ARTICLES

Enhancement of Intercalation Properties of V_2O_5 Film by TiO_2 Addition

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Although it is well-known that TiO_2 incorporation can greatly improve the cyclic stability of V_2O_5, the influences of TiO_2 addition on the Li^+ intercalation properties of V_2O_5 remain an issue of debate in literature. In this paper, we report on a systematic investigation of the preparation and intercalation properties of V_2O_5−TiO_2 mixture films. The present work demonstrates that high Li^+ intercalation rates and capacity in V_2O_5 films are achievable with TiO_2 addition. For example, the addition of 20 mol % Ti into V_2O_5 polycrystalline demonstrated an approximated 100% improvement in Li^+ intercalation performance as compared to single V_2O_5 electrodes. Such enhancement in intercalation properties of V_2O_5 films with TiO_2 addition was attributed to changes in microstructure, crystallinity, and also a possible lattice structure and interaction force between adjacent layers in V_2O_5.

Introduction

Vanadium pentoxide (V_2O_5) has attracted a lot of attention as a Li intercalation host, due to its layered structure and hence the ability to intercalate ions or molecules between adjacent layers.[1,2] Electrical energy is stored in the form of a chemical potential during intercalation, and this chemical energy is released in the form of electricity during deintercalation. This interesting electrochemical performance has created significant interest in V_2O_5 for various applications such as a cathode for high-energy density lithium batteries[3,4] and as an electrode material for electrochemical pseudocapacitors[5,6] as well as for electrochromic devices[7] and electrooptic switches.[8]

In energy storage applications, the fundamental advantage of intercalation-based high rate systems as compared to other nonfaradic reaction-based electrochemical systems is that the former are characterized by 3-D energy storage and release processes, whereby the intercalate moves into the host solid phase. This 3-D system possesses a significant advantage over conventional electrochemical capacitors, which are inherently 2-D. The energy that can be stored in a 3-D electrode structure is much larger than in conventional capacitors, but the depth of penetration by intercalation is limited by diffusion. Previous studies have indicated that the diffusion coefficient of Li^+ in crystalline V_2O_5 is inherently low (i.e., $D = \sim 10^{-12}$ cm^2/s).[9] In addition, the electrical conductivity of V_2O_5 is too low (10^{-2} to 10^{-3} S/cm) to sustain a large current density.[10,11] Many studies have been conducted to improve lithium diffusion and electrical conduction performance in V_2O_5 by crystal structure modification toward a more open structure[12−15] and by thin layer coating of V_2O_5 on highly conductive materials.[16,17]

Another approach to improve lithium interaction capacity is through doping with electrochemically active species, such as TiO_2 or V_2O_5. However, there have been some debates in the literature as to the impact of doping with TiO_2. For example, Minett and Owen[18] showed improved cyclic reversibility of mixed vanadium/titanium oxide systems over V_2O_5. However, their mixed oxide system possessed a lower capacity value than that of V_2O_5. Davies et al.[19] found that the improved cycling stability of the V_2O_5−TiO_2 system might be caused by a preferential reduction of Ti^{4+} to Ti^{3+}, which prevented a reorganization of the microstructure in the material. Özer et al.[20] found that a 5 mol % TiO_2 addition to V_2O_5 greatly improved the intercalation capacity. It is clear that although the literature agrees that the cycling stability of the mixed V/Ti−oxide system is improved, there are different findings on the Li^+ intercalation properties of V_2O_5 with the addition of TiO_2.

The roots of this disagreement on intercalation properties may lie in the fact that the electrochemical performance of the electrode is strongly dependent on its fabrication method, morphology, and crystallinity. The V_2O_5−TiO_2 systems described previously were either amorphous V_2O_5 and TiO_2 or included a rutile phase, which has a negligible Li^+ intercalation ability.[21] In the present study, we synthesized the V_2O_5−TiO_2 mixed films using solution methods and systematically investigated the intercalation properties of the films. The dependence of the intercalation properties of the V_2O_5−TiO_2 mixture films on the chemical composition, crystallinity, and microstructures has been studied in detail.

