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Lithium-ion intercalation and electrochromism in ordered V_2O_5 nanoporous layers

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ABSTRACT

Highly ordered V_2O_5 porous layers were fabricated from vanadium metal foils by self-organizing anodization. The defined porous structure of this material provides excellent lithium-ion transportation and intercalation/extraction properties. As a result the highly ordered porous structure shows a very good electrochromic performance with long term switching stability.

1. Introduction

Over the last decade, high-performance reversible lithium-ion intercalation materials have attracted wide attention as they provide a basis for ion insertion batteries or electrochromic devices [1–3]. Electrochromism (a reversible color change) is a phenomenon observed for some materials when small ions intercalate and de-intercalate in a host lattice in response to an applied potential or current [4,5]. In the material, inserted small ions (such as H^+ or Li^+) change the electronic and optical properties that result in a clear visible color change. In practice, transition metal oxides such as WO_3, MnO_2, TiO_2 and NiO are usually used as electrode materials for electrochromic devices due to the reversible redox reactions between their different valence states and their ion intercalation features [6–8].

Another transition metal oxide that has been widely investigated for application in lithium-ion intercalation is V_2O_5 due to its distinguished characteristics, i.e. reversible redox reactions among different valence states and its layered structure with an open framework. Lithium-ion intercalation in V_2O_5 typically results in a comparably strong electrochromic contrast [9,10]. Recently, both theoretical and experimental studies have been conducted in order to understand the lithium-ion intercalation mechanism and enhance the energy storage performance of V_2O_5 [11,12]. Theoretically, the process of lithium-ion intercalation into V_2O_5 can be divided into different stages and different phases of $Li_xV_2O_5$ that can be formed in each stage. According to the phase diagram of $Li_xV_2O_5$, there are five phases (depending on the amount of lithium, x), which are α ($x<0.1$), ϵ($0.35<x<0.7$), δ ($0.9<x<1$), γ ($1<x<2$), and ω ($x>2$) phases. The transitions between the different phases can be observed as plateaus at different voltages in galvanostatic charge/discharge curves.

For intercalation materials a large number of studies demonstrate that the morphologies at the nanoscale have an important influence on their performance [13,14]. Furthermore, a highly-ordered nanoporous or nanotubular structure shows three-dimensional direct open channels (1D) which are helpful for improving the electrochromic performance and long term stability due to the enhancement of ion migration and suppression of the stress during intercalation [15]. One of the most elegant and simple methods for the synthesis of ordered transition metal oxide nanostructures is self-organizing electrochemical anodization of an according metal substrate. On a wide range of transition metals, ordered arrays of nanochannels, nanotubes or nanoporous geometries can be produced (for an overview see references [16–19]). However, for a long time, the preparation of aligned V_2O_5 nanoporous or tubular layers using self-organizing anodization was a considerable challenge [20,21]. Only very recently, by using optimized anodization conditions, highly ordered and self-assembled V_2O_5 nanoporous and nanotubular layers with controllable pore size and layer thickness could be fabricated [22]. In the present work, we investigate the lithium-ion intercalation in such ordered V_2O_5 nanoporous layers and show that these structures are promising candidates for application in electrochromic devices.

2. Experimental

For anodization, vanadium foils (0.25 mm, 99.8%, Advent Materials) were used as substrates, which were ground and polished to a mirror

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finish before use, followed by rinsing with deionized (DI) water and ethanol, respectively. Electrochemical anodization was carried out at room temperature in a solution of ethylene glycol (EG, Riedel-de Haën, 99.5%) with 7 mM $(NH_4)_2TiF_6$ (Sigma-Aldrich, 99.99%) in 0.1 M HF (40 vol.%, Merck). The anodization was conducted at 120 V for 100 min to grow 20 μm thick porous V_2O_5 layers using a conventional two-electrode configuration with platinum gauze as a counter electrode. After anodization, the samples were rinsed with ethanol followed by thermal treatments using a Rapid Thermal Annealer (Jipelec JetFirst 100) at 200 °C for 3 h in air with a heating/cooling rate of 5 °C min^{-1}. A field-emission scanning electron microscope (Hitachi FE-SEM S4800) was used to investigate the morphologies and compositions of the samples. The crystal structure of the samples was evaluated from X-ray diffraction (XRD) spectra acquired with an X'pert Phillips PMD with a Panalytical X'celerator detector using graphite-monochromatized CuKα radiation. The composition and the chemical state of the samples were characterized by using X-ray photoelectron spectroscopy (XPS, PHI 5600, Perkin Elmer).

Lithium intercalation and electrochromic measurements were carried out in a classical three electrode set-up: For this, the self-assembled V_2O_5 porous layers on the metal substrates were used as working electrode; a platinum plate served as a counter electrode, and a Ag/AgCl (3 M KCl) electrode in a Haber–Luggin capillary served as a reference electrode. Electrochemical characterization including cyclic voltammograms (CV) and galvanostatic charge/discharge (chronopotentiometry) was performed on an Autolab PGSTAT 30 Potentiostat/Galvanostat (Ecochemie, The Netherlands). Reflectance measurements were carried out with a fiber optic illuminator (tungsten halogen lamp, LS-1, Ocean Optics, El Dorado Hills, CA, USA).

