



Vanadium nitride supercapacitors: Effect of Processing Parameters on electrochemical charge storage behavior



Prashanth Jampani Hanumantha^{a,b}, Moni Kanchan Datta^b, Karan Kadakia^a, Christopher Okoli^a, Prasad Patel^a, Prashant N. Kumta^{a,b,c,*}

^a Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA

^b Department of Bioengineering, University of Pittsburgh, Pittsburgh, PA 15261, USA

^c Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA

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ABSTRACT

Nanoparticulate transition metal nitride based supercapacitor electrodes have recently gained considerable attention as high capacity energy storage materials. In particular, vanadium nitride has been shown to be an excellent pseudocapacitor on account of surface reactions occurring at an oxide ex-shell. However, there is limited understanding into the exact nature of charge storage behavior and its dependence on synthesis and processing route. In the present work, we explore the effect of materials processing and electrode properties on capacitive charge storage in vanadium nitride based supercapacitor electrodes. Dependence of capacitance on particle properties and electrode properties are evaluated and reported here-in.

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1. Introduction

The development of high power energy storage devices for both stationary and mobile applications has been deemed critical for the attainment of sustainable energy storage systems to meet the global energy storage demands and the development of energy efficient global systems [1–5]. One of the outstanding challenges in this regard is to have devices with sufficiently large amount of charge stored while at the same time being able to deliver the same at rapid rates. Supercapacitor materials are capable of rapid charge storage and distribution thus ensuring short charging times and seemingly infinite cyclability with sufficiently large capacitances [6–11]. There is however, a dire need for identification of materials systems and development of simple and cost effective synthesis techniques to render supercapacitor systems suitable for large-scale commercialization [12–14]. Conventional dielectric and double layer electrochemical capacitors are generally incapable of storing such large amounts of charge. Pseudocapacitor materials involving a chain of successive reversible Faradaic reactions occurring at the surface however exhibit large specific

capacitances making them promising candidates for commercialization provided they sustain such behavior at higher rates over a number of cycles. Transition metal oxides in particular are very attractive for this genre of application on account of their ability to accept variable oxidation states. Of particular interest for pseudocapacitor applications is the ability of the surface oxide to undergo reversible hydration as in Ruthenium oxide [6,7,15–21]. However, the prohibitive price of noble metal based supercapacitors and poor electronic conductivity of oxides drives the search for alternative materials with similar energy storage capability but better electronic conductivity and low cost. Recent work by various groups has shown viability of nitrides, carbides and sulfides for catalysis and energy storage applications [22–30]. Transition metal nitrides were first shown to have promise as energy storage materials by various groups identifying molybdenum nitride as a suitable pseudocapacitor material [24,26,31–33]. A thorough investigation into transition metal nitride supercapacitors was then undertaken by Choi et. al and they determined them to be excellent supercapacitor materials in aqueous electrolytes [34–38]. Among the various nitrides evaluated, VN was found to exhibit capacitances as high as 1350 F/g [34,35,38]. This exceptional performance has been attributed to a combination of both double layer type capacitance and pseudo-capacitance occurring at the nitride surface. Vanadium is an element in Group 5 of the periodic table with a half empty d-shell allowing it to

* Corresponding author at: Department of Bioengineering, University of Pittsburgh, Pittsburgh, PA 15261, USA.

E-mail address: pkumta@gmail.com (P.N. Kumta).

accept valences of +2 to +5, thus allowing it to exhibit reversible Faradaic reactions yielding pseudocapacitance. Following this groundbreaking discovery, a number of studies have evaluated the capacitor properties of nitrides with a wide range of reported capacitances [24,26,31–34,36–61]. The large difference in capacitive charge storage obtained in VN explored by various methods indicates that charge storage in VN is very much dependent on the nature of the VN, i.e. crystallinity, particle size, surface area and the type of the surface oxide [44,45]. In addition, electrode properties could have a distinct bearing on the gravimetric and areal capacitance of VN that can be achieved [62]. In this study we have undertaken a thorough study into the various particle and electrode properties and their effect on electrochemical characteristics of vanadium nitride.

2. Experimental details

2.1. Materials Synthesis

Vanadium nitride was synthesized using a two-step ammonolysis method. In this procedure, approximately, 3 ml vanadium tetrachloride (Sigma Aldrich, Inc., 97.5–99%) was dissolved in 150 ml of anhydrous chloroform (< 5 ppm H₂O, ACROS Organics) inside an inert atmosphere glove box (Vacuum Atmospheres Inc.). The dissolved chloride was then reacted with flowing anhydrous ammonia gas (100 sccm, Valley National gas, 99.99%) to form a halide complex of the form V(NH₂)₃Cl. The solvent was then evaporated at 100 °C and the powder was recovered in a glove bag and introduced into a tube furnace. Subsequently, the powder was heat-treated in anhydrous ammonia (100 sccm) at 400 °C to convert the complex to vanadium nitride. The two-step ammonolysis procedure results in very fine VN crystallites which require surface passivation to avoid pyrophoric reactivity of the resulting nanostructured nitride upon exposure to air. A very low concentration of oxygen-argon (0.1% O₂-Ar) gas mixture was passed at 100 sccm for 4 hours to passivate the nitride nanoparticles resulting in a very thin surface oxide layer thus stabilizing the nitride against any exothermic oxidation of the nanoparticulate nitrides.

