Inorg. Chem. **2004**, *43*, 8215–8217

Inorganic Chemistry
Communication

A Direct Electrochemical Route to Construct a Polymer/Manganese Oxide Layered Structure

Masaharu Nakayama,* Hiroki Tagashira, Sayaka Konishi, and Kotaro Ogura

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

Received September 17, 2004

A layered nanocomposite with poly(diallyldimethylammonium), PDDA, intercalated between manganese oxide layers can be formed on a platinum electrode in a thin film form through a direct electrochemical route. The process involves a potentiostatic oxidation of aqueous Mn^{2+} precursors in the presence of PDDA by applying a constant potential (+1.0 V vs Ag/AgCl).

A variety of organic polymers and inorganic solids have been successfully combined to form nanocomposite structures.[1−3] Nanocomposites sometimes offer improved mechanical, catalytic, electronic, and optical properties that are distinct from those of the pure component phases and those of the related macro- and microcomposites. Layered nanocomposites are materials usually composed of an organic polymer included between layers of an inorganic host. Much effort has been devoted to developing synthetic methods for these materials, which include the following: (i) in situ polymerization of intercalated monomers; (ii) exfoliation of a layered host and subsequent adsorption of polymer and reaggregation; (iii) template synthesis of host structures in polymer-containing solutions; (iv) direct melt intercalation of polymers into hosts.[4−8]

Layered manganese oxides have attracted considerable attention due to their unique adsorptive, catalytic, and electrochemical properties. Small cations such as potassium or protons are normally located in the galleries to compensate negative charges on manganese oxide layers. Some organic ammonium ions can also be intercalated between layers by ion-exchange, accompanied by an expansion of the interlayer.[9,10] However, layered manganese oxides possess a high charge density in the interlayer, which makes it very difficult to synthesize nanocomposites intercalated with polycations by a conventional ion-exchange procedure. Recently, Liu et al. have provided a breakthrough to such a problem.[11] They prepared a layered nanocomposite with poly(diallyldimethylammonium) (PDDA) cations incorporated between manganese oxide layers by a delamination/reassembling process, where the slurry of exfoliated manganese oxides was soaked in a PDDA solution. Spontaneous layer-by-layer electrostatic assembly is a method for preparing ultrathin film, which is based on the alternate adsorption of oppositely charged polyions.[12−15] Sasaki et al. have first applied this technique to fabricate ordered multilayered films with exfoliated manganese oxide nanosheets and PDDA ions.[16] Thin films are the desirable form of metal oxides for use in electronic, optical, magnetic, and electrochemical applications.

Among various techniques for fabrication of thin metal oxide films, electrochemical deposition is one of the most promising approaches, particularly for obtaining thin and uniform films on substrates of complex shape with high reproducibility.[17] Conducting films adhering well to a substrate need no binders or conductive additives in their electrochemical use. More importantly, one can fine-tune the film thickness by simply changing the delivered electrical charge.

Herein, we present a new synthetic strategy for building a polymer/manganese oxide layered structure with a thin film form. The product is crystallized electrochemically from a homogeneous aqueous solution of PDDA and Mn^{2+} ion precursors by a potentiostatic oxidation at $+1.0$ V versus Ag/AgCl.

---

* To whom correspondence should be addressed. E-mail: nkymm@yamaguchi-u.ac.jp.

(1) Lerf, A. Intercalation Compounds in Layered Host Lattices: Supramolecular Chemistry in Nanodimensions. In *Handbook of Nanostructured Materials and Nanotechnology*; Nalwa, H., Ed.; Academic Press: New York, 2000; Vol. 5, pp 1−166.
(2) Komarneni, S. *J. Mater. Chem.* **1992**, *2*, 1219.
(3) Ozin, G. A.; Ozkar, S. *Adv. Mater.* **1992**, *4*, 612.
(4) Lerner, M. M.; Oriakhi, C. O. Polymers in Ordered Nanocomposites. In *Handbook of Nanophase Materials*; Goldstein, A., Ed.; Marcel Dekker: New York, 1997; pp 199−219.
(5) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
(6) Oriakhi, C. *J. Chem. Educ.* **2000**, *77*, 1138.
(7) Carrado, K. A.; Xu, L.; Seifert, S.; Csencsits, R.; Bloomquist, C. A. A. Polymer-Clay Nanocomposites Derived from Polymer-Silicate Gels. In *Polymer-Clay Nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; Wiley & Sons: New York, 2000; pp 47−63.
(8) Carrado, K. A. Polymer-Clay Nanocomposites. In *Advanced Polymeric Materials: Structure Property Relationships*; Advani, S. G., Shonaike, G. O., Eds.; CRC Press: Boca Raton, FL, 2003; pp 349−396.
(9) Luo, J.; Suib, S. L. *Chem. Commun.* **1997**, 1031.
(10) Brock, S. L.; Sanabria, M.; Suib, S. L.; Urban, V.; Thiyagarajan, P.; Potter, D. I. *J. Phys. Chem. B* **1999**, *103*, 7416.
(11) Liu, Z.; Yang, X.; Makita, Y.; Ooi, K. *Chem. Mater.* **2002**, *14*, 4800.
(12) Decher, G. *Science* **1997**, *277*, 1232.
(13) Kotov, N. A.; Haraszti, T.; Turi, L.; Zavala, G.; Geer, R. E.; Dékány, I.; Fendler, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 6821.
(14) Cassagneau, T.; Mallouk, T. E.; Fendler, J. H. *J. Am. Chem. Soc*. **1998**, *120*, 7848.
(15) Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. *Macromolecules* **1999**, *32*, 2317.
(16) Wang, L.; Omomo, Y.; Sakai, N.; Fukuda, K.; Nakai, I.; Ebina, Y.; Takada, K.; Watanabe, M.; Sasaki, T. *Chem. Mater.* **2003**, *15*, 2873.
(17) Therese, G. H. A.; Kamath, P. V. *Chem. Mater.* **2000**, *12*, 1195.

