

Preparation of Anion Exchangeable Layered Mixed Basic Salt $\text{Ni}_{1-x}\text{Zn}_{2x}(\text{OH})_2(\text{OCOCH}_3)_{2x}n\text{H}_2\text{O}$ Thin Film under Hydrothermal Conditions

H. Nishizawa¹ and K. Yuasa

Department of Chemistry, Faculty of Science, Kochi University, Kochi 780, Japan

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Anion exchangeable layered mixed basic salt (LMBA) $\text{Ni}_{1-x}\text{Zn}_{2x}(\text{OH})_2(\text{OCOCH}_3)_{2x}n\text{H}_2\text{O}$ thin film was deposited onto a glass slide substrate through the hydrothermal decomposition of mixed aqueous solution of zinc and nickel acetates. The molar ratio of Zn/Ni in mixed solution affected the orientation of LMBA crystals on the substrate. LMBA thin films obtained at 130°C in Zn rich solutions showed *c*-axis orientation perpendicular to the substrate surface. The acetate ions of oriented LMBA thin film easily exchanged with most of the inorganic, as well as the organic, anions without destruction of the thin film. © 1998 Academic Press

1. INTRODUCTION

The increasing demand for thin films of high quality inorganic materials for electronic, ceramic, and pigment applications has prompted industry to search for alternate processes to produce these thin films. Various methods of preparation such as sputtering, molecular beam epitaxy (MBE), laser ablation, and chemical vapor deposition (CVD) have been developed. However, these methods require high technologies and elaborate conditions, e.g., high temperature and ultrahigh vacuum. In addition, the methods usually require long preparation times to obtain films with thicknesses on the order of micrometers.

The hydrothermal decomposition method has a bright prospect of preparing higher quality inorganic thin films (1–3). Because this method possesses several advantages, that is, thin films of various inorganic compounds, including hydroxides and hydrates, may be prepared with sufficient thickness at relatively low temperature, and for a short time.

Recently, present workers have succeeded in preparing highly oriented ZnO thin films on a glass slide substrate through the hydrothermal decomposition of an aqueous solution of zinc acetate. The effects of metal cation addition

on the orientation of ZnO crystals in thin film was examined. ZnO thin films oriented in the [002] direction with a fairly smooth surface and high transparency were obtained at 150°C for 1 h by the addition of Co ions (4).

Furthermore, anion exchangeable layered mixed basic salt (LMBA), $\text{Ni}_{1-x}\text{Zn}_{2x}(\text{OH})_2(\text{OCOCH}_3)_{2x}n\text{H}_2\text{O}$, thin film was found to be deposited onto a glass slide substrate through the hydrothermal decomposition of a mixed aqueous solution of zinc and nickel acetates. LMBA is one of the anion-exchangeable layered crystals. In contrast to variety of cation-exchangeable layered crystals, anion-exchangeable ones are very rare (5).

Thus far, hydrotalcite-type layered double hydroxides (LDHs) (6–10) and a copper basic salt (11–14), $\text{Cu}_2(\text{OH})_3(\text{OCOCH}_3)\text{H}_2\text{O}$, have been known as anion-exchangeable layered crystals. The LDHs have a general formula of $[\text{M}_1^{2+}x\text{M}_2^{3+}(\text{OH})_2]^{x+}\text{Y}_x^{z-}n\text{H}_2\text{O}$. Here, M^{2+} and M^{3+} are di- and trivalent metal ions that occupy octahedral positions in brucite-like hydroxide layers, and Y^{z-} is the interlayer anion easily exchanged with various anions. The LDHs have been generally prepared by coprecipitation of metal salt solutions with sodium hydroxide at room temperature. On the other hand, the acetate ions directly coordinated to the copper ions in the copper basic salt with a botallackite-type layered structure are exchangeable with various anions. The basic copper salt is easily prepared by a partial titration of a copper acetate solution with sodium hydroxide at room temperature.

