Cathodic Behavior of MoCl_5 -Graphite Intercalation Compounds in a Dimethyl Sulfoxide Solution

Masato KURIHARA*, Akio MINAKUCHI, Takashi MIURA
and Tomiya KISHI

Received December 20, 1993; Accepted February 21, 1994

Several MoCl_5 -graphite intercalation compounds (GICs) were prepared by heating graphite and MoCl_5 in a vacuum-sealed glass tube at various temperatures (250–400°C). The cathodic behavior of MoCl_5 -GICs (mainly 2nd stage) was investigated in a dimethyl sulfoxide (DMSO) solution containing $1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiClO}_4$. Electrochemical lithium insertion to an MoCl_5 -GIC proceeded in two steps (accompanied with the reduction of Mo ions and graphite layers) as well as in the case of CrO_3 -GIC. The difference between plateau potentials of these two insertion processes was less marked for MoCl_5 -GICs than for CrO_3 -GICs probably due to the different electron affinity of these transition metal compound intercalants.

1 INTRODUCTION

As mentioned previously^{1–3}, various graphite intercalation compounds (GICs) had been investigated as a possible cathode material for lithium cells. So far, we had reported the discharge/charge behavior of CrO_3 -GIC cathode in non-aqueous solutions containing LiClO_4 ^{1–3}.

The discharge reaction of a CrO_3 -GIC consisted of two different lithium insertion processes, namely, simultaneously inserted electrons were accommodated in (i) Cr ions and (ii) CrO_3 -free graphite layers. The first discharging plateau at about 2.7 V accompanied with the reduction of Cr component and the second plateau at about 1.5 V could be observed at a relatively low current density (c.d.) of $-10 \mu\text{A} \cdot \text{cm}^{-2}$, which were not distinguished clearly from each other during cathodic lithiation at higher c.d.'s. ($\geq 250 \mu\text{A} \cdot \text{cm}^{-2}$).

However, the length of the first discharging plateau decreased with the stage number of a GIC and the transition between these discharging plateaus seemed to depend on a certain kinetic factor.

Whereas the smallest stage number of CrO_3 -GIC was 3, a lower 2nd-staged GIC can be prepared in case of another transition metal compound intercalant of MoCl_5 . The lower-staged and hence high intercalant content GIC can be expected to have a large discharge capacity per unit weight. Further, MoCl_5 -GIC is a highly oxidized transition metal compound intercalant as well as CrO_3 . In this study, the behavior of MoCl_5 -GICs as a cathode material for a lithium cell were investigated in an LiClO_4 -dimethyl sulfoxide (DMSO) solution.

2 EXPERIMENTAL

2.1 Preparation of MoCl_5 -GIC samples

Pristine graphite (from Madagascar, purified to a level of >99% by Nippon Carbon, Co., Ltd.) was crushed by a mortar and then classified by standard sieves. MoCl_5 -GICs were prepared by heating graphite flakes and the excess amount of anhydrous MoCl_5 in a vacuum-sealed borosilicate glass tube^{4,5}. Unreacted molybdenum chloride was washed out with ethanol and then with ammonia water. Preparation conditions of various MoCl_5 -GIC samples were summarized in Table 1.

Table 1 Preparation conditions of MoCl_5 -GIC samples.

no.	temp./°C	time/h	graphite size/ μm
1	150	72	100–150
2	250	72	100–150
3	300	72	100–150
4	300	48	53–75
5	400	72	100–150
6	300	68	53–75
7	300	90	53–75

2.2 Analytical procedures¹⁾

The Mo/carbon atomic ratio in a GIC was determined by thermogravimetric analysis. Powder X-ray diffraction (XRD) measurements were carried out using $\text{CuK}\alpha$ radiation. Electron diffraction (ED) measurements were performed by the transmission electron microscope (200 kV). The Raman scattering spectra were obtained by using argon ion laser beam (514.5 nm). Electron spin resonance (ESR) measurements were carried out at room temperature using the X-band.

2.3 Electrochemical measurements

The electrochemical measurements were performed galvanostatically at 25°C in a beaker cell set up in a dry box. Commercially available (from Mitsubishi Yuka) $1 \text{ mol} \cdot \text{dm}^{-3} \text{ LiClO}_4$ solution of DMSO was used as an electrolyte. MoCl_5 -GIC pressed discs of 5 mm in diameter (5 mg) were used as a working electrode after insulating their back and side faces¹⁾. The electrode potentials were measured against a reversible lithium electrode in the electrolyte and

Department of Applied Chemistry, Faculty of Science and Technology, Keio University (Hiyoshi 3-14-1, Kouhoku-ku, Yokohama, 223 Japan)

Key Words: Electrochemical Lithiation, Graphite Intercalation Compounds, Molybdenum Penta-chloride, DMSO

another lithium rod was employed as the counter electrode.