10.1021/ic048691d CCC: $27.50

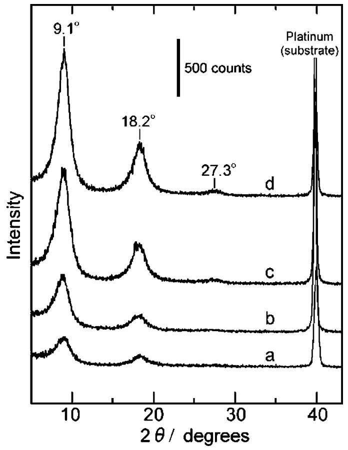

Figure 1. XRD patterns of manganese oxide films on a Pt electrode prepared from a 2 mM $MnSO_4$ and 5.6 mM PDDACl solution by applying a constant potential of +1.0 V for (a) 30, (b) 60, (c) 120, and (d) 240 min.

Poly(diallyldimethylammonium) (PDDA) chloride (20% solution in water, MW 400 000−500 000) was purchased from Aldrich and used without further purification. All solutions were prepared with doubly distilled water and deoxygenated by bubbling nitrogen gas before use. Electrochemical experiments were conducted in a conventional three-electrode cell. A platinum sheet and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Manganese oxide films with PDDA were prepared on a Pt plate (1 cm^2) electrode by applying a constant potential of +1.0 V for 30−240 min in aqueous $MnSO_4$ (2 mM) solutions containing 1−56 mM PDDACl as a monomer concentration (most experiments were carried out with a PDDA concentration of 5.6 mM). This procedure is similar to what we previously reported for the formation of thin films of layered manganese oxides intercalated with alkylammonium ions.[18,19]

The resulting Pt-supported films were rinsed with copious amounts of water and then dried under vacuum. X-ray diffraction (XRD) patterns were obtained in a Shimadzu XD-D1 spectrometer using Cu Kα radiation ($\lambda = 0.15405$ nm). X-ray photoelectron spectra were collected using a Fisons Escalab 210 spectrometer, with an Al Kα (1486.6 eV) unmonochromatic source (15 kV, 20 mA). Wide- and narrow-range spectra were collected with a pass energy of 20 eV and a channel width of 0.1 and 0.01 eV, respectively. Curve fitting was made by a mixture of Gaussian and Lorentzian functions on a Shirley-type background. Semiquantitative estimates of the atomic concentrations were obtained from the peak area ratios by considering the appropriate sensitivities: Mn $2p_{1/2} = 4.74$, N 1s $= 1.80$, and O 1s $= 2.93$.

Figure 1 displays X-ray diffraction patterns of the manganese oxide films on a Pt electrode deposited from a $MnSO_4$ solution with 5.6 mM PDDA at a constant potential of +1.0 V for indicated periods of time. We can see diffraction peaks at $2\theta = 9.1$, 18.2, and 27.3°, which are equally spaced by 9.1°, respectively. These can be indexed to the reflections of ($00l$, $l = 1-3$) for the manganese oxide layers, as previously observed for birnessite-type layered manganese oxides.[20,21] According to Bragg's equation, these 2θ values indicate d-spacings of 0.97, 0.49, and 0.33 nm, respectively, and the d_{001} value (0.97 nm) corresponds to the interlayer spacing. The peaks increase in intensity with an increase in the deposition time without changing the pattern, indicating that the bulk of the film is composed of a layer structure and the crystalline growth proceeds electrochemically. Diffraction peaks indicative of a layered structure were obtained in the potential region from +0.9 to +1.0 V (Supporting Information I), which is similar to the result observed for the alkylammonium-intercalated coumponds.[19]

