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Mica-like vanadium pentoxide-nanostructured thin film as high-performance cathode for lithium-ion batteries

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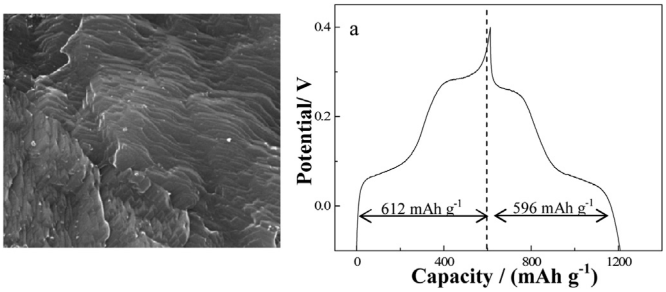
HIGHLIGHTS

- Mica-like V_2O_5 nanostructured thin-film is fabricated directly by anodic electrodeposition.
- Mica-like V_2O_5 thin-films are formed by nanosheets with thickness less than 50 nm.
- The initial discharge capacity of V_2O_5 thin-film was 596 mAh g^{-1} at 1080 mA g^{-1}.
- The fading rate of V_2O_5 thin-film was 1% per cycle at 1080 mA g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Stable and homogeneous mica-like vanadium pentoxide (V_2O_5)-nanostructured thin films are prepared directly by simple anodic deposition from V_2O_5/H_2O_2 sol solution, and then dried at ambient temperature and annealed at 500 °C in air for 1 h. The films' crystal- and microstructures, surface morphology and Li-ion intercalation properties were characterized and analyzed by X-Ray diffraction (XRD), field emission scanning electron microscopy (FSEM), thermogravimetric analysis (TGA), and electrochemical techniques. When used as a lithium-ion battery (LIB) cathode, the films exhibit a large discharge capacity of 596 mAh g^{-1} at a current density of 1080 mA g^{-1}, as well as excellent cyclic stability and a fading rate of 1% per cycle. Explanations for such significant enhancements in specific capacity, cyclic stability, and rate performance of mica-like V_2O_5-nanostructured thin films are demonstrated in this study.

1. Introduction

In recent years, both environmental and energy-resource-depletion issues have made energy conversion and storage top concerns. More environmentally benign and sustainable energy-storage systems, accordingly, are the desired future power sources [1]. In this regard, lithium-ion batteries (LIBs), with their high power output, long cycle life and high energy density, represent an attractive option for many researchers. LIBs have already been used in a wide range of applications including portable electronic devices, electric vehicles, and implantable medical devices [2–4]. The key to LIB performance enhancement, obviously, is the development of new and improved cathode materials. The maximum

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practical discharge capacity of the commercially available cathode materials available for LIBs, such as $LiCoO_2$ [5–6], $LiNiO_2$ [7], $LiMn_2O_4$ [8], $LiFePO_4$ [9,10], and their derivatives [11–13], at present, is ~300 mAh g^{-1}. However, $LiCoO_2$ toxicity and high cost have introduced environmental problems and made LIBs more expensive, while the utility of commercial $LiNiO_2$ is severely curtailed owing to its low specific capacity and insufficient cycle life. And as for $LiMn_2O_4$ cathode materials, they have been found to suffer from a severe capacity-fading problem [14].

More recently, vanadium pentoxide (V_2O_5) of a layered structure has been considered a promising LIB cathode electrode material owing to its high discharge capacity, low cost and abundance [15]. However, its poor structural stability, low electronic conductivity and slow electrochemical kinetics have hampered its LIB application. In efforts to accelerate the electrochemical kinetics, much research has focused on the synthesis and fabrication of nanostructured vanadium oxides [16]. And in fact, single-crystal V_2O_5 nanorod arrays, nanotubes, nanoroll and nanocables have been demonstrated to possess significantly enhanced electrochemical Li-ion intercalation properties [17]. Such improvement has been attributed to nanostructured materials providing shorter and simpler diffusion paths for lithium ions and allowing maximal freedom for the dimension change that accompanies lithium-ion intercalation and de-intercalation.

Among the many nanomaterial fabrication methods, which include hydrothermal treatment, the template-based method, the electrospinning method, and others, the electrodeposition method is perhaps the most low-cost, simple and easy for industrial applications. Liu [18] reported that nanostructured V_2O_5 prepared by cathodic deposition showed, as cathodes for lithium-ion intercalation, excellent electrochemical properties: specifically, a high initial discharge capacity of 402 mAh g^{-1} with a discharging current density of 200 mA g^{-1} (1.3 C). In the present study, a modified method combining sol–gel processing with anodic electrodeposition was used to fabricate mica-like V_2O_5 nanostructured thin-film electrodes. Such film in LIB applications offers the large discharge capacity of 596 mAh g^{-1} (at a current density of 1080 mA g^{-1}), which is much higher than that of V_2O_5 film prepared by the cathodic deposition method, as well as excellent cyclic stability due to its unique structure and morphology. The characteristics of the crystal structure and morphology of the V_2O_5 thin films, and their electrochemical performances, additionally, were systematically studied.

