On the Graphite Intercalation Compound Prepared Electrochemically in LiClO_4 -Propylene Carbonate Electrolyte

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INTRODUCTION

Recently, the formation of graphite intercalation compounds by the electrochemical method in organic electrolytes has been noted. For the electrochemical preparation of the compounds, two methods, the electrochemical oxidation and reduction are known. In the former case carbon net planes carry positive charges, while in the latter they carry negative charges. It was reported that the graphite intercalation compounds by the electrochemical reduction of graphite were prepared in alkali or ammonium salts-1,2 dimethoxyethane or dimethylsulfoxide electrolytes.¹⁾ On the other hand, Dunning et al.²⁾ described the formation of a graphite compound in LiClO_4 -dimethyl sulphite by the electrochemical oxidation, applying it as a cathode material for a rechargeable cell. Takada et al.^{3,4)} reported that the graphite intercalation compound could be formed similarly in LiClO_4 -propylene carbonate (PC). A lithium rechargeable cell consisting of the graphite cathode and an aluminum anode exhibited a large number of charge-discharge cycles. Ohzuku et al.⁵⁾ described a graphite perchlorate compound having characteristics as a cathode of high coulombic efficiency in the same electrolyte. However, the information concerning the structure of the graphite intercalation compound electrochemically prepared in LiClO_4 -PC has been scarcely reported.

In this report, the graphite intercalation compound was investigated by analytical, electrochemical and X-ray diffractometry measurements. The I_c spacing and the stage of the compound, and the reaction mechanism of the graphite in LiClO_4 -PC were considered.

EXPERIMENTAL

Graphite samples prepared by recrystallization of pyrolytic graphite at 3000°C were used. Graphite specimens (30–200 mg) wrapped with a platinum net (50 mesh) were employed as the sample electrode. The lattice constant and the dimension of crystallite for the 3000°C annealed pyrolytic graphite were $6.699\text{\AA}$ for $C_0(002)$ and $2825\text{\AA}$ for $L_c(002)$, respectively. Propylene carbonate was distilled under 3–5 Torr vacuum at 85°C . Lithium perchlorate was dried under vacuum at 100°C for several days. Concentration of LiClO_4 -PC electrolyte was 1.0 M, and water content in the electrolyte was less than 50 mg dm^{-3} .

Test cell for the electrochemical measurement is shown in Fig. 1. The constant current method was applied to the electrochemical oxidation and

Fig. 1 Structure of cell.

- G: Graphite electrode wrapped with Pt net
- R: Reference electrode
- L: Luggin capillary
- C: Counter electrode
- A: Argon inlet and outlet
- S: Solution inlet

reduction of the graphite. Lithium wires were used as the reference and counter electrodes. In order to obtain reproducible results, the specimen was treated with three times of oxidation-reduction process at about 50 C (coulombs) before the measurement. The measurement was carried out at 25°C.

The diffraction pattern of the graphite compound was recorded with an X-ray diffractometer (Rigaku-Denki, Ru-200PL) using monochromatized $\text{CuK}\alpha$ radiation, $2^\circ(2\theta) \text{ min}^{-1}$ of a scanning speed, 35kV and 20mA. After the surface of the graphite compound specimens ($5 \times 5 \text{ mm}^2$) was covered with liquid paraffin, the specimens were set on a sample holder with adhesive material (liquid paraffin was employed in order to protect the specimens from moisture and it was recognized that liquid paraffin did not affect X-ray patterns essentially).

The lithium content in the graphite compound was determined as follows: After being washed with pure PC, the compound was decomposed by immersing it in water for a few days. The lithium concentration in the solution which passed through a filter was determined by an inductively coupled argon plasma emission spectrometry (Nippon-Jarrell-Ash, ICAP-500) at the wavelength of 6708Å.

RESULTS AND DISCUSSION

Fig. 2 shows the relation between electrochemical oxidation-reduction electric quantity and potential of the graphite electrode. The electrode potentials are about 4.7V vs. Li^+/Li in the same electrolyte, which seems very high compared with those for the intercalation compounds prepared in aqueous solutions such as graphite bisulphate⁶⁾,

Fig. 2 Galvanostatic oxidation-reduction of a graphite electrode in LiClO_4 -PC
 $i = 0.25 \text{ mA cm}^{-2}$.

chlorosulphonate⁷⁾, etc: For example, the potential of graphite bisulphate in sulfuric acid exhibited about 1V vs. $\text{Hg}/\text{Hg}_2 \text{ SO}_4$, though a different reference electrode was used. Potential step as described elsewhere when oxidation or reduction was carried out in aqueous solutions was scarcely recognized in this case. No more than 80 C g^{-1} carbon of reduction was seen at any large electric quantity of oxidation (cut off voltage for reduction was 3.0 V vs. Li/Li^+). The value of 80 C g^{-1} carbon corresponds to C_{96} , that is, the electric quantity required to oxidize $1/96 \text{ g}$ of carbon.