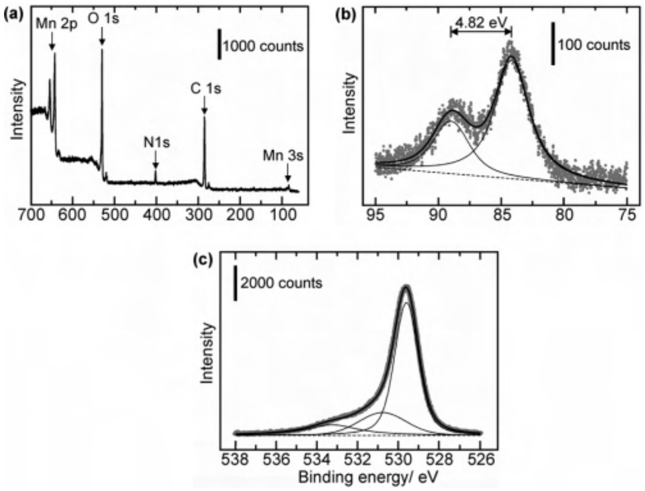

Figure 2. (a) XPS wide-scan, and (b) Mn 3s and (c) O 1s core-level spectra of the manganese oxide film on a Pt electrode. The film was prepared by the same method as that in Figure 1a.

A repeating periodicity of 0.97 nm is close to that (0.92 nm) observed for the multilayer ultrathin films composed of manganese oxide nanosheets and PDDA ions, which were prepared by Sasaki et al.[16] They attributed the spacing of 0.92 nm to the intercalation of one molecular layer of PDDA between the manganese oxide layers. This is consistent with the data that manganese oxide sheet and PDDA are 0.45 and 0.5 nm in thickness, respectively.[22,23] Therefore, we can assign the obtained d_{001} value to the accommodation of a monolayer of PDDA in parallel arrangement.

Figure 2a shows an XPS wide-scan spectrum of the electrodeposited crystalline film on a Pt electrode. Besides the Mn 2p, O 1s, and Mn 3s peaks due to manganese oxide, the N 1s peak centered at 402.1 eV and the C 1s peak at 285.0 eV are detected, which can be attributed to nitrogen and carbon coming from the incorporated PDDA. There is no peak in the Cl 2p (around 200 eV) region, confirming that PDDA exists in a polycation form and not as a chloride salt.

In Figure 2b, the Mn 3s core level spectrum exhibits multiple splitting in the form of two peaks at 89.00 and 84.18 eV. This splitting is induced by the parallel spin coupling

---

(18) Nakayama, M.; Konishi, S.; Tanaka, A.; Ogura, K. *Chem. Lett.* **2004**, *33*, 670.

(19) Nakayama, M.; Konishi, S.; Tagashira, H.; Ogura, K. *Langmuir*, in press.

(20) Golden, D. C.; Chen, C. C.; Dixon, J. B. *Clays Clay Miner.* **1987**, *35*, 271.

(21) Wang, S.-T.; Cheng, S. *Inorg. Chem.* **1992**, *31*, 1165.

(22) Post, J. E.; Veblen, D. R. *Am. Mineral.* **1990**, *75*, 477.

(23) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1996**, *12*, 3038.

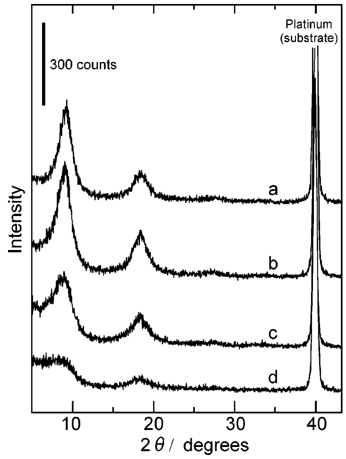

Figure 3. XRD patterns of manganese oxide films on a Pt electrode prepared by applying a constant potential of +1.0 V in 2 mM $MnSO_4$ solutions containing PDDACl with concentrations of (a) 1, (b) 5.6, (c) 25, and (d) 56 mM. The electric charge passed during electrolysis was always 330 mC cm^{-2}.