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Experimental Procedures

Preparation of Samples. Mixed vanadium/titanium solutions with different mole ratios of titanium (0, 5, 10, 20, and 30 mol %) to vanadium were synthesized by combining a water-based vanadium sol with a titanium solution. The vanadium sol was prepared using a method reported by Fontenot el al.[22] In this approach, a V_2O_5 powder (99.8%, Alfa Aesar) was first dissolved in an iced-cooled 30 wt % H_2O_2 (J. T. Baker) aqueous solution with a V_2O_5 concentration of 0.15 mol/L. After stirring for 1.5 h at room temperature, the excess H_2O_2 was decomposed by sonication, and a yellow−brown gel was obtained. The resultant gel was then redispersed in deionized water, producing a sol that has a red−brown color, containing 0.01 mol/L vanadium ions and with a pH of 2.7. The titanium solution was prepared using $TiOSO_4$ (99.99%, ca. 15 wt % solution in dilute sulfuric acid, Aldrich), which was diluted by adding deionized water to obtain a $TiOSO_4$ concentration of 0.01 mol/L. To prevent the precipitation of white colloidal particles, HCl was added to the solution while stirring vigorously. The obtained solution is transparent and contains 0.008 mol/L titanium ions and has a pH of 0.35. Without further adjusting the pH values of the individual sol and solution, the appropriate amounts of vanadium sol and titanium solution were admixed by stirring for 2 h, followed by standing for 24 h to give a stable transparent solution. A droplet of the sol or solution was applied onto the Ti-substrate and dried under ambient conditions. As the solvent evaporated from the surface of the sol or solution, the concentration at the surface or subsurface was enriched, leading to enhanced condensation and eventually a sol−gel transition near the surface. In addition, as the solvent evaporated from the surface under ambient conditions, it was likely that a local saturation developed, resulting in a slow evaporation of solvent, which in turn permits the formation of crystallized particles (needles or platelets) and relatively dense films. Such a relative slow evaporation of solvent also ensures the formation of crack-free films. After the formation of thin films upon the complete removal of solvent, the films were subjected to heat treatment at 480 °C for 1 h in air with a heating rate of 10 °C/min.

Sample Characterizations. Optical absorption spectra of solutions with various vanadium and titanium ratios were carried out in the wavelength range of 400−900 nm using a fiberoptic spectrometer (Ocean Optics PC2000). The crystalline phases that precipitated in the coated films were analyzed by X-ray diffraction (XRD) using a Phillips PW1830 diffractometer with CuKα radiation operated at 40 kV and 20 mA. Scanning electron microscopy (SEM, JEOL JSM-5200) was used to examine the morphology of the coated films with various vanadium and titanium mole ratios after heat treatment at 500 °C for 1 h.

Electrochemical Measurements. The effect of the mole ratio of vanadium and titanium on the electrochemical properties of the thin films was investigated by using a three-electrode cell with a platinum counter electrode and a silver wire in the 0.1 mol/L $AgNO_3$ solution as the reference electrode. A 1 mol/L solution of lithium perchlorate (99.99%, Aldrich) in propylene carbonate (99.7%, Aldrich) was used as the electrolyte. Cyclic voltammetric (CV) measurements were carried out between the potential limits of -1.5 and 0.5 V versus Ag/Ag^+ using a CHI605B potentiostat/galvanostat (CHI instrument). The CV curves were recorded after two cycles at a scan rate of 0.01 V/s. The chronopotentiometric measurements were carried out after CV cycles under various current densities. Unless otherwise specified, all values reported in this paper are based on the mass of applied material. The mass of material was directly calculated from the applied volume (200 μL) and the concentration of the solution that converted to the film.

