning the cathode of lithium primary battery, covalent type (CF)$_n$ (or it is also denoted as CF$_x$) has been commercialized, together with manganese oxide, however, it suffers from the relatively low discharge voltage and potential drop at the beginning of discharge. Recently it has been reported that the low discharge voltage can be somewhat improved by increasing the surface area of the sample by ball milling but it is still 2.5 V [7]. The discharge voltage of C$_x$F is higher than graphite fluorides exceeding 3 V and no potential drop is observed probably because of its higher conductivity and the nature of C—F bonding. However, the capacity of it still lower than that of graphite fluoride, therefore, preparation of C$_x$F with higher fluorine content has been extensively studied. In order to obtain C$_x$F with high fluorine content, solid-gas reaction using fluorine gas in the presence of catalysts such as solid metal fluorides, gaseous halogen fluorides, etc. has been usually employed [8–20]. Among them by using KAgF$_4$ under high F$_2$ gas pressure in anhydrous HF solution, C$_x$F with the minimum x value (highest fluorine content) of 1.2 has been prepared [18]. The discharge capacity of C$_x$F samples can reached more than 600 mAh g^{-1} with the discharge voltage higher than 3.0 V [14,16,18,20]. Fluorine-intercalated graphite can be also prepared by the electrochemical oxidation of it in aqueous hydrofluoric acid solutions [21]. However, it was difficult to obtain C$_x$F with high fluorine content was not obtained because of the narrow electrochemical window of these solutions. Before reaching the potential to obtain highly oxidized graphite, oxygen

evolution occur as the result of oxidation of water, which prevented C_xF with high fluorine contents. Therefore, in our previous paper, we have electrochemically oxidized graphite in 47% aqueous solution of HF at high current densities in order to reach the potential needed to oxidize graphite at higher levels by increasing the overpotential for oxygen evolution reaction [22]. Highly fluorinated stage 1 "bi-intercalation type" [23], $C_{2.8}F$ with an interlayer spacing of 1.15 nm was obtained when graphite was oxidized at 100 mA cm^{-2}. Moreover, a new covalent type stage 2C_xF was also successfully synthesized.

In this study, graphite was oxidized at higher current densities than 100 mA cm^{-2} in order to obtain more highly oxidized C_xF samples. The resulting materials were characterized in detail and the electrochemical performance of them was investigated.

2. Experimental

Graphite sheet electrode (PERMA-FOIL; PF type, Toyo Tanso Co., Ltd., $d(0\,0\,2) = 0.3356$ nm) was used as a working electrode. As a reference electrode, the Pb/PbF$_2$ couple was prepared by immersing Pb wire in 47% HF aqueous solution overnight. Pt plate was used as a counter electrode. Cyclic voltammetry was performed at a potential scan rate of 0.5 mV s^{-1} from OCV to various upper limit potentials of 2.2, 2.4 and 3.0 V vs Pb/PbF$_2$ (-0.344 V vs NHE). Constant current oxidation was performed at current densities of 5–800 mA cm^{-2}. The resulting materials are analyzed by X-ray diffraction (Rint-2100, CuKα) and X-ray photoelectron spectroscopy (Ulvac Phi-5000 MgKα) measurements. NMR measurements were performed using a BRUCKER AVANCE spectrometer, with working frequencies for ^{13}C, ^{1}H, and ^{19}F of 73.4, 300.1 and 282.2 MHz, respectively. A magic angle spinning (MAS) probe (Bruker) operating with a 4 mm rotor was used. For MAS spectra, a simple sequence was performed with a single $\pi/2$ pulse length of 3.5, 4 and 3.5 μs for ^{1}H, ^{19}F and ^{13}C, respectively. ^{1}H and ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS). ^{19}F chemical shifts were referenced with respect to CFCl$_3$.

Discharge characteristics of C_xF samples were investigated by constant current discharge at a current density of 20 mA g^{-1} in 1 M LiClO$_4$–EC/DMC electrolyte solution. The active materials were mixed with acetylene black as a conducting additive and PVDF as a binder at a weight ratio of 8:1:1. This mixture was sandwiched by Ni mesh and the pressed at 200 kg cm^{-2} for 5 min. As a counter electrode, Li metal was used.

