



A nanocrystalline nitride as an insertion anode for Li-ion batteries



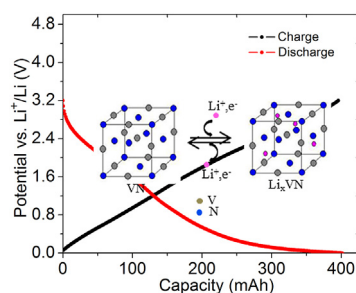
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HIGHLIGHTS

- Nanocrystalline vanadium nitride has been synthesized by a facile room temperature process.
- Carbon coated nano-VN delivers sustainable capacity of ~400 mAh/g and impressive rate performance.
- Ex-situ XRD and TEM studies reveal insertion based electrochemical reaction mechanism.
- Temperature dependent magnetic susceptibility studies confirm a change in the electronic structure of lithiated VN.

GRAPHICAL ABSTRACT



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ABSTRACT

Transition metal based binary oxides and nitrides are commonly known to undergo electrochemical conversion reaction with lithium in a lithium ion battery (LIB). Here, based on *ex-situ* X-ray diffraction and transmission electron microscopic studies, we propose an (de)insertion electrochemistry for a nanocrystalline vanadium nitride in a Li-ion cell. Upon carbon coating, the nano-VN delivers a stable capacity of 400 mAh g⁻¹, which is comparable to the (de)insertion of one lithium per VN unit. A change in the electronic structure of VN, resulting from the Li⁺ ion insertion into the structure, is confirmed by temperature dependent magnetic susceptibility measurement.

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1. Introduction

Since the commercialization of rechargeable Li-ion batteries graphite has remained the primary choice of anode material, functioning by intercalation/deintercalation of Li⁺ ions into/from

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its interlayer spacing. In the last two decades a wide variety of materials have been investigated in order to address the growing demand for high energy density batteries. Especially Sn, and Si, which undergoes alloying/dealloying reaction [1] with lithium during battery operation have received immense attention [2–12] as they offer very high specific capacity at moderate operating potential vs. Li⁺/Li. A large number of oxides of transition and non-transition metals have also been explored. [2,13–20] Among them, nanostructured oxides [20] offer high capacity and good capacity retention. These lithium alloying elements and metal oxides store lithium by electrochemical conversion reactions, which involve major reorganization of the structure, massive volume change and

consequential mechanical stress. This leads to poor coulombic efficiency in the first cycle, rapid capacity fading, and large hysteresis between charge and discharge voltages amongst others. [4,21,22] As a consequence, structurally unchangeable host materials with specific sites for Li ions to be inserted or intercalated, still remain a safer and attractive choice. In this regard, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been widely studied [23–27] and is employed in some new generation batteries (Super Charge Ion Batteries, Toshiba) due to its excellent stability, impressive rate capability, low cost, and environmental benignity. Despite the merits, low specific capacity (175 mAh g^{-1}) and overall low operating voltage (when combined with available cathode materials) limit its applicability.

Metal nitrides are interesting materials because of their high thermal and chemical stability. Some of them are resistant to moisture and other corrosive environments. [28,29] In addition, average working potentials of nitrides are lower than those of comparable oxides due to the lower electronegativity of nitrogen. Binary nitrides like silicon and tin nitrides, [30–33] Sn_3N_4 , [34] Zn_3N_2 , [35] Ge_3N_4 , [36] Cu_3N , [37] Co_3N , [38] Fe_3N , [38] CrN , [39] VN [40] have been shown to electrochemically react with lithium by conversion reaction resulting in the formation of metal nanoparticles embedded in Li_3N matrix. Among various binary nitrides, vanadium nitride is an interesting material because of its outstanding corrosion resistance, thermal and chemical stability [41]. Vanadium is highly abundant, cheap and an environmentally benign metal. Thin films of vanadium nitride made by tedious and expensive magnetron sputtering process have been reported to exhibit discharge capacity as high as 1500 mAh g^{-1} [40] by electrochemical conversion reactions with lithium. Synthesis of titanium vanadium nitride composites [42] through a high temperature mesoporous route using a reactive carbon nitride template and their electrochemical behaviour in lithium ion cells was illustrated by Cui et al. In both reports mentioned, vanadium nitride has been shown to operate by means of conversion electrochemical mechanism which can be written as $(3\text{Li}^+ + 3\text{e}^- + \text{VN} \rightarrow \text{Li}_3\text{N} + \text{V})$. Although theoretical specific capacity for the reaction is very high (1238 mAh g^{-1}), it accompany large volume expansion (~240%, calculated based on the density of VN, Li_3N and V) leading to particle–particle electronic contact loss. These severely affect the cycling efficiency and cycle life of the Li-ion cells. Very recently, Zhang et al. demonstrated highest first discharge capacity of 410 mAh g^{-1} for a VN-graphene composite [43]. They proposed a conversion reaction pathway, leaving the low first discharge capacity corresponding to an exchange of one lithium per VN unit unexplained.

