Preparation of a Polycation-Intercalated Layered Manganese Oxide Nanocomposite by a Delamination/Reassembling Process

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A layered manganese oxide nanocomposite (PDDAMO) with poly(diallyldimethylammonium chloride), PDDA, incorporated between manganese oxide sheets, was synthesized by a delamination/reassembling process. The product was characterized by powder X-ray diffraction, elemental analysis, thermal analysis, FT-IR spectroscopy, and FE-SEM observation. XRD analysis showed that the expansion of the interlayer depended on the amount of PDDA intercalated; the largest expansion was 1.09 nm, corresponding to a bilayer of PDDA chains in the interlayer. Chemical analysis results showed that the PDDA intercalation progressed by an ion-exchange mechanism, and the PDDA polymer existed in a polycation form, not as a chloride salt. PDDAMO was comprised of platelike nanocomposite particles that were 1−5 μm in width. The thickness of each plate was 30 nm on average, which corresponds to the stacking of about 20 sheets of manganese oxide. The formation of the PDDAMO nanocomposite was hardly affected by the pH of the solution. PDDAMO had a high stability against extraction by acid treatment, probably due to the strong electrostatic attraction between manganese oxide sheets and PDDA chains.

Introduction

The field of organic and inorganic nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas in materials chemistry because these materials have proved to exhibit a variety of unique properties due to the synergies of the inorganic and organic components.[1−6] A series of new synthesis methods for nanocomposite materials have been developed, such as the in situ polymerization of intercalated monomers, the exfoliation of a layered host and subsequent adsorption of polymer and reaggregation, template syntheses of host structures in polymer-containing solutions, and direct melt intercalation of a polymer into hosts.[7−9]

Layered manganese oxides are important two-dimensional layered inorganic materials due to their unique adsorptive, catalytic, and electrochemical properties.[10] Some organic alkylammonium ions have been intercalated into the interlayer by an ion-exchange reaction, accompanied by the expansion of the interlayer. The expanded layered manganese nanocomposites can be used as molecular sieves or precursors to synthesize porous manganese oxides.[11−14] However, layered manganese oxides have a higher charge density in the interlayer than the other layered materials, making the synthesis of layered manganese nanocomposites by a conventional intercalation reaction difficult with bulky guest ions or polymer in the interlayer.

The delamination/reassembling process has proved to be an alternative route for the synthesis of an interlayer nanocomposite. Because the delaminated inorganic sheets have a higher degree of freedom than the stacked sheets, the bulky guest ions or polymer molecules can be easily adsorbed onto their surface. Many layered nanocomposite materials or films with novel properties have been synthesized by this method,[15−20] for example, titanium dioxide flakes with porous aggragates,[15] a

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graphite oxide nanocomposite with a higher stability against organic solvents,[16] layered zirconium phosphate as a protonic conductor,[17] layered double hydroxides with a wide range of tunable materials,[18] smectite clay minerals,[19] and layered perovskites.[20] We were the first to succeed in the delamination of the layered manganese oxide (BirMO(H)) by intercalation of tetramethylammonium ions (TMA^+) followed by water washing.[21] The delaminated manganese oxide, which can be described as nanosheets, can be used as a suitable starting material for the preparation of layered manganese oxide nanocomposites. Layered manganese oxide nanocomposites of ultimate two-dimensionality with thickness in the subnano- to nanometer range, good crystallinity, and novel physical properties can be fabricated.

PDDA is an interesting polymer due to its high conductivity in combination with excellent stability, a relatively high transparency to visible light, and aqueous processability. Many PDDA nanostructure films or nanocomposites have been synthesized and they carry good potential for industrial use.[22−27] However, there have been no reports of a PDDA-intercalated manganese oxide nanocomposite. In this work, we succeeded for the first time in preparing a new layered nanocomposite of PDDA-intercalated manganese oxide by a delamination/reassembling process. The obtained manganese oxide nanocomposite is expected to find use as novel selective adsorbents or as a cathode material for lithium batteries.