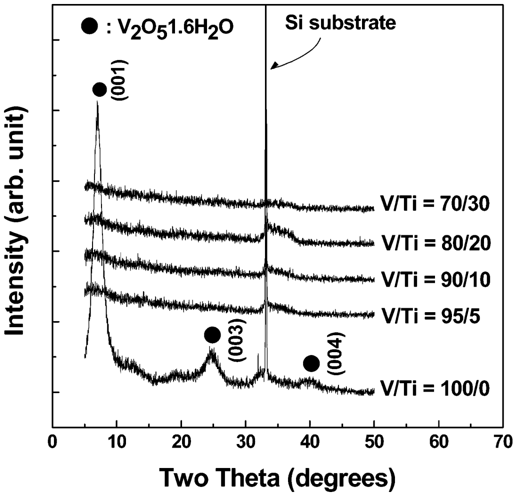

Figure 1. X-ray diffraction patterns of mixed $V_2O_5-TiO_2$ system after drying at 60 °C for 3 days.

Results and Discussion

The pure vanadium sol (0.01 mol/L, pH = 2.7) has a broad absorption peak centered around 575 nm corresponding to a red−brown color in the solution. There is a certain degree of absorbance in the entire wavelength, indicating that the solution contains a visible light absorbing or scattering media such as a colloidal dispersion. Vigolo et al.[23] established a phase diagram of stable vanadium species as a function of the concentration of vanadium ions and the pH. According to this diagram, the prepared solution with 0.01 M vanadium ions and a pH of 2.7 consists of stable hydrated V_2O_5 ribbon clusters. The pure titanium solution (0.008 mol/L, pH = 0.35) shows no absorbance peak in the entire range, and this indicates that the solution is transparent and consists of TiO^{2+} ions only. When the Ti solution was added to the vanadium sol, the color of the vanadium sol changed from red−brown to transparent. The pH of the sol decreased with an increasing amount of Ti solution and became a solution containing no vanadium oxide colloids but rather only VO_2^+ ions. In the present study, all the prepared vanadium and titanium mixed solutions consist of TiO^{2+} ions and VO_2^+ ions.

Figure 1 shows the X-ray diffraction spectra of the films dried at 60 °C for 3 days. The sol−gel derived pure vanadium film shows hydrated vanadium pentoxide ($V_2O_5{\cdot}1.6H_2O$), which is in agreement with the optical absorbance spectrum of the vanadium sol. The solution derived vanadium/titanium films show no crystalline peaks after drying and are likely to be amorphous.

Figure 2 shows the X-ray diffraction spectra of the films fired at 500 °C for 1 h. The sol−gel derived V_2O_5 film demonstrated a large deviation in relative peak intensity from the standard pattern of orthorhombic V_2O_5 powder. There was a strong preferential orientation along the [001] direction, which is in good agreement with the literature.[24] The platelet particles of the layer structured hydrate the vanadium oxide form during processing and exist in the prepared solution prior to coating. Coating aligns the platelet particles parallel on the substrate surface. Heat treating at 500 °C is unlikely to change the crystal orientation. In the titanium solution derived film, the anatase phase was precipitated during heat treatment, but there was no

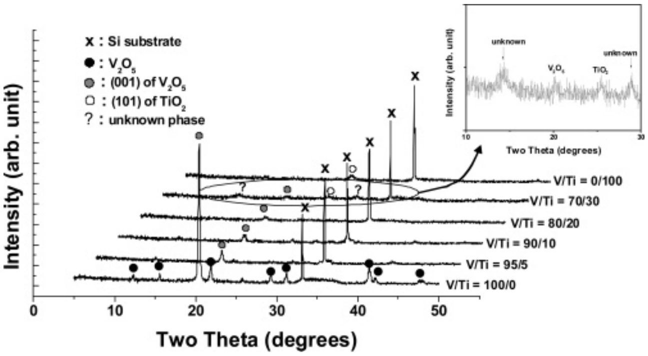

Figure 2. X-ray diffraction patterns of mixed V_2O_5−TiO_2 system after firing at 500 °C for 1 h.

sign of precipitation of the rutile phase. In all the V_2O_5−TiO_2 mixture films, the shcherbinaite phase of V_2O_5 and the anatase phase of TiO_2 were observed, while no complex vanadium/titanium oxide compounds were found. This result is also in good agreement with the phase diagram that shows neither complex oxide nor solid solutions formed in the V_2O_5−TiO_2 binary system. XRD results also indicate that there was no preferred crystal orientation, and all the XRD peaks are significantly weaker than that of single phased films. These results suggest that the crystallization started from the ion state in the amorphous films of the mixed vanadium/titanium solution system, and the coexistence of both vanadium and titanium ions hindered the crystallization process. In the film with a V/Ti = 70:30 ratio, an unknown phase was detected.