3 RESULTS AND DISCUSSION

3.1 Characterization of MoCl_5 -GIC samples

The lattice structure of MoCl_5 -GIC has been analyzed by the XRD⁵⁻⁸⁾, the ED^{7,8)} and the neutron scattering⁹⁾ measurements.

The XRD patterns of GIC samples were shown in Fig. 1, where only (00 l) reflections appeared because of the preferred orientation. The repeating distance along the c -axis (l_c) was summarized and compared with literature data⁵⁻⁷⁾ in Table 2. The stage number (n) was calculated from l_c after assuming a thickness of MoCl_5 -intercalant as 0.585 nm⁵⁻⁷⁾. The lower heating temperature was recommended so far^{5,6)} to prepare the lower-staged MoCl_5 -GIC. However, the 1st-staged sample could not be obtained in this study. In addition, the longer reaction time at 300°C resulted in the formation of the higher-staged MoCl_5 -GIC in this study. This tendency might be explained by the instability of MoCl_5 between graphite layers at 300°C, which was expected from the reported transition of MoCl_5 -intercalant to the liquid-like phase at above *ca.* 310°C⁸⁾.

Table 2 The identity period (l_c), the stage number (n) and theoretical Mo/carbon atomic ratio⁵⁾ of MoCl_5 -GIC.

no.	l_c/nm	n	Mo/carbon
ref.5,6	1.254	2	1/21.0
ref.5,6	1.602	3	1/31.4
ref.5,6	1.942	4	1/40.5
ref.7	1.937	4	1/40.5
1	—	—	—
2	1.260	2	1/21.0
3	1.262	2	1/21.0
4	1.252	2	1/21.0
5	1.590	3	1/31.4
6	1.589	3	1/31.4
7	1.920	4	1/40.5

Typical ED pattern from an MoCl_5 -GIC (No.3) was given in Fig. 2. The spots as indicated by the arrow were attributed to the ($hk0$) reflection from a honeycomb carbon lattice and the other spots were attributed to the ($hk0$) reflection from the MoCl_5 -intercalant lattice. Two-dimensional lattice constant determined from this ED pattern was identical to the literature data (orthorhombic phase, $a_0=0.621\text{ nm}$, $b_0=1.793\text{ nm}$)⁷⁾.

On the thermogravimetric curve, the weight of sample No.3 began to decrease at 280°C and became almost constant after holding at 500°C for 10h. After TG measurements, the deintercalation of MoCl_5 -intercalant from a GIC was confirmed by the XRD pattern. Thus, Mo/carbon atomic ratio was determined from the weight loss after ignition at 500°C for 48h. Sample No.3, 2nd-staged GIC (Mo/carbon=1/32), was used mainly for the electro-

Fig. 1 Powder XRD patterns of MoCl_5 -GIC samples.

1: 2nd stage (No. 3) 2: 3rd stage (No. 5)

3: 4th stage (No. 7)

(G: (00 l) reflection from unreacted graphite portion)

Fig. 2 Typical electron diffraction pattern of an MoCl_5 -GIC (No. 3).

chemical measurements below.

3.2 Discharge behavior of MoCl_5 -GICs

Discharging curve of MoCl_5 -GIC (3rd stage) in an LiClO_4 -DMSO solution at $-250\mu\text{A}\cdot\text{cm}^{-2}$ was compared with that of graphite in Fig. 3. Electrochemical lithium insertion into graphite is known to occur

Fig. 3 Discharging curves of at $-250 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution.

- 1: 3rd-staged MoCl_5 -GIC (No. 6)
 2: 3rd-staged CrO_3 -GIC 3: pristine graphite

Fig. 4 Discharging curves of 2nd-staged MoCl_5 -GIC (No. 4) in a DMSO solution.

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

at 1.7–1.0 V in a DMSO solution and the insertion limit of lithium, x_{lim} (in C_xLi), was reported as 24 for the formation of 1st-staged GIC^{1,9)}. This value corresponds to the cathodic charge of $0.335 \text{ C}\cdot\text{mg}^{-1}$ in this case (see curve 3 in Fig. 3).

On the other hand, the galvanostatic discharging potential of MoCl_5 -GIC (3rd stage) went down quickly to a plateau beginning at about 1.9 V, then it lowered gradually to the potential of about 1.5 V. The plateau potential and the final steady-state potential of an MoCl_5 -GIC were higher than those of a CrO_3 -GIC and graphite as shown in Fig. 3.

Fig. 5 A change in the length of plateau I with the current density. (2nd-staged MoCl_5 -GIC (No. 4))

Discharging curves of 2nd-staged MoCl_5 -GIC at various c.d.'s were shown in Fig. 4. There were three plateaus on each curve, i.e., plateau I at 2.2–2.1 V, the following plateau II and the final steady-state plateau III. The transition points between these plateaus were determined by differentiating the discharging potential with Q_C .