LMBA was first formed when an attempt was made to prepare a nickel basic acetate in the presence of zinc ions under hydrothermal conditions (15). The composition is $\text{Ni}_{1-x}\text{Zn}_{2x}(\text{OCOCH}_3)_{2x}\text{H}_2\text{O}$ ($0.15 < x < 0.25$). The structure, estimated on the basis of the analytical and XRD data, is isomorphous with zinc basic salts such as $\text{Zn}_5(\text{OH})_5(\text{OH})_8\text{Cl}_2n\text{H}_2\text{O}$ (16) and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_22\text{H}_2\text{O}$ (17). The nickel ions form brucite-type hydroxide layers with vacancies and the zinc ions occupy the tetrahedral sites above and below the vacant sites outside the hydroxide layers. One quarter of the octahedral sites of the nickel hydroxide layers

¹Author to whom correspondence should be addressed. E-mail: hakkun@cc.kochi-u.ac.jp.

can be vacant at maximum. The acetate ions directly coordinated to the zinc ions in LMBA are exchangeable with various anions.

The preparation of a thin film based on such material is significant with respect to the applicability to many fields. For example, this may be useful in the electronics field as an electrode, taking advantage of the layered structure and ion-exchange properties.

In the present study, the effects of the molar ratio of metal ions in mixed solutions on the orientation of crystals in the LMBA thin films prepared by the hydrothermal decomposition of Ni–Zn mixed acetate solutions are examined. The structural change of the thin film of LMBA by the anion exchange is also studied.

2. EXPERIMENTAL DETAILS

Preparation of LMBA thin films was conducted by heating a mixed metal acetate aqueous solution with the glass substrate in a microautoclave. To prepare the starting solutions, zinc and nickel acetates (Guaranteed reagent grade, Wako Pure Chemical Industry, Ltd., Osaka, Japan) with several Zn/Ni molar ratios were dissolved in distilled water in a total metal concentration of 0.5 M (mol/dm³). A glass slide (Matsunami Glass Ind. Ltd.) was used as the substrate (10 × 10 mm).

A 5-ml solution and the substrate were inserted directly into a microautoclave 13-mm ID and 70 mm deep, lined with hasteloy-C. The autoclave was heated in a furnace designed to minimize the temperature gradient in the charge. The heating rate was controlled at 6°C/min from 60° to 300°C. The temperature were measured with a potentiometer connected to chromel–alumel thermocouple attached to the outside wall of the autoclave. These temperatures are probably higher than the actual values but are meaningful as a basis for comparing the data.

Autogeneous pressures in the autoclave were monitored with a calibrated gauge. The autoclave was quenched into an ice bath immediately after the desired temperature was reached or after the temperature had been maintained for up to one day. The glass substrate was taken out and washed with distilled water, followed by drying in a desiccator at room temperature. The deposited film on one side of the glass substrate was scraped off with sand paper as the films grew on both sides. The powder samples were prepared in the same way as those of the thin film, except the glass substrate.

The deposited film on one side was subjected to structural analysis using Rigaku X-ray diffraction equipment model RAD-II-C. The chemical analysis was mainly done by the atomic absorption method on the powder sample dissolved in a hydrochloric acid solution. The microstructure and composition of the films were observed using a scanning electron microscope (SEM) and an electron probe micro-

analyzer (EPMA). The thermal behavior of the LMBA powder sample in air was followed with a MAC Science TG-DTA 2000 apparatus (heating rate 10°C/min). Typically sample weights of ca 15 mg were employed during the run.

Anion exchanging reactions were conducted by immersing the LMBA film (10 × 10 mm, ca 5 μm thick) deposited on one side of the glass substrate or the LMBA powder samples (15 mg) in the aqueous solutions, 5 ml of KX (X: F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻), K₂CO₃, and organic acid salts (concentration about 0.5 M), and allowed to react for up to 3 days at room temperature. The samples were occasionally shaken during these periods. The glass substrate was taken out and washed with distilled water, followed by drying in a desiccator at room temperature. The anion exchanged films occasionally peeled off the glass substrate but the shape of the film was preserved. The anion exchanged films and powder samples were characterized in a similar manner as the original ones.

