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Preparation and Characterization of Layered Manganese Oxide (Birnessite) and Its Intercalation Reactions

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(Manuscript submitted February 14, 2003; accepted April 11, 2003)

Abstract

Layered manganese oxide (birnessite) was prepared by oxidation of $\text{Mn}(\text{NO}_3)_2$ with H_2O_2 in NaOH solutions. The product had a composition of $\text{Na}^{+}_{0.44}(\text{Mn}^{\text{III}}_{0.44}\text{Mn}^{\text{IV}}_{0.56}\text{O}_2)^{0.44-} \cdot 0.5\text{H}_2\text{O}$ and the negative charge of the host MnO_2 layer due to Mn^{III} was counterbalanced by Na^{+} in the interlayer. This Na-birnessite was treated with a hydrochloric acid solution to exchange Na^{+} with H^{+} . The H-birnessite obtained was further treated with an *n*-propylamine solution, and the interlayer distance nearly doubled to 1.41 nm by the incorporation of propylammonium ions (PA). The PA-birnessite was suspended in a VCl_3 solution, and V ions were intercalated. The V-birnessite had a composition of $\text{V}^{5+}_{0.08}(\text{H}_{0.3}\text{Mn}^{\text{III}}_{0.7}\text{Mn}^{\text{IV}}_{0.3}\text{O}_2)^{0.4-} \cdot 0.3\text{H}_2\text{O}$, and it was found that the interlayer V ion was oxidized to 5+, possibly by Mn^{IV} in the host layer. This compound was expected to show better charge-discharge properties as a battery material than Na-birnessite, since multi-valent V^{5+} ions were likely to attract the layers more strongly and to support the layered structure more firmly.

1 Introduction

Birnessite is a layered manganese oxide composed of host MnO_2 layers with negative charges owing to Mn^{III} and of interlayer cations counterbalancing the negative charge of the host layers.[1] Its chemical composition can be expressed as $\text{M}^{n+}_{x/n}(\text{Mn}^{\text{III}}_x\text{Mn}^{\text{IV}}_{1-x}\text{O}_2)^{x-} \cdot m\text{H}_2\text{O}$, where M^{n+} stands for an interlayer cation with a charge of $n+$. The interlayer cations can be exchanged with cations in external solutions and the properties of birnessite can be altered by intercalation.

Birnessite is a potential cathode material for lithium ion batteries as manganese is an abundant resource. It can intercalate along the interlayer channels. It has been reported that a lithium intercalate has a high diffusion coefficient for Li^{+} . [2] However, with repeated charge-discharge cycles, the interlayer distance changes and the crystal structure is deformed and finally destroyed. Zinc birnessite shows better charge-discharge cycle properties because Zn^{2+} ions act as pillars between the layers.[3] Intercalation with Bi^{3+} and Pb^{2+} improved the charge-discharge properties, presumably because the layers are bound more tightly than with Na^{+} owing to the much stronger attraction by multi-valent cations.[4, 5] It has been reported that intercalation of Ca^{2+} and Zn^{2+} also improved the charge-discharge performance for similar reasons as above.[6] There has been no report, however,

on intercalation of cations with variable, higher valencies.

In this investigation, the intercalation of vanadium ions with charges from 3+ to 5+ in birnessite was attempted with the expectation that the introduction of cations with higher valencies would improve the charge-discharge properties. Direct intercalation of Na-birnessite with vanadium cations, however, did not work, and the following indirect way of intercalating vanadium cations was used: Na-birnessite was firstly treated with a hydrochloric acid solution to obtain proton (H) birnessite. The H-birnessite was further treated with an *n*-propylamine solution to introduce propylammonium (PA) into the interlayer by acid-base reaction. The interlayer distance of PA-birnessite was large enough to intercalate even hydrated vanadium cations (V). The V-birnessite obtained was characterized by various methods and the reaction mechanism is discussed.

2 Experimental

2.1 Preparation

Na-birnessite A solution of 0.6 M NaOH - 3% H₂O₂ ($M = \text{mol dm}^{-3}$) was added to a 0.3 M Mn(NO₃)₂ solution in a volume ratio of 2:1, and the mixture was agitated vigorously for 5 min. Then the mixture was allowed to stand for 24 h at room temperature. The precipitate was separated, washed with distilled water, and dried at 80°C to obtain the Na-birnessite.

H-birnessite The Na-birnessite (1 g) was suspended in 100 cm³ of 1 M HCl solution for 24 h, and the HCl solution was changed 3 times to complete the exchange of Na⁺ with H⁺. The solid was separated, washed with distilled water, and dried at 80°C to obtain the H-birnessite.

