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 Fe₂O₃, MnO₂, 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 Mo₂N 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-
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]:

\[ \text{xVN} + 3\text{Li}^+ + 3\text{e}^- \rightarrow \text{xV} + \text{xLi}_2\text{N}. \]

During lithiation, the product is metallic vanadium nanoparticles embedded in the Li$_3$N 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$_3$N, and unique metallic vanadium embedded Li$_3$N 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$_2$O$_5$ 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$_2$O$_5$·nH$_2$O nanosheets were prepared according to the procedures reported previously [30]. In brief, 2 mmol ammonium metavanadate (NH$_4$VO$_3$, Sigma-Aldrich) powders were added to 39 mL of deionized water (DW) under stirring and then 1 mL of concentrated HCl (Sigma-Aldrich, ≥ 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° [28], 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$_2$O$_5$·nH$_2$O nanosheets and (c) porous VN nanosheets with the insets presenting the corresponding high-magnification SEM images.](image-url)
were electrochemical potential measurements performed on an Ar-filled glove box (Vigor SG1200/750). Cyclic voltammetry (CV) was performed on the CHI 6144D electrochemical workstation (Shanghai CH Instrument Company, China) at a scanning rate of 0.2 mV s⁻¹ in the potential range between 0.005 and 3.0 V (versus Li⁺/Li). Galvanostatic discharging-charging (GCD) of the assembled cells was performed on a Land CT2001A system (Wuhan LAND electronics Co., Ltd., China) in the voltage range of 0–3 V (vs. Li⁺/Li). Electrochemical impedance spectroscopy (EIS) was carried out on the Zennium electrochemical workstation (Zahner, Germany) after several CV cycles for stabilization with an AC perturbation of 5 mV at different voltages during discharging process. Chronopotentiometry was employed to control the VN-based batteries in different discharging stages. After discharging to a certain potential, the batteries were equilibrated at the corresponding potential for several hours. All the electrochemical measurements were performed at room temperature.

### 3. Results and Discussion

Fig. 1a illustrates the fabrication procedures of the porous VN nanosheets. Firstly, NH₄VO₃ is dissolved in HCl under stirring for about 30 min to get a yellow solution, followed by a hydrothermal treatment to synthesize the V₂O₅·nH₂O nanosheet gel which is then freeze-dried to maintain the large surface area. Finally, the V₂O₅·nH₂O nanosheets are annealed under NH₃ [15,16,32]. The morphology of the hydrothermal product (V₂O₅·nH₂O) and final product (VN) is examined by FE-SEM, as shown in Fig. 1b and c. The hydrothermal product is composed of large-area 2D nanosheets with a smooth surface (Fig. 1b) and after annealing, the nanosheet structure is preserved but the surface becomes porous (Fig. 1c).

The crystal structure and phases are determined by XRD as shown in Fig. 2a. The diffraction peaks of the hydrothermal product can be indexed to the (001), (003), and (006) lattice planes of layered V₂O₅·nH₂O [16,33,34]. After the NH₃ treatment, the diffraction patterns are quite different and the five peaks at 37.7°, 43.8°, 63.7°, 76.4°, and 80.5° correspond to (111), (200), (220), (311), and (222) diffractions of cubic VN (JCPDS card No. 73-0528) without other impurities, revealing that V₂O₅·nH₂O has been converted into VN completely after the NH₃ treatment. The TEM images in Fig. 2b and c confirm the large-area porous nanosheet structure of the product. The diffraction rings in the selected-area electron diffraction (SAED) patterns (inset in Fig. 2b) are consistent with the cubic VN phase. Fig. 2d indicates that the final product consists of VN. The O signal may be attributed to surface oxidation of VN [35,36] and C and Cu stem from the TEM grid, since no C or Cu containing precursors are used in this work. The HR-TEM image in Fig. 2e shows lattice fringes with a spacing of 0.24 nm corresponding to the (111) plane of cubic VN. The N₂ adsorption-desorption isotherms are shown in Fig. S1. The as-prepared porous VN nanosheets have a BET specific surface area of 30 m² g⁻¹ and BJH pore-size distribution of 3.5 nm. The porous structure shortens the

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**Fig. 2.** (a) XRD patterns: (1) V₂O₅·nH₂O nanosheets and (2) Porous VN nanosheets; (b, c) TEM images and SAED (inset); (d) EDS; (e) HR-TEM image of the porous VN nanosheets.
Li$^+$ diffusion path and accommodates the lithiation-delithiation stress resulting in better Li$^+$ storage characteristics.

