Synthesis, surface chemistry and pseudocapacitance mechanisms of VN nanocrystals derived by a simple two-step halide approach

Daiwon Choa, Prashanth H. Jampanib, J.R.P. Jayakodyc,d, Steven G. Greenbaume, Prashant N. Kumta

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- Supercapacitors
- Nitrides
- Nanoparticles
- Pseudocapacitance

Abstract

Chloroamide precursors generated via a simple two-step ammonolysis reaction of transition metal chloride in the liquid phase at room temperature were heat treated in ammonia at moderate temperature to yield nano-sized VN crystallites. Grain growth inhibited by lowering the synthesis temperature (≈400 °C) yielded agglomerated powders of spherical crystallites of cubic phase of VN with particle sizes as small as 6 nm in diameter. X-ray diffraction, FTIR, mass spectroscopy (MS), and nuclear magnetic resonance (NMR) spectroscopy assessed the ammonolysis and nitridation reaction of the VCl4-NH3 system. X-ray Rietveld refinement, the BET technique and high-resolution transmission microscopy (HRTEM), energy dispersive X-ray (EDX) and thermogravimetric analysis (TGA) helped assess the crystallographic and microstructural nature of the VN nanocrystals. The surface chemistry and redox reaction leading to the gravimetric pseudo-capacitance value of (≈855 F/g) measured for the VN nanocrystals was determined and validated using FTIR, XPS and cyclic voltammetry analyses.

1. Introduction

The rocksalt structured 3d-transition metal nitrides have attracted considerable interest due to their important physical and well-known properties. Amongst the many transition metal nitrides, vanadium nitrides (VN) is well-known for its combination of unique properties including extreme hardness, high melting point (≈2300 K), high thermal conductivity, and good electrical conductivity (≈6 × 104 Ωm) [1–4]. These set of properties makes them important subject areas for technological as well as theoretical fundamental research resulting in several studies into various applications including capacitive charge storage in vanadium nitrides [5–10]. However, it is equally important to investigate nanostructured VN powder with high specific surface area which can be attractive for various catalytic studies [11], superconducting applications [12], magnetic storages devices [12], electrochemical capacitors [10,13–34] and myriad technological tasks arising within the semiconductor industries [35]. The fundamental question that still persists is the influence of reduced dimensionality on the collective unique materials properties indicated above.

The two most widely known routes for synthesizing vanadium nitrides are carbothermal reduction of vanadium pentoxide (V2O5) in N2 and direct nitridation of vanadium metal in H2/N2, NH3 and N2H4 or mixture thereof [4,11–15]. However, these routes require high temperatures (>1200 °C) and are often incomplete resulting in oxygen [19,36] and carbon contamination [22,37]. Incorporation of such impurities significantly and adversely affect the materials properties degrading the electronic, thermal and mechanical properties of the materials. Recently, other methods have been explored including microwave-assisted combustion [38–40], solid state metathesis (SSM) [18], low temperature thermal reduction and nitridation in an autoclave at 500 °C [41], transferred-arc plasma synthesis [42], aerosol reactor synthesis [43], sputtering [18,20,44], chemical vapor deposition [45,46] and anodic dissolution of the metal in an organic amine solution [47]. Even though many different synthesis routes have been developed, the fundamental reaction for obtaining VN in most approaches is the reaction between NH3 (or H2/N2 mixture) with various vanadium sources such as vanadium metal, oxides [48], chloride [49], sulfide [50], and NH4VO3 [51] at elevated temperature or in the presence of high energy.

The small value of free energy of formation due to the strong N≡N
bond in di-nitrogen molecules renders it very difficult to synthesize the corresponding nitrides of metals as compared to the more stable oxides. The presence of surface oxide however, is an essential aspect of nitride supercapacitors. Supercapacitors are high power density devices [52–55] with very high stability and the use of oxide nanoparticles as standalone supercapacitors is challenging due to their poor electronic conductivity [56]. However, the use of nanoparticle nitrides with thin oxide surfaces enables high capacitance with good electronic conductivity. The use of low temperature methods to synthesize nitrides is becoming however, increasingly relevant due to the advantages yielded by the reduction in particle sizes afforded at lower temperatures. The ammonolysis of chloride precursors is a suitable route for preparing nano-sized nitrides since chlorides undergo reduction at lower temperatures than the other sources mentioned previously. It has previously been demonstrated that the use of a two-step low temperature ammonolysis method using chloride precursors leads to several crystallographic properties and electrochemical characteristics of relevance to electrochemical charge storage [9,10]. In addition, the wet-chemical ammonolysis method is amenable for preparing doped nitrides as has been reported [57]. The liquid phase VCl4-NH3 reaction has been studied by Fowles et al. [58] and vapor-phase VCl4-NH3 reaction has also been studied by Saeki et al. [59] Further, Hojo et al. have studied the preparation of fine VN powders by a vapor-phase VCl4-NH3-H2-N2 reaction at 700–1200 °C [60]. However, not much information is at present available on the nitridation mechanism between liquid VCl4 with NH3 gas. In our study, ammonolysis and nitridation mechanism of liquid VCl4 dissolved in chloroform was investigated and the effects of reaction mechanism on the final material properties was correlated by characterizing the N/V ratio, lattice constants, surface area, crystallite size, density, and electronic conductivity. Furthermore, the final VN obtained was applied as a supercapacitor electrode where the pseudo-capacitance mechanism leading to high specific capacitance has been observed [10,13–94,61]. Herein we report detailed studies related to the surface chemistry and surface redox reaction occurring during the electrochemical process.