3. RESULTS AND DISCUSSION

(1) Hydrothermal Decomposition of Metal Acetates

Layered Ni–Zn mixed basic acetate (LMBA) with a basal spacing of 1.3 nm was obtained by the hydrothermal decomposition of Ni–Zn mixed acetate solution (Zn/Ni = 10) at 150°C. The composition of the compound was given by the formula Ni_{0.78}Zn_{0.44}(OCOCH₃)_{0.44}(OH)₂H₂O on the basis of the chemical analysis data. The diffraction peaks of the XRD pattern, shown in Fig. 1(a), can be indexed on the basis of the hexagonal cell of basic zinc chloride (*a* = 0.62 nm, *c* = 1.30 nm). These results were in fair agreement with

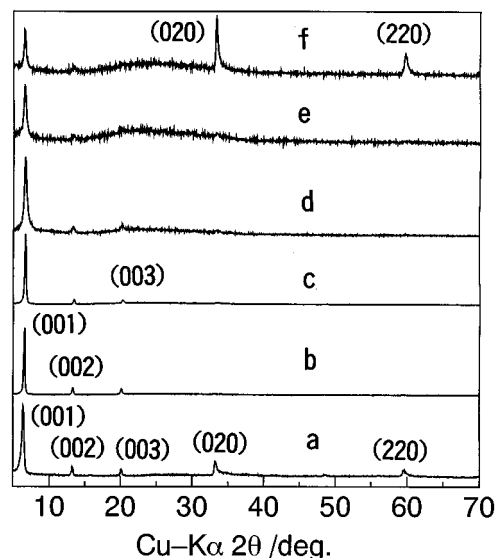


FIG. 1. XRD patterns of (a) LMBA powder and thin films obtained by hydrothermal treatment at 130°C for 1 h in Ni–Zn mixed acetate solutions; (b) Zn/Ni = 10, (c) 2.7, (d) 1.2, (e) 0.6, (f) 0.2.

those of Yamanaka (15). The LMBA was formed in a wide composition range of Ni–Zn acetate solutions, except in the pure Ni or Zn acetate solution. The Zn/Ni molar ratio of the compounds were in the range of 0.45 to 0.65 from the analytical data. The basal spacing little changed with the composition. The Zn content of the compounds was saturated at Zn/Ni = 0.65 although the Zn concentration of the mixed solution increased.

Zinc acetate was found to be hydrothermally decomposed above 120°C, resulting in the formation of polycrystalline ZnO. No impurity phase could be found. The hexagonal columnar ZnO crystals with a mean diameter of 2 μm were obtained by hydrothermal treatment of 0.3 M zinc acetate solution at 120°C for 1 h.

The hydrothermal treatment at 150 to 190°C of only Ni acetate without Zn ions resulted in the formation of a new basic Ni acetate with a layer structure of the botallackite type. At high temperature or at 150°C for a long duration (3 h), stable Ni(OH)₂ formed. Experimental results about this basic Ni acetate will be reported elsewhere.

The glass substrate surface hydrothermally treated at 140°C for 40 min in 0.3 M zinc acetate solution exhibited a homogeneous white layer of material that remained even after they were rinsed in de-ionized water. SEM observation of the films showed hemispherical grains with a mean diameter of 500 nm. At higher temperatures or even at 150°C for a longer duration (1 day), ZnSiO₃ (willemite) film formed by the reaction of the zinc acetate with the glass substrate. The effect of the addition of foreign ions such as Mn²⁺, Co²⁺, Ni²⁺, Ca²⁺, Sr²⁺ on the crystallization of ZnO on the glass substrate was examined. The addition of Ca²⁺ and Sr²⁺ gave no effect on the formation of ZnO films, while the addition of Co²⁺ and Mn²⁺ led to the formation of a transparent and colorless film on the substrate. The XRD patterns of these films showed only the (002) peak of ZnO and indicated that the films have a *c*-axis orientation perpendicular to the substrate surface. The addition of Ni²⁺ ion prevented the formation of ZnO with and without the glass substrate, resulting in the formation of LMBA powder or thin film.

(2) Polycrystalline LMBA Film on the Substrate

The films on the substrate produced at 130 for 1 h in mixed solutions with Zn/Ni molar ratio from 0.2 to 10 showed a pale green smooth surface and translucency. Figure 1 shows XRD patterns of these films. All these films showed the formation of LMBA with almost constant basal spacing of 1.27 nm which was slightly smaller than that (1.3 nm) of the LMBA powder obtained by hydrothermal treatment of the mixed solution with Zn/Ni = 10. The Zn/Ni molar ratio in these thin films were found to be almost the same value (0.5) from the EPMA analytical data and independent of the molar ratio of mixed solution. Such slightly

smaller basal spacing seemed to be due to poor Zn content of these thin films. The formation of ZnO was not observed even in Zn-rich solutions. This result was consistent with that of LMBA powder samples produced under hydrothermal conditions.