The porous VN nanosheets are assembled into 2025-type coin cells to investigate the electrochemical performance. CV is utilized to study the Li$^+$ storage mechanism in the VN nanosheets electrodes, as shown in Fig. 3a. In the first cycle, a strong peak at ~0.7 V is observed but disappears from the following cycles due to decomposition of the electrolyte and formation of a solid-electrolyte interphase (SEI) [24,37]. In the following CV cycles, a pair of broad peaks at around 1.0 V (versus Li$^+$/Li) is observed as a result of Li$^+$ extraction from and insertion into the VN nanosheets as commonly observed from transition-metal-nitride electrodes [38–40]. The steady redox peaks suggest stable lithiation and delithiation as well as a long cycle life. The reduction peaks correspond to reduction of VN to metallic V and the oxidation peaks are associated with oxidation of metallic V back to VN, as indicated by the ex-situ HR-TEM and SAED in Fig. S2 showing that the lithiation products are Li$_3$N and metallic vanadium, thereby illustrating highly reversible insertion and extraction of Li$^+$ in the VN nanosheets. The metallic vanadium increases the electronic conductivity and Li$_3$N which has high Li-ion conductivity accelerates Li$^+$ diffusion in the porous VN nanosheets [27–29]. The GDC profiles of the porous VN nanosheets at a current density of 100 mA g$^{-1}$ in the potential range between 0 and 3 V (vs. Li$^+$/Li) are displayed in Fig. 3b. The initial discharging capacity is as high as 658 mAh g$^{-1}$ and a reversible capacity of 455 mAh g$^{-1}$ is retained in the subsequent charging process, revealing a coulombic efficiency of ~70% in the first discharging-charging process. The irreversible capacity loss in the first cycle can be ascribed to the formation of the SEI film. During the initial 5 discharging-charging cycles, the VN nanosheets have stable reversible capacities with little loss.

The cycling performance shown in Fig. 3c and Fig. S3 confirms the stable cyclability of the VN nanosheets electrode. The reversible capacity at a current density of 100 mA g$^{-1}$ increases slightly to 520 mAh g$^{-1}$ after 100 discharging-charging cycles, compared to the first charging capacity of 455 mAh g$^{-1}$. The

![Graph showing cycling performance](image)

### Table 1
Comparison of the reversible capacities and rate capability of the porous VN nanosheets in this work and other transition metal nitrides and carbides reported in the literatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacity (mAh g$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.1 Ag$^{-1}$</td>
</tr>
<tr>
<td>Mesoporous VN nanosheets (this work)</td>
<td>455</td>
</tr>
<tr>
<td>VN/nitrogen-doped graphene [24]</td>
<td>220</td>
</tr>
<tr>
<td>VN nanocristallyne [21]</td>
<td>~400@C/5$^\circ$</td>
</tr>
<tr>
<td>Molybdenum oxynitride [26]</td>
<td>~600</td>
</tr>
<tr>
<td>TiO$_2$@TiO$_x$N$_y$/TiN-Graphene [54]</td>
<td>~170</td>
</tr>
<tr>
<td>Two-dimensional Ti$_2$C [55]</td>
<td>-</td>
</tr>
<tr>
<td>Two-dimensional Nb$_2$C [56]</td>
<td>-</td>
</tr>
<tr>
<td>Two-dimensional V$_2$C [56]</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ 1C = 400 mA g$^{-1}$. 
capacity increase during cycling may be attributed to the gradual activation and electrochemical milling processes [41,42] which are commonly observed from metal oxides, sulfides, and nitrides [24,43,44]. In some cases, decomposition of the SEI film may increase the capacity and decrease the coulombic efficiency. Here, the coulombic efficiency remains at near 100% after the initial 5 cycles (Fig. S3), indicating excellent stability of the SEI film and bonding well for a long cycle life. To evaluate the rate capability of the porous VN nanosheets electrode, the assembled coin cell is discharged-charged at larger current densities as shown in Fig. 3c. At a current density of 1 A g⁻¹, the initial reversible capacity is 341 mAh g⁻¹ and stable after 250 discharging- charging cycles. The capacity is steady at 75% when the current density is increased 10 times larger than that at 100 mA g⁻¹. Even though the current density is increased to 10 A g⁻¹, the capacity is more than 60 mAh g⁻¹ and stable for 250 discharging-charging cycles. The rate performance of the porous VN nanosheets electrode is presented in Fig. S4. Compared to the rate capability of other transition metal nitrides and carbides reported in the literatures, these porous VN nanosheets have better properties as shown in Table 1, for example, capacity and rate capability. It is because the porous 2D nanosheets structure increases the interfacial area between the active materials and electrolyte and shortens the Li⁺ diffusion path.

