CrO₃-Graphite Intercalation Compound Cathodes with Various Stage Numbers in a Lithium Secondary Cell

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CrO₃-graphite intercalation compounds (GICs) with various stage numbers (3, 6 and 11) were prepared by a solvent method in acetic acid and their discharge characteristics were investigated comparatively in a DMSO solution containing 1 mol·dm⁻³ LiClO₄. On the discharging curves at a low current density (c.d.) of -10 μA·cm⁻², two potential plateaus appeared at about 2.7 and 1.5 V. The length of the former plateau decreased with the stage number of a GIC. The transition between these two plateaus was likely determined by a kinetic factor even at this low c.d.

1 INTRODUCTION

In our previous studies^{1,2)}, CrO₃-graphite intercalation compounds (GICs) were investigated as a possible cathode material in a lithium secondary cell, where the most of investigations were carried out mainly at relatively high current densities ($\geq 250 \mu\text{A}\cdot\text{cm}^{-2}$) in an LiClO₄-dimethylsulfoxide (DMSO) solution.

The amount of discharge electricity before beginning of the solvent decomposition increased almost linearly with the Cr content in GIC under these conditions¹⁾. There are two kinds of interlayers in CrO₃-GICs excepting stage 1, namely, CrO₃-intercalated layers and CrO₃-free layers having distances of 0.812 and 0.335 nm, respectively. Hence, the discharge reaction was considered to consist of two different lithium insertion processes, namely, simultaneously inserted electrons were accommodated in (i) Cr ions and (ii) CrO₃-free graphite layers.

Furthermore, the anodic extraction of inserted lithium proceeded in two steps²⁾, which could not be distinguished from each other clearly during cathodic lithiation at a high current density (c.d.). On the first recharging curve, there appeared two plateaus at about 1.7 and 3.0 V.

In this work, the effects of a stage number of CrO₃-GICs on their cathodic behavior in a lithium cell were investigated at a low c.d. of -10 μA·cm⁻² in order to characterize electrochemical lithium insertion processes to an originally intercalated material of CrO₃-GIC.

2 EXPERIMENTAL

2.1 Preparation of CrO₃-GIC samples

CrO₃-GIC samples with various stage numbers were prepared by a solvent method as previously¹⁾,

where the stage number was controlled by changing a reaction temperature according to Metz *et al.*³⁾. Pristine graphite (from Madagascar, pretreated at a high temperature by Nippon Carbon, Co., Ltd.) was crushed by a mortar and then classified by standard sieves. Preferable preparation conditions of GIC samples were summarized in Table 1.

Table 1 Preparation conditions of CrO₃-GIC samples by the acetic acid method

sample	temperature	time	graphite size
A	120 °C	4 h	75–100 μm
B	80 °C	24 h	100–150 μm
C	25 °C	120 h	150–250 μm

2.2 Analytical procedures¹⁾

The Cr/carbon atomic ratio in GIC samples was determined from a weight loss after ignited at 900 °C. The (001) and (*hk*0) reflections from GIC crystals were obtained by X-ray powder diffraction (XRD) with CuK_α radiation and by the electron diffraction (ED, 200 kV) measurement, respectively. The electron spin resonance (ESR) measurements were performed at a room temperature using an X-band¹⁾.

2.3 Electrochemical measurements

The electrochemical measurements¹⁾ were performed galvanostatically at 25 °C in a beaker cell set up in a dry box. Commercially available (from Mitsubishi Yuka) 1 mol·dm⁻³ LiClO₄ solution of DMSO was used as the electrolyte. 5–10 mg of GIC flakes were pressed into discs of 5 mm in diameter at 2000 kg·cm⁻² without any binder. GIC disc electrodes were made after insulating their back and side faces. A reversible lithium electrode in the electrolyte was employed as the reference, and another lithium wire was used as the counter electrode.

3 RESULTS AND DISCUSSION

3.1 Characterization of CrO₃-GIC samples

Characterization of GIC samples prepared in this work were summarized in Table 2. After igniting at 900 °C under air atmosphere, Cr₂O₃ was obtained as a residue and the Cr/carbon ratio in a GIC was determined from the weight of this residue. The stage number (*n*) was determined from XRD patterns as in Fig. 1 after assuming a diameter of the inter-

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Fig. 1 XRD patterns of CrO_3 -GIC samples (See Table 2, G: (002) reflection from unreacted graphite portions)

Table 2 The stage number (n), the degree of penetration (α) and the Cr/carbon atomic ratio of CrO_3 -GIC samples

sample	n	α	Cr/carbon
A	3	1.00	1/19.9
B	6	0.88	1/33.7
C	11	0.81	1/71.2

calant as $0.477 \text{ nm}^{1,4}$). The degree of penetration (α)³, a measure for the intercalated portion of a starting graphite material was derived from the integrated intensity of the strongest XRD peak from a GIC and that of (002) reflection from graphite. When (002) peak from graphite disappeared perfectly, α reached at the unity. This α -value became higher with elevating the reaction temperature or with decreasing the size of graphite particles.

