A Novel Electrochemical Method for Preparation of Thin Films of Layered Manganese Oxides

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(Received March 5, 2004; CL-040250)

Thin films of layered manganese oxides with alkylammonium and alkali-metal ions in the interlayer were formed on a platinum electrode by a one-step electrochemical route. The interlayer distance was determined by the size of the electrolyte cations used.

Manganese oxides with various valence states and crystalline structures, such as spinel, layered, and 1-D tunnel, have been extensively studied on their synthesis, structures, and physicochemical properties. As with other electroactive metal oxides, manganese oxide stores electrical charge by simultaneous insertion of electrons and cations into the solid. Recently, layered manganese oxides, in particular birnessite, have received increasing attention because of their unique adsorptive, catalytic, electrochemical, and ion-exchange properties. Birnessite has a 2-D layered structure, composed of edge-sharing [MnO_6] octahedra, with water molecules and cations occupying the interlayer space. Bach et al. have reported that Na–birnessite (birnessite with Na^+ in the interlayer) has a large discharge capacity as electrode materials in rechargeable Li batteries.[1] Long et al. have found that sol–gel-derived thin films of Na–birnessite cast on a transparent glass electrode showed high electrochromic efficiency due to facile mobility of the interlayer cations.[2] The preparation of birnessites with larger interlayer space were accomplished by using a two-step method, where organic ammonium ions were intercalated into the layers of synthesized proton birnessite by an ion-exchange mechanism.[3,4] Furthermore, it has been suggested that the birnessite with larger cations can be converted to electroactive nanosheets of MnO_2 by disintegrating the layered material into single sheets.[5]

A number of procedures have been developed for the synthesis of birnessite-type manganese oxide. However, no studies have yet been published on their electrochemical formation. The electrodeposition method provides very thin and uniform films even on substrates of complex shapes with high reproducibility. Thin conducting films adhered well to a substrate need no binders and conducting agents in their electrochemical use. In addition, one can precisely control the film thickness by monitoring the delivered electrical charge, thus making the process attractive for device fabrication.

We report here a one-step electrochemical route for preparing thin films of the birnessite-type layered manganese oxides with interlayer alkylammonium and alkali-metal ions. The process is constituted by potentiostatic oxidation of Mn^{2+} ions in aqueous solutions containing alkylammonium and alkali-metal chlorides.

Tetrabutylammonium (TBA) chloride (99%, Fluka) and tetraethylammonium (TEA) chloride (98%, Tokyo Kasei) were used as received. All electrolytic solutions were prepared with doubly distilled water and deoxygenated by bubbling purified nitrogen gas just prior to use. Electrochemical experiments were conducted in a standard three-electrode cell. A platinum sheet and an Ag/AgCl electrode were used as the counter and reference electrode, respectively. Films of manganese oxides with alkylammonium ions were deposited on a Pt plate (1 cm^2) electrode by applying a constant potential of +1.0 V in aqueous $MnSO_4$ (2 mM) solutions with 50 mM TBACl and TEACl. A film of potassium birnessite was similarly obtained with KCl instead of alkylammonium chloride. X-ray diffraction (XRD) experiments were performed using a Shimadzu XD-D1 spectrometer with Cu Kα radiation. An electron probe microanalyser (EPMA, Horiba EMAX-7000) was used to measure the molar ratio of carbon to manganese in the films.

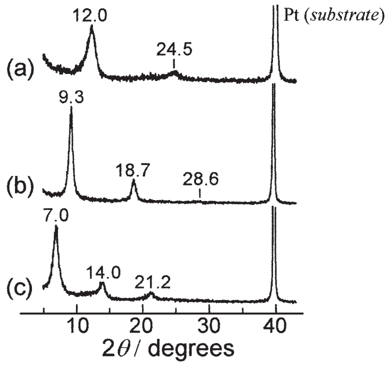

Figure 1. XRD patterns of manganese oxide films deposited on a Pt electrode by applying a constant potential of +1.0 V for 30 min in 2 mM $MnSO_4$ solutions with 50 mM KCl (a), TEACl (b) and TBACl (c).

Figure 1 shows XRD patterns of the films deposited on a Pt plate from the solutions with KCl (a), TEACl (b) and TBACl (c). In Figure 1a, two peaks were observed at the 2θ values of 12.0° and 24.5°, along with that due to Pt substrate. These values correspond to the d spacings of 0.73 and 0.36 nm, respectively. According to the literature, the 0.73 and 0.36 nm peaks can be indexed to the 001 and 002 reflections of potassium birnessite with an interlayer distance of 0.73 nm.[6] In the presence of TEA (Figure 1b), three peaks appeared at 9.3°, 18.7° and 28.6°. These peaks can be attributed similarly to the 001, 002, and 003 planes, respectively. When the largest ion TBA was introduced, a set of three peaks were shifted to lower angle, as shown in Figure 1c. These peaks are the same as those of the chemically-prepared TBA–birnessite which was obtained by treating proton birnessite with an aqueous TBAOH solution.[3,4] The interlayer distances of the manganese oxides deposited from TEA- and TBA-containing solutions correspond to 0.96 and 1.26 nm, respectively. These findings clearly demonstrate the formation of the films of birnessite-type manganese oxides. The interlayer distance is determined by the size of the electrolyte cations.