To determine the charge transfer and Li⁺ diffusion kinetics of the porous VN nanosheets during lithiation, EIS after several CV cycles for stabilization are acquired at different voltages during discharging process, as the lithiation products in different states have great effect on the resistance of the electrode [45,46]. As shown in Fig. 4a, all the Nyquist plots contain two semicircles at the high to medium frequencies and a straight line at low frequencies. They are fitted by equivalent circuits as shown in the inset of Fig. 4a in which \( R_r \) stands for the total resistance of the electrolyte, separator, and contacts. The semicircles at high frequencies represent the resistance of the SEI film (\( R_I \)) whereas that at high to medium frequencies is the charge transfer resistance (\( R_c \)). The straight lines are associated with the diffusion process through the porous VN nanosheets. Fig. 4b presents the relationship between the real impedance (\( Z' \)) and inverse of the square root of the angular frequency (\( \omega^{-1/2} \)) in the low frequency region at different voltages during lithiation. It can be fitted by a straight line and the slope is the Warburg impedance coefficient (\( \sigma_{\omega} \)). The square of \( \sigma_{\omega} \) is inversely proportional to the Li⁺ diffusion coefficient, that is, \( D_{Li+} \times 1/\sigma_{\omega}^2 \), meaning that the difference in \( D_{Li+} \) can be derived from \( \sigma_{\omega} \) indirectly [47–49]. The fitted values of the \( R_r \), \( R_c \), and \( \sigma_{\omega} \) are displayed in Fig. 4c. \( R_c \) and \( R_r \) are nearly constant at all voltages during lithiation as a result of the stable electrolyte and SEI film during the process and being consistent with the high coulombic efficiency during cycling because the porous 2D structure works as a buffer for the volume change during lithiation [50–52]. This is also the reason why the porous VN nanosheets have a long cycle life.

\( R_r \) and \( \sigma_{\omega} \) change during lithiation. \( R_r \) is steady as the voltage is decreased from 3 to 1.5 V, increases when the voltage is reduced to 1 V, and decreases slightly as the voltage approaches 0 V. \( R_c \) increases to a higher level at voltages below 1.5 V on account of the newly formed Li₃N with poor electron conductivity during discharging, since lithiation occurs at around 1 V as shown by CV and previous works [22,24–26,53]. \( R_c \) decreases slightly finally as a result of metallic vanadium being embedded in Li₃N increasing the electron conductivity and accelerating electron transport. \( \sigma_{\omega} \) is steady before 1.5 V but decreases sharply when the voltage is decreased from 1.5 to 0 V, implying that Li⁺ diffusion increases sharply when the voltage is below 1.5 V. It is because the lithiation product of Li₃N has high Li-ion conductivity to accelerate Li⁺ diffusion [27–29]. The plots of the imaginary parts versus frequencies of the VN nanosheets at different voltages in Fig. 4d disclose a similar conclusion that the time constant reaches 7.7 ms.

**Fig. 4.** (a) Nyquist plots of the VN nanosheets at different discharge voltages with the inset showing the equivalent circuit; (b) Linear relationship between the real impedance (\( Z' \)) and inverse of the square root of the angular frequency (\( \omega^{-1/2} \)) in the low frequency region of the VN nanosheets at different discharge voltages; (c) Calculated resistances and Warburg impedance coefficient (\( \sigma_{\omega} \)) of the VN nanosheets at different discharge voltages; (d) Plots of the imaginary parts versus frequencies at different discharge voltages.
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.08.023.

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Supporting Information

Lithiation Kinetics in High-Performance Porous Vanadium Nitride Nanosheet Anode

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**Figure S1.** Adsorption-desorption isotherms of VN and pristine V$_2$O$_5$·nH$_2$O. The inset shows the BJH pore size distribution of the VN nanosheets.
Figure S2. (a) HR-TEM image and (b) Corresponding SAED pattern of the VN nanosheets electrode after discharging to 0.01 V.
Figure S3. Cycling performance of the porous VN nanosheets in the potential range between 0 and 3 V (versus Li+/Li) at a current density of 100 mA g⁻¹.
Figure S4 Rate performance of the as-prepared porous VN nanosheets electrode.