It was difficult to prepare a series of well-penetrated ($\alpha \approx 1$) GIC samples having different stage numbers and the same particle size. The minimum value of α in this work was 0.81. The particle size of obtained GICs was the smaller for the higher stage numbered sample owing to the longer preparation time under mechanical agitation. However, each GIC sample had almost comparable particle size (75–150 μm).

The in-plane structure of GICs could not be analyzed by XRD because of the (00 l) preferred orientation. Instead, ED pattern as in Fig. 2 gave the structural information for a small single crystalline portion. The relatively strong spots as indicated by the arrow could be attributed to the ($hk0$) reflection from graphitic carbon honeycomb layers and the other weak spots were attributed to the ($hk0$) reflections from the CrO_3 -intercalant lattice.

The two-dimensional intercalant lattice constant of sample A was determined as 0.820 nm by analyzing the reciprocal lattice vectors, which was identical to the literature⁴) data for a 5th-staged CrO_3 -GIC. Further, for our 6th- and 11th-staged samples, almost the same intercalant lattice constant as above was obtained. These results showed that the arrangement of a CrO_3 -intercalant was independent of the stage

Fig. 2 Typical electron diffraction pattern of CrO_3 -GIC sample A (arrow: ($hk0$) reflections from honeycomb carbon lattice)

Fig. 3 Typical discharging curves of CrO_3 -GIC sample A (3rd staged) in a DMSO solution

1: $-10 \mu\text{A}\cdot\text{cm}^{-2}$ 2: $-50 \mu\text{A}\cdot\text{cm}^{-2}$
3: $-250 \mu\text{A}\cdot\text{cm}^{-2}$ 4: $-500 \mu\text{A}\cdot\text{cm}^{-2}$

number.

3.2 Discharge behavior of CrO_3 -GICs

3.2.1 Effects of a current density

As mentioned above, two different lithium insertion steps to CrO_3 -GIC, namely, one into CrO_3 -intercalated layers and another into CrO_3 -free graphite layers, could not be distinguished from each other on galvanostatic discharging curves so far¹⁾. In this work, however, a rather high potential plateau I at about 2.7 V was found out in addition to a lower plateau II at about 1.5 V, when we applied a low c.d. of $-10 \mu\text{A}\cdot\text{cm}^{-2}$ as seen on curve 1 in Fig. 3. The former plateau I shifted to lower potential and became shorter with increasing the discharge c.d. Especially at high c.d.s. of -250 and $-500 \mu\text{A}\cdot\text{cm}^{-2}$, it was difficult to confirm the presence of plateau I on the scale of abscissa as in Fig. 3. When a GIC had a large particle size (0.5–0.7 mm) as in the previous work¹⁾, a higher discharging plateau I did not appear even at $-10 \mu\text{A}\cdot\text{cm}^{-2}$. Presumably, the exposure of active edge faces of a lamellar GIC crystals to the

Fig. 4 Typical discharging curves of graphite and CrO_3 -GIC in DMSO solution at $-10 \mu\text{A}\cdot\text{cm}^{-2}$
 1: graphite 2: 3rd staged GIC
 3: 6th staged GIC 4: 11th staged GIC

Fig. 5 ESR spectra of CrO_3 -GIC (A) before and (B) after discharging ($e/\text{Cr}=1.3$)

electrolyte played an important role. When we consider the exposed area of active edge faces at a constant GIC weight, it should be the smaller for the larger GIC particles. Consequently, the larger particles show the shorter plateau at 2.7 V.

Discharge curves of GICs at a low c.d. of $-10 \mu\text{A}\cdot\text{cm}^{-2}$ were compared with that of graphite in Fig. 4, where the amount of electricity was given in coulomb·mg⁻¹. It is clear that a higher plateau I at 2.7 V was absent in case of graphite and hence this plateau was characteristic for GICs.

