Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O composite films as host materials for Li$^+$ intercalation

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Received 5 April 2005, revised 25 April 2005, accepted 27 April 2005
Published online 29 April 2005

PACS 61.10.Nz, 68.37.Hk, 82.45.Xy, 82.47.Aa

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We have prepared Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O composite films by dispersing Ag nanowires into V$_2$O$_5$·nH$_2$O sol and have investigated electrochemical properties of the films for Li$^+$ intercalation applications. With the molar ratio of Ag nanowires to V$_2$O$_5$·nH$_2$O as 0.1, such prepared films are composed of metallic Ag nanowires embedded in the matrix of Ag$_{0.08}$V$_2$O$_5$·nH$_2$O, due to partial Ag reacted with V$_2$O$_5$·nH$_2$O. At a current density of 85 mA/g, such Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O film can intercalate about two equivalents of Li ions and delivers twice the capacity of the V$_2$O$_5$·nH$_2$O xerogel film. Such improved electrochemical performance is ascribed to the changes in the microstructure and crystallinity of the Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O films including (i) further amorphization of V$_2$O$_5$·nH$_2$O, (ii) increased porosity, and (iii) enhancement of electrical conductivity.

1 Introduction
Vanadium pentoxide (V$_2$O$_5$) has a layered structure and is a promising cathode material for lithium secondary batteries [1]. Amorphous or low-crystalline V$_2$O$_5$·nH$_2$O has higher Li$^+$ intercalation capacity than its crystalline analogue, due to several advantages such as small particle size, low density, and most importantly, no phase transition limits [2]. However, V$_2$O$_5$·nH$_2$O films share the same disadvantage of low conductivity with its crystalline analogue, due to several advantages such as small particle size, low density, and most importantly, no phase transition limits [2]. However, V$_2$O$_5$·nH$_2$O films share the same disadvantage of low conductivity with its crystalline analogue. The use of metal intercalation compounds such as Ag nanowires into the Ag$_{x}$V$_2$O$_5$·nH$_2$O matrix to improve the electrochemical properties as host materials for Li-ion intercalation applications is to prepare metal-doped vanadium pentoxide, such as M$_{x}$V$_2$O$_5$ (M = Cu, Ag, and Ni) by introducing metal ions between the layers of the V$_2$O$_5$ structure [4].

The present work combines these two methods by incorporating Ag nanowires into the Ag$_{x}$V$_2$O$_5$·nH$_2$O matrix to prepare the Ag–Ag$_{x}$V$_2$O$_5$·nH$_2$O composite film and investigates its electrochemical properties as host materials for Li-ion intercalation. The relationship between the intercalation properties, electrical conductivity, and crystallinity has been discussed.

2 Experimental
The detailed synthetic process of silver nanowires can be found in the previous publications of Xia’s group [5]. V$_2$O$_5$·nH$_2$O sols were synthesized with V$_2$O$_5$ (Alfa Aesar) and 30% H$_2$O$_2$ (J. T. Baker) as precursor. 0.136 g of V$_2$O$_5$ powder was dissolved in 7 ml H$_2$O and a brown clear sol was obtained. The Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O composite film was prepared by dispersing Ag nanowires into V$_2$O$_5$·nH$_2$O sol and have investigated electrochemical properties of the films for Li$^+$ intercalation applications. With the molar ratio of Ag nanowires to V$_2$O$_5$·nH$_2$O as 0.1, such prepared films are composed of metallic Ag nanowires embedded in the matrix of Ag$_{0.08}$V$_2$O$_5$·nH$_2$O, due to partial Ag reacted with V$_2$O$_5$·nH$_2$O. At a current density of 85 mA/g, such Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O film can intercalate about two equivalents of Li ions and delivers twice the capacity of the V$_2$O$_5$·nH$_2$O xerogel film. Such improved electrochemical performance is ascribed to the changes in the microstructure and crystallinity of the Ag–Ag$_{0.08}$V$_2$O$_5$·nH$_2$O films including (i) further amorphization of V$_2$O$_5$·nH$_2$O, (ii) increased porosity, and (iii) enhancement of electrical conductivity.