The effect of the reaction temperature on the formation of the thin film was examined for constant reaction time, 1 h. At a reaction temperature below 120°C, no film was obtained on the glass substrate. The films of single phase LMBA formed between 130°C and 200°C were obtained. The formation of willemite (ZnSiO₄) with LMBA was observed at 250°C. The single phase of NiO was obtained above 300°C. The film of NiO may form on the glass substrate after the film of LMBA and ZnSiO₄ peeled off.

XRD patterns of these films obtained at 130°C shows that the relative intensities of peaks changes with Zn/Ni molar ratio in Ni–Zn mixed acetate solutions (Fig. 1). The relative intensity of basal reflections increased with increasing the content of Zn. The pattern of Zn/Ni = 10 is consistent with the notion that all the crystallites are oriented with (001) planes parallel to the film surface plane, because only basal plane reflections are evident in the pattern. The intensities of the basal plane reflections decreased with decreasing Zn/Ni molar ratio. The pattern of Zn/Ni = 0.2 showed that basal plane reflections were very weak and contrarily the peaks (220) and (020) were clearly observed.

The SEM photographs of these films are shown in Fig. 2. The film surface of Zn/Ni = 0.2 appeared as networks like honeycomb with 0.1 to 1 μm pore size at approximately right angles to the film surface (Fig. 2a). This shows that the lamella LMBA crystals with the developed (001) basal plane grows perpendicularly to the glass substrate, that is, in the direction parallel to the (001) basal plane. On the other hand, the film of Zn/Ni = 10 shows the stacking of lamella ZnO crystals (Fig. 2b). The LMBA crystals seem to grow in the direction parallel to the substrate glass. The film morphology as evident from the micrographs suggests that the film grows according to the following process: In Zn-rich solutions, first (001) preferred oriented ZnO microfilm (which unfortunately cannot be detected) forms on the glass substrate and then the LMBA crystals epitaxially grow only perpendicularly to the (001) basal planes. In Zn-poor solutions, the basal planes of LMBA crystals grow in the direction parallel to the glass substrate due to the lack of a ZnO microfilm.

TG and DTA curves for LMBA powder obtained by hydrothermal decomposition of Ni–Zn mixed solution (Zn/Ni = 10) are shown in Fig. 3. The first endothermic peak due to the dehydration of interlayer water was observed at 94°C. The basal spacing of LMBA was reduced by ca 0.3 nm on dehydration. The spacing reverted to the initial value on rehydration by standing in air. Furthermore, peaks, endothermic peak at ca 250°C and exothermic peak at ca 300°C, are poorly resolved and correspond to the