SEM micrographs of the oxides films corresponding to the X-ray diffraction patterns in Figure 2 are shown in Figure 3. Pure vanadium oxide films show some voids throughout the film. As titanium oxide incorporated into the vanadium oxide, there was a development of randomly oriented rodlike particles. Although our EDAX results are not conclusive, the rodlike particles are most likely to be TiO_2. However, V_2O_5 is known to form rodlike particles easily, and more detailed experiments are underway to determine the composition of the rodlike particles. The amount of rods increases with an increasing Ti content in the films. The grain size of vanadium pentoxide was difficult to analyze in the films heat treated at 500 °C for 1 h. Therefore, some films were heat treated at 500 °C for 10 h for better microstructure analyses. The SEM micrographs of the films heat treated at 500 °C for 10 h are shown in Figure 4. As one can see, the average grain size of V_2O_5 is remarkably reduced with an increasing TiO_2 content from 1 μm to 50 nm.

Figure 5 shows typical cyclic voltammograms of the mixed vanadium/titanium oxide films measured using a scan rate of 0.01 V/s. Although anatase TiO_2 is known as a Li^+ intercalating material (up to $x = 0.5\sim1$ in Li_xTiO_2) depending on the processing conditions,[25,26] the cyclic voltammetric experiments revealed no detectable Li^+ intercalation in anatase TiO_2 within the given potential limit. The cyclic voltammogram of the pure vanadium oxide film shows two cathodic reduction peaks at −0.25 and −0.5 V, which are attributed to Li^+ intercalation, and anodic peaks at −0.2 and −0.05 V, which correspond to Li^+ extraction. With 5 mol % titanium incorporation, each of the two cathodic and anodic peaks (due to Li^+ intercalation/deintercalation of V_2O_5) were still distinguishable. However, these cathodic and anodic peaks merged together as a single cathodic and a single anodic peak when more than 10 mol %

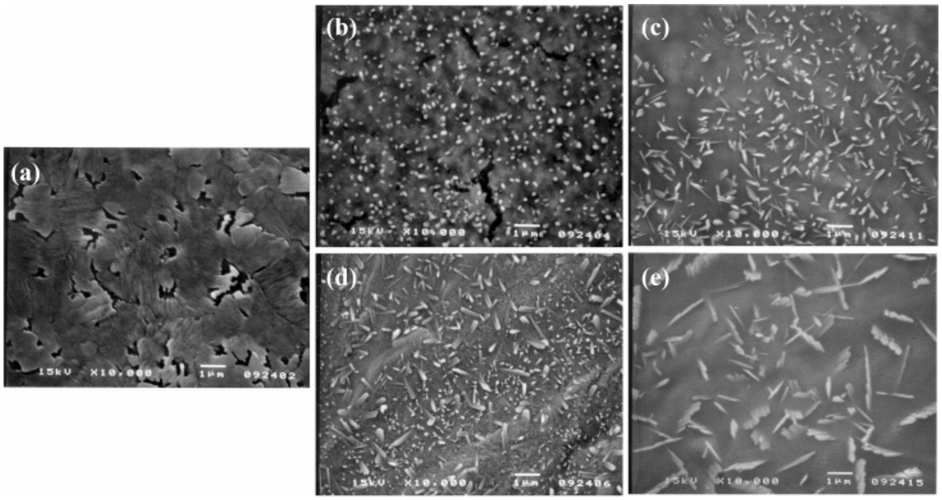

Figure 3. SEM micrographs showing surface morphologies of mixed V_2O_5−TiO_2 system with various V/Ti mol ratios after heat treatment at 500 °C for 1 h. (a) V/Ti = 100:0, (b) V/Ti = 95:5, (c) V/Ti = 90:10, (d) V/Ti = 80:20, and (e) V/Ti = 70:30, respectively.