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amount of Ag(0) and Ag(+1) in the composite film cannot be distinguished with X-ray photo-electron spectroscopy (XPS) [6]. Therefore, we measured XRD of a certain amount of silver and calculated the amount of metallic Ag in the Ag–Ag$_{x}$V$_{2}$O$_{5}$·nH$_{2}$O composite film by comparing the peak height of Ag(0) in such composite film to that of the known amount of Ag(0). For the composite film with molar ratio Ag/V$_{2}$O$_{5}$·nH$_{2}$O = 0.1, the metallic Ag was found to be 20% of entire silver in the composite film, i.e., x = 0.08 in Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O. Electrochemical properties of V$_{2}$O$_{5}$·nH$_{2}$O film and Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O film electrode were investigated using a standard three-electrode cell, with the 1M-LiClO$_{4}$ solution in propylene carbonate as the electrolyte, Pt mesh as the counter electrode and Ag as the reference electrode.

3 Results and discussion

Figure 1a shows the SEM micrograph of silver nanowires dried on the glass substrate. The Ag nanowires have a diameter of ~300 nm and a length up to several tens of microns. These Ag nanowires are smooth, uniform, and mono-dispersed, which ensures their well-separated dispersion into V$_{2}$O$_{5}$·nH$_{2}$O. Figure 1b shows the SEM micrograph of Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O composite film (molar ratio Ag/V$_{2}$O$_{5}$·nH$_{2}$O = 0.1) deposited on ITO substrate (top view). It can be seen that Ag nanowires are embedded in the relatively fine and smooth film. Cross section of the same film is shown in Fig. 1c. XRD patterns of (1) V$_{2}$O$_{5}$·nH$_{2}$O film and (2) Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O film on ITO substrate.

Figure 2 X-ray diffraction patterns of (a) V$_{2}$O$_{5}$·nH$_{2}$O film and (b) Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O film on ITO substrate.

Figure 3 a) Cyclic voltammograms of Ag–Ag$_{0.08}$V$_{2}$O$_{5}$·nH$_{2}$O film and V$_{2}$O$_{5}$·nH$_{2}$O film in a potential range from −1.6 V to 0.4 V vs. Ag/Ag$^+$ and under the scan rate of 10 mV/s. b) Potential (vs. Ag/Ag$^+$) vs. x, i.e. equivalents of lithium intercalated, for the V$_{2}$O$_{5}$·nH$_{2}$O xerogel film and Ag–Ag$_{x}$V$_{2}$O$_{5}$·nH$_{2}$O films that have different molar ratio Ag/V$_{2}$O$_{5}$·nH$_{2}$O. Current density 800 mA/g.

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The molar ratio is 0.1) and V2O5·

talllic Ag nanowires embedded in the matrix of

Ag–Ag0.08V2O5·

V2O5·

The electrochemical property of Ag–Ag x

be higher than those presented in Fig. 4. The improved

V2O5·

gram of Ag–Ag 0.08V2O5·

V2O5 layers and causes the layers to be closer

Figure 4 summarizes the Li

x

n
H2O films. We calculated the capacity based on the

H2O film and two Ag–Ag

H2O composite film and V 2O5·

Ag–Ag0.08V2O5·nH2O composite film and V 2O5·nH2O film. However, peaks in the cyclic voltammo-

Ag–Ag0.08V2O5·nH2O film are flatter, possibly due to more amorphization in Ag–Ag 0.08V2O5·nH2O film as indicated in its XRD pattern and discussed above. Although the Li’ extraction/intercalation behaviors were found similar in the Ag–Ag 0.08V2O5·nH2O composite film and V 2O5·nH2O film, the discharge capacity of Ag–Ag 0.08V2O5·nH2O composite film is higher than that of V 2O5·nH2O film and increases with the amount of Ag. Figure 3b shows the chronopotentiometric curves of V 2O5·nH2O film and two Ag–Ag 0.08V2O5·nH2O films that have different molar ratio Ag/V2O5·nH2O, i.e., 0.1 and 0.15 respectively.

