

Enhanced performance as a lithium-ion battery cathode of electrodeposited V_2O_5 thin films by e-beam irradiation

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Abstract The influence of electron beam irradiation on the electrochemical properties of electrodeposited V_2O_5 thin films was investigated. V_2O_5 thin films were deposited electrochemically onto indium tin oxide-coated glass from an aqueous vanadyl sulfate hydrate ($VOSO_4 \cdot nH_2O$) solution using Pt and Ag/AgCl as the counter electrode and reference electrode, respectively. Electrodeposition was performed potentiostatically at 1.7 V vs. Ag/AgCl. Electrodeposited samples were then subjected to a 1-MeV electron beam using an electron beam accelerator at the Korea Atomic Energy Research Institute. For comparison, a control sample was not irradiated with the electron beam. Crystallinity change before and after electron beam irradiation was investigated by X-ray diffraction and the oxidation state of vanadium determined by X-ray photoelectron spectroscopy. Scanning electron microscopy was utilized to examine surface morphology. It was observed that electron beam irradiation altered the oxidation state of vanadium and increased crystallinity. Significant morphological changes of V_2O_5 thin films were also observed with electron beam irradiation. Cyclic voltammetry was

employed to evaluate the electrochemical properties of the synthesized V_2O_5 films in terms of their application as electrodes of lithium-ion battery. Compared with the control sample, which was not irradiated with an electron beam, the electron beam-irradiated V_2O_5 specimens showed much higher capacitance.

Keywords Lithium-ion battery · Electrodeposition · e-beam irradiation · Vanadium oxide (V_2O_5)

Introduction

Transition metal oxides have attracted considerable interest owing to their high capacity and high power density [1–5]. In particular, vanadium oxide (V_2O_5) is of particular interest for its potential applications in energy storage devices, such as lithium-ion batteries and pseudocapacitors, on account of its high intercalation properties, large specific capacity, and good stability [6–8].

The synthesis of electrodeposited V_2O_5 is also of great interest due to the versatility in energy storage device with respect to bulk materials [9]. Especially, electrochemical methods for the fabrication of thin films have many advantages over other methods in terms of economics and flexibility [10]. Electrodeposition is carried out at low temperatures and pressures.

Electron beam irradiation is known as an effective method to improve the stability and performance of electrodes by varying the chemical and physical properties of materials. It has been reported that surface morphology, oxidation state, optical properties, and electrochemical properties can be modified by electron beam irradiation [11–15].

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In this study, the influence of electron beam irradiation on the electrochemical properties of V_2O_5 was investigated. An electrochemical method was employed to fabricate V_2O_5 thin films, and an electron beam was then irradiated on electrodeposited V_2O_5 thin films. Electrochemical properties of electron beam-irradiated V_2O_5 thin films were investigated in terms of their potential application as electrodes of lithium-ion battery, and changes of the physical and chemical properties before and after electron beam irradiation were examined.

Experimental

V_2O_5 thin films were electrochemically fabricated onto indium tin oxide (ITO)-coated glass from an aqueous solution of vanadyl sulfate hydrate ($VOSO_4 \cdot nH_2O$). The electrolyte was prepared by dissolving 1.90 g of $VOSO_4 \cdot nH_2O$ in 17.5 g of water and 17.5 g ethanol. All electrodepositions in this study were carried out under a constant potential (1.7 V vs. Ag/AgCl) in a three-electrode electrochemical cell at room temperature. Pt and Ag/AgCl in saturated KCl solution were used as the counter electrode and the reference electrode, respectively. Prior to electrodeposition, the ITO-coated glass was ultrasonically washed for 20 min in a 1:1 mixture of acetone and isopropanol and finally rinsed with distilled water.

An electron beam was irradiated onto V_2O_5 thin films using an electron beam accelerator at the Korea Atomic Energy Research Institute with various irradiation doses (30–70 kGy). The electron beam irradiation was performed by an electron accelerator, and the electron beam was extracted by a potential of 1 MeV applied between the electron source and the sample target at room temperature. The distance between the source and sample was 400 mm

and the electron beam current was 1 mA. For comparison, a control sample was not irradiated with the electron beam.

