AOBO₄ Type Electrode Materials for Rechargeable Lithium Battery

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1 INTRODUCTION

Materials with many vacancies or interstices in their structures have a possibility of application as a cathode for rechargeable lithium battery. This type of inorganic materials have layered structures, framework structures, and some clusters. They have been studied widely since the lithium secondary battery was established in 1970s. These studies have made it clear that the larger and three dimensional open spaces are advantageous for the rapid lithium diffusion in the electrode material.

ReO₃ is built from cubic close-packed oxygen array, in which 1/4 sites of each oxygen layer are vacancies. The structure of this type of material, therefore, consists of vertice-sharing MO₆ octahedra and have many vacancies, which is in contrast with the ordered rock salt or spinel type materials. AOBO₄ compounds are formed from the ReO₃ type framework, but have more defects in each oxygen layer. Two modifications are known in these compounds, α and β types, which consist of vertice-sharing octahedral AO₆ and tetrahedral BO₄ groups^{1,2)}. In α structure, each tetrahedron shares all its vertices with octahedra and each octahedron shares four vertices with tetrahedra and two with other octahedra as shown in Fig. 1a. In β type compounds, the linkage pattern of AO₆ and BO₄ polyhedra is different as shown in Fig. 1b³⁾. This arrangement in β type results in more dense structure than α type. Both structures form the three dimensional path way for lithium

diffusion and can be a new type of cathode materials. In this study, the electrode behaviors of AOBO₄ (A=V, Mo; B=P) are discussed.

2 EXPERIMENTAL

β -VOPO₄ and α -MoOPO₄ were prepared and tested as the cathode. β -VOPO₄ was synthesized in an evacuated silica tube by reacting V₂O₅ and P₂O₅ (1:1 mole ratio) at 600°C for 72h. α -MoOPO₄ was prepared by reacting Mo, MoO₃ and P₂O₅ (1:5:3 mole ratio) at 500°C for 36h. XRD measurements of the products showed that MoOPO₄ was produced in a single α phase and VOPO₄ was produced in a β phase including some slight unindexed lines presumably due to impurities.

Electrochemical measurements were done by using a two-electrode coin cell. Cathode was a mixture of AOBO₄ powder, acetylene black and PTFE (50:10:1 weight%). The electrolyte was a 1.0M LiClO₄ in PC-DME solvent. Charge-discharge was carried out at a current density of 0.4mAcm⁻² or 1.0mAcm⁻². Appropriate cutoff voltages were determined for each cell.

Fig. 1 The structures of α (a,top) and β -AOBO₄(b,bottom).

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3 RESULTS AND DISCUSSION

Charge-discharge curves of β -VOPO₄ in the first 20 cycles are shown in Fig. 2. The cell was cycled between 2.5 and 4.5 V, because of its high initial voltage (about 4.0 V vs. Li). The first discharge and charge curves show a larger polarization compared to the following cycles, which is often observed for the lithium insertion electrode. The high voltage plateau, high reversibility and small specific capacity in curves after the fifth cycle are recognized as the intrinsic characteristics of β -VOPO₄. High potential of β -VOPO₄ can be clearly resulted from V⁵⁺ ions as same as V₂O₅, although the voltage profiles are different in each other. While, the small capacity is due to its crystal structure. In the β type structure, the interstitial sites between VO₆ octahedra are all occupied by the P atoms. Thus, the intercalated Li atoms have to be located between VO₆ and PO₄ polyhedra⁴⁾. This site is also surrounded by six oxygen atoms, but forms much distorted octahedra. As a result, β type structure like β -VOPO₄ cannot realize a fast Li ion transport and the capacity is limited under the high rate charge-discharging.

The electrochemical behavior of α -MoOPO₄ having α structure was examined. Figure 3 shows the charge-discharge curves of α -MoOPO₄ at a current density of 1 mAcm⁻². These curves are characterized by the low discharge voltage and the large specific capacity. The potential of AOBO₄ is determined by the A and B cations. This is supported by the fact that the average discharge voltage of MoOPO₄ and VOPO₄ are much similar with those of MoO₃ and V₂O₅, respectively. Therefore, the low discharge voltage such as about 2.0 V in MoOPO₄ is due to Mo⁵⁺ ions and the potential might be improved by the replacement of Mo⁵⁺ by other cations.

On the contrary to β type electrode, highly reversible lithium intercalation is realized in the compositional range of $0 < x < 1.0$ for α -Li_xMoOPO₄. This behavior is attributed to the α type structure, which has more loosely packed oxygen array than the β type structure. α -LiAOBO₄ is formed from AO₆ octahedra with their interstitial sites occupied by the B and Li atoms alternately. Consequently, the Li atoms are surrounded by five oxygen atoms, which

results in higher lithium mobilities in α type than β type. High current densities above 1 mAcm⁻² can be applicable for the α -MoOPO₄. The better cycling property and larger capacity than β -VOPO₄ indicate that the α structure is more suitable for the cathode of lithium battery.

4 CONCLUSION

AOBO₄ compounds have two kinds of polymorphs indicated as α and β type in the text. α -AOBO₄ has more opened structure than β type, which enables the reversible fast lithium ion transport. The high discharge potential will be realized by the selection of the best combination of the A and B cations.

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Fig. 2 Charge-discharge curves of β -VOPO₄ at 0.4 mAcm⁻².

Fig. 3 Charge-discharge curves of α -MoOPO₄ at 1 mAcm⁻².