Amorphous Iron Orthovanadate (FeVO_4) as Cathode Active Materials for Rechargeable Lithium Cells

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The amorphous iron orthovanadate (FeVO_4) was prepared and applied for a cathode active material for rechargeable lithium cells. The charge-discharge reaction with the insertion and deinsertion of lithium ion proceeded reversibly to give good cycling behavior.

1 INTRODUCTION

A variety of feasible studies have been presented for cathode active materials of rechargeable lithium cells. Some workers including us have recommended amorphous cathode materials to improve cycling behavior. A V_2O_5 - P_2O_5 glassy material as a typical example reported by Sakurai and Yamaki would be an interesting cathode in practical application.¹⁾

There have been many studies on the application of vanadium containing oxides for the cathode. Among these oxides little attention has been denoted to iron orthovanadate (FeVO_4) though expected to be one of the promising cathode materials from the crystal structure analysis.^{2,3)}

The charge-discharge characteristics of the crystalline FeVO_4 prepared by thermal reaction of V_2O_5 and Fe_2O_3 were briefly reported in patent literature, and were poor in the cycling behavior.⁴⁾ In this study the authors have tried to prepare amorphous FeVO_4 ⁵⁾ and applied for the cathode active material of rechargeable lithium cells.

2 EXPERIMENTAL

2.1 Preparation of amorphous FeVO_4

A 100 ml of 0.04M $\text{Fe}(\text{NO}_3)_3$ ($\text{M}:\text{mol dm}^{-3}$) was added dropwise to a solution (100 ml) of 0.04M NH_4VO_3 at room temperature to precipitate iron vanadate, which was dissolved by adding 6M HNO_3 to establish a pH of 1. The resulting solution was then neutralized by 6M NH_3 to reprecipitate iron oxide-free iron vanadate. The precipitate was filtered off, dried under reduced pressure at room temperature and used for the further series of experiments.

An anhydrous and amorphous FeVO_4 were prepared by the thermal treatment of the precipitate based on the data of thermal and XRD analyses. The crystalline FeVO_4 was also prepared by heating the precipitate at 600 °C for 2 h (precipitation method) and an equimolar mixture of Fe_2O_3 and V_2O_5 at 650 °C for 6 h (solid state method).

2.2 Measurement of electrochemical characteristics

A disk type of cathode (diameter : 1.3 cm, thickness : 0.3 mm) was prepared by rolling a mixture of FeVO_4 , acetylene black and Teflon (5:3:2 by weight) by the method reported previously.⁶⁾ Anode (1.33 cm^2) and reference electrode were lithium. The gap between the anode and cathode was 1.5 cm, and about 2 ml of electrolyte was filled in a Teflon cell. The electrolyte was a

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1M LiClO₄-propylene carbonate with water content less than 20 ppm (Mitsubishi Petrochemical Co.).

Charge and discharge curves were measured at a constant current density per 1 g of FeVO₄ (mA g⁻¹). All electrochemical experiments were carried out in dry Ar atmosphere at 25 °C.

2.3 Characterization

The lithium ion, vanadium and iron were determined by an atomic absorption spectroscopy (Japan Jarrel Ash AA-855) after dissolving the sample with 6M HNO₃. The thermal analysis (sample weight : about 10 mg) was carried out in air atmosphere at a heating rate of 10 °C min⁻¹ by TG/DTA 30 (Daini Seikousha). The X-ray diffraction (XRD) patterns were recorded with a diffractometer using Cu K_α radiation by RAD-7A (Rigaku Denki) equipped with a monochromator.

3 RESULTS AND DISCUSSION

3.1 Preparation of amorphous FeVO₄

The atomic ratio of iron to vanadium in the precipitate obtained was confirmed to be 1.0. The precipitate was then characterized by a thermal analysis as shown in Fig.1. The weight loss with an endothermic reaction was observed from 80 to 250 °C, followed by the constant weight region with an exothermic reaction at 420 °C.

Fig.1 Thermal analysis of the precipitate at 10 °C min⁻¹ in air.

The precipitate was obtained by the reaction of Fe(NO₃)₃ and NH₄VO₃.

