

New Route for Preparation of Layered Manganese Oxides with Multivalent Metals in the Interlayer

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Fe(III)-, Cr(III)-, Al(III)- and La(III)-buserite type manganese oxides were synthesized from a hydrothermally treated, well-crystallized Na⁺-birnessite through a two-step ion-exchange route, M/Mg²⁺ ion exchange subsequent to Mg²⁺/Na⁺ exchange. The ion-exchange reactions progressed smoothly and the layered manganese oxides with multivalent metal ions in the interlayer could be obtained at room temperature.

Recent progress in understanding porous manganese oxide materials and interest in their applications as cathode materials for secondary ion batteries, selective adsorbents, catalysts and new magnetic materials have given rise to a number of studies on the incorporation of different elements into the matrix manganese oxide materials. Buserite and birnessite are both layered manganese oxides. Buserite has double layers of hydrates whereas birnessite has only one. The layered materials are precursors to one-dimensional tunnel materials, among which todorokites with tunnels of [3×3] MnO₆ units are generally synthesized hydrothermally from buserite.^{1–3} It has been found that only buserite, stable at least at room temperature and under common humidity conditions, can be hydrothermally converted to todorokites.³ Therefore, the preparation of stable metal-incorporated buserite controls the incorporation of metal ions into todorokites.

Earlier studies^{4–6} have shown that only a few group II or transition metal ions, such as Mg²⁺, Ni²⁺, Ca²⁺, are capable of formation of buserite derivatives with basal spacings of 10 Å from Na-birnessite. Recently, a double-aging method³ has been developed to prepare stabilized Na-buserite, into which over 25 kinds of ions were ion-exchanged, forming various stable metal-buserites. However, the preparation of stabilized Na-buserite is difficult because of the low hydration energy of Na⁺ ions. Many methods have been used for preparation of birnessite,⁷ but Na-buserite obtained from Na-birnessite in most cases is unstable.⁴ Buserite incorporating some multivalent cations, e.g., Cr³⁺, Fe³⁺, etc., has not been attainable by an ion-exchange method up to now. In this work, we propose a new formation route using stabilized Mg²⁺-buserite, which is more stable than Na⁺-buserite. Buserite or birnessite with multivalent metals in the interlayer can be simply synthesized from the Mg²⁺-buserite with a good reproducibility. A hydrothermally treated, well-crystallized Na-birnessite was used as the starting material; some trivalent cations, Fe³⁺, Cr³⁺, Al³⁺, La³⁺ and a tetravalent cation Zr⁴⁺ were used for testing the effectiveness of our method.

Na-birnessite was prepared as reported in the literature.^{8–10} A 810 cm³ solution of 0.6 mol·dm⁻³ NaOH was mixed with 90 cm³ of 2 mol·dm⁻³ H₂O₂, and then poured into 450 cm³ 0.3 mol·dm⁻³ Mn(NO₃)₂. After stirring for 25 minutes, the precipitate was filtered and washed with distilled water several times

until pH < 8. To improve the crystallinity of the obtained birnessite, the precipitate was hydrothermally treated in a solution of 2 mol·dm⁻³ NaOH at 150 °C for 16 h. The product was filtered and washed, and then dried at 70 °C.

Na⁺/Mg²⁺ exchange was carried out by soaking Na-birnessite (1 g) in an aqueous solution of 0.5 mol·dm⁻³ MgCl₂ (50 cm³) for 1 day with stirring. The Mg-buserite obtained was washed and filtered, and subsequently soaked in a 0.5 mol·dm⁻³ solution (50 cm³) of CrCl₃, FeCl₃, LaCl₃, Al(NO₃)₃, or ZrO(NO₃)₂, with stirring for 1 day.