2. Experimental procedure

All manipulations were conducted inside a glove box (VAC: model EE-493, ≥5 ppm O2 + H2O) filled with Ultra high purity (UHP-Ar, Grade 5). The VCl4 (99.9% Aldrich) precursor was dissolved in chloroform (CHCl3: HPLC grade, 99.8%, ACROS) (purified by A4 molecular sieves (10–18 mesh, ACROS) and refluxed over CaCl2 (anhydrous 96%, ACROS)). 0.3 M of each transition metal chlorides were dissolved in chloroform (500 ml) and stirred for 30 min inside the glove box (VAC: model EE-493, ≥5 ppm O2 + H2O). The solution was mixed for 1 h and transferred to Ar-filled glove bag (Atmosbag: Aldrich) connected to an inert gas handling Schlenk line setup where dissolved vanadium tetra-chlorides solution were exposed to anhydrous NH3 gas (flow rate = 100 cc/min) for 10 h. Upon completion of the reaction, the solvent was evaporated at 100 °C under continuous NH3 gas flow and the as-prepared powders were collected and stored inside the glove box until execution of the final heat-treatment. For the final nitridation step, ≈10 g of as-prepared powder was heat-treated inside a mullite tube furnace under anhydrous NH3 atmosphere (flow rate = 130 cc/min, heating and cooling rate = 5 °C/min). When heat-treated below 500 °C, the powders were oxygen passivated by flowing UHP-Ar containing 0.1% oxygen for 4 h to prevent pyrolysis of the nano-sized powders when exposed to air. Fig. S1 depicts the synthesis procedure along with the compositions of the intermediate species and final product obtained.

The VCl4 salt dissolved in chloroform was analyzed using FTIR (Mattson Galaxy FTIR spectrometer) for any possible adduct formation. The solution of VCl4 (b.p = 154 °C at 1 atm) dissolved in chloroform was mixed for 2 h inside the glove box and few drops of the solution were placed on a NaCl plate which was dried inside the vacuum chamber for 4 h. After evaporating the solvent, the plate was covered by another NaCl plate and sealed in an air-right liquid FTIR cell. The as-prepared powder sample was also recovered inside the glove box and placed in a screw-end type FTIR cell.

The powders were subjected to phase analysis by X-ray diffraction (X’pert Pro, Philips) using CuKα radiation (λ = 1.5418 Å) with detector (X’celerator, Philips) and 0/20 goniometer between 10° and 80° with 0.0334 step size and 50 s exposure time. Reitveld X-ray refinement yielded the lattice parameters using X’pert Highscore plus software (Philips) and crystallographic structure was obtained using the Scherrer equation from the XRD peak broadness using Profit software (Philips).

In order to perform NMR measurements, the as-prepared powder and the corresponding heat-treated to 200 °C, 300 °C, and VN obtained at 400 °C under NH3 atmosphere were packed inside an Ar glove box into 5 mm (OD) x 25 mm NMR tubes and sealed by paraffin film. 1H (I = 1/2), 31V (I = 7/2) and 35Cl (I = 3/2) NMR spectra were collected at B0 = 7.05 T, 301 MHz; 31V, 79.2 MHz; 35Cl, 29.5 MHz) on a Chemagnetics CMX-300 spectrometer. The static 1H spectra were obtained using a wide-line low proton background probe with single-pulse excitation with a 10 μs pulse width. The 31V and 35Cl spectra were correspondingly acquired using a multi nuclear probe with quadruple echo and single-pulse sequences with 4 μs and 14 μs pulse widths respectively. All the spectra were acquired for the current study were acquired at ambient temperature (20 °C).