PA-birnessite The H-birnessite (0.2 g) was further treated with 40 cm³ of 40% *n*-propylamine solution for 24 h at 40°C to introduce propylammonium (PA) in the interlayer.

V-birnessite The PA-birnessite (0.26 g) was suspended in 10 cm³ of 0.05 M VCl₃ solution for 1 h at 40°C in a sealed 100 cm³-plastic vessel. The solid was washed with distilled water, and dried in a vacuum for 1 h at 40°C to obtain the V-birnessite.

2.2 Characterization

XRD The crystal structure of the birnessites was determined with Philips X'pert-MPD.

ICP and AAS The birnessite samples were dissolved with hydroxyl ammonium chloride solution, and the contents of metal ions were determined with Shimadzu ICPS-1000IV and Hitachi Z-6000.

Titration with oxalic acid The amount of electrons necessary to reduce the manganese ions of birnessite to Mn²⁺ was determined to evaluate the oxidation number of Mn.

TG-DTA The amounts of interlayer water and structure water in the host layer were determined with Shinku Riko MTS-9000.

3 Results and Discussion

3.1 Na-birnessite

Figure 1, curve (a) shows the XRD pattern of Na-birnessite. All the diffraction peaks could be indexed as a monoclinic form with the lattice parameters: $a=0.51$ nm, $b=0.28$ nm, $c=0.73$ nm, and $\beta=103^\circ$. The (001) and (002) peaks are related to interlayer spacings and the interlayer distance is 0.71 nm. The (020) peak indicates a regular arrangement of atoms along layers. The composition of Na-birnessite was determined according to the following procedure: If the oxidation number of manganese is expressed by x and the number of interlayer water molecules by y , the chemical formula is given by Na_{4- x} MnO₂ · y H₂O. By titration with oxalic acid, manganese ions in birnessite, Mn ^{x +}, are reduced to Mn²⁺ according to:

Then the ratio of the amount of electrons necessary for the reduction of birnessite e and the manganese content Mn is $(x-2)$. The value of x is known from the e/Mn value in Table 1, and this gives the amount of Na^+ . The amount of interlayer water was measured by TG-DTA (Table 2), and the value of y is obtained. The composition determined was: $\text{Na}^+_{0.44}(\text{MnO}_2)^{0.44-} \cdot 0.5\text{H}_2\text{O}$. The Na content in this formula determined by the charge balance with the host layer agrees with the ICP and AAS results (Table 1).

3.2 H-birnessite

The H-birnessite formed by proton intercalation of Na-birnessite shows a similar XRD pattern as Na-birnessite (Fig. 1, curve b). It has a hexagonal form with the lattice parameters: $a=0.28$ nm and $c=0.73$ nm, and all the diffraction peaks could be indexed. The original (020) peak remains as the (110) peak here, indicating that the original atomic arrangement in the host layer is retained after the acid treatment. The interlayer distance evaluated from the (001) peak is 0.72 nm, which is about the same as that of the original Na-birnessite. This similar interlayer distance can be explained by the fact that the size of water molecules supporting the interlayer is about the same as that of sodium ions. Its chemical composition determined from the analytical results (Tables 1 and 2) is: $\text{H}_{0.3}\text{Mn}^{\text{III}}_{0.3}\text{Mn}^{\text{IV}}_{0.7}\text{O}_2 \cdot 0.3\text{H}_2\text{O}$. Here the amount of intercalated protons was determined by the charge balance of the host layer, and it agrees with that measured by TG-DTA as structure water (Table 2). This composition shows that H-birnessite is more oxidized than Na-birnessite, probably due to a disproportionation reaction of Mn^{III} by the acid treatment.

3.3 PA-birnessite

In the preparation of PA-birnessite the acid and base reaction between H-birnessite and *n*-propylamine appears important because direct cation exchange reactions between Na-birnessite and *n*-propylammonium ions did not occur. All the XRD peaks could be indexed as a hexagonal form with the lattice parameters: $a=0.28$ nm and $c=1.41$ nm (Fig. 1, curve c). The (001) peak at low angles and (110) peak at high angles indicate this material to be a layered compound. The (001) peak shifted to a low diffraction angle and the interlayer distance increased to 1.41 nm, which is twice that of H-birnessite. This expansion of the interlayer can be explained by the presence of propylammonium ions (0.75 nm) larger than water molecules. With exposure to the air the intensity of the (001) peak decreased, possibly because the intercalated propylammonium escapes as amine to the air. A chemical analysis of PA-birnessite was therefore impossible due to weight changes with time. The PA-birnessite finally returned to the H-birnessite and it did not intercalate vanadium ions. The intercalation of vanadium ions into birnessite was carried out immediately after the preparation of PA-birnessite.

