SYNTHSIS OF VANADIUM-ION INTERCALATED MANGANESE OXIDE (BIRNESSITE) VIA BUSERITE

S. Kawanami, T. Takeda, H. Tamura, S. Kikkawa

Graduated School of Engineering
Hokkaido University
Sapporo, 060-8628 Japan

Introduction

Layered manganese oxide (birnessite) can be a cathode material for lithium ion secondary batteries because lithium ions are (de)intercalated from or into the oxide depending on the oxidation state of Mn ions. However with charge-discharge cycle the layer structure is destroyed and the discharge capacity is decreased. The insertion of multi-valent metal ions like vanadium in the interlayer would improve the charge-discharge cycle properties of the oxide by acting as a pillar attracting the layers strongly. The authors have reported that vanadium ions are intercalated into birnessite after expanding the interlayer by the introduction of n-propylamine through several reaction steps [1]. (The n-propylamine method)

In this investigation, more straightforward intercalation of vanadium ions was attempted using the reaction with buserite (layered manganese oxide with an expanded interlayer distance due to excess water, an early stage of the birnessite formation). The product was characterized with respect to the crystal structure and the chemical composition. Also its electric conductivity was measured as one of the important properties of battery materials.

Experimental

Synthesis: A solution of 0.7M NaOH – 3% H_2O_2 (M=mol dm^{-3}) was added to a 0.3M $Mn(NO_3)_2$ solution in a volume ratio of 2:1, and the mixture was agitated vigorously for 5 min. After adding 0.2M VCl_3 solution, the mixture was agitated for 24 hours in an N_2 atmosphere at pH around 6. The product was separated from supernatant liquid by centrifugation, and dried enough at 60℃.

Characterization: Crystal structure of the product was analyzed by XRD and the content of V by ICP. The product was made into a pellet by uniaxial pressing and then CIPed. Pt was sputter deposited as electrodes for their electrical conductivity measurement.

Results and discussion

Figure1 shows the XRD patterns of (a) V-birnessite obtained by the n-propylamine method and (b) the product of this study. Both patterns are very similar. The diffractions of 001and 002 are characteristic of layered structure. These results indicate V ions were directly intercalated into the expanded interlayer of buserite. The V ions were assumed to be oxidized to V^{5+} during the intercalation by the MnO_2 host layer. Electrical conductivity of the present product is interesting because Na-birnessite should be a mixed conductor. Table 1 shows the DC conductivity of (a) V-birnessite, (b) Na-birnessite and (c) battery MnO_2 international common sample 12(IC12). And the Electrical conductivity of birnessites are much smaller than that of battery MnO_2 (IC12).

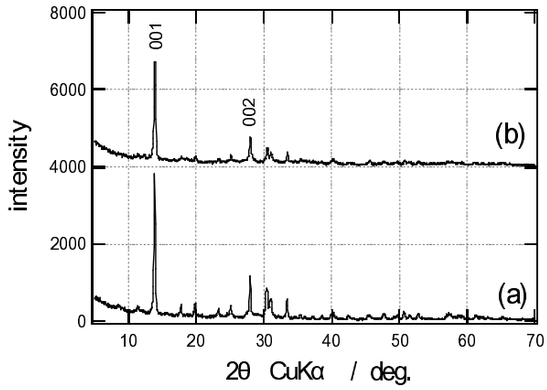

Fig.1 XRD patterns of (a) V-birnessite prepared by n-propylamine method, (b) the present product.

Table.1 DC electrical conductivity of V-birnessite, Na-birnessite and MnO_2.

(a) V-birnessite	1.06×10^{-4} S/m
(b) Na-birnessite	0.53×10^{-4} S/m
(c) MnO_2 (IC12)	4.10×10^{-2} S/m

Reference

[1] H. Tamura, K. Nakamura, T. Takeda, S. Kikkawa, J.ION EXCHANGE, 14, 133-136 (2003).