Following electrodeposition and electron beam irradiation, synthesized samples were subjected to more detailed analyses. Crystallinity change before and after electron beam irradiation was investigated by X-ray diffraction (XRD; Rigaku, D/max-2200), and the oxidation state of vanadium was determined by X-ray photoelectron spectroscopy (Thermo-scientific, ESCA 2000). The morphologies were investigated by scanning electron microscopy (SEM; Hitachi Ltd., S-4200). Cyclic voltammetry measurements were employed to evaluate the electrochemical properties of V_2O_5 thin films with a conventional three-electrode system in 1 M $LiClO_4$ /propylene carbonate. I - V measurements were carried out with a voltage range from -1.5 to 1.5 V vs. Ag/AgCl at room temperature.

Results and discussion

SEM images were used to examine the influence of electron beam irradiation on surface morphology, and Fig. 1 compares SEM images of as-electrodeposited V_2O_5 , 50-kGy electron beam-irradiated V_2O_5 , and 70-kGy electron beam-irradiated V_2O_5 samples. As-electrodeposited V_2O_5 film showed a relatively smooth surface with porous structure, which is a typical feature of an electrodeposited metal oxide. The electrodeposited sample was dried in the atmosphere for 1 day after electrodeposition; the pores can form during this drying process to allow solvent evaporation.

With electron beam irradiation, significant morphology change was clearly observed. With 50-kGy irradiation, the

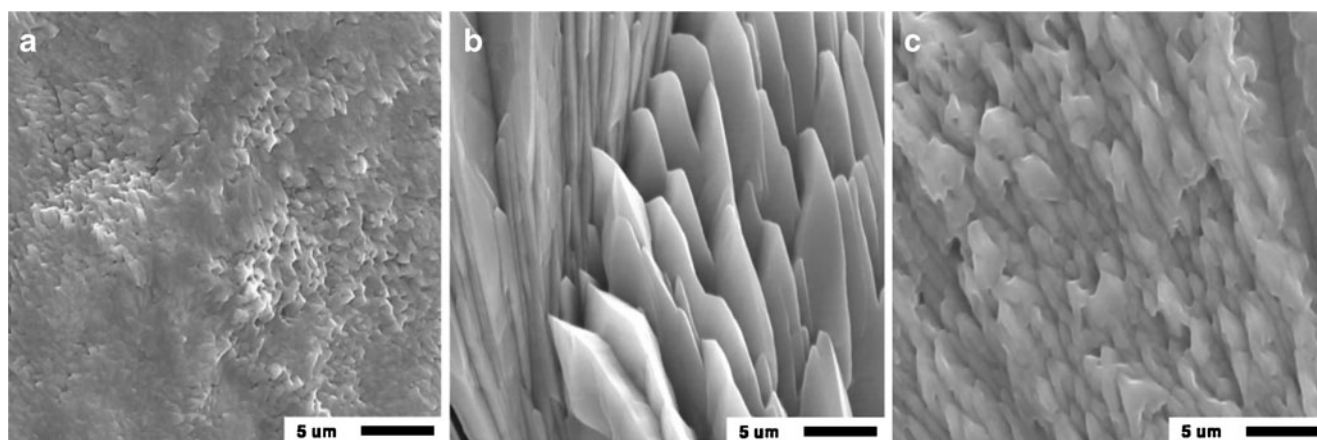


Fig. 1 Scanning electron microscopy (SEM) images of V_2O_5 thin films as a function of irradiation dose: **a** as-electrodeposited, **b** 50 kGy, and **c** 70 kGy

surface became very rough with sharp rods, which were not originally found in the as-electrodeposited sample. When the sample was irradiated for a longer time (above 60 kGy), the needle-like surface collapsed. The change of surface morphology is likely due to the mechanical energy of electrons and increased temperature. When the surface was irradiated with an electron beam below 50 kGy, it was etched and became very rough. With long irradiation (above 60 kGy), however, the film surface was reformed by high temperature. It can be concluded that the mechanical energy of electrons changes the surface morphology at low electron beam dose, and the thermal energy changes the film surface at high dose. This morphology change corresponds with the change of X-ray diffraction patterns. The surface temperature increased with electron beam irradiation, resulting in morphology and crystallinity change.