The specific surface area was measured using a multi-point (8) Brunauer-Emmett-Teller (BET) technique (Quantachrome Inst., NOVA-2000) and the density was measured using pycnometer (Quantachrome Inst., Ultrapycnometer).

Differential thermo-gravimetric analyses (DTGA: Cahn Inst., TG-171) were conducted on the as-prepared powder in anhydrous NH3 and the synthesized nitrides in air to understand the nitridation mechanism and to estimate the nitrogen content of the final nitride obtained, respectively. For both DTG analyses, a heating rate of 5 °C/min was employed from room temperature to 1000 °C and the gases released during heat-treatment in anhydrous NH3 atmosphere was analyzed using mass spectropy (MS, Automass) starting from 50 °C to 650 °C.

Scanning electron microscope (SEM: Philips XL30 FEG-SEM) with energy dispersive X-ray spectrometer (EDS: EDAX) was used for elemental mapping of the nitride samples. High-resolution transmission electron microscope (HRTEM: Philips Tecnai 20 FEG) was used for crystallite size and morphology analysis.

The chemical bonding nature, surface chemistry and ionization state of vanadium in VN nanocrystal surface before and after electrochemical cycling in 1 M KOH electrolyte were investigated using FTIR and XPS. The surface composition of VN and the possible valence states of V in VN was analyzed by using the X-ray photo-electron spectrometry (XPS)/electron spectroscopy for chemical analysis (ESCA) system (Perkin-Elmer PHI-5600). The VN powders were pressed into a pellet (diameter 1 cm) employing pressure of 7000 lbs using Carver press for analysis. A monochromated aluminum anode was used as the X-ray source, combined with a multi-channel detector, a sample stage cooling attachment, and a small spot (30 μm) electron lens. The XPS spectra were obtained using 0.4 eV binding energy resolution averaged over 10 scans. An inert gas sputtering source (PHI-04-303) was used for simultaneously cleaning the sample and acquiring depth profiles. The obtained XPS spectra peaks were de-convoluted using the CasaXPS software.

The electrical resistivity of the synthesized transition metal nitrides was measured using a four-point probe technique. The nanocrystalline nitrides was compacted into a pellet (diameter: 1 cm) by pressing 1 g of the powder employing a uniaxial pressure of 7000 lbs using Carver press. The electrical resistivity of pellets were then measured using the four-point probe measuring equipment, which comprised of 3-D adjustable probes and a digital source meter (Keithley 2400, voltage from ± 5 μV (sourcing) and ± 1 μV (measuring) to ± 200 V DC and current ranging from ± 10pA to ± 1A). The distance between the
probes used for the measurement was set at 1 mm.

Cyclic voltammetry (CV) was mainly used for understanding the pseudocapacitance behavior of VN using a three-electrode cell setup equipped with a working electrode, platinum wire counter electrode, and an Hg/HgO (in 1 M KOH) reference electrode. The working electrode was comprised of a nickel disk coated with the VN (active material), super-P (conductive carbon additive) and poly(vinylidene fluoride) (PVDF) (binder) dispersed in N-methylpyrrolidinone (NMP) solution in weight ratio of 85:5:10, respectively (Active material loading ~ 0.02 mg/cm²). The CV was performed at various scan rate (2-100 mV/s) in 1 M KOH electrolyte solution at 25 °C between ~ 1.2 V and 0 V (vs. Hg/HgO). The specific capacitance was calculated from the enclosed area of the anodic/cathodic curves in the CV plot using the following equation:

\[
\text{Capacitance } C \text{ (in F/g)} = \frac{\int V \, dV}{s + 2V + m}
\]

where

\[
\int V \, dV = \text{Area of the cyclic voltammogram}
\]

\[s = \text{scan rate in V/s}
\]

\[V = \text{voltage window}
\]

\[m = \text{Mass of active material in grams}
\]

The impedance response at different potentials was investigated by fitting equivalent circuit model to experimentally obtained impedance Nyquist plot using Zview software (Scribner Associates Inc.) Elemental analysis of the electrolyte collected after 100 cycles of CV testing, was performed by conducting inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 duo Thermo Fisher) to determine the amount of V that was leached out of the supercapacitor electrode into the solution, which yielded valuable pertinent information about the electrochemical stability/durability of the nitride material.

