Electrochemical properties of vanadium oxide coatings grown by APCVD on glass substrates

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ARTICLE INFO

ABSTRACT

The growth of vanadium pentoxide was carried out on SiO_2-precoated glass substrates by atmospheric pressure chemical vapor deposition at 300 °C. The as-grown coatings were characterized using X-ray diffraction, Raman spectroscopy, scanning electron microscopy and UV–vis spectroscopy. The electrochemical properties of the oxides were evaluated utilizing cyclic voltammetry. The analysis showed that the N_2 gas flow rate through the bubbler of the vanadium precursor influenced the structure, morphology and the electrochemical performance of the oxides. X-ray diffraction and Raman spectroscopy revealed the presence of amorphous vanadium pentoxide. Scanning electron microscopy showed granular surface only for the sample grown for flow rate of 0.8 L min^{-1}, while the others presented featureless surfaces. In addition, the same coating exhibited the best electrochemical activity with maximum attained current density of 0.8 mA cm^{-2} and the highest intercalated charge of 9.82 mC cm^{-2} due to the presence of single-phase of V_2O_5. This as-grown oxide reached a specific capacitance of 246 F g^{-1}.

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1. Introduction

Vanadium pentoxide (V_2O_5) is a promising candidate as a cathode material in Li$^+$ batteries because of its high electrochemical activity, high energy density and high stability towards lithium intercalation [1]. The Li$^+$ intercalation/deintercalation process of the V_2O_5 can be described by the following redox reaction [2]:

$$V_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xV_2O_5.$$
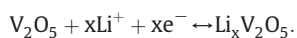
However, one of the main drawbacks in utilizing V_2O_5 as a cathode material is the low capacity during Li$^+$ intercalation because of the small diffusion coefficient of lithium ($D \approx 10^{-12}$ cm^2 s^{-1} [2]). Since, its performance is dependent on the morphology and crystallinity, a lot of interest has been focused on the growth of V_2O_5 to achieve higher specific capacities and better cyclability [3]. It has been shown that nanostructured cathodes offer larger capacities than thin film cathodes, because of the shorter Li$^+$ diffusion length and the larger surface area.

Nevertheless, they degrade after only a few intercalation and deintercalation scans [4–6]. In addition, it has been found that crystalline V_2O_5 presents high specific capacity, but exhibits a weak cyclability due to a damaged crystal structure during the scans [7]. On the other hand, amorphous and low crystallinity V_2O_5 allows faster Li$^+$ diffusion and displays remarkable cyclability. Since, amorphous materials exhibit better electrochemical properties compared to crystalline ones, they have been investigated extensively by a number of groups [2,7–21]. For example, Sakurai et al. reported that the amorphous materials exhibit superior cyclic performance compared to the crystalline ones [12]. Bates et al. demonstrated the use of amorphous V_2O_5 thin films as rechargeable thin film lithium microbatteries with high energy densities and long cycle lives [13]. Kim et al. presented the Pt doping effect on amorphous V_2O_5 films during the charge–discharge measurements revealing evidence for the close relationship between the cycling properties and microstructure of the V_2O_5 cathodes [14]. In addition, Nabavi et al. showed that the insertion process is more reversible in the case of the amorphous V_2O_5 contrary to the crystalline ones [15].

In this paper, atmospheric pressure chemical vapor deposition (APCVD) route is chosen for the production of vanadium oxide coatings on glass substrates, since the structure of the coatings may simply be controlled by tuning the vapor flows in the coating zone and the growth temperature. In addition, the operation of the CVD at atmospheric pressure makes it compatible with in-line glass manufacturing processes. It has been shown in previous papers that vanadium oxides can be

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obtained from the APCVD using vanadium (IV) chloride (VCl_4) [22,23], vanadium oxytrichloride ($VOCl_3$) [24], vanadyl acetylacetonate ($VO(C_5H_7O_2)_2$) [25] and vanadium (V) isopropoxide ($VO(OC_3H_7)_3$) [26] as vanadium sources at temperatures >400 °C. The selective APCVD of monoclinic VO_2 on patterned Cu at 150 °C with the presence of various vanadium oxide phases at higher temperatures using $VO(OC_3H_7)_3$ is also reported [27]. This work presents the deposition of cost-effective amorphous V_2O_5 using $VO(OC_3H_7)_3$ as the vanadium precursor on commercial SiO_2-precoated glass at 300 °C. The relationship of the morphology with the N_2 gas flow rate through the bubbler of the vanadium precursor towards the enhancement of the electrochemical properties of the samples is considered.

2. Experimental

2.1. Coating deposition

The APCVD reactor used in this work is an in-house design and consists of a cold-wall reactor connected to an arrangement of stainless-steel heated pipes and bubblers as reported previously [21,28]. Vanadium (V) isopropoxide ($VO(OC_3H_7)_3$ (96%, Alfa Aesar)) precursor was placed in a bubbler and heated at 60 °C, while the gas lines were kept at 80 °C to avoid any condensation. The carrier gas during all operations of the reactor was N_2 (99.9%). The substrates used for all the experiments were commercial SiO_2-precoated glass (Pilkington Glass, UK), all of dimensions 5 cm × 5 cm × 0.3 cm. Prior to coating, all substrates were cleaned with H_2O and detergent, rinsed thoroughly with H_2O and deionized H_2O, and allowed to dry. The temperature of the reactor was set at 300 °C by heating the carbon susceptor (on the top of which the substrate was) containing three pencil heaters, which were controlled by K-type thermocouples. Finally, the deposition time was 15 min, while the N_2 gas flow rates through the bubbler of the vanadium precursor were 0.8, 1, 1.2 and 1.4 L min^{-1}. The total gas flow rate in all CVD experiments was 12 L min^{-1}. Once the allotted time was complete, the reactor heater was turned off and the substrate allowed cooling under an atmosphere of nitrogen. The substrate was removed from the reactor below 200 °C. All samples were handled and stored in air.