X-ray diffraction patterns were used to investigate the crystallinity change before and after electron beam irradiation. Figure 2a shows the XRD patterns of the V₂O₅ thin films as a function of irradiation time. The as-electrodeposited V₂O₅ showed poor crystallinity, and only one peak was observed at 21.2° in the XRD patterns (Fig. 2a). The peak is similar to previously reported findings, and it can be assigned as a characteristic peak of V₂O₅ [16]. With an increase of irradiation time, the peak increased, indicating that V₂O₅ was crystallized. These phenomena can be explained by two factors: temperature increase and generation of ozone. The temperature of the sample surface may increase as a result of electron beam irradiation, and amorphous V₂O₅ can be crystallized at high temperature. Furthermore, it is known that electron beam irradiation in air generates ozone from oxygen,

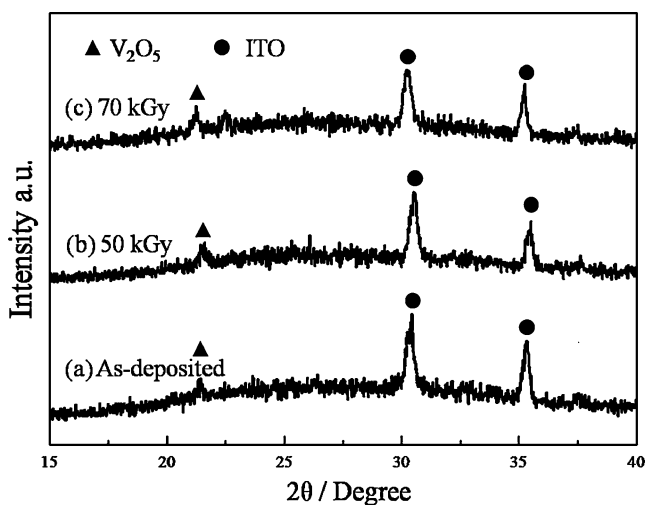


Fig. 2 X-ray diffraction (XRD) patterns of electron beam irradiated V₂O₅ films: **a** as-electrodeposited, **b** irradiated with 50-kGy electron beam, and **c** irradiated with 70-kGy electron beam (circle ITO substrate, triangle V₂O₅)

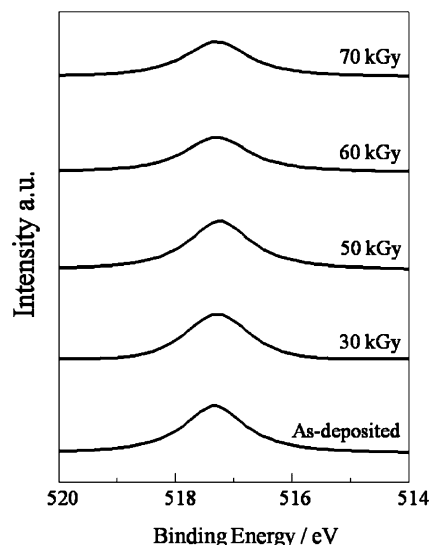


Fig. 3 X-ray photoelectron V 2p spectra of V₂O₅ thin films as a function of electron beam dose

which can oxidize the sample surface. With an increase of irradiation time, the surface temperature increased and the time that the sample surface was exposed to ozone increased, resulting in an increase of crystallinity. Among the samples tested, the V₂O₅ thin film irradiated with a 70-kGy electron beam showed the highest crystallinity (Fig. 2c).

Figure 3 shows the V 2p X-ray photoelectron spectra of V₂O₅ films with electron beam irradiation, and the main peak positions are listed in Table 1. For all samples, the main peak was observed at around 517 eV. The as-electrodeposited film showed main peak at 517.28 eV, which can be assigned as a V–O–V bond [17]. With electron beam irradiation longer than 50 kGy, the peak was observed to shift to higher binding energy, as shown in Table 1. Oxidation by both ozone and increased temperature could account for peak shift. X-ray photoelectron spectroscopy results indicated that V is partially oxidized at high dose, and these results correspond to XRD results. From the above results, it can be concluded that electron beam irradiation strongly affects crystallinity, surface morphology, and oxidation state.