In contrast to these studies, herein, we report an electrochemical (de)insertion behaviour of lithium for a room temperature synthesized nanocrystalline vanadium nitride. Upon electrochemical cycling in a Li-ion cell lithium ion (de)insert into the vacant tetrahedral sites of rock-salt vanadium nitride lattice ($\text{VN} + \text{Li}^+ + \text{e}^- \rightarrow \text{LiVN}$) as opposed to conversion electrochemical pathway. The insertion mechanism enables a sustainable capacity of $\sim 400 \text{ mAh g}^{-1}$ with high coulombic efficiency for an *in-situ* carbon coated nano-VN. A very good rate performance is also demonstrated by the carbon coated nano-VN, delivering 200 mAh g^{-1} at 1C rate (here, 1C rate corresponds 400 mA g^{-1} of current density). We propose a Li ion insertion mechanism for lithium cycling based on *ex-situ* XRD, and TEM investigation of the cycled VN electrode. Finally, modification in the electronic structure of VN, as expected to happen for V^{3+} to V^{2+} redox switch upon electrochemical discharge reaction has been probed by temperature dependent magnetic susceptibility measurement.

2. Experimental

2.1. Synthesis of nanocrystalline VN

Nanocrystalline vanadium nitride was synthesized by a room temperature reduction-nitridation technique, following the process described by Chen et al. [44] Vanadium tetrachloride (VCl_4 , 99+%) and sodium amide (NaNH_2 , 99+%) were used as obtained. All the manipulations were carried out in an argon filled glove box as both VCl_4 and NaNH_2 are sensitive to air and moisture. In a typical process, 0.01 mol of VCl_4 was added dropwise to NaNH_2 under magnetic stirring. The addition was carried out for a duration of about 30 min. The dripping of VCl_4 into NaNH_2 was accompanied by a highly exothermic reaction leading to formation of the black vanadium nitride powder. The product was taken out of the box and washed thoroughly with cold distilled water to remove excess sodium amide and sodium chloride byproducts. Finally, the product was washed with ethanol and dried at 60°C under vacuum. The overall chemical reaction can be written as follows:



2.2. Carbon coating of nanocrystalline VN

Carbon coating of the VN nanoparticles was achieved by lactose decomposition. VN was combined with 15 wt% of lactose in presence of water to ensure a homogeneous mixing. The mixture was dried under vacuum at $50\text{--}60^\circ\text{C}$. The resulting dry mixture was finally heated to 600°C for 4 h with a heating ramp of 100°C/h under nitrogen atmosphere. After cooling to room temperature black carbon coated VN was obtained.

2.3. Characterizations

Structural characterization was performed with powder X-ray diffraction, using Bruker D8 diffractometer equipped with position sensitive detector and Cu K_α radiation. Data were collected in the 2θ range of $10^\circ\text{--}90^\circ$ with a step size of 0.02° and an exposure time of 5 s. For the *ex-situ* XRD characterization, the electrode was removed from the half-cell after electrochemical discharge and put into a small cavity of a plastic sample holder. The cavity, tailor made to accommodate the current collector was then covered with a Mylar® film using silicone oil followed by a scotch-tape on top to minimize the exposure to air during analysis. All the manipulations were done in argon atmosphere. The samples were also characterized by transmission electron microscopy (Philips CM30ST). Powder sample was dispersed in THF (tetrahydrofuran) and a drop of the resultant ink was put onto a carbon coated copper grid for TEM analysis. For the TEM analysis of the electrochemically lithiated VN, discharged electrode was washed with anhydrous THF and the electrode material was scratched out of the current collector and dispersed in the anhydrous THF. The obtained ink was dropped onto a carbon coated copper grid. TEM sample preparation was done in an argon filled glove-box and the copper grid was transferred to the microscope in a sealed glass vial. Carbon and nitrogen contents of the samples were determined by micro-elemental analysis (LECO). Temperature dependence of the magnetic susceptibility was measured with superconducting quantum interference device (SQUID, MPMS-5S). SQUID sample preparation also involved careful manipulation of the discharged electrode material in the inert atmosphere (glove-box).

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