2. Experimental

According to the procedure reported by Fontenot et al. [19], V_2O_5 powder (Shanghai Shenjiang Chemical Factory) was added to a solution of 30% H_2O_2 ($n(V_2O_5):n(H_2O_2) = 1:12.25$) and de-ionized water at room temperature and stirred vigorously until the complete dissolution of V_2O_5 yielded, after 60 min, a clear dark red liquid. This sol was further dispersed and then diluted to the vanadium concentration of 3.2 mol L^{-1}. In the preparation of V_2O_5 thin films, one Platinum (Pt) plate was used as the deposition substrate on the positive side, and another as a counter electrode on the negative side. The distance between the electrodes was maintained constant at 2.5 cm while 10 min of electrodeposition was carried out; the deposition area of the positive electrode was 0.5 cm^2, and the deposition voltage was 5 V. The thin films were dried in air completely over 12 h in order to prevent cracking from the drastic volume change; subsequently they were annealed in a 500 °C ambient atmosphere for 1 h followed by a slow cool-down. All of the samples finally were stored in air preparatory to characterizations and performance measurements.

The crystal phases and crystallite sizes of the V_2O_5 thin films were characterized by X-ray diffraction (XRD, Japan Shimadzu, XRD-6000), and their surface morphologies were examined under field emission scanning electron microscopy (FESEM, JSM-7100F). The films' thermogravimetric properties, meanwhile, were investigated by thermogravimetric analysis (TGA; Shimadzu DTG-60H thermal analyser) in air, from room temperature to 600 °C at the heating rate of 10 °C per minute.

The electrochemical performances of the V_2O_5 thin-film electrodes were tested at room temperature using a standard three-electrode system: 1 mol L^{-1} $LiClO_4$ in propylene carbonate (PC) as the electrolyte, a Pt plate as the counter electrode, and Ag/AgCl as the reference electrode. Cyclic voltammetric (CV) tests on the electrodes were carried out between −0.2 V and 0.6 V (*vs.* Ag/AgCl) at a scan rate of 5 mV s^{-1}, and their charge–discharge properties were investigated by chronopotentiometric (CP) measurement within the −0.1 V to 0.4 V range (*vs.* Ag/AgCl) for various current densities. Both the CV tests and CP measurements were performed using an electrochemical analyzer (CH Instruments, Model 660B).

3. Results and discussion

Fig. 1 compares the XRD patterns of as-deposited V_2O_5 films prepared by anodic deposition from sol solution at room temperature and with those annealed at 500 °C in air for 1 h. As is apparent, the as-deposited films showed an intense (001) peak centered around 8.1° and indexed to hydrous vanadium pentoxide ($V_2O_5 \cdot nH_2O$) of layered structure, as is consistent with the literature [20,21], the broad (001) peak suggesting, moreover, an amorphous structure. The crystallite size as estimated by Scherrer Equation was 4.2 nm, and the interlayer distance calculated by Bragg's law was 10.94 Å, which indicated a crystalline water composition in this sample of $n < 1.5$ [22]. The series of (00*l*) peaks reflected the preferred orientation of a V_2O_5 layered structure effected by anodic deposition, while the missing (002) peak suggested the formation of double V_2O_5 sheets in each layer [23].

After each V_2O_5 thin-film sample was annealed at 500 °C in air for 1 h, it was completely dehydrated, thus transitioning to the pure orthorhombic phase with good crystallinity, as shown in the XRD pattern. The interlayer distance along the c-axis was calculated as 4.23 Å, slightly short relative to the crystalline structure of

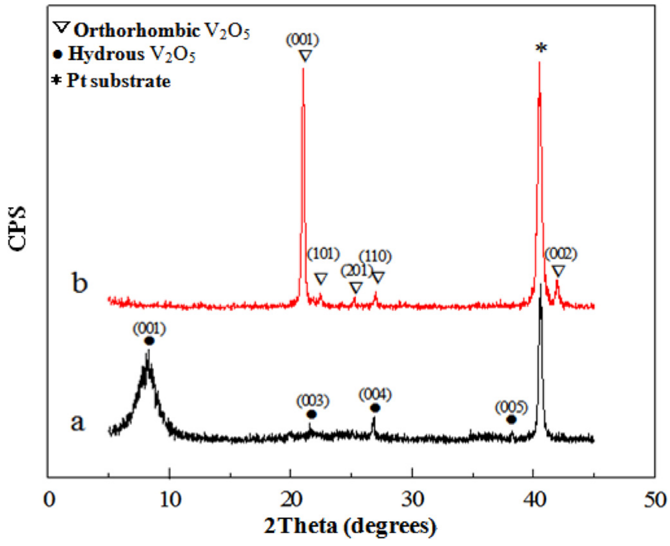

Fig. 1. XRD patterns of V_2O_5 films: a) before annealing; b) after annealing at 500 °C in air for 1 h.