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Electrochemical Intercalation of Organic Molecules into Thin Film of Layered Oxide MoO_3

Hideyuki TAGAYA,* Kensuke ARA, Tateaki OGATA, Koichi MATSUSHITA, † Jun-ichi KADOKAWA, Masa KARASU, and Koji CHIBA

Department of Materials Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992

† Department of Electrical and Information Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992

Electrochemical reduction of vacuum evaporated MoO_3 thin film in organic electrolyte solution resulted in the formation of organic intercalation compounds of pyridine, 4-methylpyridine and 4-propylpyridine. Interlayer spacings of MoO_3 increased to 12-19Å by the intercalation, and reduction of MoO_3 was confirmed by XPS measurement.

MoO_3 has a typical layered structure in which distorted MoO_6 octahedra share edges and vertices to form two-dimensional sheets which are separated by van der Waals gap,[1,2] and acts as a neutral host lattice having conductivity in intercalation reaction. It is believed that when the host lattice is neutral, electron donation from guest species to host lattice is a primary step of intercalation reaction.[3-5] Therefore, intercalation of a weak Lewis base organic by conventional thermal method is quite difficult. It has been already reported that chemical reduction of MoO_3 in an aqueous solution of $Na_2S_2O_4$ results in formation of $MoO_3^{x-}(Na^+)_x$.[6] The ion exchange reaction of $MoO_3^{x-}(Na^+)_x$ with a organic cation was relatively easy and various new organic intercalates were obtained.[7] However, the presence of a Na^+ ion by the incomplete ion exchange was not excluded. It is well known that intercalation reactions can be performed electrochemically. In this case the host lattice having conductivity such as transition metal dichalcogenides serves as the cathode of an electrochemical cell.[4]

Organic intercalation compounds into inorganic layer compounds are expected to have novel characteristics as a nano composite.[8-10] In this study we have prepared organic intercalates of MoO_3 by electrochemical reduction of MoO_3 in organic electrolyte instead of chemical reduction method to avoid undesirable co-intercalation. Although electrochemical reduction of MoO_3 in an aqueous solution was already reported by Schöllhorn, hydrated MoO_3 bronzes, $A_x(H_2O)_yMoO_3^{x-}$ where A is inorganic or organic guest, were products.[11]

Electrochemical reduction was carried out by using two types of MoO_3 electrode. They were MoO_3 powder bound by Teflon resin and MoO_3 thin film. Teflon binding MoO_3 electrode was used to get information on electrochemical properties of MoO_3. MoO_3 powder (5 g) was mixed with water suspension of Teflon resin (30%, 1 g) and dried to get gum state materials. Platinum mesh was held within the gum state MoO_3 as the

cathode.

The thin film of MoO_3 was prepared by vacuum evaporation of MoO_3[12] from electrically heated tungsten boats onto ITO conductive glass at a pressure range 4 to 8×10^{-5} Torr. Thickness of the MoO_3 thin films recorded using Sloan DEKTAK 3030 were 500 - 1000 nm. The film was amorphous. By heating the film at 400 ℃ for 2 h in a stream of oxygen gas, crystallized film was obtained as shown in Fig. 1 (b) and (c).

Each of the two types of the MoO_3 electrodes was dipped into 0.1 M organic perchlorate acetonitrile solution and polarized. Platinum and saturated calomel electrode were used as the counter and reference electrodes. After the reaction the sample electrode was washed with acetonitrile before dried.

In the cyclic voltammogram of Teflon binding MoO_3 electrode in acetonitrile solution of 4-propylpyridine, a reduction peak corresponding to the reduction of the host lattice and insertion of a propylpyridinium ion into the host lattice was observed at -1.0 to -1.3 V vs. SCE. The oxidation peak observed at about 0.3 V vs. SCE indicates the oxidation of host and deintercalation of guest ions which were confirmed by decoloration of the MoO_3 electrode.