3. Results and discussion

Fig. 1 shows the self-assembled and highly ordered V_2O_5 nanoporous layers used in this work. The structures have a length of 20 μm and pore diameter of 12 nm. These as-formed layers are amorphous but can be crystallized by an adequate heat treatment. The XRD pattern of the V_2O_5 layer in Fig. 2a shows that the anodic layer crystallizes as orthorhombic V_2O_5 phase after a heat treatment at 200 °C for 3 h. XPS confirms after annealing a composition of V_2O_5 with the peak position of $V2p_{1/2}$ and $V2p_{3/2}$ located at 524.47 and 517.04 eV respectively, which is typical for V^{5+} in V_2O_5 [23].

To characterize lithium-ion intercalation and electrochromic properties we used reflectance measurements that were performed during voltage pulsing between a lithium extraction potential (2 V vs. Ag/AgCl) and different lithium intercalation potentials (from 0.7 to −0.7 V vs. Ag/AgCl) as shown in Fig. 3a. An apparent electrochromic contrast induced by the lithium-ion intercalation/extraction process can be found over a wide voltage window. With increasing the applied voltage, much higher electrochromic contrasts are induced due to the enhanced lithium-ion kinetics during the intercalation/extraction process. The CV curve (Fig. 3b) shows a symmetrical shape with two pairs of redox peaks (reduction peaks at −0.22 and −0.56 V, oxidation peaks at 0.92 and 1.26 V) which can be assigned to reversible lithium intercalation/extraction. Combined with the in situ visually observed color contrast changes during reflectance measurement as shown in Fig. 3f, the cathodic peak at −0.22 V is assigned to the visible color contrast change from yellow to green, while the cathodic peak at −0.56 V is assigned to a further color contrast change from green to dark. The observed two-step lithium-ion intercalation and color contrast change are due to the reversible phase transitions between different lithium intercalated V_2O_5 phases, i.e. $Li_xV_2O_5$, which are induced by the particular structure characteristics of V_2O_5. The first

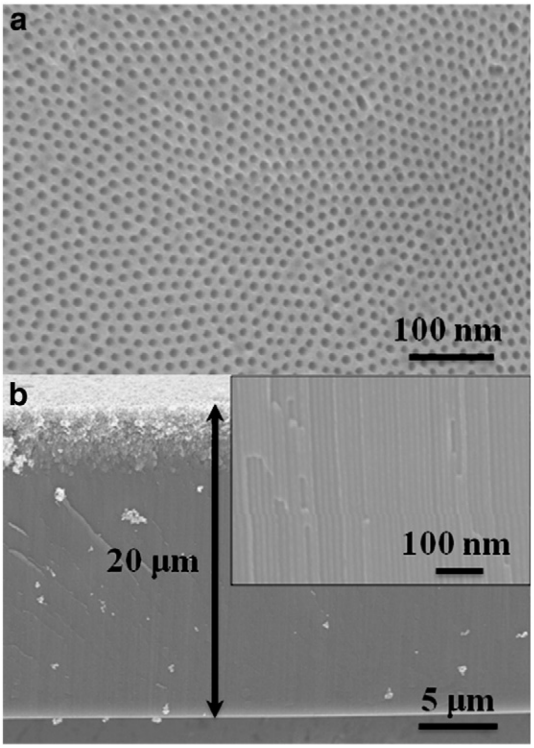

Fig. 1. SEM images of V_2O_5 porous layers: (a) surface image; (b) cross-section image with high magnification in the inset.

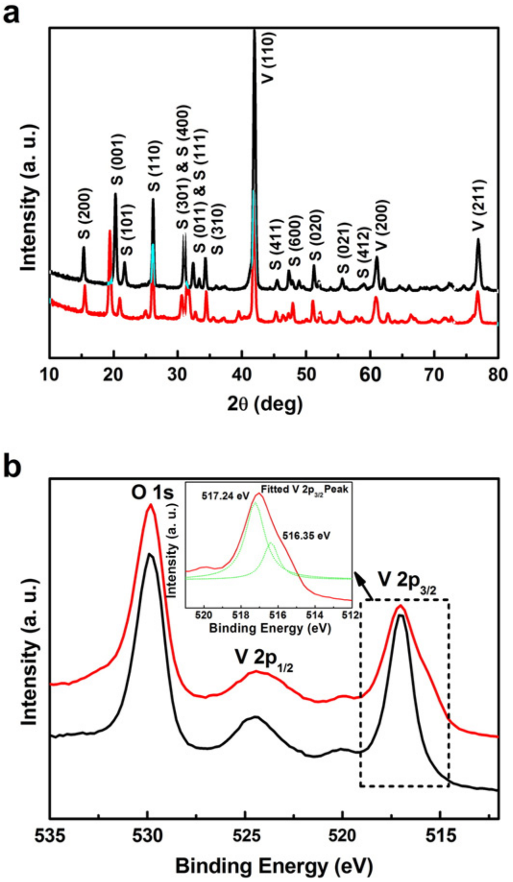

Fig. 2. Structure characterization and investigation of vanadium valence states in the V_2O_5 porous layers before (black line) and after (red line) lithium-ion intercalation: (a) XRD patterns, S: orthorhombic phase of V_2O_5, V: metal vanadium substrate; (b) XPS spectra of V2p and O1s peaks. The inset of (b) shows the fitted $V2p_{3/2}$ peaks represented as green dot lines.