3. Results and discussion

Before examining the VCl₄-NH₃ reaction product, the VCl₄-CHCl₃ solution was examined for possible chloroform adduct formation with the VCl₄. When highly reactive liquid vanadium chloride is used as a starting material, organic adducts can easily form with various polar solvents, which can be source of oxygen and/or carbon contamination and can significantly increase the nitridation temperature. Therefore, the interaction between VCl₄ and CHCl₃ solvent during mixing was first investigated using FTIR. The characteristic IR modes of CH₃Cl are shown in Fig. 1(a) and those of VCl₄ and CHCl₃ solvent during mixing are shown in Fig. 1(b). The peak positions are summarized in Table 1. The FTIR spectrum of the solution residue was similar to that of chloroform with some shifts in absorption peaks indicating possible adduct formation. The peaks at 3683 cm⁻¹, 3024 cm⁻¹ and 2400 cm⁻¹ dedicated to ν₁ + ν₂, ν₁ and ν₁ − ν₂ peaks of C−H stretching have shifted close to 2898 cm⁻¹ [62–65]. The significant shifts of ν₁ + ν₂ and ν₁ − ν₂ peaks are due to disappearance of the ν₂ mode of CHCl₃ at 675 cm⁻¹ when chloroforam interacts with VCl₄. The weakening of C−Cl stretching mode accompanied by shift in H stretching mode signify some type of interaction between VCl₄ and CHCl₃ solvent. Such an interaction is likely to occur between VCl₄ and the hydrogen atom in an aliphatic C−H bond of chloroform (CHCl₃) which is uncommonly reactive. Even though the shape of the chloroform molecule is spheroidal and permanent dipole moment is not very large (~1D), it is reported that hydrogen atom in an aliphatic C−H bond can even form hydrogen bonding [65,66]. Similar shift in C−H stretching bands to lower frequency has been observed when chloroform is chemisorbed onto zeolites [66]. Chloroform adsorbed on the stronger basic site through its hydrogen atom leads to a weaker C−H bond accompanied by shift to lower C−H stretching frequency but participation of chlorine during the chemisorption leading to disappearance of ν₂ mode (C−Cl stretching)

![Fig. 1. FTIR spectra of (a) pure chloroform and (b) chloroform-VCl₄ mixture, (c) NH₄Cl and (d) as-prepared powder obtained after VCl₄-NH₃ reaction for 10 h (flow rate 130 cc/min).](image)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>Frequency (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁</td>
<td>C−H s stretching</td>
<td>3021 [16,26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₂</td>
<td>C−Cl s stretching</td>
<td>680 [16,26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₃</td>
<td>C−Cl s deformation</td>
<td>363 [26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₄</td>
<td>C−H d bending</td>
<td>1220 [26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₅</td>
<td>C−Cl d stretching</td>
<td>774 [26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₆</td>
<td>C−Cl d deformation</td>
<td>261 [26,27]</td>
<td></td>
</tr>
<tr>
<td>ν₁</td>
<td>N−H s stretching</td>
<td>3048 [21,30–33]</td>
<td></td>
</tr>
<tr>
<td>ν₂</td>
<td>N−H₄ a bending</td>
<td>1716 [30–33]</td>
<td></td>
</tr>
<tr>
<td>ν₃</td>
<td>N−H₄ a stretching</td>
<td>3126 [21,30–33]</td>
<td></td>
</tr>
<tr>
<td>ν₄</td>
<td>N−H t bending</td>
<td>1403 [21,30–33]</td>
<td></td>
</tr>
<tr>
<td>ν₅</td>
<td>N−H₄ z c-trans-optic</td>
<td>186 [31,32]</td>
<td></td>
</tr>
<tr>
<td>ν₆</td>
<td>N−H₄ t librational</td>
<td>389 [30–32]</td>
<td></td>
</tr>
<tr>
<td>As-prepared powder</td>
<td>N−H stretching</td>
<td>3000–3300 [34–38]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N−H bending</td>
<td>1604 [34–38]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N−H₂ wagging or twisting</td>
<td>1270/974 [35–38]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N−H₂ rocking</td>
<td>696 [34–38]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V−Cl stretching</td>
<td>433 [32,34]</td>
<td></td>
</tr>
</tbody>
</table>

(c: symmetric, d: double degenerated, t: triple degenerated, *: lattice mode).