Stage 1 type C_xF sample with $x = 2.5$ (based on the weight change during reaction) was prepared by the reaction of graphite powder with the mixture of HF (1 atm) and F$_2$ (1 atm) gases at room temperature. After 24 h of reaction, F$_2$ gas was added to compensate the consumed amount of it and then the reaction was continued for 8 h. Finally, the reactor was evacuated at room temperature for 1 h and then at 100 °C for 12 h. Graphite oxide (hereafter GO) was also synthesized by the method based on the Brodie's one according to our previous study [24]. These were used as references.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram of graphite sheet in 47% HF aqueous solution at the scan rate of 0.5 mV/s. The curve measured with the upper limit of 3.0 V vs Pb/PbF$_2$ was almost the same as that reported in our previous study [22], considering that the difference of the potentials of reference electrodes, Pb/PbF$_2$ and Cu/CuF$_2$ couples. Three broad oxidation peaks at around 2.0, 2.38 and 2.6 V vs Pb/PbF$_2$ were observed. On the other hand, only one reduction peak at 1.3 V vs Pb/PbF$_2$ was observed, indicating that covalent C—F bonding formed. When the upper limit potential was 2.2 V vs Pb/PbF$_2$, a reduction peak at 1.8 V vs
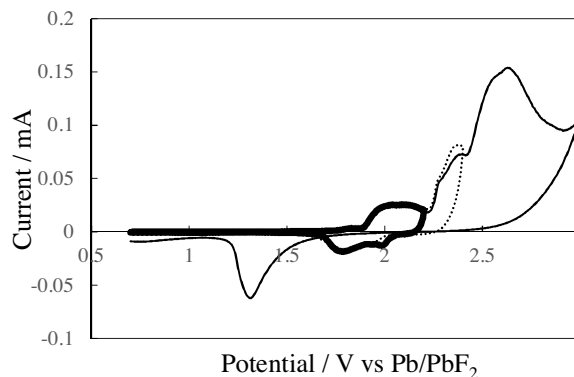

Fig. 1. Cyclic voltammograms of graphite at a scan rate of 0.5 mV s^{-1} with various upper limit potentials of 2.2 (thick), 2.4 (broken) and 3.0 (thin) V.

Pb/PbF$_2$ appeared, together with small one at 1.95 V vs Pb/PbF$_2$, indicating that graphite electrode was reversibly oxidized and reduced. On the other hand, no reduction peak corresponding to that at 2.38 V vs Pb/PbF$_2$ was not observed and this peak disappeared during the subsequent cycles. At this potential, some irreversible reaction occurs. These results suggest that reversible intercalation/de-intercalation of HF$_2^-$ occurs below 2.2 V and covalent type of C_xF formed above 2.4 V vs Pb/PbF$_2$.

Fig. 2 shows the variation of potential during electrochemical oxidation of graphite at various current densities. When the current density was 800 mA cm^{-2}, the potential linearly increased and then reached a plateau after charged 0.1 F mol^{-1} (C$_{10}^+$). In the other cases, two potential plateaus were observed. The second plateau started after graphite was oxidized to less than C$_5^+$ (0.2 F mol^{-1}), which was accompanied by the vigorous oxygen gas evolution. The potential values of the first and second plateaus are summarized in Fig. 3. In case of the sample oxidized at 5 mA cm^{-2}, as already reported, stage 2 type $C_xHF_2^-$ formed at the beginning of the electrochemical oxidation and as the increase in the charge passed through the cell, covalent type stage 2C_xF gradually formed [22]. This is well explained by the results obtained above. The first plateau of 2.17 V is lower than 2.2 V, therefore, ionic type material was formed. On the other hand, the second plateau of 2.71 V vs Pb/PbF$_2$ is enough high to form covalent type stage 2C_xF, though considerable charge passed through the cell was consumed by the oxygen evolution. Considering that stage
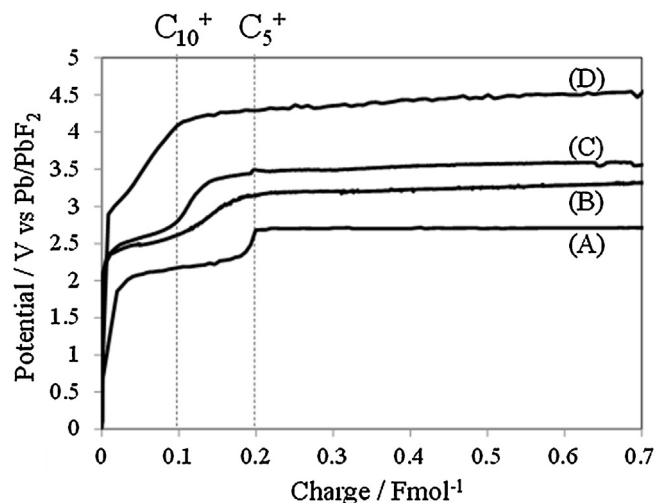

Fig. 2. Variation of the potential during constant current oxidation of 5, 50, 200 and 800 mA cm^{-2}.