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Superior Sodium Storage of Vanadium Pentoxide Cathode with Controllable Interlamellar Spacing

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ABSTRACT

The orthorhombic and hydrated vanadium pentoxide (V_2O_5) films are fabricated via a facile electrodeposition method followed with a controllable annealing process. Served as sodium ion batteries (SIBs) cathode, the hydrated V_2O_5 film exhibits enhanced sodium storage performance over the orthorhombic V_2O_5 film, originating from faster diffusion reaction kinetics, better electrochemical reaction reversibility, and smaller electrochemical reaction resistance. To be specific, the hydrated V_2O_5 film maintains a high capacity of 166 mAh g^{-1} after 100 charge-discharge cycles at 200 mA g^{-1} between -1.5 V and 0.5 V (vs. an Ag/Ag$^+$ reference electrode). Moreover, it reveals outstanding rate capability with reversible discharge capacities of 133 mAh g^{-1} at 1000 mA g^{-1} and 121 mAh g^{-1} at 2000 mA g^{-1}, which are higher than those of orthorhombic V_2O_5 film (41 mAh g^{-1} at 1000 mA g^{-1} and 34 mAh g^{-1} at 2000 mA g^{-1}). The significant enhancement in sodium-ion storage capacity and high-rate performance of the hydrated V_2O_5 film is mainly due to its lager interlamellar spacing, which can promote the insertion/extraction of Na$^+$, and the presence of V^{4+} accompanied with oxygen vacancies, which might improve the electronic conductivity and alleviate the stress caused by volume expansion.

1. Introduction

Sodium-ion batteries (SIBs) have attracted increasing attention as a potential alternative to lithium-ion batteries (LIBs) for large-scale electric energy storage applications, due to the wide availability, low cost and suitable redox potential of metallic sodium [1,2]. Over the past few years, various SIBs cathode materials, mostly mimicked from LIBs, have been developed in the fields of SIBs [3–6], for example, manganese oxides with a special structure comprised of wide tunnels [7–9], AMO$_2$-type layered oxides (M = Co, Mn, Ni and combinations) [10–12], NASICON-type materials [13,14], sodium compounds with olivine structure [15–17], and layered sodium iron fluorophosphates [18], etc. Nevertheless, some obvious challenges still exist in these SIBs cathode materials, such as the low-lying theoretical capacity, poor capacity retention, and unsatisfied rate capability. Thus, it is

generally accepted that engineering novel construction is essential for SIBs cathode materials [19–21].

Vanadium pentoxide (V_2O_5) with typical lamellar structure has been studied as cathode material for LIBs over decades due to its high theoretical capacities, relatively safer, large abundant, and ease of synthesis [22–26]. When "borrowed" as cathode for SIBs, generally, layered V_2O_5 can reversibly accommodate sodium ions to form Na$_2$V$_2$O$_5$ and release a considerable specific capacity of 236 mAh g^{-1} [27]. Furthermore, some studies have proved that hydrated V_2O_5 with larger interlayer spacing is more suitable for the reversible insertion/extraction of sodium ion, and delivers higher specific capacity than the orthorhombic one [27,28]. For example, the orthorhombic V_2O_5 nanoarrays released a specific capacity of 120 mAh g^{-1} at 25 mA g^{-1} [29]. While, the V_2O_5 nanobelt with large (001) distance layers ($\sim$11.5 Å) can exhibit a high discharge capacity of 231.4 mAh g^{-1} at 80 mA g^{-1} [27]. And the nanocrystalline V_2O_5 with a large interlayer spacing (11.6 Å) showed a reversible capacity of 220 mAh g^{-1} under a current density of 10 mA g^{-1} [30]. Specifically, 2D $V_2O_5 \cdot n$H$_2$O flake, which possessed a large interlayer, exhibited a striking initial discharge capacity of 338 mAh g^{-1} under 50 mA g^{-1} [28]. In despite of these

efforts achieving high specific capacities, unfortunately, the capacity retention, cyclic stability, and rate capability can hardly satisfy the SIBs applications. Furthermore, the electrochemical storage performance and interfacial reactions are directly bound up with the chemical environment of sodium ions, viz., the crystalline state, surface/bulk defects, and/or activity pair of bulk material. For example, the previous studies have proven that the existence of V^{4+} and oxygen vacancies in V_2O_5 can improve the conductivity of V_2O_5 [31]. Therefore, it is of vital importance to systematically investigate the impact of different crystal forms and chemical compositions of V_2O_5 on the sodium storage behaviors. when considering the fact that the hydrated V_2O_5 displays an interlayer spacing ranged from 8.8 to 13.8 Å [32], while the interlayer spacing of orthorhombic V_2O_5 is around 4.5 Å. Unfortunately, few study has focused on this important research topic. More importantly, the underlying reason of such influence in sodium storage performance has not been clarified in detail.

In this paper, to investigate the influence of crystal forms of V_2O_5 cathode on the sodium storage, orthorhombic and hydrated V_2O_5 films have been designed by cathodic electrodeposition method followed by a controllable annealing process. The binder-free V_2O_5 films can avoid the influence (partly decreasing the energy density and raising the resistance) of polymer binder, and enhance the electrons transport between electrode and current collector during charge/discharge processes. It is revealed that, the larger spacing, the more V^{4+}/defect and more rough surface of hydrated V_2O_5 film contribute a great deal to its better performance than the orthorhombic V_2O_5 film.