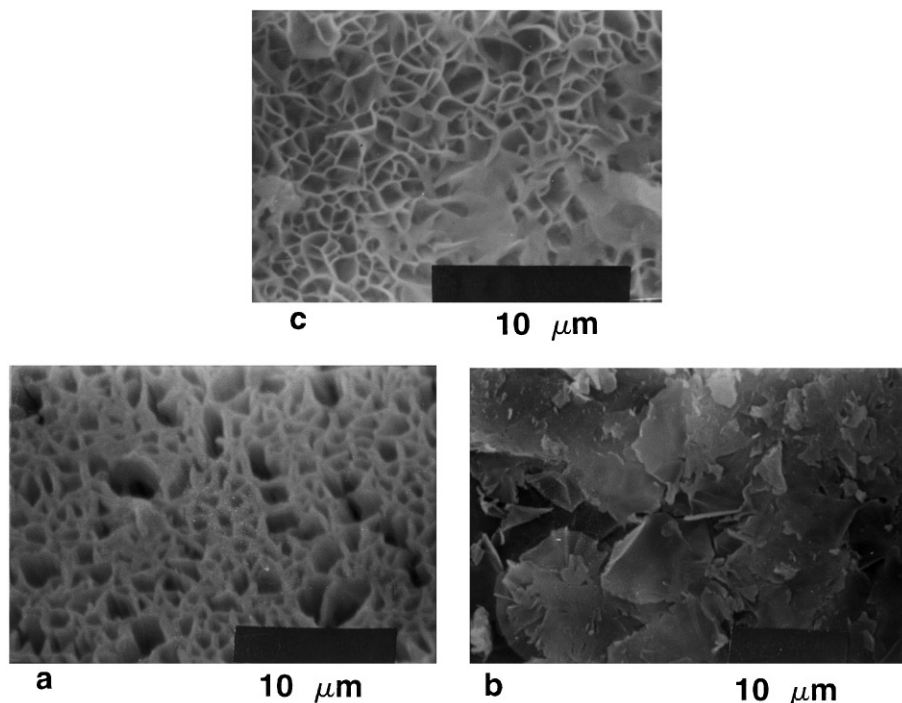


FIG. 2. SEM photographs of thin films obtained by hydrothermal treatment at 130°C for 1 h in Ni-Zn mixed acetate solutions: (a) Zn/Ni = 0.2, (b) 10, (c) heated; (a) in air at 400°C.

complete thermal decomposition. It should be noted that the dehydration of OH bound with Ni and the combustion of acetate bound with Zn partially overlap. These thermal changes were very similar to those of $\text{Cu}_2(\text{OH})_3(\text{OCOCH}_3)\text{H}_2\text{O}$ (14). The crystallization of NiO and ZnO occurred at ca 600°C. The thin film of LMBA mechanically peeled off from the glass substrate showed the same thermal changes as the powder sample. The microstructure of the thin film, shown in Fig. 2c, was almost unchanged after heating to 400°C.

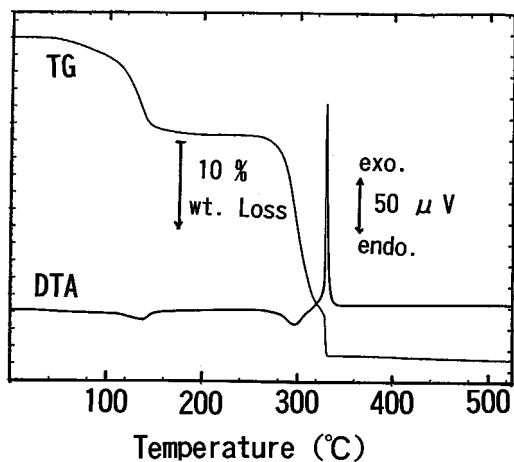


FIG. 3. TG-DTA of LMBA powder obtained in air with a heating rate of 10°C/min.

(3) Anion Exchanging Reaction of LMBA Thin Film

The appearance of LMBA (Zn/Ni = 10) thin film was unchanged after the anion exchanging reaction in a variety of potassium salt solutions such as KX ($X: \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-$), K_2CO_3 , and organic acid salts (concentration about 0.5 M). Figure 4 shows the XRD patterns of the

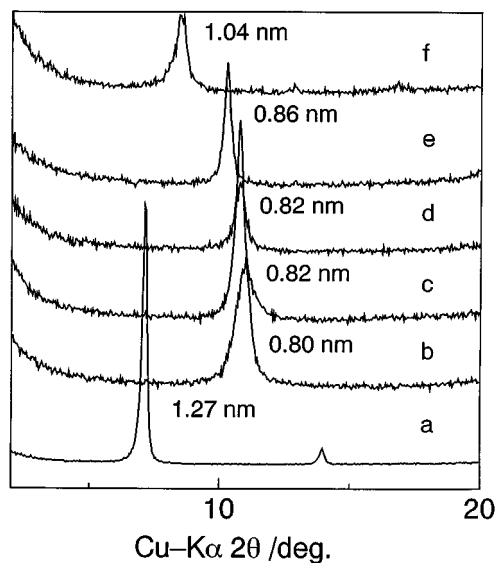


FIG. 4. XRD patterns of (a) original LMBA and (b)-(f) anion exchanged LMBA (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , respectively).

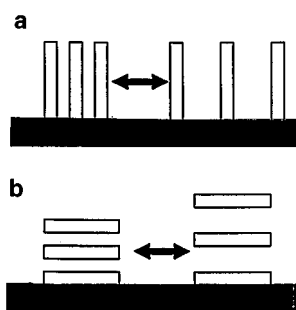


FIG. 5. Basal spacing changes of LMBA thin films with (001) basal plane (a) perpendicular and (b) parallel to the glass substrate.

resulting exchanged forms. Despite only 1 h for the exchanging reaction time, all anion exchanging reactions were completed. The basal spacing of the exchanged forms changed with the size of the exchanging anion. When the same anion exchanging procedure for LMBA ($\text{Zn}/\text{Ni} = 0.2$) thin film was conducted, the film tended to crack and peel off. This may be due to the evolution of the gap on the substrate caused by the change of the basal spacing of the resulting exchanged forms (Fig. 5). Such a difference can be explained by the preferred orientation of the LMBA crystals in the thin film. In the anion exchange of LMBA ($\text{Zn}/\text{Ni} = 10$), no gap between the substrate and film evolved because the changing of basal spacing occurred perpendicularly to the substrate. As the changing of basal spacing occurred parallel to the substrate in LMBA ($\text{Zn}/\text{Ni} = 0.2$), some gap between the substrate and the film evolved.

