Electrochemical energy storage of nanocrystalline vanadium oxide thin films prepared from various plating solutions for supercapacitors

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ABSTRACT

Nanocrystalline V_2O_5 is electrochemically deposited onto an indium tin oxide substrate in $VOSO_4$—based solution with various acetate additives, i.e., lithium acetate, sodium acetate, and potassium acetate. The deposition conditions including pH value and acetate additive are found to be crucial factors in influencing the deposition rate, crystallinity, and porous structure of V_2O_5 electrodes. The electrochemical capacitive behavior of the deposited V_2O_5 electrodes in KCl electrolyte is investigated by cyclic voltammetry at various scan rates, ranged from 5 to 200 mV s^{-1}. The specific capacitance of V_2O_5 electrode prepared from the potassium acetate containing plating solution is up to 350 F g^{-1}, indicating that the level of K$^+$ occupancy reaches as high as 0.71. This suggests that the occupancy of K$^+$ ions is in tetrahedral and eight coordinated sites in V_2O_5 crystals. The capacitance retention at 200 mV s^{-1} compared to that at 5 mV s^{-1} reaches to 75% for this electrode. The enhanced performance is mainly attributed to the highly porous structure which significantly increases the active sites, imparts oxide/electrolyte interfaces for energy storage, and subsequently enhances the rate of insertion/extraction of K$^+$ ions. The V_2O_5 electrode is capable of delivering high energy density up to 48.6 Wh kg^{-1}, demonstrating a significant potential for thin-film energy storage devices.

1. Introduction

Supercapacitors have attracted increasing attention owing to their advantages involving high power density, fast charge—discharge rate, wide operating temperature range, long cycle life, and high safety. Generally, supercapacitors can be classified into two types: (i) electric double layer capacitors and (ii) electrochemical pseudocapacitors. The former is capable of storing energy, based on a physical adsorption of ions (within the electrolyte) on the surface of the electrode materials without any chemical reactions. The later one is related to fast and reversible faradic redox reactions that occur near an electrode surface over an appropriate range of potentials [1,2]. The active materials in electrodes of pseudocapacitors are typically transition metal oxides, such as Mn, Ru, V, Ni, Co and Mo oxides, which are able to offer theoretical capacitances of >1000 F g^{-1} [3,4].

Vanadium oxides, including VOOH [5], VO_2 (A) [6,7], VO_2 (B) [8,9], V_6O_{13} [10,11], and V_2O_5 [12,13], have been used in the energy storage devices due to their excellent electrochemical performance. Among the oxides, V_2O_5 is considered as a potential electrode materials for supercapacitors because high oxidation state variation of vanadium leads to the possibility of storing more than one electron per formula unit and the ability to form layered structure during ion intercalation process. Numerous techniques such as hydrothermal [14], electrospun [15], sol—gel [16], template-assisted growth [17], electrodeposition [18] and many others [19,20] have been adopted to obtain various V_2O_5 nanostructures. As compared to the other methods, electrodeposition shows great feasibility for commercialization since the oxide thickness, morphology, crystallinity, and chemical states can be easily engineered by adjusting the

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electrochemical parameters such as applied charge, current, potential, temperature, and electrolyte composition [21–24].

It has already been shown that the deposition potential of metal oxide is close to the decomposition potential of water, making the deposition of the metal−oxide very cumbersome. To address this problem, some researchers have proposed strategies to electrochemically deposit metal oxide coating layer with good uniformity. Broughton et al. [25] electrodeposited hydrous MnO_2 thin films from $MnSO_4$ solutions, which were mixed with acetate−based electrolytes, for electrochemical capacitive applications. This finding reveals that the presence of acetate ion has a significant effect on the deposition potential and enables further control over the deposition process. Therefore, a homogeneous deposition can be achieved at a lower potential with the acetate additive. It is important to note that although acetate ions have significant impact on the deposition potential; the influence of these additives on the capacitance is minor. Hu et al. [26] prepared hydrous ruthenium oxide by anodic deposition from $RuCl_3 \cdot xH_2O$ in aqueous media with/without adding acetate ions as the complex agent. They observed that the onset and the peak potentials were negatively shifted, and the peak current density increased monotonously with increasing the concentration of $NaCH_3COO$ [26]. It has been proposed that the formation of Ru−Cl−AcO complexes can promote the deposition rate of $RuO_2 \cdot xH_2O$ [26]. In our previous work [27], we successfully prepared V_2O_5 electrodes from 0.2 M $VOSO_4$ solution with 0.2 M $NaCH_3COO$ addition. In the same work, we also discussed the effect of deposition potential on the electrochemical performance [27]. However, to the best of our knowledge, the effect of various acetate additives on the pseudocapacitive behavior of electrodeposited V_2O_5 electrodes has not been studied so far.

Accordingly, the present work adopts an electroplating method to deposit nanocrystalline V_2O_5 onto indium tin oxide (ITO) substrates. Three kinds of $VOSO_4$−based solutions with lithium acetate, sodium acetate, and potassium acetate were used as plating electrolyte in this study. The influence of electrolyte type is found to be a crucial factor in affecting the crystallinity, porous structure, and electrochemical performance of the obtained electrodes. The intercalation/de-intercalation level of K^+ in the V_2O_5 crystals is discussed based on the experimental results. The major contribution of this work is delineating the influence of various plating electrolyte additives on the electrochemical performance of the deposited films for supercapacitor applications.