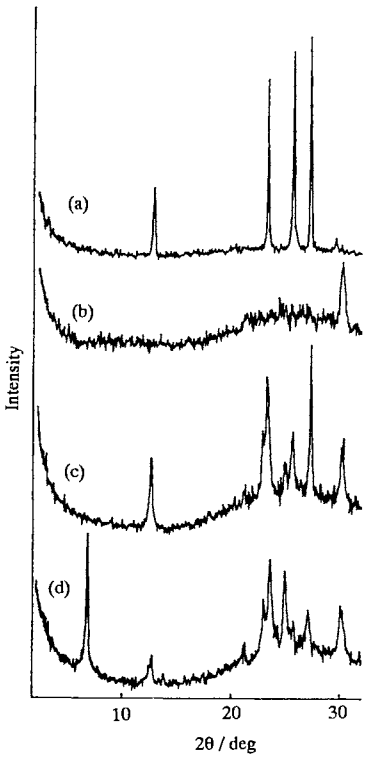
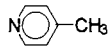
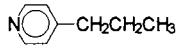
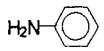
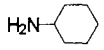


Fig. 1. XRD patterns of (a) MoO_3 powder, (b) MoO_3 thin film as prepared, (c) MoO_3 thin film after heat treatment of (b), and (d) after electrochemical reaction of (c) in the solution of methylpyridinium perchlorate.

By cathodic reduction of Teflon binding MoO_3 electrode in the solution of propylpyridinium perchlorate at -1.5 V vs. SCE, the working electrode turned dark blue immediately and interlayer spacing of MoO_3 increased from 6.9 to 19.2 and 12.6 Å in the reaction for 5 h. When the guest was pyridinium perchlorate, interlayer spacing increased to 12.4 Å. Table 1 shows the interlayer spacings of organic intercalation compounds obtained by electrochemical reduction. When the guests were methyl- and propylpyridines, two values of interlayer spacing were observed. Therefore, two conformation were

Table 1. Interlayer spacings of intercalation compounds obtained electrochemically

Guest	Interlayer spacing/Å
	12.4
	12.7,18.0
	12.6,19.2
	14.4
	17.9

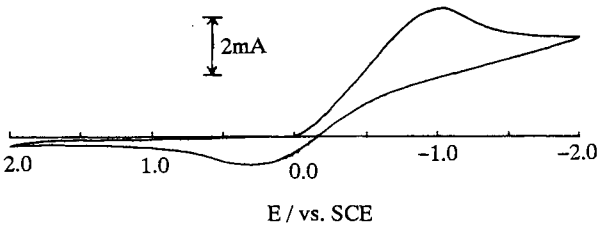


Fig. 2. Cyclic voltammogram of MoO_3 thin film in the solution of 4-propylpyridinium perchlorate.

suggested. The large interlayer expansion was twice as large as the size of aromatic ring and small one corresponded to the size of aromatic ring. Therefore, bilayer and single layer conformation were suggested. Bilayer conformation between MoO_3 layers was suggested by O'Hare et al. when the guest was 2-aminoethylferrocene.[13] The presence of two conformation should be caused by difference of concentration of guest molecules in the interlayer. Steric restriction by the presence of aliphatic chain was also important. When the guest molecules have no aliphatic chain, guest species are supposed to be placed as a single layer independent on its concentration. Certainly, in the case of pyridine, only one phase was obtained as shown in Table 1. Chemical formula of the 4-propylpyridine intercalate by chemical reduction method was $(propylpyridine)_{0.13}(Na)_{1.3}MoO_3$. Chemical formula by electrochemical reduction was $(propylpyridine)_{0.11}MoO_3$.

In the cases of aniline and cyclohexylamine the values of layer expansions were near to molecular size of aniline and cyclohexylamine.