Commercially procured vanadium nitride (STREM, Goodfellow, 99.5% V) was simultaneously examined as-obtained for

comparison of material properties. In addition, high energy mechanical milling was performed on the commercial VN in a high energy shaker mill (SPEX CertiPrep 8000 M) for up to 10 hours (in a stainless steel (SS) vial using 20 SS balls of 2 mm diameter (~20 g) with a ball to powder weight ratio 10:1. The aim of this procedure was to characterize the change in materials properties of commercial VN and compare the same with VN derived by the two-step ammonolysis method.

2.2. Materials Characterization

In order to perform qualitative phase analysis, the synthesized materials were characterized by X-ray diffraction (XRD) using Philips XPERT PRO system employing CuK α ($\lambda = 0.15406$ nm) radiation with operating voltage and current set at 45 kV and 40 mA, respectively. The XRD peak profile was analyzed using the Pseudo-Voigt function to determine the Lorentzian and Gaussian contribution of the peaks. The integral breadth of the Lorentzian contribution, determined from peak profile analysis using single line approximation method after eliminating the instrumental broadening and lattice strain contribution, was implemented in the Scherrer formula to calculate the effective crystallite size of the VN derived by ammonolysis method, the commercially procured VN and the milled samples of the commercial VN [63,64]. The lattice parameter and molar volume of VN was calculated using the least square refinement techniques.

To investigate the microstructure of the VN derived by ammonolysis and the commercial VN before and after milling, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were conducted. Philips XL-30FEG comprised of an ultrathin beryllium window and Si (Li) detector operating at 20 kV was employed for executing the secondary electron (SE) image. The nitride powder was homogeneously spread out over a carbon background to obtain the SEM images. High resolution transmission electron microscopy (HR-TEM) analysis was conducted on the sample using JEOL JEM-2100F to investigate the particle size and morphology. A dispersion of the nitride particles (in methanol) was coated onto 300 mesh copper TEM grids (TED Pella, Inc.) and used for the TEM imaging. In addition, the oxygen and nitrogen content in the VN samples prepared by the ammonolysis method and the commercial VN before and after milling were independently analyzed using inert gas fusion analysis [LECO TC600 analyzer (Alternative Testing Laboratories, Inc.)]. The inert gas fusion technique analyzes oxygen content by allowing the oxygen to react with carbon and analyzing carbon dioxide formed using infrared spectroscopy. Nitrogen content is measured by using a thermal conductivity cell. The analysis was performed by Alternative Testing Laboratories, Inc. Finally, the specific surface area (SSA) of the VN was also measured using a Micromeritics ASAP 2020 (Accelerated surface area and porosimetry) system. Nitrogen adsorption and desorption partial pressures were measured and a BET (Brunauer Emmett Teller) type adsorption was assumed to obtain the surface area. Multi-point BET surface area is reported in this work using an adsorption-desorption isotherm over partial pressure values P/P₀ going between 0.06 and 0.35.

Since the electronic conductivity of the active material is a crucial parameter affecting the supercapacitor performance, a four point probe was used to measure the electronic conductivity of the VN derived by the various methods. To measure the electronic conductivity, pellets were prepared by compaction of the VN powder using a uniaxial pressure of 7000 lb in a manual press (Carver Inc.). A FPP 5000 four-probe conductivity instrument (Miller Design & Equipment, Inc.) was used for the measurements. The thickness of the pellets was measured and they were depressed against the four tips on the resistivity meter using a

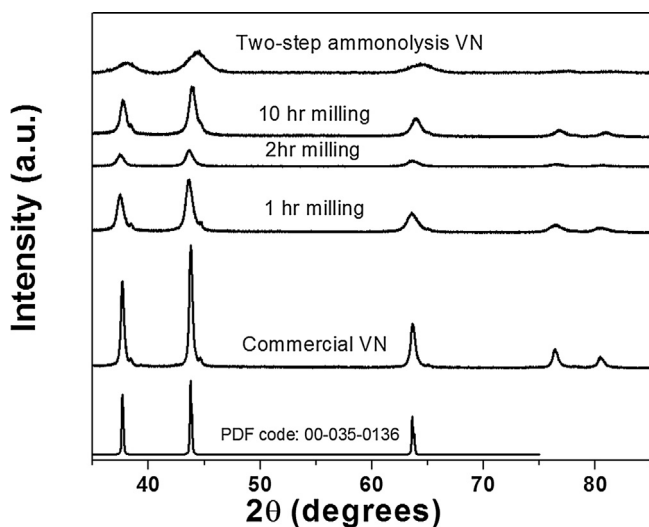


Fig 1. X-ray diffraction patterns obtained on as-procured commercial VN, commercial VN milled for varying amounts of time and chemically synthesized VN are shown along with the standard pattern for VN (PDF code: 00-035-0136).

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