2. Experimental

2.1. Material Preparation

Vanadium pentoxide gel was prepared as following: 0.25 g of V_2O_5 powders (99.8%) were added into 3.85 mL of de-ionized water and 1.15 mL of H_2O_2 (30 wt%) to form a solution with V_2O_5 concentration (C_V) of 0.3 M (n (H_2O_2): n (V) of 8:1). The obtained solution was stirred for 15 min at room temperature in water bath. After sonicated for 10 min, this resulted solution was diluted to C_V = 0.056 M with 50 mL of de-ionized water and then continuously sonicated for 60 min until the final solution revealed brownish-green V_2O_5 gel. After rest for another 12 h, the gel was further diluted to C_V = 0.008 M used as electrolyte.

Via an electrodeposition, the V_2O_5 films were deposited on stainless steel sheet (with a thickness of 50 um) used as the working electrode, and a platinum electrode was used as the counter electrode. The electrodepostion was performed at a constant voltage of 2.5 V for 20 min. Subsequently, the as-grown samples were dried at ambient condition for 48 h, and finally annealed at 400 °C and 100 °C for 1 h in air to obtain the orthorhombic and hydrated V_2O_5 films (marked as V_2O_5-i and V_2O_5-ii, respectively).

2.2. Characterization

The surface morphology of the films was observed by a Hitachi-SU8010 type field-emission scanning electron microscopy (FE-SEM). Transmission electron microscopy (TEM, JEOLJEM-3000F) and atomic force electron microscope (AFM, Bruker Multimode 8) were used to verify the nanostructure and topography of the samples. X-ray power diffraction (XRD) patterns were collected by a X'Pert³ Powder X-ray diffractometer using Cu K$_\alpha$ radiation (λ = 1.5406 Å) in a 2θ ranged of 5° ~ 70°. The water content of the samples was measured via thermogravimetric analysis (TGA, SDTQ600) at air ranging from 25 °C to 600 °C with a ramping rate of 10 °C min^{-1}. Fourier-transform infrared (FTIR) spectra were obtained on a Nicolet iS10 Spectrometer by using KBr as the dispersant. Raman analysis was carried out with a confocal Micro Raman Spectrometer with LabRAM HR800 system (HORIBA) between 200 cm^{-1} and 1800 cm^{-1}. To identify the valence state of vanadiumin in the obtained samples, X-ray photoelectron spectroscopy (XPS, VGESCA- LAB MKII) was carried out with Al K$_\alpha$ radiation as the X-ray source for excitation.

2.3. Electrochemical Performance

Electrochemical measurements were performed using a standard three-electrode device [33]. It is worth noted that the
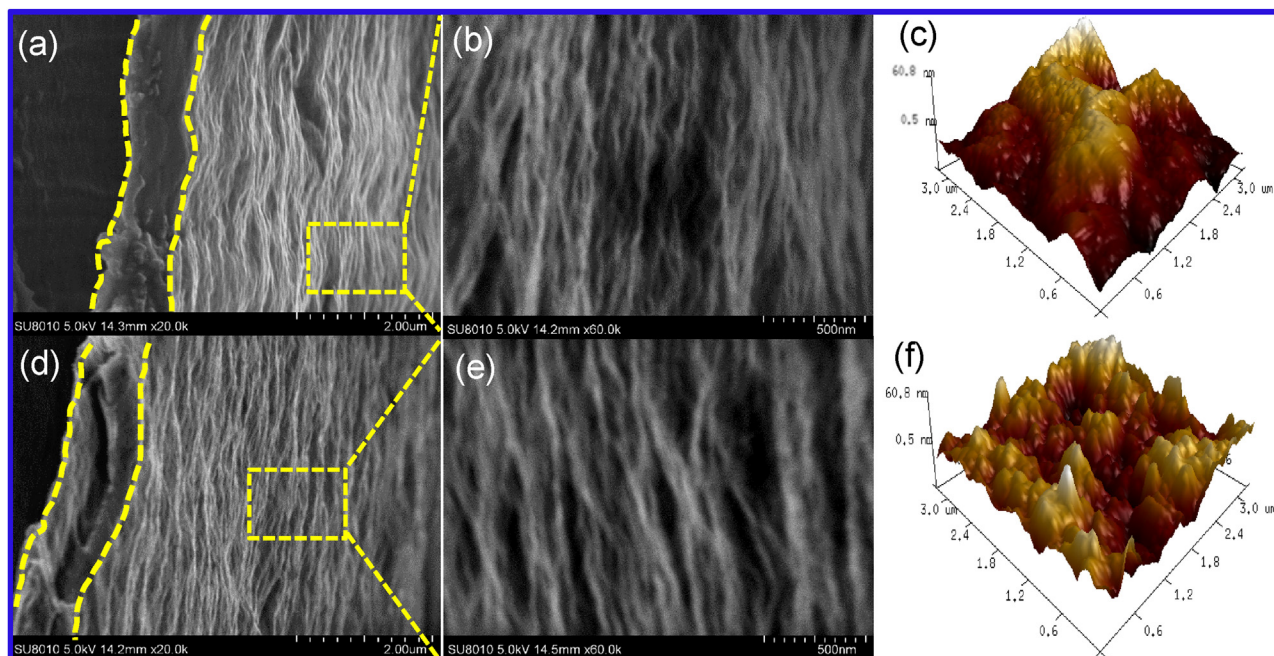

Fig. 1. FESEM and 3D AFM images of the (a, b, c) V_2O_5-i and (d, e, f) V_2O_5-ii films.