The exchanged film with NO_3^- was reversibly converted to LMBA ($\text{Zn}/\text{Ni} = 10$) in an 1 M CH_3COONa solution.

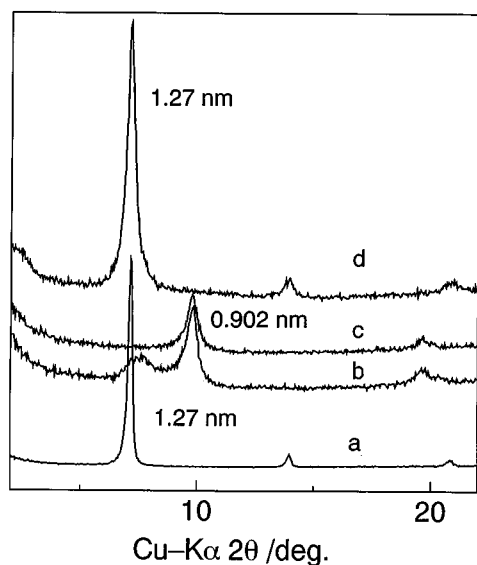


FIG. 6. Reversible anion exchanging process between acetate and NO_3^- : (a) original LMBA, (b) anion exchanging in KNO_3 solution for 10 min, (c) for 50 min, and (d) anion exchanging of (c) in CH_3COONa solution for 10 min.

XRD patterns of the anion exchanged thin film were shown in Fig. 6. The anion-exchanging process from acetate to NO_3^- took about 50 min. It took only 10 min for the reverse change. It is an important characteristic of LMBA thin films that the anion exchange takes place more rapidly than that of powder LMBA.

Figure 7 shows XRD patterns of thin film and powder exchanged with *p*-aminobenzoic acid at room temperature. In powder, the original LMBA remains even after 24 h of the exchanging reaction. It is reported to need several days to reach equilibrium for such ion exchanging (18–19) and the intercalation reaction (20). The original LMBA was

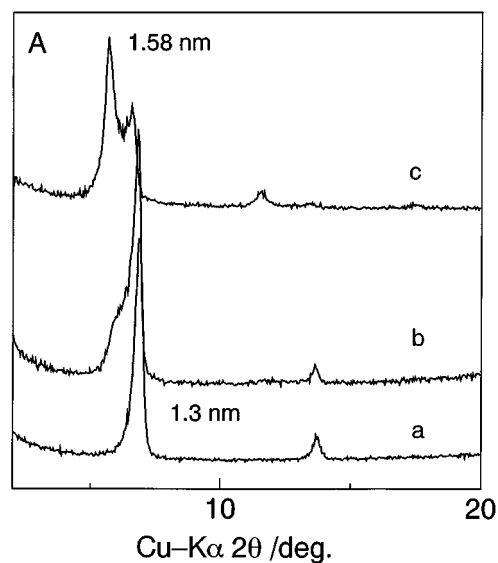


FIG. 7. Comparison of exchanging reaction rate with *p*-aminobenzoic acid between (A) powder; reaction time (a) 0 h, (b) 3 h, (c) 24 h; (B) thin film, reaction time (a) 0 h, (b) 3 h, (c) 12 h.

completely exchanged within 3 h and a new diffraction peak appeared at 1.5 nm in the thin film. These results on reaction rate are consistent with a model involving nucleation followed by two-dimensional diffusion of the guest ions into the host lattice (21). Because the propagation of nucleation and two-dimensional diffusion of the guest ions seems to be more favorable to the thin film than the powder sample.

There was apparently no change of structure and anion exchanging efficiency of the film, even after performing these reversible changes 10 times. Further study is now under way to make the best use of anion exchangeable thin films and will be reported subsequently.

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