The length of plateau I (Q_I , in $\text{C}\cdot\text{mg}^{-1}$) decreased with increasing the c.d. as seen on curve 1 in Fig. 5, and the transition from plateau I to plateau II was probably dominated by a kinetic factor. However, the j - Q relationship was somewhat different from that expressed by modified Sand equation, $jQ = \text{const}$ (see curve 2), under the semi-infinite linear diffusion control. In fact, plateau I could be divided into two parts when a lower c.d. of $-10 \mu\text{A}\cdot\text{cm}^{-2}$ was applied.

Thus, Q_I depended on a c.d. and the potential of plateau I (ca. 2.2 V) was lower than that for CrO_3 -GIC (ca. 2.7 V) at a low c.d.. We supposed that the reduction of the transition metal intercalant in MoCl_5 -GIC proceeded on plateau I as well as in the case of CrO_3 -GIC and that the difference in discharging potentials between MoCl_5 - and CrO_3 -GICs was caused by the different electron affinity of these intercalants.

On the other hand, the total amount of electricity to the end of plateau II, Q_{I+II} , was independent of a c.d.. The discharging curves of various MoCl_5 -GICs were compared in Fig. 6, where plateau I was observed only for a 2nd-staged sample. Although Q_{I+II} per unit weight of a GIC increased with the Mo/carbon ratio, Q_{I+II} per Mo atom was roughly constant at about $2e/\text{Mo}$ for each sample. This value corresponds to the apparent valence change of Mo from +5 to +3. Similar experimental data had been obtained for CrO_3 -GICs¹⁾, corresponding to the

Fig. 6 Discharging curves of MoCl_5 -GICs at $-250 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution. (The vertical arrows indicate the depth of discharge of $2e/\text{Mo}$)

1: 2nd stage (No. 4) 2: 3rd stage (No. 6)
3: 4th stage (No. 7)

Fig. 7 ESR spectra of 2nd-staged MoCl_5 -GIC (No. 4) after discharged at $-250 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution.

1: $6.5 e/\text{Mo}$ 2: $9.1 e/\text{Mo}$

apparent valence change of Cr from +6 to +3.

Moreover, plateau III was higher than that of CrO_3 -GICs. As seen in Fig. 7, ESR spectra of an MoCl_5 -GIC changed after discharged to $6.5 e/\text{Mo}$ or to $9.1 e/\text{Mo}$. Several papers¹⁰⁻¹²⁾ described that the transition metal chloride-intercalants such as FeCl_3 and CoCl_2 are reduced to a lower oxidation state upon electrochemical lithiation. Analogously, the

Fig. 8 Powder XRD patterns of 2nd-staged MoCl_5 -GIC (No. 3) after discharged at $-10 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution.

1: $0.17 e/\text{Mo}$ 2: $0.25 e/\text{Mo}$
3: $0.70 e/\text{Mo}$ 4: $1.40 e/\text{Mo}$

reduction of Mo component in GIC probably proceeded on plateau III, although this plateau had the length of $10 e/\text{Mo}$ twice longer than that required for the change from Mo^{5+} to Mo^0 . This result suggested that the decomposition of DMSO occurred competitively on plateau III. In case of graphite, the reductive decomposition of DMSO occurred on the final steady-state potential at *ca.* $1.0 \text{ V}^{1,9)}$.

3.3 Structural Changes of MoCl_5 -GIC after discharge

The XRD patterns of 2nd-staged MoCl_5 -GIC after discharged at $-10 \mu\text{A}\cdot\text{cm}^{-2}$ were given in Fig. 8. The diffraction intensity decreased with increasing the depth of discharge, and the XRD peaks disappeared at $0.70 e/\text{Mo}$ on plateau II. These facts showed that the periodical layer structure of 2nd-staged GIC was disordered by lithium insertion, which was the case also for 3rd- and 4th-staged GICs.

The insertion of solvated large Li^+ ions should cause lattice expansion in general. If the inserted solvated ion is unstable in a GIC lattice, its intralayer decomposition may lead to the destruction of periodical lamellar structure as confirmed by XRD patterns in Fig. 8. Thus, solvated Li^+ ions were considered to be inserted on plateau II.

Murakami *et al.*¹³⁾ investigated the structural changes accompanied with the intercalation of potassium to 3rd- and 4th-staged MoCl_5 -GICs and reported that a heterostructure (HS)-GIC formed, in which both the acceptor intercalant of MoCl_5 and the donor intercalant of K were inserted periodically. In case of electrochemical insertion of sulfuric acid to an MoCl_5 -GIC¹⁴⁾, the formation of an acceptor

Fig. 9 ESR spectra of 2nd-staged MoCl_5 -GIC (No. 3) after discharged at $-10 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution.

