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 V2O5 xerogel were investigated and compared with V2O5 prepared by conventional heat-treatment. X-ray diffraction revealed that the V2O5 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 V2O5 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. Aubach et al. reported an electrolyte solution that allowed Mg to dissolve and deposit reversibly.1,2 Novak et al. reported V2O5 to be a candidate cathode material.3,4 Imamura et al. reported Mg2+ intercalation into a composite prepared from a V2O5 xerogel and carbon. They reported that the V2O5/carbon composite has a large interlayer distance and short diffusion length compared to the V2O5 xerogel without carbon.5 In this study, we focus attention on the drying process of the V2O5 xerogel, which is known to develop a narrow interlayer distance by thermal drying over 50°C.6 Microwave (MW) irradiation under vacuum was employed to dry the V2O5 xerogel in an attempt to achieve a longer interlayer distance than that prepared by conventional heat-treatment.

2. Experimental

V2O5 xerogel was prepared by a sol-gel process. V2O5 (1 g) was added to 10 wt% H2O2 aqueous solution (100 mL) under electromagnetic stirring. The hydrogel was dried overnight to produce a dark brown xerogel of V2O5. The V2O5 xerogel was placed in a glass vessel and irradiated with MWs (500 W, 2.45 GHz) for 4 min under vacuum. For comparison, V2O5 xerogels were dried at 200 and 300°C for 8 h. The structure of the V2O5 xerogel was examined by X-ray diffraction (XRD; Rigaku, RINT 2000).

Electrodes were prepared using a 7:2:1 weight-ratio mixture of V2O5 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-V2O5 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(ClO4)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. Mg2+/Mg) 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 V2O5 products. The V2O5 xerogel dried at 300°C for 8 h (Fig. 1c) was generally equivalent to that of crystalline V2O5. These results are similar to those reported by Hibino et al.7 In contrast, XRD profiles of the V2O5 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 2θ = 7 and broad and weak peaks around 2θ = 23 and 31°, which indicate structurally-preserved xerogel.8 These peaks were

![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.](http://dx.doi.org/10.5796/electrochemistry.80.421)
The interlayer distance was calculated by using the Bragg equation. Prepared by MW irradiation (d = 11.96 Å) was longer than by heat-treatment (d = 11.58 Å). Williamson-Hall plots of the XRD peaks are shown in Fig. 2. The slope of V$_2$O$_5$ prepared by MW irradiation was more inclined than that prepared by conventional heat-treatment, which indicates that the crystal structures of V$_2$O$_5$ 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$_2$O$_5$ was 77 mAh g$^{-1}$ (Fig. 3c), which is similar to that reported by Yu et al. $^{10}$ The first discharge capacity of V$_2$O$_5$ prepared by heat-treatment $^{7}$ at 200°C was 138 mAh g$^{-1}$ (Fig. 3b). The second discharge capacity was comparable with the first. In contrast, the first discharge capacity of V$_2$O$_5$ prepared by MW irradiation was 175 mAh g$^{-1}$ (Fig. 3a) and the second discharge capacity was increased 2.66 times, which indicates that Mgb$^{2+}$ 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$_2$O$_5$ xerogel was 483 mAh g$^{-1}$. It is indicated that interlayer distance of V$_2$O$_5$ prepared by MW irradiation is similar in long to V$_2$O$_5$ xerogel.

Figure 4 shows cyclic voltammograms for the prepared xerogels. V$_2$O$_5$ 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$_2$O$_5$. These results indicate that Mg$^{2+}$ ions inserted to interlayer of V$_2$O$_5$ and that MW irradiation increases Mg$^{2+}$ insertion sites. In contrast, V$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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.

References