—Communication—

Cathode Properties of Amorphous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ Powders Obtained by Mechanical Milling Technique

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Amorphous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ (mol%) powders were synthesized by mechanical milling treatments of the mixture of crystalline V_2O_5 and FeOOH at room temperature in air. The mechanochemically synthesized amorphous powders worked as a cathode in a cell with lithium metal as an anode. The amorphous cathode materials maintained the high capacities over 200 mAh g^{-1} at least up to the 50th cycle at an apparent current density of 0.5 mA cm^{-2} at room temperature. Amorphous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ powders obtained by mechanical milling is one of the promising candidates as cathode materials for lithium secondary batteries.

Key Words : Mechanical Milling, Lithium Secondary Batteries, Amorphous Cathode Material, $\text{V}_2\text{O}_5\text{-FeOOH}$ System

1 Introduction

Recently, lithium secondary batteries have been rapidly developed with the spread of cordless electronics devices like cellular phones. Many investigations on cathode materials have been carried out in order to obtain batteries of higher capacity. In particular, various V_2O_5 -based lithium intercalation materials prepared by a melt quenching technique and a precipitation method, *etc.* have been studied as high-capacity cathode materials for lithium secondary batteries. Vanadium oxide glasses in the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ system were prepared by a melt quenching technique and the powdery glasses as a cathode material exhibited the high capacity and good cycle life, compared with those with crystalline V_2O_5 .¹⁾ Machida have reported that the pure V_2O_5 glass was prepared by a twin-roller rapid quenching technique and this glass also worked as a cathode with a good rechargeability.²⁾ Sugawara have reported that amorphous FeVO_4 , including two transition metals, were prepared by a precipitation method and this material as a cathode exhibited good cycling behavior compared with that using crystalline FeVO_4 .³⁾ These results means that the amorphization of V_2O_5 -based oxide systems is effective to develop cathode materials with excellent charge-discharge performances.

On the other hand, it is known that mechanical milling technique is one of the effective processes to synthesize the powdery amorphous materials. Recently, we have reported that SnO -based amorphous oxides were synthesized by mechanical milling using planetary ball-mill at room temperature and the amorphous fine powders worked as a high capacity anode for lithium secondary batteries without pulverizing procedures.^{4, 5)} Such mechanical milling techniques have been found to be effective for preparation of active materials in batteries.

In the present study we have tried to synthesize amor-

phous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ powders by mechanical milling of starting crystalline V_2O_5 and FeOOH at room temperature in air. In this case, crystalline FeOOH was used to promote the amorphization. In addition, we can expect that transition metal element Fe in the amorphous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ may also play a role in an electrochemical redox reaction. Thus these powders obtained by mechanical milling treatments of V_2O_5 and FeOOH might exhibit the high capacity. This paper reports the preparation of the amorphous powders by mechanical milling and the charge-discharge behaviors of the lithium cells using the powders in lithium ion conducting liquid electrolyte.

2 Experimental

V_2O_5 (Wako pure chemical) and FeOOH (Kanto chemical) were used as starting materials. These materials were weighed and mixed in air. Then the mixture was milled by a planetary ball mill (Fritsch Pulverisette 5) rotating at 150 rpm in air at room temperature. Both pot and balls were made of stainless steel (SUS 304). The volume of the pots and the number of the balls with 10 mm in diameter were 80 ml and 20, respectively. X-ray diffraction measurements were performed to identify the crystalline phase in the samples obtained by changing the milling time.

The powders obtained by mechanical milling and acetylene black using as a high electron conductive material were dried in vacuum at 150°C , respectively. The cathode was prepared from the powders obtained by mechanical milling for 100 h. This powder (65% by weight), acetylene black (20% by weight), and polyvinylidene fluoride (PVDF) (15% by weight) dissolved in N-methyl pyrrolidinone (NMP) were mixed in an agate-motor in the dry N_2 -filled glove box. The stainless steal mesh on

which the mixtures were painted were dried at *ca.* 120°C in the dry N₂ and pressed under *ca.* 800 kg cm⁻² to use as a working electrode. Lithium foil was used as a counter and a reference electrode. The mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1:1 volume ratio containing 1 mol dm⁻³ LiClO₄ was used as the electrolyte. The electrode properties at room temperature were tested by charge-discharge measurements at the potential range from 2.0 to 4.1 V.