Fig. 6 Typical discharging curves of CrO_3 -GICs in a DMSO solution at $-250 \mu\text{A}\cdot\text{cm}^{-2}$
 1: 3rd stage 2: 6th stage 3: 11th stage

As seen in an ESR spectrum of CrO_3 -GIC (Fig. 5(A)), a sharp signal ($g=1.98$) was observed. The g -value was determined from the peak position of the integrated curve of ESR spectrum. This sharp signal was identified with that from Cr(V) by referring the literature data^{1,5)}. On the other hand, in an ESR spectrum after discharged on plateau I (Fig. 5(B)), a broad signal appeared in addition to a sharp one. Since these sharp and broad ESR signals correspond to Cr(V) and Cr(III) , respectively¹⁾, the broad signal after discharge proved that electrons injected simultaneously with Li^+ ions were accommodated in Cr species. Thus, lithium insertion to GICs accompanied by the reduction of Cr component took place on plateau I.

So far, the lithium insertion potential of chromium oxides such as Cr_2O_5 and Cr_2O_3 in non-aqueous solutions were reported^{6,7)} as 3.0 V approximately. The electrochemical insertion of solvated lithium ions to well-graphitized carbon from an LiClO_4 -DMSO solution, on the other hand, was reported^{1,8)} to occur at 1.7–1.6 V.

3.2.2 Effects of a stage number of GICs

The discharge curves of GIC samples at a high c.d. of $-250 \mu\text{A}\cdot\text{cm}^{-2}$ were given in Fig. 6, where the amount of discharge electricity before reaching at the final steady-state potential of about 1.1 V (probably due to the decomposition of DMSO) was about 4 electrons per chromium atom (e/Cr) independent of the stage number as discussed in a previous paper¹⁾. This value might be considered as the sum of two components, namely, 3 (e/Cr) due to an apparent change in the oxidation number of Cr from +6 to +3 and the rest of 1 (e/Cr) due to lithium insertion to CrO_3 -free graphite layers. Only a slight difference in discharge potentials could be recognized in the initial

Fig. 7 Typical discharging curves of CrO_3 -GICs in a DMSO solution at $-10 \mu\text{A}\cdot\text{cm}^{-2}$

Fig. 8 Schematic representation of electrochemical lithium insertion into CrO_3 -GICs at plateau I

(●: Li, ■: CrO_3 -intercalant layer, —: graphite layer) stage of $(e/\text{Cr}) \leq 1$.

When we applied a low c.d. of $-10 \mu\text{A}\cdot\text{cm}^{-2}$, on the other hand, the length of plateau I decreased markedly with a stage number as can be seen in Fig. 7. Besides, the length of plateau I was considerably smaller than 3 (e/Cr) and might not correspond to the limiting value of lithium insertion, because the charging plateau at about 3.0 V was confirmed to be longer than 2 (e/Cr) on the 1st recharging²⁾. A certain kinetic factor probably caused to the transition from potential plateau I to plateau II.

Both the particle size and the arrangement of the intercalant in a GIC can affect the kinetics of lithium insertion in general. In the present work, however, the particle size of GIC samples was almost identical and the in-plane structure of the intercalant was independent of the stage number.

When we consider the charge transfer between graphite layers and the acceptor intercalant in a GIC like as CrO_3 , the graphite layers adjacent to the intercalant has a lower electron density than the other graphite layers as a result of the staging structure. Ohno *et al.*⁹⁾ calculated the band structure and

the local charge distribution along the c -axis of a higher staged GIC ($n=2-6$). Several experimental results such as Raman scattering¹⁰⁾ so far supported the non-uniform charge distribution along the c -axis.

On the discharging plateau I, lithium should be inserted not to the intercalant-free graphite layers but to CrO_3 -intercalated layers owing to this non-uniform charge distribution. Of course, the entrance for lithium to a GIC or graphite is not the (001) lamellar plane but ($hk0$) edge planes. Quite schematically, we illustrated in Fig. 8 the effects of a stage number on the kinetics of electrochemical lithiation under diffusion control in a GIC phase. In this figure, the number of inserted lithium ions is equal for every case after assuming the constant c.d. Lithium insertion to the intercalant-free layers may begin when the concentration of lithium at the edge surface exceeds a certain threshold value. Since the charge density on intercalant-free layers was almost the same as that on pristine graphite due to the localized charge distribution in a GIC, lithium accommodation in these layers should occur at 1.7–1.6 V, which had been reported^{1,8)} as the lithiation potential of graphite in a DMSO solution. In fact, the observed plateau II was located closely to this potential. Accordingly, plateau I was the longer for a GIC having the lower stage number and at the same time the more CrO_3 -intercalant.

4 CONCLUSIONS

Both the first discharging plateau I at about 2.7 V accompanied with the reduction of Cr component and the second plateau II at about 1.5 V could be observed at a relatively low c.d. of $-10 \mu\text{A}\cdot\text{cm}^{-2}$, where the length of the former plateau decreased with the stage number of GICs. The lower staged GIC showed the longer plateau I and the transition from plateau I to plateau II was likely determined by a kinetic factor.

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