Electrode Performance of Vanadium Pentoxide Xerogel Prepared by Microwave Irradiation as an Active Cathode Material for Rechargeable Magnesium Batteries

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ABSTRACT

Vanadium pentoxide xerogel was prepared by irradiation with microwaves and successfully applied as the active cathode material of a magnesium rechargeable battery. The structure and electrochemical properties of the V_2O_5 xerogel were investigated and compared with V_2O_5 prepared by conventional heat-treatment. X-ray diffraction revealed that the V_2O_5 xerogel prepared by MW irradiation has low crystalline structure. Charge-discharge tests revealed a specific capacity of 463 mAh g^{-1} , which was much larger than of V_2O_5 prepared by conventional heat-treatment (190 mAh g^{-1}).

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1. Introduction

Magnesium rechargeable batteries, which have been studied for a long time, have begun to draw attention for next generation power storage applications. Magnesium is a low-cost material, safe to handle, environmentally-friendly and naturally abundant.

However, there have been a limited number of materials available as the cathode for magnesium rechargeable batteries. Aurbach et al. reported an electrolyte solution that allowed Mg to dissolve and deposit reversibly.^{1,2} Novak et al. reported V_2O_5 to be a candidate cathode material.^{3,4} Imamura et al. reported Mg^{2+} intercalation into a composite prepared from a V_2O_5 xerogel and carbon. They reported that the V_2O_5 /carbon composite has a large interlayer distance and short diffusion length compared to the V_2O_5 xerogel without carbon.⁵ In this study, we focus attention on the drying process of the V_2O_5 xerogel, which is known to develop a narrow interlayer distance by thermal drying over 50°C .⁵ Microwave (MW) irradiation under vacuum was employed to dry the V_2O_5 xerogel in an attempt to achieve a longer interlayer distance than that prepared by conventional heat-treatment.

2. Experimental

V_2O_5 xerogel was prepared by a sol-gel process. V_2O_5 (1 g) was added to 10 wt% H_2O_2 aqueous solution (100 mL) under electromagnetic stirring. The hydrogel was dried overnight to produce a dark brown xerogel of V_2O_5 . The V_2O_5 xerogel was placed in a glass vessel and irradiated with MWs (500 W, 2.45 GHz) for 4 min under vacuum. For comparison, V_2O_5 xerogels were dried at 200 and 300°C for 8 h. The structure of the V_2O_5 xerogel was examined by X-ray diffraction (XRD; Rigaku, RINT 2000).

Electrodes were prepared using a 7:2:1 weight-ratio mixture of V_2O_5 xerogel, acetylene black and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone solvent, and spreading the resulting slurry (5 mg cm^{-2}) on carbon paper. The electrode was dried at 110°C for 1.5 h. Cyclic voltammetry (CV) was measured for the three-electrode cells using an electrochemical measurement system (Hokuto Denko, HZ-3000) with Ag/AgCl as the reference electrode. The electrode charged with magnesium ions was used as a

counter electrode. As a counter electrode, that is, S- V_2O_5 prepared by our method⁶ was charged with magnesium ions and used as a counter electrode. This electrode shows the same potential changes as a magnesium alloy plate. Magnesium alloy plate was used as the reference electrode. Thus, electrode performance was evaluated using three-electrode cells. 0.3 M $Mg(ClO_4)_2$ dissolved in propylene carbonate (PC) was used as the electrolytic solution. Charge-discharge tests were conducted between cut-off potentials of 0.9 and 2.4 V (vs. Mg/Mg^{2+}) at a constant current of 60 mA g^{-1} (0.1C rate). All three-electrode cells set up in a nitrogen atmosphere and they were closed container. All measurements were conducted at room temperature (25°C).

3. Results and Discussion

Figure 1 shows XRD patterns of the V_2O_5 products. The V_2O_5 xerogel dried at 300°C for 8 h (Fig. 1c) was generally equivalent to that of crystalline V_2O_5 . These results are similar to those reported by Hibino et al.⁷ In contrast, XRD profiles of the V_2O_5 xerogel irradiated with MWs for 4 min (Fig. 1a) and that dried at 200°C for 8 h (Fig. 1b), both of which had a broad and strong diffraction peak around $2\theta = 7$ and broad and weak peaks around $2\theta = 23$ and 31° , which indicate structurally-preserved xerogel.⁸ These peaks was

Figure 1. XRD patterns of vanadium pentoxides prepared by (a) MW irradiation for 4 min, (b) heat-treatment at 200°C for 8 h, and (c) at 300°C for 8 h.