Experimental Section

Preparation. The proton-type birnessite manganese oxide (BirMO(H)) was prepared by the acid treatment of highly crystallized sodium-type birnessite (BirMO(Na)) in a 0.1 M HCl solution.[28] The acid-treated sample has a chemical formula of $H_{3.49}Na_{0.21}Mn_{12}O_{23}\cdot 9.5H_2O$ and cation-exchange capacity of 2.70 mmol/g. Delamination of BirMO(H) was carried out by the method described in the literature.[21] BirMO(H) (0.5 g) was treated in a 0.35 M aqueous solution of tetramethylammonium hydroxide (TMAOH) (125 cm^3) for 7 days at room temperature. The amount of TMAOH added was 25-fold that of the exchangeable capacity of BirMO(H). After soaking, the colloidal suspension was centrifuged at a speed of 13 000 rpm for 20 min and washed with 100 cm^3 of distilled water four times to obtain a delaminated BirMO slurry. The filtrates in the wet state were subjected to XRD analysis by an X-ray diffractometer equipped in a humidity-/temperature-controllable chamber at a humidity around 90% and temperature at 30 °C. Water washing caused a partial deintercalation of TMA^+ ions; the remaining TMA^+ content was 1.67 mmol/g in the dried BirMO slurry.

The delaminated BirMO slurry was poured into an aqueous solution of poly(diallyldimethylammonium) (PDDA) chloride with a monomer concentration of 0.03 M. PDDA ($M_w \approx$ 300 000) was purchased from Wako Pure Chemical Co. and used without further purification. The ratio ($R_{PD/Mn}$) of diallyldimethylammonium monomer (mmol) to birnessite (H) (mmol) was adjusted to 1 and the pH of the solution to 10.0 with a 0.5 M aqueous ammonia solution. The mixture was maintained overnight while stirring at room temperature. The product was collected by centrifugation, washed with distilled water, and then dried for 1 day at 70 °C. The PDDA-intercalated layered manganese oxide nanocomposite was designated as PDDAMO.

The influences of the initial PDDA concentration and pH on the nanocomposite structure were studied by changing the $R_{PD/Mn}$ value and the pH of the PDDA solution. Deintercalation of PDDA polycations from the interlayer was studied by mixing the PDDAMO sample with a 0.1 M HNO_3 solution at room temperature for 3 days.

Characterization. X-ray diffraction (XRD) analysis was carried out using a Rigaku-type RINT 1200 X-ray diffractometer with a graphite monochromator at room temperature. Infrared spectra were obtained by the KBr method on a Perkin-Elmer infrared spectrometer (1600 Series FTIR). TG-DTA curves were obtained on a MAC Science thermal analyzer (system 001, TG-DTA 2000) at a heating rate of 10 °C/min. FE-SEM observation was carried out with a JEOL-type JSM-890 high-resolution scanning electron microscope.

The TN (total nitrogen) and TC (total carbon) contents of samples obtained at different conditions were determined by a Sumigraph-type NCH-21 analyzer. The Mn contents of samples were determined by atomic adsorption spectrometry after they were dissolved in a mixed solution of HCl and H_2O_2. The Cl^- content was analyzed by Mohr's method after the samples were dissolved in a mixed solution of HNO_3 and H_2O_2, with $KCrO_4$ as an indicator and $NaHCO_3$ as the pH controller.

Results and Discussion

Formation Process of Layered Manganese Oxide Nanocomposite, PDDAMO. The direct intercalation reaction of PDDA polymer was studied using the BirMO(H) and a 0.03 M PDDA solution at pH 10.0 and room temperature for 3 days. The XRD pattern showed no change after the treatment, indicating that the intercalation of PDDA molecules rarely progresses by conventional intercalation reaction.

The XRD diffraction patterns of the starting BirMO(H), delaminated BirMO slurry, and the final product, PDDAMO, are shown in Figure 1. Starting BirMO(H) has a layered structure with a basal spacing of 0.73 nm (Figure 1a). An unidentified peak is observed at $2\theta = 26.1°$, probably due to the presence of a minor amount of impurities. Similar peaks are also observed for the interlayer manganese oxide compounds described below. The XRD pattern of the colloidal suspension itself (Figure 1b) gives no clear peaks but only an amorphous halo, in striking contrast to that of the unwashed sample. The halo can be interpreted as scattering from the nanosheets, which are aggregated irregularly, similar to the case of layered titanic acid.[29,30] This indicates that water washing causes the delamination of stacked manganese oxide plates to the individual primary plates. We have studied the delamination process of the layered manganese oxide in the previous paper.[21] A suitable sheet charge density accompanied by a low ionic concentration is required for the delamination of layered manganese oxides. Water washing causes a simulta-

