Microwave-assisted hydrothermal synthesis of vanadium oxides for Li-ion supercapacitors: The influences of Li-ion doping and crystallinity on the capacitive performances

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HIGHLIGHTS

► $VO_x \cdot nH_2O$ with excellent capacitive behavior can be synthesized rapidly by an MAHS method.
► The crystal size and spacing distance of two adjacent layers are affected by the MAHS temperature and adding LiCl.
► The above two factors show great influences on the Li-ion intercalation capacity and rate.
► Doping Li ions into $VO_x \cdot nH_2O$ enlarges the spacing distance of adjacent layers and crystal size of $VO_x \cdot nH_2O$.
► Doping Li ions into $VO_x \cdot nH_2O$ enhances its specific capacitance and prolongs its cycle life.

ABSTRACT

Vanadium oxides ($VO_x \cdot nH_2O$) with long cycle-life for Li-ion supercapacitors have been successfully synthesized by means of the microwave-assisted hydrothermal synthesis (MAHS) method, a faster and more energy-saving method than the conventional hydrothermal synthesis. Such oxides show capacitor-like, lithium-ion intercalation/de-intercalation responses in aqueous media. Although electrochemical activation is required to reveal the capacitor-like behavior of $VO_x \cdot nH_2O$, doping Li ions by adding LiCl into the precursor solution not only effectively shortens the activation time but also enhances the specific capacitance of $VO_x \cdot nH_2O$. This kind of materials shows the promising application potential in the aqueous-based Li-ion supercapacitors. X-ray diffraction (XRD), Raman spectroscopic, and X-ray photo-electron spectroscopic (XPS) analyses are employed to identify the fine tune-up in microstructures of various $VO_x \cdot nH_2O$.

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1. Introduction

Vanadium oxides in multiple oxidation states/various forms with layered structures have been found to show redox intercalation ability for various cations [1–3]. Hence, many vanadium oxides are considered as important electrode materials in the electrochemical energy storage applications, such as lithium-ion batteries (LIBs) [4] and electrochemical capacitors (ECs) [5,6]. However, the intrinsic requirements for rechargeable batteries and ECs are different [7–10]. For example, ECs, also called supercapacitors or ultracapacitors, generally show the high power and long cycle-life

characteristics with an acceptable energy density [7,9,11]. How to improve the electron conductivity and the ion diffusion/penetration rate and to inhibit the degradation of electrode materials are the major considerations in developing an ideal electrode material for such applications [12,13]. Moreover, the redox reactions of electrochemically active materials often involve the superficial region in order to ensure the excellent electrochemical reversibility for ECs [8], leading to a lower energy density in comparison with batteries. While rechargeable batteries usually show much higher energy densities by utilizing the bulk phase of electroactive materials (e.g., the Li-ion intercalation capability of vanadium oxides). Consequently, the low ion-diffusion rate within the bulk phase of active materials generally limits the power performance of devices [13,14] although power-oriented LIBs [13–16] have been developed for the usage in hybrid and pure electric vehicles (HEV and EV) recently. On the other hand, all the above concepts and viewpoints

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agree that tuning/designing a desirable microstructure of electrochemically active materials for meeting the intrinsic requirements of individual electrochemical energy storage system is the key to enhance their respective performances.

In order to meet the requirements for the high-power ability, acceptable energy density, and very long cycle-life with an improved energy storage/delivery efficiency of ECs [7,9,11], developing an effective method for tuning the microstructure of vanadium oxides is very important. Such synthesis methods are not only important to the energy storage systems but also very interesting to other applications, e.g., catalysts, smart windows [17–19], and semiconductors [20]. Several wet chemical methods have been proposed to synthesize vanadium oxides, including sol–gel [17,21], hydrothermal [19,22–30], reverse micelle [31,32], and electrochemical deposition [5,6,33,34], etc. While it is still lack of full understanding on any method for effectively controlling/tuning the microstructures of crystalline vanadium oxides although hydrothermal synthesis with a long reaction time (sometimes even longer than 1 week) seems to be widely studied [19,22–29,35]. From the practical application viewpoint, the cycle-life issue is still a big challenge for vanadium oxides in ECs due to the structure collapse or phase transition during intercalation/de-intercalation of Li ions [14,36,37], although vanadium oxides with the well-known layered structure showed a promising applicability to LIBs [25,38–40] and ECs [5,6,23,35,41,42]. Hence, developing new/improving existed methods for manufacturing vanadium oxides with properties meeting the above requirements is very important.

In general, the microwave-assisted hydrothermal synthesis (MAHS) method is a homogeneous heating process and creates the possibilities in obtaining new and modified forms of materials [43,44] through the direct energy transfer from the water molecules to the precursors in comparing with conventional hydrothermal synthesis. Such a unique "molecular heating" method has been shown to provide several merits in materials preparation, e.g., rapid volumetric heating, high reaction rate, short reaction time, high reaction selectivity, and energy saving [43,44]. Recently, microwave-assisted hydrothermal/solvothermal methods have been tried to fabricate metal oxides [45–47] although they have been widely applied to organic synthesis. Consequently, it is still lack of detailed discussion on the fabrication of metal oxides through such interesting methods. In this work, vanadium oxides were proposed to be synthesized by means of the MAHS route for the EC application.