between electrons in 3s and 3d energy levels during the photoelectron ejection. The separation of the peak energy (ΔE) is sensitive to the oxidation state of manganese. When the mean oxidation state decreases, the 3s peak splitting increases due to more electrons in the 3d orbital.[24-26] According to a linear relationship in the literature[26] between the oxidation state of manganese and the ΔE value, the value (4.82 eV) obtained corresponds to an oxidation level of 3.8−3.9. The O 1s spectrum (Figure 2c) is composed of three contributions originating from the Mn−O−Mn bond (529.6 eV), the Mn−OH bond (530.8 eV), and structural water (533.2 eV).[27] Their relative percentages were 65.3%, 19.4%, and 15.3%, respectively. Using the O 1s and Mn $2p_{1/2}$ peak area ratios and their sensitivities, the molar ratios of O^{2-} and OH^- to Mn were estimated to be 1.89 and 0.56, respectively. The Mn $2p_{1/2}$ and N 1s peak areas gave the PDDA/Mn molar ratio of 0.40. Hence, the film can be written as a chemical formula of $(C_8H_{16}NH_2)_{0.40}MnO_{1.89}(OH)_{0.56}\cdot(H_2O)_{0.44}$ (Supporting Information II). This formula leads to a manganese valence of 3.9, which is consistent with that estimated from the energy splitting of Mn 3s doublet.

XRD and XPS analyses revealed that the PDDA polycations were not ion-exchanged with protons or alkali metal cations such as K^+. Similar behavior was previously observed for the PDDA/MnO_2 nanocomposite prepared by Liu et al.[11]

Figure 3 shows XRD patterns of the films obtained from the solutions containing different concentrations of PDDA, where the electric charge passed during electrolysis was always 330 mC cm^{-2}. The crystallinity of the electrodeposited film strongly depends on the PDDA concentration. The amorphous nature of the film deposited with a PDDA concentration of 56 mM is confirmed by the XRD pattern. This may be accounted for by an increase in the hydrophobic interaction of polycations, which relatively weakens the electrostatic attractive force between the cations and negative charges on manganese oxide during electrodeposition.

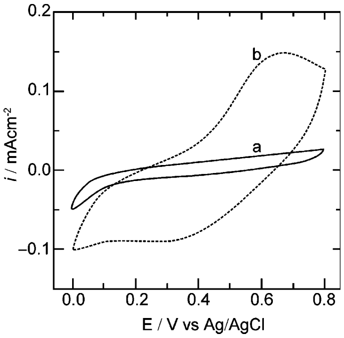

Figure 4. Cyclic voltammograms of the film coated-Pt electrodes in a 0.1 M KCl solution at a scan rate of 20 mV s^{-1}. The films were prepared from 2 mM $MnSO_4$ solutions containing (a) 5.6 and (b) 56 mM PDDACl by applying a constant potential of +1.0 V for 30 min.

Figure 4 compares typical cyclic voltammograms (measured in 0.1 M KCl at a scan rate of 20 mV s^{-1}) of the layered PDDA/Mn oxide film versus the amorphous counterpart. As shown in curve b, the amorphous film exhibits an oxidation wave peaked at +0.65 V on the positive going scan and a reduction wave at around +0.30 V on the reverse scan. These peaks are attributable to the oxidation/reduction of Mn^{3+}/Mn^{4+} in the oxide, accompanying the exclusion/inclusion of cations, respectively.[28] This CV curve means that the amorphous surface of manganese oxide is accessible to charge compensating cations in the electrolyte (K^+ and/or H^+). However, the response for the crystalline film is diminished dramatically (Figure 4a). The PDDA ions in the interlayer cannot be replaced by electrolyte cations, as described above. Accordingly, the manganese oxide surface remains associated with the intercalated polymer and inaccessible to the electrolyte cations. Such an obvious difference in the electrochemical responses implies that most of the manganese oxide surface of the crystalline film is present inside the layer structure, not on the external surface. This enables us to think that the electrodeposited layer structure is well-ordered over the entire film.

In summary, we have demonstrated a direct electrochemical route for building a polymer nanocomposite with layered manganese oxide. The new approach is simple, fast, reproducible, and inexpensive. This technique offers researchers a strategy for forming a wide variety of advanced organic−inorganic composites. Although the exact electrodeposition mechanism is not clear, it is certain that the polycations act as a template during the nucleation and growth of manganese oxide. Further study on the film formation process is now in progress and will be published elsewhere.

Acknowledgment. This research was supported in part by the Japan Society of the Promotion of Science (16750175).

Supporting Information Available: XRD patterns of the films prepared at different potentials and XPS data for quantification. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048691D

---

(24) Chigane, M.; Ishikawa, M. *J. Electrochem. Soc.* **2000**, *147*, 2246.

(25) Carver, J. C.; Schweitzer, G. K.; Carlson, T. A. *J. Chem. Phys.* **1972**, *57*, 973.

(26) Toupin, M.; Brousse, T.; Bélanger, D. *Chem. Mater.* **2002**, *14*, 3946.

(27) Casella, I. G.; Gatta, M. *Anal. Chem.* **2000**, *72*, 2969.

(28) Córdoba de Torresi, S. I.; Gorenstein, A. *Electrochim. Acta* **1992**, *37*, 2015.