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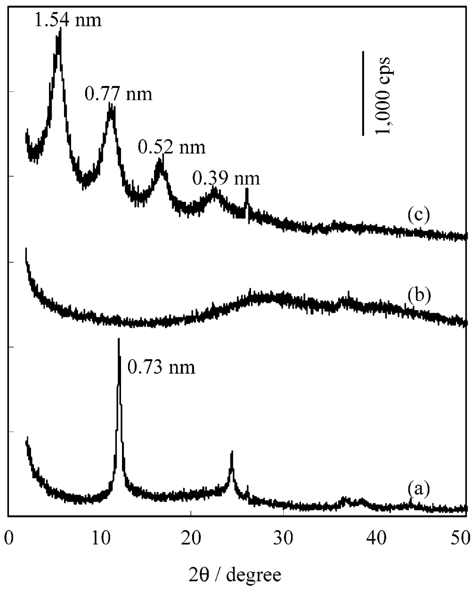

Figure 1. XRD patterns of (a) the starting BirMO(H), (b) delaminated BirMO slurry, and (c) the final product, PDDAMO.

neous decrease of both the sheet charge density and the interlayer salt concentration. The TMA^+ content decreases from 2.34 to 1.67 mmol/g by water washing, which corresponds to the decrease of sheet charge density from 3.6 to 2.5 unit charge/nm^2. The decrease of the sheet charge density results in a decrease of electrostatic attractive force between interlayer cations and anionic sheets. The decrease of the ion concentration of the interlayer solution strengthens the repulsive force between the manganese oxide sheets, owing to the decrease of the shielding effect provided by the interlayer ions. The decreases in ion concentration and surface charge density result in the delamination of a stacked manganese oxide.

The delaminated BirMO slurry was added to the PDDA solution (pH = 10.0) at room temperature and stirred for a day. After stirring, the precipitates were washed with water and dried at 70 °C for a day. The product PDDAMO shows a new phase with a basal spacing of 1.54 nm (Figure 1c). The presence of several diffraction harmonics suggests that the manganese oxide sheets are stacked in an ordered manner. This result shows that the reassembling of delaminated sheets progresses by only mixing with PDDA ions followed by air-drying. The expansion of the layer indicates the intercalation of PDDA polymer into the interlayer. Considering the thickness (0.45 nm) of the manganese oxide sheet,[31] the net interlayer expansion is evaluated as 1.09 nm. Since the effective thickness of PDDA is known to be about 0.5 nm,[23] the interlayer distance corresponds to two molecular layers of PDDA chains. The delamination/reassembling technique is a simple and effective method for the preparation of the layered manganese oxide nanocomposite with large ions or molecules in the interlayer.

Table 1. Chemical Analysis Results of Samples Obtained at Different $R_{PD/Mn}$ and Their Acid-Treated Samples[a]

$R_{PD/Mn}$	TC (mmol/g)	TN (mmol/g)	TC/TN	Mn (mmol/g)
BirMO slurry	6.5	1.6	4.0	8.9
0.1	5.5 (2.5)	1.1 (0.3)	5.1 (8.1)	8.4
0.5	8.8 (8.7)	1.2 (1.1)	7.4 (7.9)	8.3
1	13.0 (12.7)	1.8 (1.6)	7.3 (7.9)	8.2
5	12.0 (11.9)	1.6 (1.5)	7.5 (7.9)	8.2

[a] The numbers in parentheses are post-acid treatment data.

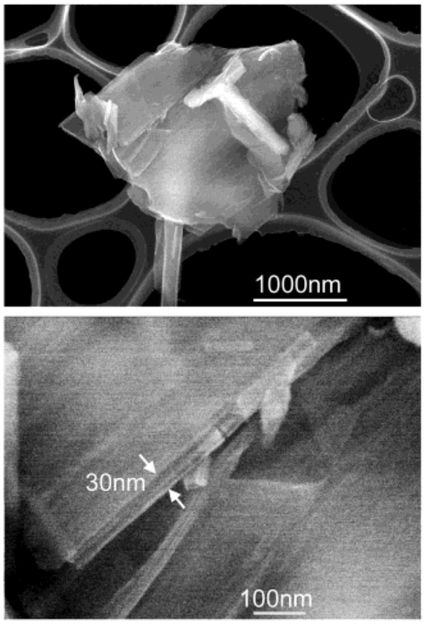

Figure 2. FE-SEM photograph of the PDDAMO nanocomposite.