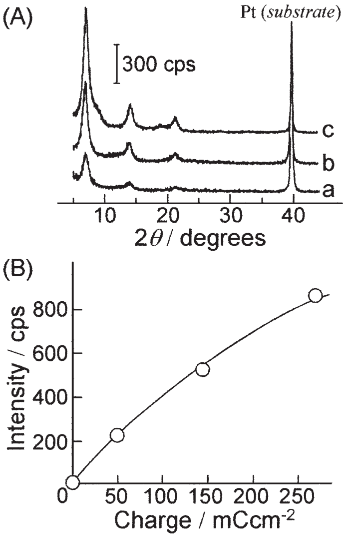

Figure 2. (A) XRD patterns of the TBA-incorporated films prepared by applying a constant potential of +1.0 V for 10 (a), 30 (b) and 60 (c) min. (B) Plots of the peak intensity at the 001 reflection in Figure 2A versus the quantity of charge passed.

Figure 2A shows the XRD patterns of the TBA-incorporated films obtained by changing the electrolysis time, and the intensity of the 001 peak was plotted against the quantity of charge passed during the electrolysis. In these figures, the peak intensity increases with an increase in the film thickness without changing the pattern, revealing that the bulk of the film consists of the layered structure, and the crystalline growth proceeds electrochemically.

Birnessite is denoted as a chemical formula of $A_xMnO_2 \cdot nH_2O$ (A = H, Na, K, etc.) Assuming that the electroformation of the birnessite film takes place similarly to that of the electrochemical manganese dioxide (γ-MnO_2),[7] the formation process can be described as follows:

$$\begin{aligned} &Mn^{2+} + (2+n)H_2O + xA^{+} \\ &\quad \rightarrow A_xMnO_2 \cdot nH_2O + 4H^{+} + (2-x)e^{-} \end{aligned}$$

where the amount of incorporated cations should be determined by the oxidation state of manganese. In fact, the films grown at other potentials (+0.9 and +1.1 V) exhibited no diffraction peaks for all the cations examined, indicating the crystallographically amorphous nature. On the basis of the EPMA analysis, the TBA/Mn mole ratio of the electrodeposited film was estimated to be 0.33, similar to the values of chemically-prepared birnessites with small cations.[8]

The TBA-incorporated manganese oxide film was immersed in a 0.001 M KCl solution for given periods of time, and the dried samples were subjected to XRD analysis. Time variation of the XRD pattern is shown in Figure 3. Three peaks due to the TBA-incorporated phase immediately decreased in intensity, and the pattern attributable to K–birnessite became predominant after 10 min and then increased gradually. This indicates the deintercalation of the TBA ions, accompanied with a shrinking of the interlayer. In this figure, we cannot find any mixture of the individual patterns from the TBA- and K-intercalated phases, which may mean uniformity of the electrodeposited film.

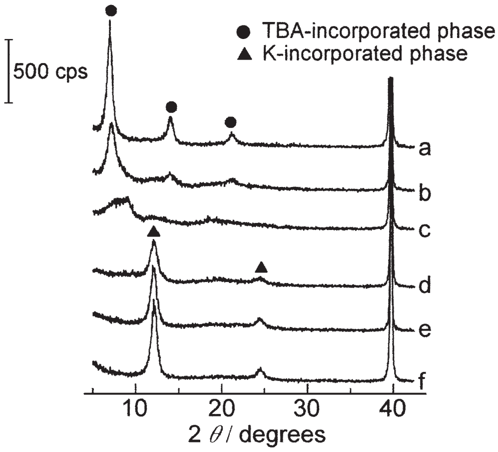

Figure 3. XRD patterns for the TBA-incorporated manganese oxide film after immersing in a 0.001 M KCl solution for 0 (a), 0.25 (b), 1 (c), 10 (d), 60 (e) and 720 (f) min. The film was prepared by the same way as that in Figure 1c.

In summery, the potentiostatic electrolysis of Mn^{2+} in the presence of alkali-metal and organic ammonium ions yields thin films of birnessites with different interlayer spacing. This technique can provide in principle electroactive nanosheets or ultrathin films by controlling the delivered charge.

This research was supported by the Japan Society of the Promotion of Science (No. 14750658) and the Saneyoshi Scholarship Foundation.

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Published on the web (Advance View) May 10, 2004; DOI 10.1246/cl.2004.670