Figure 2. Williamson-Hall plots of V_2O_5 prepared by (a) MW irradiation and (b) heat-treatment at 200°C . The vertical width of the plot represents a deviation.

Figure 3. Charge-discharge curves of V_2O_5 prepared by (a) MW irradiation, (b) at 200°C , and by (c) heat-treatment at 300°C .

(001), (003) and (004) face. The peak intensity of the MW irradiated V_2O_5 was lower than that of the heat-treated V_2O_5 , and the diffraction peaks of the former were shifted to lower angles, which indicates that MW irradiation results in lower crystallinity and longer interlayer distances than conventional heat-treatment, because MW selectively heats only water molecules in the xerogel. The interlayer distance was calculated by using the Bragg equation. Prepared by MW irradiation ($d = 11.96 \text{ \AA}$) was longer than by heat-treatment ($d = 11.58 \text{ \AA}$). Williamson-Hall plots of the XRD peaks are shown in Fig. 2. The slope of V_2O_5 prepared by MW irradiation is more inclined than that prepared by conventional heat-treatment, which indicates that the crystal structures of V_2O_5 prepared by MW irradiation is characterized by distorted layers. Therefore, it is considered that hydrate waters are instantaneously eliminated by MW irradiation.

Charge and discharge capacity curves are shown in Fig. 3. The capacity of crystalline V_2O_5 was 77 mAh g^{-1} (Fig. 3c), which is similar to that reported by Yu et al.¹⁰ The first discharge capacity of V_2O_5 prepared by heat-treatment at 200°C was 138 mAh g^{-1}

Figure 4. Cyclic voltammograms (1 mV s^{-1} , 2nd cycle) of V_2O_5 prepared by (a) MW irradiation, (b) heat-treatment at 200°C and (c) heat-treatment at 300°C .

(Fig. 3b). The second discharge capacity was comparable with the first. In contrast, the first discharge capacity of V_2O_5 prepared by MW irradiation was 175 mAh g^{-1} (Fig. 3a) and the second discharge capacity was increased 2.66 times, which indicates that Mg^{2+} insertion increased after the first cycle. The second discharge capacity was 463 mAh g^{-1} . These results may be considered that the surface became enlivened as electrode of nickel-hydride battery and the interlayer distance was increased by the first-cycle insertion of Mg^{2+} ions. Theoretical capacity of V_2O_5 xerogel was 483 mAh g^{-1} . It is indicated that interlayer distance of V_2O_5 prepared by MW irradiation is similar in long to V_2O_5 xerogel.

Figure 4 shows cyclic voltammograms for the prepared xerogels. V_2O_5 prepared by MW irradiation had a cathodic peak around -0.15 V vs. Ag/Ag^+ , and the cathodic response started in the early stage compared with that for the heat-treated V_2O_5 . These results indicate that Mg^{2+} ions inserted to interlayer of V_2O_5 and that MW irradiation increases Mg^{2+} insertion sites. In contrast, V_2O_5 prepared by conventional heat-treatment at 200°C did not display a same cathodic peak, because the interlayer distance was as short as that reported by Hibino et al.⁹ However, V_2O_5 prepared by heat-treatment at 300°C had a cathodic peak around -0.45 V . This result may indicate that Mg^{2+} ions were inserted to around apical oxygen.¹¹ Therefore, the CV results are consistent with the XRD and charge-discharge test results.

4. Conclusions

V_2O_5 xerogel prepared by MW irradiation had low crystallinity and distorted layers. The first cycle capacity was 175 mAh g^{-1} , which is almost the same as V_2O_5 prepared by conventional heat-treatment. However, the second discharge capacity of the former was 463 mAh g^{-1} , which is 2.66 times larger than that of the latter.

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