Chemical analysis showed that the manganese content decreased from 8.9 mmol/g of the BirMO slurry to 8.2 mmol/g for the sample at $R_{PD/Mn} = 1$, due to the intercalation of the PDDA polycation. Total carbon and total nitrogen contents of PDDAMO were 15.6 and 2.5%, respectively. The TC/TN molar ratio was 7.3, which is close to the C/N molar ratio (C/N = 8) of the PDDA monomer (Table 1). This indicates that the organic component in the interlayer consists mainly of the PDDA polycation. The TMA^+ ions used for the delamination process or NH_4^+ ions used for pH control are rarely left in the interlayer. The Cl^- content was less than 0.5%, indicating that most of the amine group in PDDA exists in a form of ammonium ions, and not as chloride salt. The chemical composition of PDDAMO can be written as $Na_{0.15}H_{0.94}(C_8H_{16}NH_2)_{2.61}Mn_{12}O_{23}{\cdot}5H_2O$, where the water content was calculated from the weight loss by heating at 200 °C. The ion-exchange sites on BirMO(H) are not fully exchanged with the PDDA polycations. This may be because the size of the PDDA polycation is too large to exchange with the available sites of the manganese oxide sheet.

Physical Properties of PDDAMO. A FE-SEM image of the PDDAMO nanocomposite is shown in Figure 2. Platelike nanocomposite particles of 1−5 μm in size were readily observed. The smooth surface suggests that the PDDA polymers are homogeneously distributed along the manganese oxide sheets. No other particles on the surface suggest that most of the PDDA polymers are intercalated into the interlayer of the sheets. The thickness of the plate was evaluated at about 30 nm on average from the high-magnification FE-SEM images. Therefore, each plate may consist of about 20 sheets of manganese oxide that are attached

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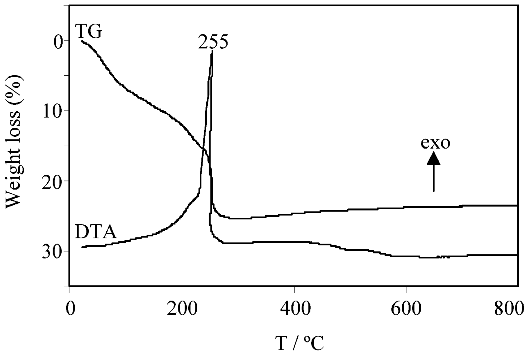

Figure 3. TG-DTA curves of the PDDAMO nanocomposite.

to each other in parallel arrangement. In the previous paper, we studied the morphology of the exfoliated manganese oxide by SEM observation using a freeze-dried sample.[21] It had a flaky appearance with irregular orientation, different from that of PDDAMO. The reassembling process may occur smoothly merely by drying the mixed solution of the exfoliated BirMO slurry and PDDA polymers.

The TG and DTA curves of PDDAMO are shown in Figure 3. A weight loss of 7.6% up to 120 °C is due to the dissipation of the interlayer water. A further weight loss (21.1%) observed from 120 to 400 °C is attributed to the decomposition of PDDA polycations in the interlayer. The amount of the weight loss is close to the PDDA contents of PDDAMO (20.5) calculated by using the total carbon content. The weight loss is associated with a sharp exothermic peak around 255 °C. The peak is lower than the decomposition temperature of PDDA salt (about 350 °C). Since the PDDA polymer is intercalated in a polycation form, but not as a PDDA salt, the polymer in the interlayer is probably less stable against heat treatment. A small weight loss (1.95%) between 420 and 580 °C is due to the reduction of manganese from tetravalent to trivalent form accompanied by the evolution of oxygen.[32]

Infrared spectra for manganese oxide samples are given in Figure 4 with the spectrum of PDDA chloride. Bands around 3420 and 1630 cm^{-1} were observed for all the samples, due to the presence of interlayer or surface water. The dried BirMO slurry has sharp bands at 1487 and 948 cm^{-1}, which are assigned to the absorption of TMA^+ ions in the solid.[33] PDDA chloride shows the characteristic absorption bands due to the C−H asymmetric and C−H symmetric stretching frequencies (2942 and 2867 cm^{-1}, respectively), CH_2 bending vibrations (1474, 1326, 1244, and 960 cm^{-1}), and C−N symmetric stretching vibration (1125 cm^{-1}).[34] PDDAMO also shows similar absorption bands, but the bands due to the stretching vibrations are shifted to lower frequencies. The shift of the band suggests a more anisotropic conformation of the interlayer PDDA polycations.[35] The absence of the sharp bands at 1487 and 948 cm^{-1} on the PDDAMO spectrum shows that most of the TMA^+ ions are replaced by PDDA polycations.