1: 0.70 e/Mo 2: 1.40 e/Mo
3: 2.10 e/Mo

Fig. 10 Relationship between the depth of discharge at $-10 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution and ΔH_{pp} (width between peak tops) in ESR spectra. (see Fig. 9)

-acceptor HS-GIC was proposed. After electrochemical lithiation up to 0.25 e/Mo , however, such an HS-GIC was not observed by the XRD patterns as seen in Fig. 8.

The ESR signal at $g=1.94$ was observed both before and after electrochemical lithiation up to 2.1 e/Mo as seen in Fig. 9. The line width of integrated curves, on the other hand, became narrower with the depth of discharge as in Fig. 10. Although Q_{I+II} of 2 e/Mo suggested the reduction of Mo(V) to Mo(III) , it was difficult to deconvolute ESR signals into Mo(V) and Mo(III) contributions.

Fig. 11 Raman spectra of 2nd-staged MoCl_5 -GIC (No. 3) after discharged at $-10 \mu\text{A}\cdot\text{cm}^{-2}$ in a DMSO solution.

1: 0.30 e/Mo 2: 0.70 e/Mo

The E_{2g} intralayer Raman band of highly oriented graphite appeared at around 1582 cm^{-1} and shifted owing to the charge transfer from/to the intercalant to/from graphite layers, especially intercalant-sandwiching graphite layers, in case of a GIC¹⁵⁾. There were a strong peak at 1620 cm^{-1} and a weak peak at 1590 cm^{-1} in Raman spectrum of 2nd-staged MoCl_5 -GIC shown in Fig. 11. With increasing the depth of discharge, the former and latter peaks tended to become weaker and stronger, respectively, and the reduction of graphite layers was suspected to proceed on plateau II. Plateau II was slightly higher than $1.7\text{--}1.6 \text{ V}$, where solvated Li^+ ions are inserted

to pristine graphite from a DMSO solution^{1,9)}. Since there was the electron transfer from graphite layers to the MoCl_5 -intercalant in a GIC, the reduction potential of graphite layers should be higher for a GIC than for pristine graphite. In summary, the reduction of both the intercalant and graphite layers took place upon electrochemical lithiation also for MoCl_5 -GICs.

4 CONCLUSIONS

As well as CrO_3 -GIC cathodes, electrochemical lithium insertion to an MoCl_5 -GIC proceeded in two steps accompanied with the reduction of both Mo ions and graphite layers, when discharged in a DMSO solution. The difference between plateau potentials of these two insertion processes is smaller for MoCl_5 -GICs than for CrO_3 -GICs presumably due to the different electron affinity of these transition metal compound intercalants.

The present authors would like to thank Prof. Dr. Hiroshi Nishihara and Noriyuki Ohno at our Faculty for their experimental support and helpful suggestions to analyze Raman spectra. A part of this work was supported by the foundation of Katoh Kagaku Shinkou-kai.

REFERENCES

- 1) M. Kurihara, T. Miura and T. Kishi, *Denki Kagaku* **59**, 696 (1991).
- 2) M. Kurihara, T. Miura and T. Kishi, *Denki Kagaku* **60**, 412 (1992).
- 3) M. Kurihara, T. Kurata, T. Miura and T. Kishi, *Denki Kagaku* **61**, 1357 (1993).
- 4) R.C. Croft, *Austr. J. Chem.* **9**, 186 (1956).
- 5) Yu. N. Novikov, V.A. Semion, Y.T. Struchkov and M.E. Vol'pin, *Strukt. Khim.* **11**, 880 (1970).
- 6) A.V. Zvanykina, Yu.S. Karimov, M.E. Vol'pin and Yu.N. Novikov, *Sov. Fiz. Tverd. Tela* **13**, 28 (1971).
- 7) A.W. Syme Johnson, *Acta Cryst.* **23**, 770 (1967).
- 8) M. Suzuki, L.J. Santodonato, I.S. Suzuki, B.E. White, Jr. and E.J. Cotts, *Phys. Rev.* **43**, 5805 (1991).
- 9) P. Schoderböck and H.P. Boehm, *Synth. Met.* **44**, 239 (1991).
- 10) Ph. Touzain, A. Chamberod and A. Briggs, *Mat. Sci. Eng.* **31**, 77 (1977).
- 11) R. Yazami, G. Chouteau, P. Touzain and A. Briggs, *J. Physique* **46**, 1961 (1985).
- 12) G.K. Ngnessan and Ph. Touzain, *Synth. Met.* **34**, 267 (1989).
- 13) Y. Murakami, T. Kishimoto and H. Suematsu, *Synth. Met.* **34**, 205 (1989).
- 14) H. Shioyama, K. Tatsumi, I. Souma and R. Fujii, *Tanso* **145**, 220 (1990).
- 15) S.A. Solin, *Physica* **99B**, 443 (1980).