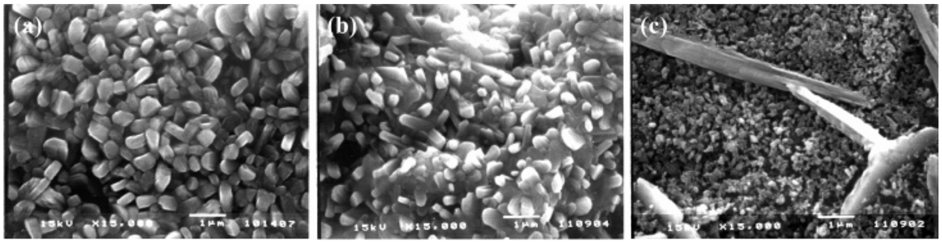

Figure 4. SEM micrographs showing grain size decrease with increased TiO_2 content in the mixed V_2O_5−TiO_2 system after heat treatment at 500 °C for 10 h. (a) V/Ti = 100:0, (b) V/Ti = 95:5, and (c) V/Ti = 80:20, respectively.

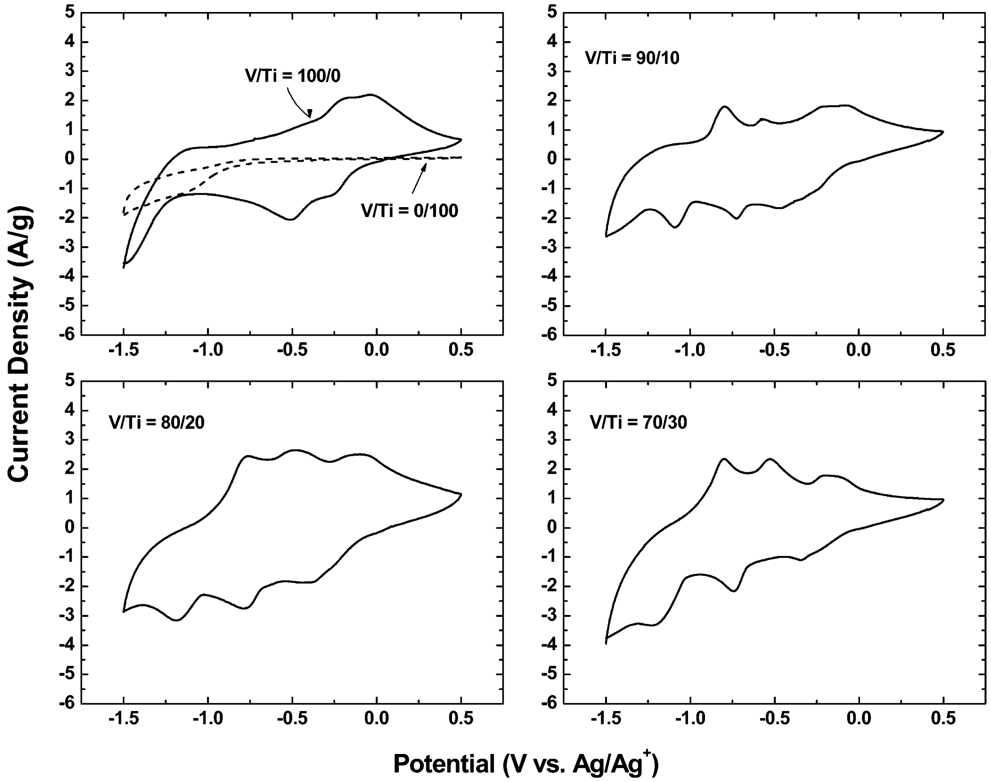

Figure 5. Cyclic voltammograms of mixed $V_2O_5-TiO_2$ films using a scan rate of 0.01 V/s.

of titanium was incorporated into the films. The cyclic voltammograms of the vanadium/titanium oxide films also show extra cathodic peaks at -0.74 ± 0.02 and -1.15 ± 0.04 V and extra anodic peaks at -0.5 ± 0.08 and -0.78 ± 0.02 V. The exact mechanisms that may induce such intercalation and extraction is not known; however, it is possible to attribute these extra cathodic and anodic peaks to Li^+ insertion and extraction of V_2O_5 with poor crystallinity or in the amorphous form. The area and shape of the CV curves for TiO_2 incorporated V_2O_5 films remained the same after the 30th cycle, which supports cyclic stability of the mixed $TiO_2-V_2O_5$ system that has been widely reported in the literature.[18,19]