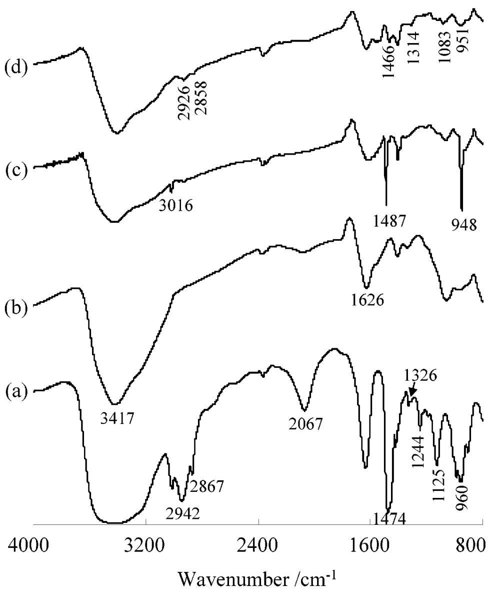

Figure 4. IR spectra of (a) PDDA chloride, (b) BirMO(H), (c) dried BirMO slurry, and (d) PDDAMO sample at $R_{PD/Mn} = 1$.

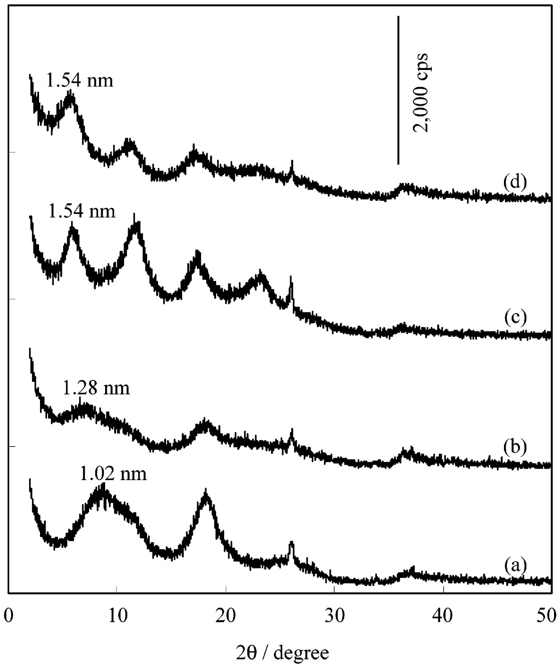

Figure 5. Changes of the XRD patterns of PDDAMO nanocomposites with different starting PDDA concentrations: (a) $R_{PD/Mn} = 0.1$, (b) $R_{PD/Mn} = 0.5$, (c) $R_{PD/Mn} = 1$, and (e) $R_{PD/Mn} = 5$.

Effect of PDDA Concentration on Nanocomposite Structure. The effect of $R_{PD/Mn}$ in preparation on a nanocomposite structure was studied by changing the starting PDDA concentrations. A broad peak with a basal spacing of 1.02 nm was observed for the sample prepared at a markedly low $R_{PD/Mn}$ ratio of 0.1 (Figure 5a). The basal spacing is similar to that (0.96 nm) observed for TMA^+-intercalated manganese oxide in the previous study.[21] Total nitrogen content decreased slightly from 1.6 to 1.1 by the PDDA treatment, while the TC/TN ratio increased from 4.0 to 5.1 (Table 1). Since the TN value is markedly larger than the monomer amount (0.26 mmol/g) of added PDDA, a considerable amount of TMA^+ ions remain in the interlayer after

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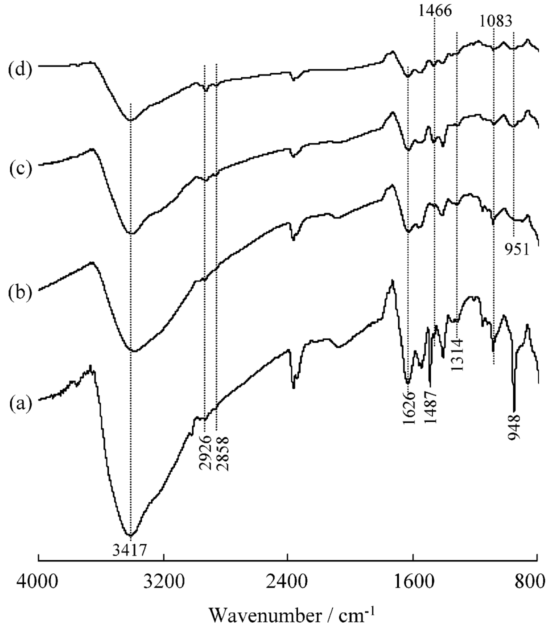