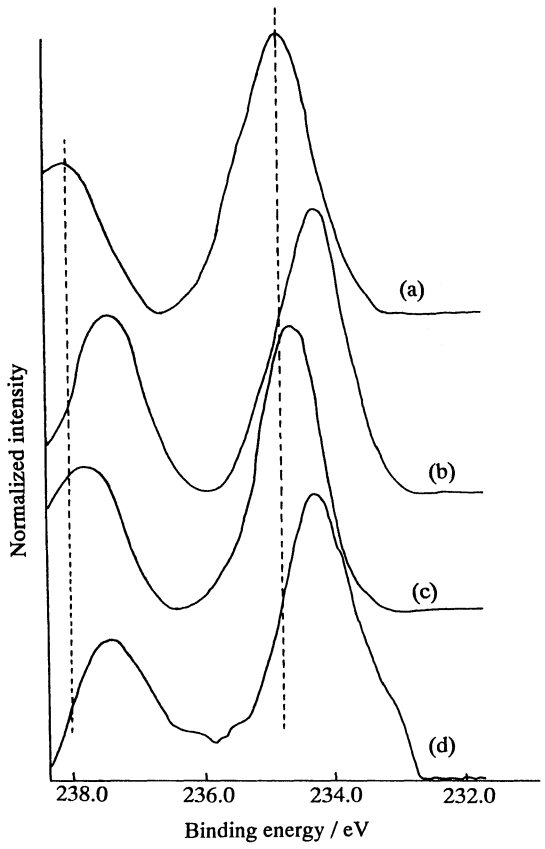


Fig.3. XPS patterns of (a) MoO_3 powder, (b) MoO_3 thin film in amorphous state, (c) (b) after heat treatment, and (d) (c) after electrochemical reaction.

Figure 2 shows the cyclic voltammogram measured in acetonitrile solution of 4-propylpyridinium perchlorate using the crystallized thin film electrode. The shape and positions of a reduction and oxidation peaks were similar with those of Teflon binded MoO_3 electrode. However, when the reduction of the thin film electrode was carried out at -1.5 V, ITO surface turned to black indicating the occurrence of undesirable reaction of ITO glass. Certainly, no intercalation reaction occurred. Cyclic voltammogram showed that alkylammonium and anilinium perchlorates were not reduced under -1.0 V vs. SCE. Actually, no reaction was observed by the reduction of them at -0.5 V vs. SCE. However, reduction of alkylpyridines occurred at - 0.5 V vs. SCE as shown in Fig. 2. Therefore, electrochemical reduction of MoO_3 thin film on ITO glass was carried out at -0.5 V vs. SCE in alkylpyridinium perchlorates. Reaction time was 1 min because a long reaction time led to exfoliation of thin film by swelling. Figure 1 (d) shows the XRD pattern of crystallized film after electrochemical treatment in the solution of methylpyridinium perchlorate. The interlayer spacing increased from 6.9 to 12.8 Å. The value was almost the same with 12.7 Å when Teflon binding MoO_3 electrode was used.

Valence state of Mo was measured by XPS spectroscopy which was calibrated by standard MoO_3.[7] Mo metal of vacuum evaporated MoO_3 thin film was in slightly reduced state as shown by XPS spectrum

in Fig. 3 (b). It was probably because of the oxygen lacking caused by heating in *vacuo*. After heat treatment of it in a stream of oxygen gas, peaks of MoO_3 itself appeared as shown in Fig. 1 (c). It indicated that the oxygen was recovered by the heat treatment in the presence of oxygen, and the reconstruction of crystallized structure occurred. After the electrochemical reactions, the peaks of XPS shifted to low energy levels as shown in Fig. 3 (d) indicating reduction of Mo metal.

Although two interlayer spacings were observed in the case of Teflon binding MoO_3, one interlayer spacing was observed in the case of organic intercalation into MoO_3 thin film. Probably the reaction time 1 min is too short to form intercalation compound with guest of high concentration.

In this study we have established the electrochemical intercalation method for MoO_3 thin film, and prepared organic intercalates of MoO_3 thin film. This electrochemical intercalation methods are expected to contribute the preparation of new classes of useful thin layer materials.

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