3.4 V-birnessite

The reaction between PA-birnessite and VCl_3 solution was affected by the ratio of these reactants. With the addition of 0.26 g of PA-birnessite to 10 cm³ of 0.05M VCl_3 solution, the external solution became yellow. The color of vanadium species changes with the oxidation number and solution pH. According to the color, these vanadium ions would be VO_2^+ and so PA-birnessite appears to oxidize V^{3+} in solution. However, the solid showed sharp XRD peaks of birnessite (Fig. 1, curve d), suggesting that the PA-birnessite intercalated vanadium ions. Most of the XRD peaks could be indexed as a monoclinic form with the lattice parameters: $a=0.59$ nm, $b=0.56$ nm, $c=0.79$ nm, and $\beta=103^\circ$. The (001) and (020) peaks indicate this material to have the original layered structure. The b parameter is twice that of Na-birnessite. The chemical composition was determined from the analytical results in Tables 1 and 2 as $\text{V}^{5+}_{0.08}(\text{H}_{0.3}\text{Mn}^{\text{III}}_{0.3}\text{Mn}^{\text{IV}}_{0.7}\text{O}_2)^{0.4-} \cdot 0.3\text{H}_2\text{O}$. Here the amounts of vanadium and manganese were determined by ICP and the valency of manganese by titration with oxalic acid. The amount of layer protons was determined as structure water by TG-DTA. The valency of vanadium ions was determined from

both the charge of the host layer and the amount of vanadium ions. The process of incorporation of V^{5+} may be explained as follows: Vanadium ions with the oxidation number 5 exist as VO_2^+ or VO_3^- and cannot exist as V^{5+} in aqueous solutions. After the experiment the external solution contained VO_2^+ ions as described above. However, this VO_2^+ ion does not directly intercalate into PA-birnessite as separate experiments indicate. Thus it is likely that, before being oxidized by birnessite, V^{3+} ions enter into the interlayer, and the interlayer V^{3+} ions are oxidized by the layer Mn^{IV} . The oxidation number of layer Mn here is lower than that of H-birnessite. The V^{3+} ions in external solutions were also oxidized as the intercalated V^{3+} by the host MnO_2 layer. The large b parameter value may be related to the lower number of interlayer cations owing to the high valency here than other birnessites. It is likely that the periodical atomic arrangement has changed due to the decrease of cations as well as water molecules in the interlayer.

With the addition of a smaller amount of PA-birnessite (0.20 g) to the VCl_3 solution, the solid became amorphous and most of the PA-birnessite would have been subject to reductive dissolution by V^{3+} and become amorphous. However, the color of the external solution remained green, indicating that unreacted V^{3+} ions dominated in the solution. With the addition of a larger amount of PA-birnessite (0.30 g) to the VCl_3 solution, the external solution became colorless and the solid showed no sharp XRD peaks. The colorless solution indicates that vanadium ions exist as VO_3^- anions, possibly because of a pH increase caused by excess propylamine brought with PA-birnessite. The vanadium anion cannot be intercalated and it is likely that PA-birnessite lost the intercalated propylamine with time in a random manner.

In this investigation the intercalation of V^{5+} ions into birnessite was accomplished. This intercalate is expected to show good charge-discharge properties as a battery material, and a battery test is under investigation.

Fig. 1 XRD patterns of Na-, H-, PA-, and V-birnessites

Table 1 Compositions of birnessites and amounts of electrons to reduce Mn^{x+} to Mn^{2+}

	Metal ion content		Amount of electrons e^-/Mn
	Na/Mn	V/Mn	
Na-birnessite	0.49	-	1.6
H-birnessite	0	-	1.7
V-birnessite	0	0.077	1.3

Table 2 Amounts of interlayer and structure waters

	Water content /%	
	Interlayer H_2O	Structure H_2O
Na-birnessite	9.1	-
H-birnessite	6.3	3.3
V-birnessite	5.8	2.9

References

- 1) J. E. Post and D. R. Veblen, *Am. Mineral.*, **75**, 477-489 (1990).
- 2) P. G. Bruce, A. Lisowska-Oleksiak, M. Y. Saidi, and C. A. Vincent, *Solid State Ionics*, **57**, 353-358 (1992).
- 3) L. Liu, Q. Feng, K. Yanagisawa, G. Bignall, and T. Hashida, *J. Mat. Sci.*, **37**, 1315-1320 (2002).
- 4) Y. F. Yao, N. Gupta, and H. S. Wroblowa, *J. Electroanal. Chem.*, **223**, 107-117 (1987).
- 5) R. Renuka and S. Ramamurthy, *J. Power Sources*, **87**, 144-152 (2000).
- 6) P. Le Goff, N. Baffier, S. Bach, and J. P. Pereira-Ramos, *Mat. Res. Bull.*, **31**, 63-75 (1996).