3 Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the samples after mechanical milling for 60 and 100 h of V₂O₅ using as the starting material at room temperature in air. Diffraction peaks of the samples after milling for 60 and 100 h are in good agreement with those of the starting crystalline V₂O₅. However the peaks of the samples after mechanical milling for 60 and 100 h are broader than those of the starting crystalline V₂O₅. These results suggest that the starting powders V₂O₅ become more fine and/or amorphous partly after mechanical milling.

Figure 2 shows the X-ray diffraction patterns of the samples of the nominal composition 66.7V₂O₅ · 33.3FeOOH obtained by mechanical milling of the mixture of V₂O₅ and FeOOH for various periods at room temperature in air. Patterns of starting V₂O₅ and FeOOH in fig. 2 were also shown to compare with the samples after mechanical milling. Diffraction peaks of starting V₂O₅ almost disappear after milling for 40 h. Although the X-ray diffraction shows halo pattern, the peaks of starting FeOOH are confirmed. X-ray diffraction pattern after mechanical milling for 60 h is also similar to that after mechanical milling for 40 h. On the other hand, all peaks of starting V₂O₅ disappear and weak peaks of starting FeOOH are only confirmed after milling for 100 h. The pattern of the sample after mechanical milling for 100 h shows more halo than those of the samples after mechanical milling for 40 and 60 h. Since weak peaks of starting FeOOH are observed, a slight amount of FeOOH

Fig. 1 X-ray diffraction patterns of the samples after mechanical milling for various periods of V₂O₅ using as the starting material at room temperature in air.

Fig. 2 X-ray diffraction patterns of 66.7V₂O₅ · 33.3FeOOH obtained by mechanical milling of the mixture of V₂O₅ and FeOOH for various periods at room temperature in air.

Fig. 3 Charge-discharge curves under an apparent current density of 0.5 mA cm⁻² for the amorphous 66.7V₂O₅ · 33.3FeOOH after mechanical milling for 100 h.

which could not react with V₂O₅ will probably remain after mechanical milling for 100 h. It was found that amorphous material in the V₂O₅-FeOOH system was obtained by mechanical milling treatments of V₂O₅ and FeOOH at room temperature in air. Therefore these results suggest that crystalline FeOOH using as starting material must be used to promote the amorphization.

Figure 3 shows the first charge-discharge curves under an apparent current density of 0.5 mA cm⁻² for the amorphous 66.7V₂O₅ · 33.3FeOOH after mechanical milling for 100 h. The first discharge capacity from open circuit potential (*ca.* 3.7 V) to 2.0 V shows a high value of 245 mAh g⁻¹. It was found that the discharge potential gradually decreased without any step with an increase in time. Such discharge behavior was similar to that of other amorphous electrodes. Therefore the result of the electrochemical lithium insertion into the mechanically milled samples also suggests that the sample should be amorphous material. On the other hand, the first charge

Fig. 4 Cycle performances under various apparent current densities (0.5 , 1.0 , and 5.0 mA cm^{-2}).

capacity from 2.0 to 4.1 V is 200 mAh g^{-1} . The amorphous powders obtained by mechanical milling technique can work as the rechargeable electrode.

Figure 4 shows cycle performances at various apparent current densities. In this case, the measurements were carried out for same electrode. The discharge capacities from 2nd to 50th cycle at 0.5 mA cm^{-2} (63 mA g^{-1}) show relatively high values of *ca.* 200 mAh g^{-1} . The discharge capacities versus cycle number at 1.0 mA cm^{-2} (126 mA g^{-1}) and 5.0 mA cm^{-2} (631 mA g^{-1}) show the values of *ca.* 180 mAh g^{-1} and *ca.* 80 mAh g^{-1} , respectively. When charge-discharge measurements for this electrode are carried out again under current density of 0.5 mA cm^{-2} (cycle number : 70-100), the discharge capacities show *ca.* 200 mAh g^{-1} . In addition, the coulomb efficiencies show about 100%, except 1st cycle. It was found that

amorphous materials obtained by mechanical milling exhibited good cycle performances in a conventional liquid electrolyte.

In conclusion, amorphous $66.7\text{V}_2\text{O}_5 \cdot 33.3\text{FeOOH}$ powders were obtained by mechanical milling technique at room temperature in air. The obtained powders worked as a rechargeable electrode in lithium ion conducting liquid electrolyte and exhibited high capacity and good charge-discharge efficiency at the potential range from 2.0 to 4.1 V (vs. Li/Li^+). The amorphous materials in the $\text{V}_2\text{O}_5\text{-FeOOH}$ system are one of the promising candidates as cathode materials for lithium secondary batteries of high energy densities using anode materials such lithium metal and lithium alloy.

Acknowledgments

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