Figure 6a compares the initial discharge capacities of the mixed $V_2O_5-TiO_2$ films with V/Ti ratios of 100:0, 95:5, 90:10, 80:20, and 70:30 under a constant current density of 0.27 A/g. The chronopotentiometric curve of V/Ti = 100:0 shows a typical discharge curve of crystalline V_2O_5 with a stepwise shape due to the phase change of $Li_xV_2O_5$ during Li^+ intercalation.[27,28] The curves observed in V/Ti = 95:5 and 90:10 are similar to pure V_2O_5 film, but they have broader changes and higher capacitances. However, the curves observed in V/Ti = 80:20 and 70:30 show an intercalation behavior typical of amorphous phases because there is only a gradual potential decrease without any distinct steplike potential drop.[29] Figure 6b summarizes the Li^+ intercalation capacity of the mixed $V_2O_5-TiO_2$ films as a function of current density. In the given current density range, it is clearly shown that Ti incorporation improved the Li^+ intercalation capacity. The changes in discharge capacity with different V/Ti mole ratios at a given current density are also shown in Figure 7. It is clearly shown that the film with V/Ti = 80:20 has the most promising performance in the Li^+ intercalation process. The capacity values that are reported here were based on the total amount of V_2O_5 and TiO_2. If only the active V_2O_5 mass is concerned, the actual discharge capacities of $V_2O_5-TiO_2$ will be higher than the reported values.

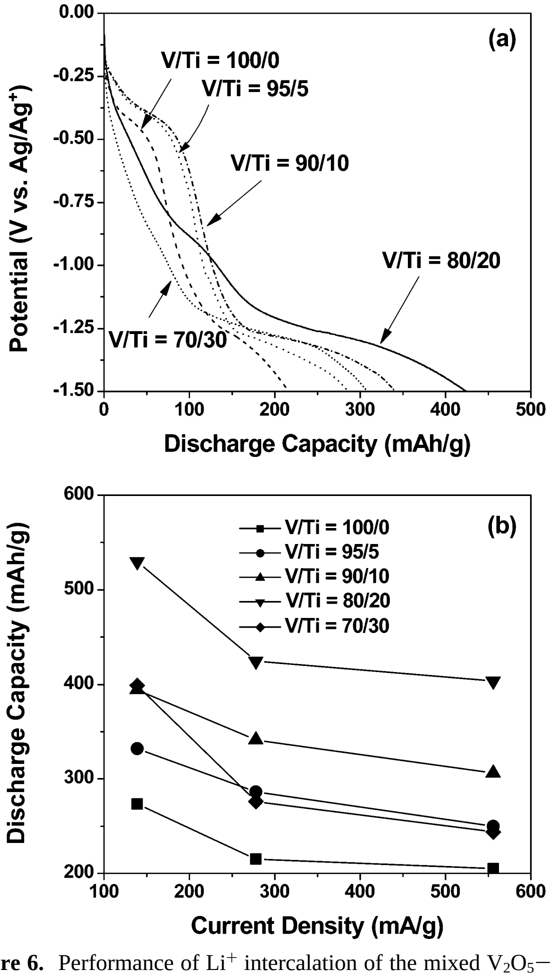

Figure 6. Performance of Li^+ intercalation of the mixed $V_2O_5-TiO_2$ system with various V/Ti ratios. (a) The initial discharge capacities at constant current density of 0.27A/g and (b) discharge capacities as a function of current density.