Figure 6. IR spectra: (a) PDDAMO sample at $R_{\mathrm{PD/Mn}} = 0.1$, (b) sample (a) after acid treatment in 0.1 M HNO_3, (c) PDDAMO sample at $R_{\mathrm{PD/Mn}} = 1$, and (d) sample (c) after acid treatment in 0.1 M HNO_3.

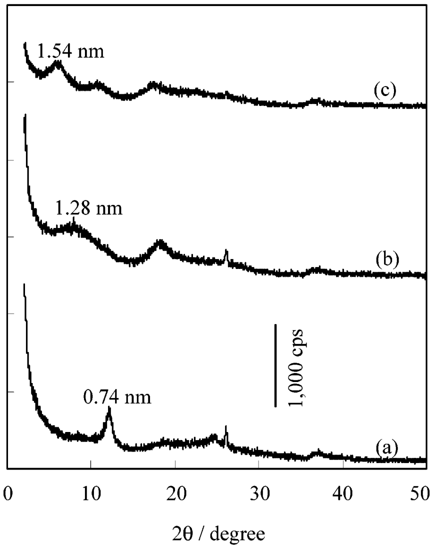

Figure 7. XRD patterns of the acid-treated PDDAMO samples: (a) $R_{\mathrm{PD/Mn}} = 0.1$, (b) $R_{\mathrm{PD/Mn}} = 0.5$, and (c) $R_{\mathrm{PD/Mn}} = 5$.

the PDDA treatment, even when all the PDDA are intercalated in the interlayer of manganese oxide sheets. The infrared spectrum also shows the coexistence of TMA^+ ions; the bands corresponding to TMA^+ ions are observed in addition to those from PDDA polymer (Figure 6a).

A new peak corresponding to a basal spacing of 1.28 nm was observed for the sample obtained at $R_{\mathrm{PD/Mn}} = 0.5$, but the peaks were broad and weak compared to those of the other PDDA-intercalated samples (Figure 5b). Contrary to the case of $R_{\mathrm{PD/Mn}} = 0.1$, the TN value is 1.3 mmol/g and the TC/TN ratio is 8, suggesting that the interlayer TMA^+ are mostly replaced by PDDA polycations at $R_{\mathrm{PD/Mn}} = 0.5$. The interlayer distance is evaluated as 0.83 nm, which is smaller than the thickness (1 nm) of a PDDA bilayer, but larger than that (0.5 nm) of a PDDA monolayer. Since the PDDA polymers are flexible, they can form a monolayer with polymers arranged in a tortuous manner. Each chain may go side by side of of manganese oxide sheets to have a interlayer distance of 0.83 nm.

A layered structure with a basal spacing of 1.54 nm was obtained at $R_{\mathrm{PD/Mn}} = 1$ (Figure 5c). The basal spacing and TN value for the sample obtained at $R_{\mathrm{PD/Mn}} = 5$ are nearly equal to those obtained at $R_{\mathrm{PD/Mn}} = 1$, although the PDDA is in sufficient excess to the ion-exchange capacity. This shows that the amount of PDDA intercalation is limited to about 1.7 mmol/g, probably due to the steric effect or due to the limited availability of exchangeable sites. The intercalation above two molecular layers of PDDA may be strongly suppressed due to a weak interaction between neighboring PDDA polymers.

Acid Treatment of PDDA-Loaded Samples. The acid treatment of the PDDA-loaded sample obtained at a low $R_{\mathrm{PD/Mn}}$ ratio of 0.1 resulted in the decrease of the TN value from 1.1 to 0.3 with a change of TC/TN from 5.1 to 8.1 (Table 1). This suggests that the TMA^+ ions are deintercalated from the interlayer by the acid treatment, but most of the intercalated PDDA ions remains. The infrared spectrum shows that the bands corresponding to the PDDA polymer remain after the acid treatment, but those corresponding to TMA^+ ions disappear (Figure 6b). These results indicate that the TMA^+ ions in the interlayer are deintercalated easily by the acid treatment with a 0.1 M HNO_3 solution, while the PDDA polymers adsorbed are hardly deintercalated by the acid treatment. The XRD analysis showed a decrease of the basal spacing from 1.02 to 0.74 nm (Figure 7a), being close to that (0.73 nm) of birnessite. In the previous paper,[21] we have observed the induction region of swelling in the case of TMA^+ intercalation to birnessite; a short-range swelling was not observed despite a considerable amount of TMA^+ intercalation. Similarly, a small amount of PDDA may be able to intercalate to the interlayer without an increase in the basal spacing.