The X-ray diffraction (XRD) patterns of all the samples were obtained by Rigaku RINT 2100, using Cu Kα radiation, with a graphite monochromator. Metal ion contents were analyzed by atomic absorption spectrophotometry or inductively coupled plasma spectrophotometry (Seiko Instrument Co., Ltd,

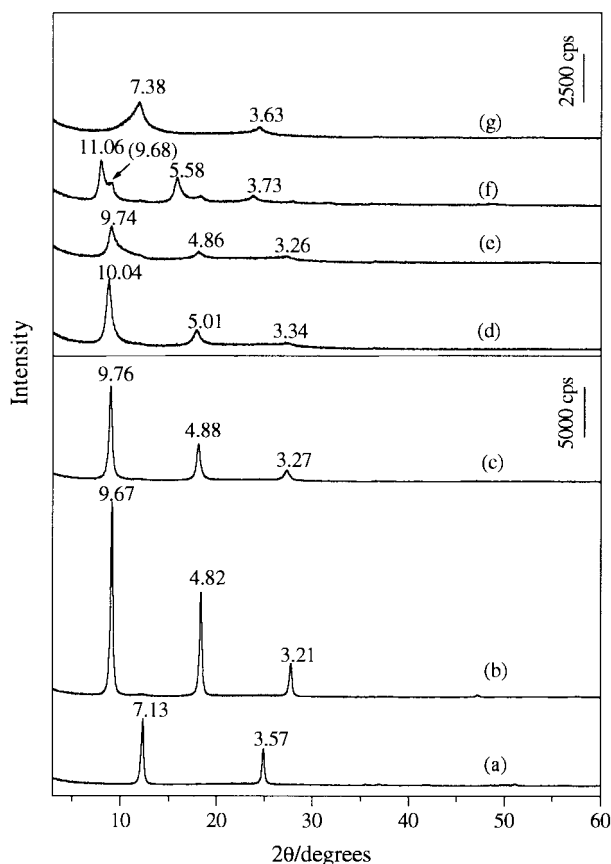


Figure 1. XRD patterns of (a) Na-birnessite, (b) Mg-buserite, and the samples incorporating (c) Al(III), (d) Cr(III), (e) Fe(III), (f) La(III), and (g) Zr(IV). d-values in Å.

Table 1. Compositional data for Na-birnessite, Mg-buserite and samples after ion exchange

Incorporated ion	Z _{Mn} ^a	Composition ^b
Sodium (I)	3.63	Na _{4.18} Mn ₁₄ O _{27.5} ·11.7H ₂ O
Magnesium (II)	3.63	Na _{0.13} Mg _{1.95} Mn ₁₄ O _{27.4} ·30.1H ₂ O
Aluminum (III)	3.58	Na _{0.014} Mg _{0.069} Al _{1.16} Mn ₁₄ O _{26.9} ·31.2H ₂ O
Chromium (III)	3.76	Na _{0.012} Mg _{0.017} Cr _{1.25} Mn ₁₄ O _{28.2} ·38.5H ₂ O
Iron (III)	3.78	Na _{0.007} Mg _{0.043} Fe _{2.82} Mn ₁₄ O _{30.8} ·43.7H ₂ O
Lanthanum (III)	3.53	Na _{0.033} Mg _{0.41} La _{1.03} Mn ₁₄ O _{26.7} ·37.9H ₂ O
Zirconium (IV)	3.63	Na _{0.011} Mg _{0.056} Zr _{0.57} Mn ₁₄ O _{26.6} ·28.2H ₂ O

^aAverage oxidation state of manganese. ^bThe water contents were evaluated from the weight loss by heating up to 400 °C in TG curves.

SPS 7800 type) after dissolving the specimens in a mixed HCl and H₂O₂ solution. The average oxidation state of manganese was evaluated as indicated in the standard oxalic acid method¹¹ by determining the available oxygen content. The specimens were subjected to TG-DTA analysis (on a MAC Science thermal analyzer, system 001, TG-DTA 2000) at a heating rate of 10 °C/min. The water contents were determined from the weight loss by heating up to 400 °C.