2.2. Materials characterization

X-ray diffraction (XRD) measurements were performed using a Siemens D5000 Diffractometer for $2\theta = 10.0$–$60.0°$, step size 0.05° and step time 30 s/°. Raman measurements were carried out in a Nicolet Almega micro-Raman system using the 473 nm line for a range of 100–1100 cm^{-1}. Scanning electron microscopy (SEM) was accomplished in a JEOL JSM-7000F field-emission microscope. Prior to measurements, it was necessary to deposit a thin film of gold on the samples to improve their conductivity. Optical measurements were carried out using a Perkin-Elmer Lambda 950 UV–vis spectrophotometer in the wavelength range of 300–800 nm.

2.3. Cyclic voltammetry

Cyclic voltammetry experiments were done using a three-electrode single compartment Pyrex glass cell as already reported from our group [29–32]. Platinum, Ag/AgCl and as-grown vanadium oxides on SiO_2-precoated glass substrates were used as the counter, reference and working electrodes respectively. The working electrode area was 0.7 cm^2. The measurements were performed in 1 M $LiClO_4$/propylene carbonate solution, which acted as the electrolyte, at a scan rate of 0.02 V s^{-1} through the voltage range of −1000 V to +1000 V. The samples were scanned for 1, 100, 250 and 500 times. To study Li$^+$ intercalation/deintercalation process with respect to time, chronoamperometry was carried out at −1000 V and +1000 V for a step of 200 s. Finally, chronocoulometry was performed at the

same potential values for a step of 10 s to calculate the electrochemical reversibility of the samples using the intercalated (Q_i) and the deintercalated (Q_{di}) charges as shown in Eq. (1) [33].

$$\text{reversibility} = \frac{Q_i}{Q_{di}} \quad\quad\quad (1)$$

3. Results and discussion

The aim of this work was to investigate the possibility of the vanadium oxide growth at a temperature as low as 300 °C for various N_2 gas flow rates through the bubbler of the vanadium precursor. The coatings produced were yellow and they had poor adhesion due to the low growth temperature. Higher gas flow rates led to an increase in transmittance from 55% (0.8 L min^{-1}) to 75% (1.4 L min^{-1}). In addition, the thickness was estimated to be 60 ± 10 nm and 40 ± 10 nm for the 0.8 L min^{-1} and the 1.4 L min^{-1} samples respectively as derived from SEM cross-section images. A possible explanation of this observation was either the depletion of the gas-phase vanadium precursor from the pre-reaction at surrounding hot surfaces [34] or the site-blocking effect in which the adsorption of $VO(OC_3H_7)_3$ (0.8 L min^{-1}) decomposition products decreases the pre-reaction rate of the excess of vanadium precursor (>0.8 L min^{-1}) on the surface [35].

3.1. Structure

XRD patterns of all the as-deposited coatings showed one broad peak at 25° related with the substrate indicating that the samples are amorphous (Fig. 1 inset). On the other hand, Fig. 1 shows the V_2O_5 Raman spectrum of the as-grown coating using gas flow rate of 0.8 L min^{-1} indicating peaks at 144, 198, 286, 408, 486, 530, 702, and 995 cm^{-1}. The peak positions agree with the literature to within ±2 cm^{-1} [29–32,36]. Raman measurements of the other samples showed no appreciable signal, a behavior that could be attributed either to the lower thickness (as confirmed from the transmittance measurements) or to the non-stoichiometry of vanadium oxide (V_xO_y).

Although, XRD gave no indication for the presence of vanadium oxide in the as-grown coatings, Raman analysis revealed the presence of well-defined V_2O_5 phase. This occurs because XRD is known to probe the long-range order crystallinity of materials, while Raman is a probe of the influence of even localized short-range order to the vibrational modes of bond configurations [36,37]. Therefore, this suggests that the films are mainly amorphous retaining however a short range, within a few neighboring atoms, crystalline ordering.
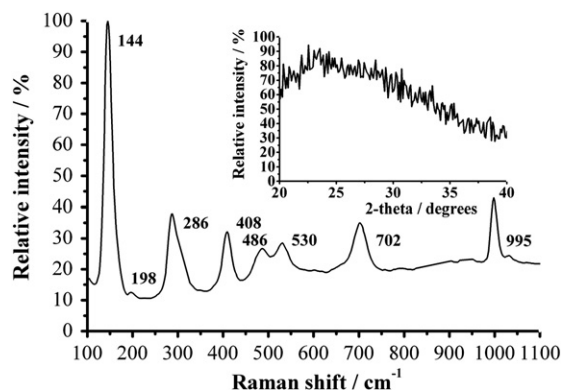

Fig. 1. Raman spectrum and XRD (inset) of vanadium oxide coatings grown for N_2 gas flow rate of 0.8 L min^{-1} at 300 °C.