Contrary to the case of $R_{\mathrm{PD/Mn}} = 0.1$, only 10% of the TN value decreased and the basal spacing of 1.28 nm remained (Figure 7b) after the acid treatment for the sample obtained at $R_{\mathrm{Pd/Mn}} = 0.5$. The TN value (1.1 mmol/g) and TC/TN ratio (7.9) of the acid-treated sample are close to those (TN = 1.3 mmol/g, TC/TN = 8) of the PDDA-loaded sample. These results indicate that the PDDA polycations in the interlayer are hardly deinterlalated by the acid treatment. Above $R_{\mathrm{Pd/Mn}} \geq 1$, the layered structure rarely changes (Figure 7c) and more than 90% of TN remains after the acid treatment. In addition, the infrared spectra are barely changed by the acid treatment (Figure 6c,d). These results indicate that the intercalated PDDA polycations are stable enough to remain in the interlayer against the acid treatment.

Effect of pH on Nanocomposite Structure. The effect of pH on the formation of PDDAMO nanocomposite was studied by changing the pH between 7.0 and 10.5 at $R_{\mathrm{PD/Mn}} = 1$. No marked change of the basal spacing was observed over the pH range; it increased only slightly from 1.49 to 1.54 nm with the increase of pH. Chemical analysis showed that the amount of the intercalated PDDA polymers increased slightly from

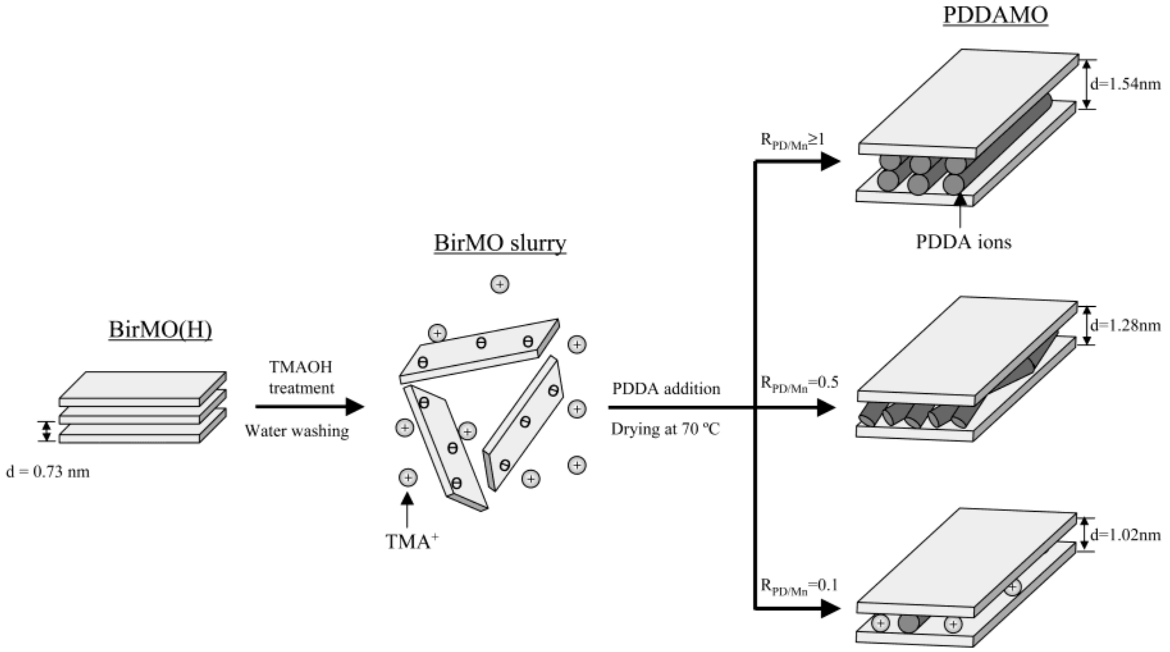

Figure 8. Schematic representation of the structural change for PDDA intercalation involving a delamination/reassembling process.

