

# Electrochemical Synthesis and Characterization of Birnessite-Type Layered Manganese Oxides

Masaharu Nakayama,\* Sayaka Konishi, Hiromoto Tagashira, and Kotaro Ogura

Department of Applied Chemistry, Yamaguchi University  
2-16-1 Tokiwadai, Ube 755-8611, Japan

Thin films of layered birnessite-type manganese oxides with tetrabutylammonium ( $\text{Bu}_4\text{N}^+$ ), tetraethylammonium ( $\text{Et}_4\text{N}^+$ ), and ammonium ions occupying the interlayer space were formed on a platinum substrate by a one-step electrochemical route. The interlayer distance can be controlled by the size of the electrolyte cations used.

## Introduction

Layered manganese oxides, in particular birnessite, have recently received widespread attention because of their unique adsorptive, catalytic, ion-exchange, and electrochemical properties. Birnessite consists of edge-sharing  $\text{MnO}_6$  octahedra that form a layer structure with cations and water molecules between layers. So far, a number of procedures have been developed for the synthesis of birnessite-type manganese oxides. However, no studies have yet been published on their electrochemical formation, despite the electrodeposition method provides very thin and uniform films even on substrates of complicated shape with high reproducibility. In addition, this technique enables one to control the film thickness precisely by monitoring the delivered electrical charge. We report here a one-step electrochemical route for preparing thin films of birnessite-type layered manganese oxides with different interlayer distances.<sup>1</sup> The process is constituted by potentiostatic oxidation of  $\text{Mn}^{2+}$  in aqueous solutions containing tetraalkylammonium ions with different methylene chain lengths.

## Experimental

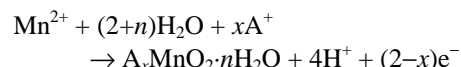
Manganese oxide thin films were prepared on a Pt plate electrode by applying constant potentials for 30 min in aqueous 2 mM  $\text{MnSO}_4$  solutions containing  $\text{Bu}_4\text{NCl}$ ,  $\text{Et}_4\text{NCl}$ , and  $\text{NH}_4\text{Cl}$  at a concentration of 50 mM. Pt sheet and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. Sample films on a Pt substrate were subjected to X-ray diffraction (XRD) analysis in their dry state, using Cu  $K\alpha$  radiation (30 kV, 30 mA).

## Results and Discussion

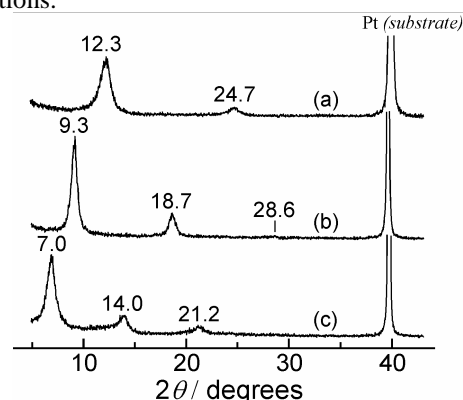
Figure 1 shows XRD patterns of the films deposited at +1.0 V from the solutions with  $\text{NH}_4\text{Cl}$  (a),  $\text{Et}_4\text{NCl}$  (b) and  $\text{Bu}_4\text{NCl}$  (c). In Fig. 1a, two peaks were observed at  $2\theta$  values of  $12.3^\circ$  and  $24.7^\circ$ , along with that due to Pt substrate. These values correspond to  $d$  spacings of 0.73 and 0.36 nm, respectively, according to Bragg's law. On the basis of the literature data, the 0.73 and 0.36 nm peaks can be indexed to the 001 and 002 reflections of the birnessite with an interlayer distance of 0.73 nm.<sup>2</sup> In the presence of  $\text{Et}_4\text{N}^+$  (Fig. 1b), three peaks appeared at  $9.3^\circ$ ,  $18.7^\circ$ , and  $28.6^\circ$ , which can be attributed similarly to the 001, 002 and 003 reflections, respectively. When the largest cation  $\text{Bu}_4\text{N}^+$  was introduced (Fig. 1c), a set of three peaks moved to lower angles and correspondingly larger  $d$  spacings. These peaks are the same as those reported for the  $\text{Bu}_4\text{N}^+$ -incorporated birnessite that was obtained chemically by the intercalation of  $\text{Bu}_4\text{N}^+$  ions into proton birnessite.<sup>3</sup> The basal spacings of the manganese oxides deposited from  $\text{Et}_4\text{N}^+$  and  $\text{Bu}_4\text{N}^+$  solutions correspond to 0.96 and 1.26 nm, respectively.

These findings clearly demonstrate the electroformation of birnessite-type manganese oxides, where the interlayer distance is determined by the size of the electrolyte cations.

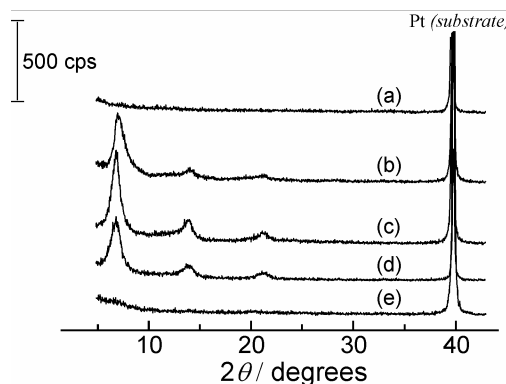
XRD patterns of the manganese oxide films prepared with  $\text{Bu}_4\text{NCl}$  by applying different fixed potentials are shown in Figure 2. It is clear from this figure that the diffraction lines indicative of the layered phase are observed only in the potential region between +0.95 and +1.05 V. Birnessite is denoted as a general formula  $\text{A}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$  ( $\text{A}=\text{H}, \text{Na}, \text{K}, \text{etc.}$ ). Assuming that the electroformation of the birnessite films proceeds similarly to that of the electrochemical manganese dioxide ( $\gamma\text{-MnO}_2$ ), the formation process can be written as follows:



Thus, the cation content in the film is governed by the oxidation state of manganese, which depends strongly on the applied potential. Indeed, the  $\text{Bu}_4\text{N}^+$  to Mn ratio in the film deposited at +1.0 V was evaluated to be 0.33 by electron probe microanalysis, which is in agreement with the values reported for the typical birnessites with small metal cations.



**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  $\text{MnSO}_4$  solutions with 50 mM  $\text{NH}_4\text{Cl}$  (a),  $\text{Et}_4\text{NCl}$  (b), and  $\text{Bu}_4\text{NCl}$  (c).



**Figure 2** XRD patterns of manganese oxide films obtained from a  $\text{Bu}_4\text{N}^+$ -containing manganese solution by applying constant potentials of +0.9 (a), +0.95 (b), +1.0 (c), +1.05 (d), and +1.1 V (e).

## References

1. M. Nakayama, S. Konishi, A. Tanaka, and K. Ogura, *Chem. Lett.*, **33**, 670 (2004).
2. Q. Feng, Y. Miyai, H. Kanoh, and K. Ooi, *Chem. Mater.*, **7**, 1226 (1995).
3. J. Luo and S. L. Suib, *Chem. Commun.*, **1997**, 1031.