The X-ray diffraction patterns of the graphite intercalation compounds are shown in Fig. 3. The oxidation electric quantities of the samples A, B and C in Fig. 3 correspond to those of a, b and c points in Fig. 2, respectively. The spacing of the reactant material, Ic for the sample A was determined as $17.20 \text{ \AA}$. This value of Ic is close to $17.65 \text{ \AA}$, Ic of the 4th stage graphite perchlorate compound prepared in aqueous HClO_4 solution⁸⁾, and the position of a in Fig. 2 is in the vicinity of C_{96} , it is supposed that the stage of this compound is the 4th stage. In a similar manner, the stages of the compounds for B and C would be the 5th and 6th, respectively. Each values of Ic and apparent thickness of reactant layer, D are shown in Table 1. On further oxidation of the graphite, almost the same X-ray pattern of the compound

Fig. 3 X-ray diffraction patterns of graphite intercalation compounds,
 $\text{CuK}\alpha$, 35 kV, 20mA.

Table 1 Stages and spacings of graphite intercalation compounds.

Stage	LiClO ₄ -PC		Aqueous HClO ₄ ⁸⁾	
	Ic	D	Ic	D
4th	17.20	3.80	17.65	4.25
5th	20.45	3.70	21.00	4.25
6th	23.70	3.60	24.35	4.25

Ic: Periodic distance of reactant layer

D: Apparent thickness of reactant layer

as A was observed. This phenomenon would be consistent with the results that the maximum reduction electric quantity of the graphite intercalation compound corresponds to C₉₆. The 4th stage of the compound prepared in LiClO₄-PC seems, therefore, to be the lowest one. X-ray measurements were carried out immediately after the specimen was taken out from the electrolyte, and when the specimen was left in air, the X-ray pattern exhibited that the stage was shifted to the higher one. Fig. 4 shows the change of the X-ray diffraction patterns at various stages in elapse of time. Decomposition process seemed faster when the specimen was allowed to stand in contact with the atmosphere than in a desiccator. The X-ray

Fig. 4 Decomposition process of a graphite perchlorate intercalation compound occurring in air as shown by the X-ray diffraction.

- 1: after 1 hour
2: 3 hours
3: 24 hours

Fig. 5 X-ray diffraction patterns of a graphite compound after the electrochemical reduction (1) and a 3000°C annealed pyrolytic graphite (2).

Fig. 6 Analysis of lithium in graphite intercalation compounds.

- *1 The reduced compound after oxidation of 80 coulombs
*2 The original graphite

pattern also proved that the compound was nearly converted to the original graphite by the electrochemical reduction. The X-ray pattern of the sufficiently reduced specimen is shown in Fig. 5, which represents that the peaks of the intercalation compound disappeared substantially.

Fig. 6 shows the relation between oxidation electric quantity and lithium content in the graphite compound found by the emission spectrography. After the quantity of lithium reached to the maximum value, 3.4 mg g⁻¹ carbon, it kept almost constant even at larger electric quantity. The value of 3.4 mg g⁻¹ carbon corresponds to 0.55 mole of lithium per 1/96 g-atom carbon. Moreover, existence of ClO₄⁻ was confirmed colorimetrically by adding methylene blue to the lithium solution and observing the complex for-

mation. Accordingly, it is supposed that 1/2 mole of LiClO₄ per 1 mole of C₉₆ClO₄ is contained as a spacer.

From the facts described above, the most probable reaction mechanism on the electrochemical oxidation and reduction of the graphite in LiClO₄-PC was considered as follows.

The quantity of a spacer in the graphite intercalation compound prepared in PC would be less than that in the aqueous solution, due to the fact the value of D determined by the X-ray analysis was smaller. Consequently, it was suggested that the ratio of ionic bond between graphite and ClO₄ would be low.

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学振第 117 委員会第 174 回会議

学振第 117 委員会第 174 回会議が昭和 58 年 5 月 6 日 (金), 7 日 (土), 市ヶ谷私学会館において開催された。各分科会には下記の資料が提出され, 活発な討論がなされた。

- 117-174-A-1 カーボンフレークの生成とその構造
(武蔵工大) 菱山幸宥ほか
- 117-174-A-2 熱処理炭の微細構造と灰分の影響
(早稲田大) 樋口真次ほか
- 117-174-A-3 コールタールピッチおよび A 240 からの可溶性メソフェーズの調整とその化学構造
(九大生研) 光来要三ほか
- 117-174-A-4 酸接触改質したエチレンタールからのメソフェーズピッチの調製
(九大生研) 持田 勲ほか
- 117-174-A-5 常温溶融塩法によるナフタレンピッチ
(群大工) 亀山光男ほか

- 117-174-B-1 炭素製品の高温特性の簡易評価法に関する研究
(大工試) 藤井祿郎ほか
- 117-174-B-2 Electrochemical Characteristics of Graphite Intercalation Compounds with Fluorine-Lithium Cells
(京大) 渡辺信淳ほか
- 117-174-B-3 電位差法を用いた黒鉛材料の破壊力学
(豊橋技科大) 逆井基次ほか
- 117-174-B-4 銅添加ポリアクリロニトリルの電子物性
(日大理工) 池田真智子ほか
- 117-174-B-5 高温ガス炉用黒鉛の機械的性質に及ぼす酸化の効果
(原研) 衛藤基邦ほか
- 117-174-C-1 炭素繊維-アルカリ二次電池の特性
(群大工) 田草川 尚ほか
- 117-174-C-2 炭素・黒鉛材料のヘリウム中水蒸気及びヘリウム中二酸化炭素による反応
(原研) 今井 久ほか