Lithiation Kinetics in High-Performance Porous Vanadium Nitride Nanosheet Anode

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ABSTRACT

Vanadium nitride (VN) is promising in lithium ion battery (LIB) anode due to its high energy density, chemical stability, and corrosion resistivity. Herein, porous VN nanosheets are synthesized hydrothermally followed by an ammonia treatment. The porous nanosheets offer a large interfacial area between the electrode and electrolyte as well as short Li^+ diffusion path and consequently, the VN nanosheets electrode has high capacity and rate capability as an anode in LIB. The VN anode delivers a high reversible capacity of 455 mAh g^{-1} at a current density of 100 mA g^{-1} and it remains at 341 mAh g^{-1} when the current density is increased to 1 A g^{-1}. The charge transfer and Li^+ diffusion kinetics during the lithiation process is studied systematically. A highly stable SEI film is formed during the initial discharging-charging cycles to achieve a long cycle life and sustained capacity at a high level for 250 discharging-charging cycles without deterioration. This work demonstrates the preparation of high-performance LIB anode materials by a simple method and elucidates the lithiation kinetics.

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1. Introduction

Driven by large-scale usage of electric vehicles, portable consumer electronics, and hybrid vehicles, the demand for high-energy and long-cycle-life lithium ion batteries (LIBs) is growing. However, the traditional graphite anode used commercially in LIBs is limited by the small theoretical capacity of 372 mAh g^{-1} and poor cyclability [1]. Hence, a variety of new anode materials are being investigated for new-generation LIBs in order to achieve a larger energy density, higher rate capability, and improved cycle stability [2–4]. Among the various anode materials, Sn and Si which can react with lithium during discharging-charging offer a high specific capacity at a moderate potential vs. Li$^+$/Li. However, the lithiation-delithiation process produces large volume change causing rapid capacity fading during cycling [5,6]. Transition metal oxides (TMOs) with better capacity and more stable cycling such as

Fe$_2$O$_3$, MnO$_2$, CoO, and NiO have been proposed for future LIB anodes and supercapacitor electrodes [7–12], but the poor rate performance remains the main obstacle stifling wider application because the semiconducting nature of TMOs impedes the kinetics of electrons [13,14]. Inspired by the high capacity and stable cyclability of TMOs, transition metal nitrides (TMN) such as TiN, VN, and Mo$_2$N derived from the corresponding oxides should not only inherit the merits of oxides, but also improve the properties due to the improved electrical conductivity, large capacity, as well as chemical stability [15–18]. Moreover, the working potentials of nitrides are lower than those of the corresponding oxides because of the lower electronegativity of nitrogen compared to oxygen [19–21].

Among the various metal nitrides, vanadium nitride (VN) is very attractive on account of the high capacity, superior dynamic and structural stability, corrosion resistance, environmental friendliness, and low cost [22–24]. Fu et al. [22] have produced a VN thin film with a high initial discharging capacity of 1500 mAh g^{-1} and stable reversible capacity of ∼800 mAh g^{-1} and Cui et al. [24] have shown that the hybrid of VN and nitrogen-

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doped graphene has excellent capacity and rate capability. The reversible conversion reaction between VN and metallic lithium can be expressed as follows [22,24–26]:

$$xVN + 3xLi^+ + 3xe^- \leftrightarrow xV + xLi_3N.$$

During lithiation, the product is metallic vanadium nanoparticles embedded in the Li_3N matrix. This means that the structural and chemical changes can be monitored and identified during cycling. The lithiation products including the electron-conductive metallic vanadium, ion-conducting Li_3N, and unique metallic vanadium embedded Li_3N structure affect the kinetics of the VN anode such as charge transfer and Li^+ diffusion [27–29]. In order to develop better anode materials, it is imperative that the conversion kinetics is better understood but the kinetics pertaining to charge transfer and Li^+ diffusion during lithiation in the VN anode is still not well understood.

In our previous experiments, V_2O_5 nanosheets were synthesized by a hydrothermal reaction and mesoporous VN nanowires or nanobelts were obtained by a thermal treatment in NH_3 [16,30,31]. In this paper, a hydrothermal method followed by ammonia treatment is described to produce large-area VN nanosheets with a mesoporous structure, as schematically illustrated in Fig. 1a. The porous nanosheets have a large capacity, high rate capability, and long cycling life due to the large specific surface area, increased interfacial area between the active materials and electrolyte, short path length for fast Li^+ storage and electron transport, as well as accommodation of the lithiation/delithiation stress. A reversible capacity of 455 mAh g^{-1} is attained at a current density of 100 mA g^{-1} and even at a large current density of 1 A g^{-1}, the reversible capacity is 341 mAh g^{-1} for 250 discharging-charging cycles. By means of electrochemical impedance spectroscopy, the charge transfer and Li^+ diffusion kinetics during lithiation is investigated.