Table 1 X-ray photoelectron spectroscopy peak position of V 2p_{3/2} (V–O–V) as a function of electron beam dose

| Electron beam irradiation dose (kGy) | V 2p _{3/2} (V–O–V, eV) |
|--------------------------------------|---------------------------------|
| Non | 517.28 |
| 30 | 517.28 |
| 50 | 517.28 |
| 60 | 517.33 |
| 70 | 517.33 |

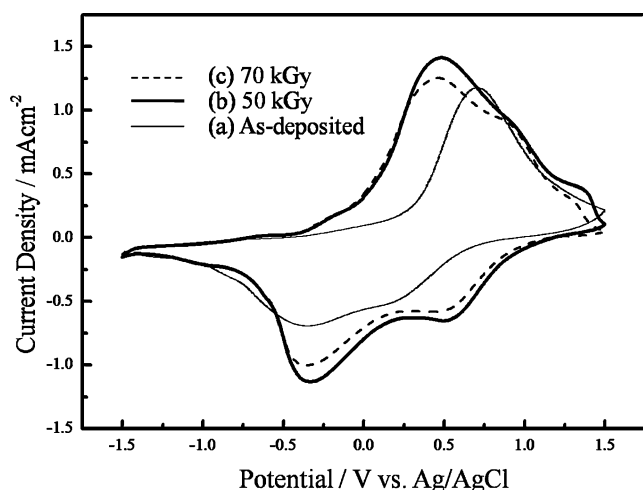


Fig. 4 Cyclic voltammograms of electron beam irradiated V_2O_5 electrodes (scan rate 10 mV s^{-1}): **a** as-electrodeposited V_2O_5 (thin line), **b** V_2O_5 irradiated with a 50-kGy electron beam (thick line), and **c** V_2O_5 irradiated with a 70-kGy electron beam (dashed line)

X-ray photoelectron spectroscopy results indicated that V is partially oxidized at high dose, and these results correspond to XRD results. From the above results, it can be concluded that electron beam irradiation strongly affects crystallinity, surface morphology, and oxidation state.

In order to examine the electrochemical properties of electron beam-irradiated V_2O_5 , cyclic voltammetry measurements were carried out. Figure 4 shows cyclic voltammograms of V_2O_5 thin films with different electron beam doses (0, 50, and 70 kGy) in 1 M LiClO_4 , and the dependence of electrochemical activity on electron beam irradiation dose was clearly observed. The curves show asymmetric shape in the range of -1.5 V to 1.5 V vs. Ag/AgCl , indicating that all electrodes have excellent electrochemical properties. Compared to the as-electrodeposited V_2O_5 film, both electron beam-irradiated films exhibited higher current density within all potential ranges and showed higher integrated area of each cathodic and anodic current density. Moreover, compared with the as-electrodeposited V_2O_5 film, all the peaks from electron beam-irradiated vanadium oxides were shifted to lower

Table 2 Specific capacitances of V_2O_5 electrodes with different electron beam dose

| Electron beam irradiation dose (kGy) | Capacitance (Fg^{-1}) |
|--------------------------------------|----------------------------------|
| Non | 230 |
| 30 | 331 |
| 40 | 312 |
| 50 | 343 |
| 60 | 278 |
| 70 | 280 |

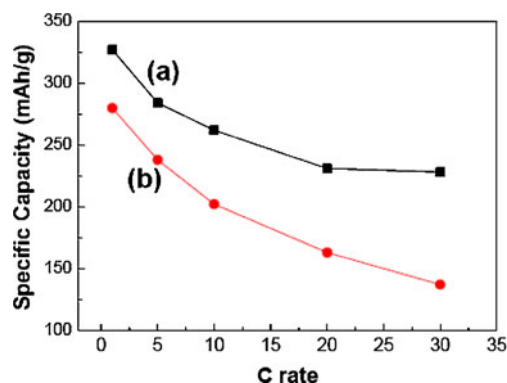


Fig. 5 Specific capacities of synthesized V_2O_5 films as a function of C rate: **a** V_2O_5 irradiated with a 50-kGy electron beam, **b** as-electrodeposited V_2O_5

potentials, indicating easier intercalation and deintercalation of lithium ions. These results entail that the capacitance of the V_2O_5 electrode is enhanced by electron beam irradiation.