XRD patterns and chemical compositions of the investigated samples are shown in Figure 1 and Table 1. Mg²⁺-buserite has a basal spacing of 9.67 Å. Using M³⁺/Mg²⁺ ion exchange, M(III)-buserite is obtained with the basal spacing larger than that of Mg-buserite. Due to the larger hydration energy for trivalent metal ions than for divalent ones, water content increases by the M³⁺/Mg²⁺ exchange. The La-buserite sample has two basal spacings (Figure 1 (f)). The smaller basal spacing (9.68 Å) can be assigned to that of residual Mg-buserite, being consistent with the high magnesium content. The larger basal spacing (11.06 Å) can be assigned to that of La-buserite, and agrees well with that (11.2 Å) found in literature.³ The basal spacing of M(III)-buserite increased in the sequence Fe³⁺, Al³⁺ < Cr³⁺ < La³⁺. The sequence agrees well with the increase in ionic radius of these ions (0.69, 0.68, 0.76, 1.17 Å, respectively). This suggests that most of the studied metal ions are in the interlayer as intercalated ions.

The amount of Mg²⁺, Cr³⁺, La³⁺, or Al³⁺, shown in Table 1, when compared with that of Na⁺, denotes that the ion exchange reaction proceeds during the formation of buserite. The Na and Mg contents of Mg-buserite indicate that 97% of Na⁺ ions are exchanged for Mg²⁺ ions. From chemical compositions of M³⁺-buserite, the exchange rates of M³⁺/Mg²⁺ are 99, 96, and 80% for Cr³⁺, Al³⁺, and La³⁺, respectively. From these results the selectivity sequence can be evaluated as Na⁺ < Mg²⁺ < La³⁺ <

Al³⁺ < Cr³⁺. The extremely high ferric content in the Fe³⁺-buserite can be explained by the presence of hydrolyzed species of ferric ions that appeared due to the hydrolysis of Fe³⁺, beginning at about pH 1. The measured pH value, 1.22, for the FeCl₃ solution with the buserite specimen indicates that the dinuclear species, Fe₂(OH)₂⁴⁺, and mononuclear species, FeOH²⁺ and Fe(OH)₂⁺, may also be formed.¹² Since the valence of ferric ions is roughly estimated as 1.4 from the chemical composition of Fe³⁺-buserite, a considerable amount of the ferric ions is considered to be in a hydrolyzed form in the interlayer.

Zirconium ions show an ion exchange behavior different from trivalent metal ions. After the Mg²⁺-buserite soaked into ZrO(NO₃)₂ solution (pH = 0.5), a sample (with the composition shown in Table 1) having a basal spacing of 7.38 Å, markedly smaller than that of buserite, was obtained. This shows apparently that zirconium ions are not intercalated in the interlayer. However, SEM-EDX and thermal analysis results have suggested some portions of zirconium ions incorporated in the interlayer.

The SEM images shown in Figure 2 illustrate that the Na-birnessite and Cr-buserite particles are composed of plate-like particles. Similar images were observed for the other ion-exchanged samples. They indicate that the present Na-birnessite is well crystallized, and the formation of buserite by ion exchange does not change the morphology of the particles of starting materials.

In the present work, M(III)-buserites were not obtained by the direct M³⁺/Na⁺ exchange using well-crystallized Na⁺-birnessite. The M³⁺/Na⁺ (where M = Fe, Cr, Al or La) and M²⁺/Na⁺ (where M = Cu, Co or Mn) exchange resulted in manganese oxides with a basal spacing of 7 Å, except for Mg²⁺ and Ni²⁺. The results agree well with those reported by Golden et al.,⁶ and by Luo et al.³ when the unstabilized Na-buserite was used. These results show that Mg²⁺-buserite contributes greatly to the formation of M(III)-buserites.

In summary, Mg²⁺-stabilized buserite is a useful intermediary for the preparation of layered manganese oxides with multivalent ions in the interlayer.

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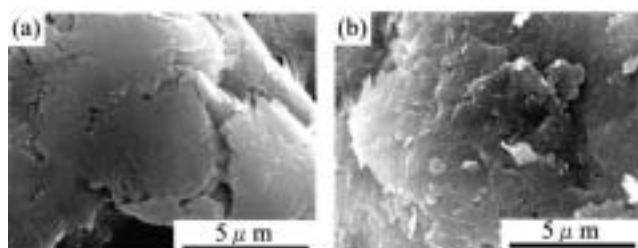


Figure 2. SEM micrographs of 70 °C-dried (a) Na-birnessite and (b) Cr-buserite.