2. Experimental method

The vanadium oxides were electrochemically deposited onto ITO substrate (thickness: 0.7 mm; electrical resistivity: 7 Ω) in a 0.2 M $VOSO_4$ (Sigma-Aldrich, 99.9%) aqueous solution containing 0.2 M $LiCH_3COO$ (Sigma-Aldrich, 99%), $NaCH_3COO$ (Sigma-Aldrich, 99%), and KCH_3COO (Sigma-Aldrich, 99%), respectively. The ITO substrates with an exposed area of 1×1 cm^2 were cleaned by sonication in ethanol and deionized water prior to the electrochemical deposition process. In a three-electrode electrochemical cell, a platinum mesh and an Ag/AgCl electrode (in 3 M KCl) were used as the counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) was performed to examine the electrochemical behavior at a sweep rate of 5 mV s^{-1}. The deposition process was conducted using a potentiostat (Autolab model 302 N) at constant voltage of 0.75 V to deposit the oxide layers onto the ITO substrates at ambient temperature. The total mass of deposited oxide layers was controlled via imposing a limiting electric flux density of 0.3 C cm^{-2}.

The microstructures of the deposited oxide layers were examined using field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The crystallinity of samples was characterized by synchrotron X-ray diffraction (XRD, Beamline 01C, National Synchrotron Radiation Research Center, Taiwan). The X-ray wavelength used in this work was 1.5418 Å. Chemical composition was studied via X-ray photoelectron spectroscopy (XPS, Thermo VG-Scientific, Sigma Probe). An automated adsorption apparatus (Micromeritics, ASAP, 2020) was employed to assess the surface area of the deposited samples, using N_2 physisorption at −196 °C. Specific surface areas of the samples were evaluated with the Brunauer-Emmett-Teller equation. The pseudocapacitive properties were analyzed with cyclic voltammetry (CV) in 3 M KCl electrolyte at room temperature. The pH value was adjusted to 2.4 by HCl solution. The voltage window of −0.2−0.8 V with various scan rates of 5, 10, 25, 50, 100, 150, and 200 mV s^{-1} was employed. The electrochemical cell utilized here was identical to that used for LSV and electrodeposition.

3. Results and discussion

The LSV was employed to characterize the electrochemical behavior of oxide-growth. Fig. 1(a) shows the LSV profiles of the ITO substrate at 5 mV s^{-1} measured in the plating solutions of 0.2 M $VOSO_4 \cdot xH_2O$ (denoted as V) and 0.2 M $VOSO_4 \cdot xH_2O$ + 0.04 M H_2O_2 (denoted as V + H_2O_2). As shown in Fig. 1, the first oxidation peak in V and V + H_2O_2 plating solutions occurs at 0.5 V, and the second oxidation peak takes place at about 1.1 V. The second oxidation peak is usually attributed to the oxygen evolution reaction. As shown in Fig. 1, for similar overpotentials, the current density obtained with V + H_2O_2 plating solution is lower compared to V solution. This is attributed to the presence of H_2O_2 that results in a partial oxidation of V^{4+} to V^{5+} and consequently reduces the concentration of V^{4+} ions [28]. The samples prepared from V, V + H_2O_2, V + Li, V + Na, and V + K plating solutions are illustrated in Fig. 1(b)–1(f). According to Fig. 1(b) and (c), the electrodes deposited from the plating solutions of V and V + H_2O_2, contain almost no vanadium oxide on the ITO substrates. To facilitate vanadium oxide deposition, various acetates are added to the plating solution. The LSV graphs for the plating solutions containing $LiCH_3COO$, $NaCH_3$−COO, and KCH_3COO have been denoted as V + Li, V + Na, and V + K, respectively, in Fig. 1. The LSV profiles reveal that the oxidation potentials shift towards more negative potentials if the acetate additives are present within the solution. Therefore, the deposition
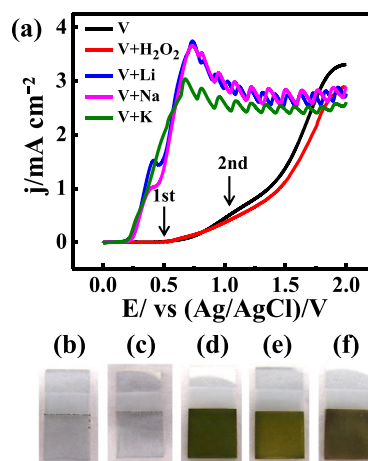

Fig. 1. (a) Linear sweep voltammogram of ITO substrates measured in 0.2 M $VOSO_4$ plating solution with and without 0.04 M H_2O_2 additive and 0.2 M $VOSO_4$ plating solution mixed with 0.2 M $LiCH_3COO$, 0.2 M $NaCH_3COO$, and 0.2 M KCH_3COO, scanned from 0 V to 2 V at a rate of 5 mV s^{-1}. Optical images of ITO substrates after deposition from 0.2 M $VOSO_4$ plating solution without (b) and with (c) 0.04 M H_2O_2 and mixed with (d) 0.2 M $LiCH_3COO$, (e) 0.2 M $NaCH_3COO$, and (f) 0.2 M KCH_3COO.