In our previous work [5,6,33,34], hydrous vanadium oxides deposited at potentials equal to/positive than 0.4 V showed promising capacitive performances in aqueous media containing concentrated Li ions. Such vanadium oxides have been found to possess highly reversible Li-ion intercalation/de-intercalation behavior in 12 M LiCl between −0.2 and 0.8 V. Since the tunnels of Li-ion diffusion should be affected by the crystallinity of vanadium oxides [14,48], this work employs the MAHS process to synthesize vanadium oxide nanocrystals in order to shorten the Li-ion diffusion length. Moreover, this work demonstrates the idea that doping of Li ions can tune the Li-ion diffusion tunnels within vanadium oxide nanocrystals in order to enhance the Li-ion intercalation/de-intercalation rate for the application of ECs.

2. Experimental

All vanadium oxides (denoted as $VO_x \cdot nH_2O$) were synthesized by means of the microwave-assisted hydrothermal synthesis (MAHS) method. An aqueous solution containing 25 mM $VOSO_4 \cdot nH_2O$ was utilized as the main precursor solution, and hydrogen peroxide was added to adjust the V^{4+}/V^{5+} ratio equal to one. LiCl was used as the lithium-ion source in the precursor

solution for doping Li ions into the oxides. The pH value of the precursor solutions was adjusted to 2.7 with 1 M H_2SO_4 and 2 M NaOH. Synthesis of $VO_x \cdot nH_2O$ was performed through a microwave reactor, Discover SP™ (CEM, USA), with temperatures equal to 140, 180 or 200 °C for 10 min. The products were washed with deionized water several times.

The chemical environments of $VO_x \cdot nH_2O$ were analyzed through XPS by means of an ESCA210 spectrometer (Kratos Axis Ultra DLD). The XRD patterns were obtained from an X-ray powder diffractometer (CuKα, Ultima IV, Rigaku) at an angle speed of $4°$ (2θ) min^{-1}. Raman spectra were measured using a 3D nanometer scale Raman PL microspectrometer (Tokyo Instruments, INC) with 632.8 nm radiation of a HeNe laser, which was focused in a circle area less than 1 μm in diameter. The doping mount of Li ions into $VO_x \cdot nH_2O$ was determined by means of an inductively coupled plasma–mass spectrometer (ICP–MS, SCIEX ELAN 5000), Auger electron spectrometer (AES, ULVAC-PHI AES 650), and Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS, TOF.SIMS IV). The electrochemical properties of $VO_x \cdot nH_2O$ were examined by an electrochemical analyzer system, CHI 633c (CH Instruments, USA) in a three-compartment cell. An Ag/AgCl electrode was utilized as the reference and a piece of platinum gauze was employed as the counter electrode. A Luggin capillary was used to minimize errors due to iR drop in the electrolytes.

All solutions used in this work were prepared with deionized water produced by a reagent water system (Milli-Q SP, Japan) at 18 MΩ cm. All reagents, not specified, without further purification are Merck, GR. The electrolyte, 12 M LiCl, used for electrochemical characterization was maintained at 25 °C and degassed with purified N_2 for 25 min before measurements. This nitrogen flow was passed over the solutions during the measurements. The solution temperature was maintained at the specified temperature by a water thermostat (Haake DC3 and K20).

3. Results and discussion

3.1. Effects of the MAHS temperature on the electrochemical behavior of $VO_x \cdot nH_2O$

The electrochemical properties of various $VO_x \cdot nH_2O$ samples prepared at different MAHS temperatures were examined in 12 M LiCl between −0.2 and 0.8 V. Curves 1–3 in Fig. 1 show the typical electrochemical behavior measured at a scan rate of 25 mV s^{-1} for
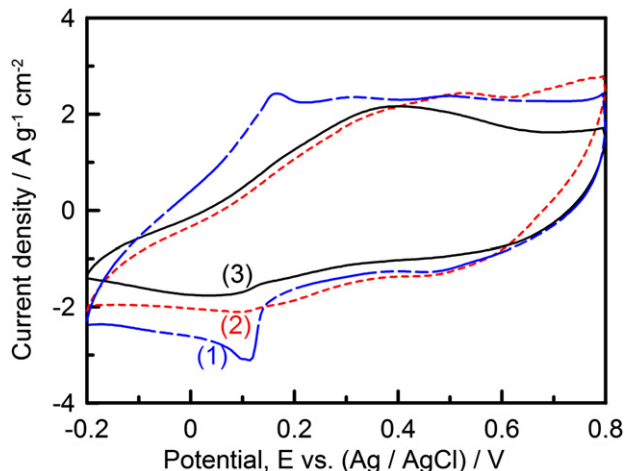

Fig. 1. Cyclic voltammograms (the 2nd cycle) of $VO_x \cdot nH_2O$ synthesized by means of the MAHS method at (1) 140, (2) 180, and (3) 200 °C.