1.67 mmol/g at pH 7.5 to 1.81 mmol/g at pH 10.0, but no obvious change was observed. This indicates that the amount of interlayer PDDA polymers is hardly affected by the preparation pH. Since PDDA is a strong basic polyelectrolyte and has a high positive charge at all pH values, the polycation property of PDDA may hardly be affected by the pH of the solution.[23] In the previous pH titration study, we obtained the dissociation constants (pK_a) of 3.2 and 6 for birnessite and observed a small difference in the Na^+/H^+ exchange capacity (about 0.3 mmol/g) between pH 7 and pH 10.[21] Only the TMA^+-exchanged sites may be involved in the intercalation reaction of PDDA, but most of the residual protonated sites may not be, due to their low dissociation ability in the pH region studied.

Schematic Model for PDDA Intercalation Involving Delamination/Reassembling. A schematic representation of structural change for PDDA intercalation involving delamination/reassembling is given in Figure 8. Starting BirMO(H) contains one molecular layer of water between the manganese oxide sheets with a basal spacing of 0.73 nm. The TMA^+ intercalation followed by water washing results in the exfoliation of manganese oxide sheets. When the BirMO slurry of exfoliated sheets is soaked in a PDDA solution, a PDDA-intercalated nanocomposite is obtained after air-drying at 70 °C. The intercalation reaction progresses mostly by the PDDA polycation/TMA^+ ion-exchange reaction. Since the affinity of the PDDA polycation may be markedly higher than that of TMA^+, the PDDA polycations in the solution probably exchange selectively with TMA^+ ions, which are present in the slurry as countercations. The PDDA polycation/TMA^+ exchange may bring the smooth reassembling of manganese oxide layers since PDDA polycations can interact simultaneously with two layers of manganese oxide. The interlayer spacing of a manganese oxide nanocomposite depends on the amount of PDDA loading, as is shown in Figure 8. The expansion of the layer is limited to two molecular layers of PDDA at a basal spacing of 1.54 nm, probably due to the steric and electrostatic effects of PDDA polycations.

The charge density of manganese oxide sheets can be calculated on the basis of the structural model of birnessite, assuming that Mn(IV) and Mn(III) atoms are uniformly distributed over the manganese oxide sheet. According to the results in the literature,[31] 13.6 manganese atoms are present per nm^2 of oxide sheet. Since the dried BirMO slurry contains 1.67 mmol/g TMA^+ and 8.87 mmol/g manganese atoms, the sheet charge density can be derived from the TMA^+/Mn ratio as 2.56 u.c./nm^2, which corresponds to an area per unit charge of 0.39 nm^2. The area per diallydimethylammonium ion ($PDDA^+$) was calculated as 0.42 nm^2 by a semiempirical MO method using a MOPAC program, assuming a rectangular form for the ions. Since the PDDA ions are a little larger in size than the area per unit charge, PDDA ions may not be able to form one molecular layer in a fully exchanged state. However, the PDDAMO derived from $R_{PD/Mn} = 0.5$ has a cation content of only 1.2 mmol/g, which corresponds to an area per unit charge of 0.5 nm^2. Therefore, in this case PDDA ions can exist as one molecular layer because of their having a sufficiently small area for exchangeable ion sites. The PDDA chain may interact with manganese oxide sheets on both sides alternately. At the fully exchanged state with PDDA ions of 1.67 mmol/g, the bilayer structure is more advantageous from the steric point of view. Since the negative charges are distributed on both sides of the manganese oxide sheet, the area per unit charge is 0.78 nm^2 for each side. The surface charge density is sufficiently low for the full exchange of $PDDA^+$ ions. Each PDDA polymer may adsorb separately on either side of the manganese oxide sheets by electrostatic interaction, subsequently forming a bilayer of PDDA molecules. The hydrophobic interaction between the bilayer of PDDA molecules may stabilize the stacked layered structure of the manganese oxide sheet−PDDA nanocomposite.

Conclusion

PDDA-intercalated layered manganese oxide nanocomposite (PDDAMO) can be prepared by a new route involving a delamination/reassembling process. The interlayer distance of the layered structure depends on the amount of PDDA intercalated. The synthesized PDDAMO has a higher stability against extraction by acid treatment, giving the product a bright prospect for developing novel selective adsorbents or cathode materials for lithium batteries. The new method is promising for the synthesis of many kinds of bulky guest molecules or polycation manganese oxide nanocomposites.

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