Figure 2 shows the XRD patterns of the products formed by the thermal treatment of precipitate. The well-crystallized product formed at 600 °C is identified as iron orthovanadate (FeVO₄) in the XRD pattern.⁷⁾ The poor crystalline product is obtained at a temperature of 400 °C close to the exothermic peak in DTA, which indicates the transition from amorphous state to crystalline one. Accordingly, it is confirmed that the one formed below 350 °C is amorphous FeVO₄.

The starting material is FeVO₄ · 3H₂O with 3 moles of water of crystallization from the value of weight loss in TGA, and the dehydration proceeds according to equation (1).

From these results the amorphous FeVO₄ was prepared by heating the precipitate at 350 °C for 2 h, and used for the following electrochemical experiments.

Fig.2 XRD patterns of the product formed by heating FeVO₄ · 3H₂O at various temperatures.

3.2 Discharge and charge characteristics

Figure 3 shows the discharge curves of FeVO₄ prepared as above. The amorphous and

crystalline FeVO_4 (precipitation method) give higher discharge capacity than that of crystalline one prepared by the solid state method. There is no significant difference in the capacity discharged to 2 V between the amorphous and crystalline active materials from the precipitation method. The discharge potential of amorphous FeVO_4 is slightly high in the early stage of discharge. Accordingly, when the iron orthovanadate is used, the precipitation method would be preferable to increase the discharge capacity.

The discharge capacity increased with decreasing current density. Since no remarkable increase in the capacity was observed in the measurements at a current density less than 100 mA g^{-1} , the results obtained at 100 mA g^{-1} were described below.

Fig.3 Discharge curves of amorphous and crystalline FeVO_4 in $1\text{M LiClO}_4/\text{PC}$ at 200 mA g^{-1} .

Amorphous FeVO_4 : prepared by heating at 350°C for 2 h

Figure 4 shows the charge-discharge curves in the first cycle for the amorphous and crystalline FeVO_4 prepared by the precipitation method. The cathode was first discharged to 2 V, and charged for the same period as that of discharge after a rest period of 30 min. At the first cycle as shown in Fig.4A, both crystalline and amorphous FeVO_4 exhibited good charge-discharge characteristics. However, a marked decrease in the discharge capacity was observed after several cycles for the

Fig.4 First cycle of charge-discharge curves(A) and cycling behavior(B) of amorphous and crystalline FeVO_4 by precipitation method in $1\text{M LiClO}_4/\text{PC}$ at 100 mA g^{-1} .

Amorphous FeVO_4 : prepared by heating at 350°C for 2 h

crystalline FeVO_4 (Fig.4B). The amorphous FeVO_4 showed an almost constant discharge capacity after an initial decrease during several cycles.

Figure 5 shows the charge-discharge curves for the further cycles in the experiment shown in Fig.4. It can be seen that the comparable charge-discharge curves are recorded after the initial several cycles. The good cycling behavior of amorphous cathode active material in this study may be attributed to the isotropic, flexible and low-density structures which suppress the deterioration of the cathode during charge-discharge cycles.⁽¹⁾

3.3 Insertion and deinsertion of lithium ion

Figure 6 shows the content of lithium ion in the cathode during the first charge-discharge cycle. The solid line(a) shows the

Fig.5 Charge-discharge curves of amorphous FeVO₄ in the subsequent cycles measured under the same conditions as that in Fig.4.

calculated value for the insertion of one mole of lithium ion by one-electron transfer. Since the discharge over one electron reduction gives the deviation from the calculated value, the reaction must be discussed by considering some by-processes such as the insertion and decomposition of solvent. The authors have, at present, no idea to explain this result.

The line(b) shows that about 5-10 % of the lithium ion inserted remains in the cathode after the recharge for the same period as that of discharge. This should cause the decrease in the capacity of the second cycle. After several cycles, the lithium ion inserted was quantitatively deinserted to give the good cycling behavior as shown in Fig.4B.

It is considered from these results that the amorphous FeVO₄ is one of the promising cathode active materials for rechargeable lithium cells.

Fig.6 Li⁺ content in amorphous FeVO₄ after discharge(a) and charge(b) in 1M LiClO₄/PC at 100 mA g⁻¹.

Amorphous FeVO₄: prepared by heating at 350 °C for 2 h

The cathode was discharged by a given electricity(depth), and then charged for the same period as that of discharge process to determine Li⁺ content in the charge process.

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