2. Experimental details

2.1. Sample preparation

The $V_2O_5 \cdot nH_2O$ nanosheets were prepared according to the procedures reported previously [30]. In brief, 2 mmol ammonium metavanadate (NH_4VO_3, Sigma-Aldrich) powders were added to 39 mL of deionized water (DW) under stirring and then 1 mL of concentrated HCl (Sigma-Aldrich, $\geq$ 37%) was added dropwise before putting in a sealed 50 mL Teflon-lined autoclave. It was maintained at 200 °C for 1 hour and cooled to room temperature in the furnace afterwards. The product was washed in DW for several times and then freeze-dried (SCIENTZ-10N, Ningbo Scientz Biotechnology Co., Ltd., China) for more than 48 hours followed by an NH_3 treatment at 550 °C for 3 hours.

2.2. Characterization

The morphology and microstructure of the samples were examined by field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano), X-ray diffraction (XRD, Bruker AXS D2 Phaser) with Cu Kα irradiation between 5° and 90° (2θ), and transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with energy-dispersive X-ray spectroscopy (EDS). The specific surface area and pore-size distribution were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using a surface area analyzer (Micromeritics ASAP 2020) at 77 K.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using 2025-type stainless coin cells. To prepare the working electrodes, a
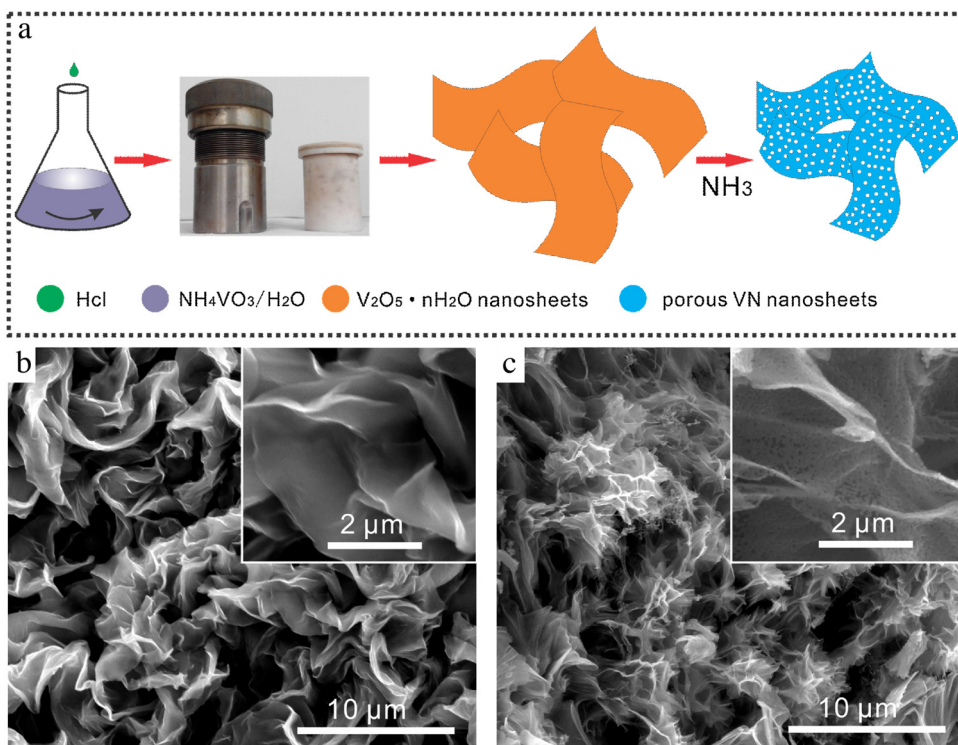
Fig. 1. (a) Schematic illustration of the fabrication procedures of porous VN nanosheets; SEM images: (b) $V_2O_5 \cdot nH_2O$ nanosheets and (c) porous VN nanosheets with the insets presenting the corresponding high-magnification SEM images.