Figure 4 illustrates the Li’-intercalation capacity as a function of current density for Ag–Ag 0.08V2O5·nH2O and V 2O5·nH2O films. We calculated the capacity based on the total mass including V 2O5·nH2O (n = 1.6 for xerogel dried under ambient condition [8]) and the entire amount of Ag, though the metallic Ag remaining in the zero-valence state (nanowires seen in SEM and indicated in XRD) is not electrochemically active. This indicates our results are conservative and the real capacity of Ag–Ag 0.08V2O5·nH2O should be higher than those presented in Fig. 4. The improved electrochemical property of Ag–Ag 0.08V2O5·nH2O composite film can be ascribed to changes in microstructure such as more amorphization and better electrical conduction resulting from the embedment of metallic Ag nanowires in the Ag–Ag 0.08V2O5·nH2O matrix. Formation of Ag–Ag 0.08V2O5·nH2O due to partial Ag reacting with V 2O5·nH2O can contribute to better electrical conduction as well, since metallic silver can be generated during the reduction cycle by the reduction of the silver ions intercalated in the material [4]. In addition, Ag–Ag 0.08V2O5·nH2O exhibits both ionic conductivity arising from ion diffusion of Ag+ and H2O and electron conductivity due to electron hopping between V5+ and V4+. The conductivity of Ag–Ag 0.08V2O5·nH2O (molar ratio Ag/V2O5·nH2O = 0.1) film was measured by four-point probe method and was found to be about 0.1 S/cm. This conductivity is higher than the value of V 2O5·nH2O xerogel film (0.001 S/cm measured in the present study and also reported in literature [4]) by two orders magnitude, due to the Ag nanowires and formation of Ag–Ag 0.08V2O5·nH2O in the composite film. In comparison with pure Ag–Ag 0.08V2O5·nH2O of the same Ag/V molar ratio [4], the Ag–Ag 0.08V2O5·nH2O film also shows higher electrical conductivity by one order of magnitude, due to the presence of Ag nanowires. In addition to enhanced electrical conductivity and porous crystallinity, introduction of Ag nanowires to the film and partial reaction with V 2O5·nH2O may result in introducing more porosity to the films. The apparent volume of the Ag–Ag 0.08V2O5·nH2O film can be computed to be 5.0 × 10−4 cm3 from the geometric area (0.5 cm2) and the thickness (1 µm from cross-section SEM image (Fig. 1c). Therefore, the density of the film is calculated to be 1.4 g/cm3, which is much lower than the reported density of V 2O5·nH2O (2.87 g/cm3) [10]. The porosity of the composite film is estimated to be ~48%. In summary, Ag–Ag 0.08V2O5·nH2O composite films have been synthesized through a simple sol–gel processing method and by dispersing pre-synthesized Ag nanowires into V 2O5·nH2O sol. The improved electrochemical performance of Ag–Ag 0.08V2O5·nH2O compared to V 2O5·nH2O film is ascribed to further amorphization, increased porosity, and the enhanced electrical conductivity. Further improvement in the intercalation capacity of Ag–Ag 0.08V2O5·nH2O films can be achieved with increased amount of Ag.

Acknowledgements Y.W. would like to acknowledge the financial support from the Ford Motor company fellowship. H. M. S. acknowledges the graduate fellowship from the Joint Institute of Nanoscience, University of Washington and Pacific Northwest National Laboratories. The authors would like to thank Cheng-Chun Lee for his help in using the FPP-5000 4-point probe.

References

[8] Y. W. would like to acknowledge the financial support from the Ford Motor company fellowship. H. M. S. acknowledges the graduate fellowship from the Joint Institute of Nanoscience, University of Washington and Pacific Northwest National Laboratories. The authors would like to thank Cheng-Chun Lee for his help in using the FPP-5000 4-point probe.

Figure 4 Relationship between current density and equivalents of lithium intercalated by Ag–Ag0.08V2O5·nH2O (Ag/V2O5·nH2O molar ratio is 0.1) and V2O5·nH2O xerogel film from chronopotentiometric measurements. x is equivalents of lithium intercalated for the V2O5·nH2O xerogel film and Ag–Ag0.08V2O5·nH2O films.