The specific capacitances calculated from the following equation are summarized in Table 2. Here, I is the discharge current, Δt is the discharge time, m is the mass of an active material (V_2O_5), and ΔV is the potential change during discharging.

$$C = \frac{I \times \Delta t}{\Delta V \times m}$$

All the irradiated V_2O_5 films exhibited higher specific capacitances than the as-electrodeposited film, implying that electron beam irradiation yielded improved electrochemical properties of V_2O_5 thin films. With an increase of electron beam irradiation dose, the capacitance increased and reached a maximum capacitance of 343 Fg^{-1} when a 50-kGy electron beam was irradiated. However, with irradiation exceeding 50 kGy, the electrochemical activity decreased. Among all the samples tested, V_2O_5 irradiated

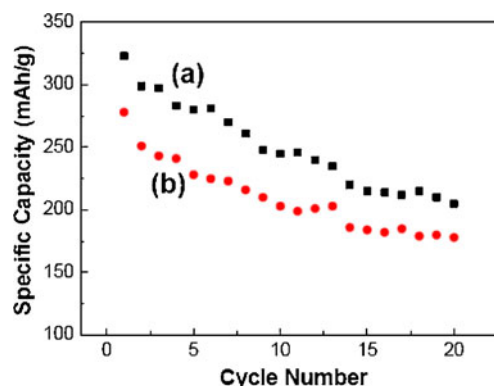


Fig. 6 Specific capacities of synthesized V_2O_5 films as a function of cycle number: **a** V_2O_5 irradiated with a 50-kGy electron beam, **b** as-electrodeposited V_2O_5

with 50 kGy showed the highest capacitance, i.e., 1.5 times higher capacitance than the as-electrodeposited sample (343 and 230 Fg^{-1} , respectively).

To compare specific capacities with respect to C rate between V_2O_5 irradiated with 50 kGy and as-electrodeposited sample (control sample), vanadium oxide films were employed as cathodes in a lithium battery cell. The C rate is defined as inserting one lithium per V_2O_5 in 1 h, which corresponds to a current density of 147 mA/g. The specific discharge capacities were calculated from the galvanostatic test when the samples were cycled between 4 and 1.1 V (vs. lithium electrode) and are summarized in Fig. 5. Although the specific capacities decreased with increasing C rate for both electrodes due to the decrease of lithium insertion, V_2O_5 film irradiated with 50 kGy was observed to have much higher capacity than nonporous structure at the all of rates tested. At 1C rate, the V_2O_5 film irradiated with 50 kGy and control sample deliver reversible capacities of 327 and 280 mAh/g, respectively. In the case of V_2O_5 film irradiated with 50 kGy, however, the specific capacity showed a much slower decrease with the increase of C rate compared with nonporous vanadium oxide electrode. For example, at a very high discharge rate of 50 C, the V_2O_5 film irradiated with 50 kGy delivers 228 mAh/g, which is 70% of the capacity at a 1C rate, while the capacity of the control sample was 137 mAh/g, which is 60% of the capacity at 1C rate.

Figure 6 shows the capacity retention of the two films at constant discharge rate (1C rate). Although both of the two electrodes revealed good cyclability, V_2O_5 film irradiated with 50 kGy showed a much higher specific retention capacity than the control sample. After 20 cycles, specific capacities of 50 kGy irradiated and control V_2O_5 films showed 205 and 178 mAh/g, respectively.

The V_2O_5 thin film that was irradiated with 50 kGy showed a very rough surface and had partially oxidized V species. The improvement in capacitance and specific capacity can be explained by morphology change, crystallinity increase, and change of the oxidation state, as previously mentioned.

Conclusions

Electrodeposited V_2O_5 thin films were treated by electron beam irradiation with various electron beam doses. Crystallinity, surface morphology, and oxidation state were significantly changed by electron beam irradiation and were found to be strongly dependent on irradiation time. Temperature increase and ozone generation may play important roles in the modification of the surface morphology, crystallinity, and oxidation state of V.

The electrochemical property is evaluated by cyclic voltammetry experiment, and among all the samples tested, V_2O_5 irradiated with 50 kGy showed the highest capacitance, i.e., 1.5 times higher capacitance than the as-electrodeposited sample. The enhanced electrochemical properties can be attributed to high surface area and facilitated charge transfer resulting from electron beam irradiation.

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