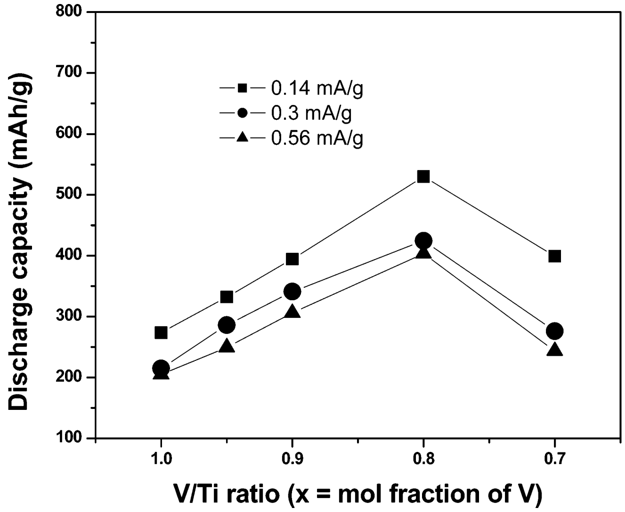

Figure 7. Summary of the initial discharge capacities of the mixed $V_2O_5-TiO_2$ system with various V/Ti ratios as a function of current density.

The possible mechanisms of enhancement in intercalation properties of V_2O_5 by the incorporation of TiO_2 are discussed as follows. The first possible mechanism is due to a reduced particle size and thus increased interface area of V_2O_5 films containing TiO_2. It is well-known that the particle size and surface area of the electrode dramatically affect the intercalation rate and capacity because Li^+ diffusion within the electrode material is slower and more difficult than in a liquid electrolyte or along the grain boundaries. Therefore, a short diffusion distance due to the small particle size will prevent concentration polarization of Li^+ within the $V_2O_5-TiO_2$ electrode, allowing retention of the cell voltage that results in delaying termination of the discharge up to the maximum capacity of the material. A high surface area due to small particle size can lower the Li^+ insertion rate density per unit area during the discharging process. This lower insertion rate also delays the capacity loss associated with concentration polarization to higher discharge current density. The second possible mechanism is related to the poor crystallinity or partially amorphous phase within the $V_2O_5-TiO_2$ films. As shown in Figure 3, the mixed $V_2O_5-TiO_2$ films show poor crystallinity as compared to the pure V_2O_5 film. It has been reported in various papers that amorphous vanadium oxides have a higher Li^+ intercalation capability than crystalline vanadium oxides due to their more open structure.[30,31] As shown in Figure 6a, the large capacitance of V/Ti = 80:20 film was attributed to the reduction plateau at around −1.15 V (vs Ag/Ag^+). Although it is known that TiO_2 and V_2O_5 do not form a solid solution, it might be possible that a trace amount of Ti was incorporated into vanadium oxide structure in the present study. The films used in this work were synthesized from solutions that consist of both Ti and V ions homogeneously mixed; such a homogeneous mixing state would likely be retained in the resultant films upon evaporation of solvent. Such a homogeneous mixture at the atomic level makes it possible to achieve partial substitution at the V site by a Ti ion during firing. Surca et al.[32] mentioned the possibility of the substitution of V by Ti in amorphous state V_2O_5. The valence state of the Ti ion is smaller than V ion in V_2O_5, and the ionic radius of tetravalent titanium is greater than that of pentavalent vanadium; thus, the size and shape of the polyhedron may change, which may result in distortion of the pyramidal chain array of VO_5 and render more open space for Li^+ insertion. The decrease in discharge capacity of the 30% Ti incorporated film is still uncertain and requires further investigation, but it may be attributed to the reduced amount of the active vanadium oxide due to the formation of unknown phases.

Conclusions

Mixed $V_2O_5-TiO_2$ films with excellent intercalation properties have been prepared by a solution method. The addition of TiO_2 greatly reduced the particle size and crystallinity of V_2O_5 in the films, resulting in a significant enhancement of Li^+ insertion capacity and intercalation rates of the mixed $V_2O_5-TiO_2$ films. Such enhancement is ascribed to the combined effects of reduced Li^+ diffusion distance, which prevents concentration polarization of Li^+ in the $V_2O_5-TiO_2$ electrode and poor crystallinity offering more Li^+ intercalation. For the TiO_2 ratios studied, the highest discharge capacity was found in V/Ti = 80:20, showing 530 mAh/g at 0.14 A/g. This discharge capacity is almost 2-fold higher than that of crystalline V_2O_5 (270 mAh/g) at the same current density.

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