is also possible. Further studies are warranted to completely understand the nature of this bonding and will be reported in a future manuscript. The as-prepared powder obtained after the ammonolysis reaction followed by evaporation of the solvent was also characterized by FTIR shown in Fig. 1(d) and the characteristic IR modes of NH₄Cl are summarized in Table 1 [62–64,67–76]. No traces of chloroform peaks are observed even though it can be embedded in other peaks. Major peaks
observed were from NH₄Cl, which is the by-product of the ammonolysis reaction verifying the numbers of chlorine groups replaced during the reaction. The IR active component of NH₄Cl is ν₃, ν₄, and ν₅ modes of which strong absorption bands at 3139 cm⁻¹ and 1402 cm⁻¹ are obviously from the ν₃ and ν₅ modes of NH₄Cl. Other weak additional peaks are also present at 2811 cm⁻¹, 1984 cm⁻¹, 1718 cm⁻¹, 1074 cm⁻¹ which is likely to be 2ν₄, ν₂ + ν₆, κν₄, and ν₄ − ν₅ bands, respectively [67]. The band at 663 cm⁻¹ is possibly due to N—Cl stretching mode of NH₄Cl where, the weaker bands are generally related to the lattice vibration modes of NH₄Cl. When FTIR spectra of the as-prepared powder was compared to that of pure commercial NH₄Cl as shown in Fig. 1, additional peaks other than that from NH₄Cl were present. These peaks are from the amide groups formed when the chloride groups are replaced during the ammonolysis of VCl₄ and the characteristic IR modes are summarized in Table 1. The broad peak around 3000–3300 cm⁻¹ and sharp peak at 1604 cm⁻¹ are due to the N—H stretching and the bending modes, respectively. The peaks at 696 cm⁻¹ are rocking mode of NH₂ group. The peaks at 1270 cm⁻¹ and 974 cm⁻¹ are not clear but can be either NH₂ wagging and twisting mode, which is reported to be sensitive to the coordination and can vary significantly. The 433 cm⁻¹ peak is due to the V—Cl stretching band. These results show the presence of amide groups with some chlorine remaining in the VCl₄. Consequently, the as-prepared powder is most likely to be V(NH₂)₃Cl₄-x (1 ≤ x ≤ 3) but the number of chlorine groups replaced is unknown. Fowles et al. have previously studied the reaction between pure VCl₄ and liquid NH₃ wherein they observed that three chlorine groups are replaced by amide groups (x = 3) in their proposed reaction as shown below [58]:

\[
\text{VCl}_4 + \text{NH}_3(\text{excess}) \xrightarrow{\text{RT}} V(\text{NH}_2)_3\text{Cl}_{4-x} + x\text{NH}_4\text{Cl} \quad (1 \leq x \leq 4)
\]

When the amido-chlorides obtained were subjected to further heat-treatment in vacuum at 200 °C and 400 °C, compositions leading to VNCl₃ and VNCl type structure were obtained, respectively [58]. However, the intermediate states and final products when the vanadium amido-chlorides are heat-treated in NH₃ have not been examined as in the present study.

Fig. 2 shows the XRD patterns of the as-prepared powder and VN powders obtained after heat-treatment. The as-prepared powder is mainly a mixture of dark brownish amorphous vanadium amido-chloride and crystalline NH₄Cl, verified by both FTIR and XRD. The as-prepared precursor transforms into cubic VN at temperature as low as 400 °C wherein the broad XRD peaks indicate the formation of nano-sized crystallites. The stoichiometry of the nitrided samples summarized in Table 2 indicate formation of stoichiometric crystalline VN at 1000 °C.

Understanding the overall ammonolysis and nitridation requires detailed knowledge of the as-prepared powder but the number of chlorine replaced by amide group (—NH₂) in vanadium amido-chloride is difficult to analyze due to the presence of NH₄Cl by-product. However, the number of amides replacing chlorines are calculated from the amount of NH₄Cl present, measured by the TGA if the decomposition of NH₄Cl and nitridation of vanadium amido-chloride occurs at different temperatures. In addition, the possible chemical species of the as-prepared powder other than NH₄Cl can be deduced from the weight change between the initial as-prepared powder and the final VN obtained. Therefore, correspondingly, the nitridation mechanism of the as-prepared powder during heat-treatment was studied by TGA-MS analysis under anhydrous NH₃ atmosphere as shown in Figs. 3 and 4.

From the TGA evolution plot, the nitridation reaction commences at 150 °C and NH₄Cl begins to decompose into NH₃ and HCl gas at 360 °C. From the weight change occurring during heat-treatment, the amount of each component in the as-prepared powder and possible VCl₄-NH₃ reaction products are measured and calculated, respectively. It can be seen from the TGA plot, the overall weight remaining is 22.13 wt% which can relate to the presence of either V(NH₂)₃Cl or V(NH₂)Cl with the amount of NH₄Cl produced by the VCl₄-NH₃ reaction is different when

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Table 2: Crystallite size, specific surface area, lattice constants, density, and composition of cubic VN powders synthesized at different temperatures under anhydrous NH₃ gas including specific capacitance.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Heat-Treatment Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>Crystallite Size (nm)</td>
<td>6.3</td>
</tr>
<tr>
<td>Spec. Surf. Area (m²/g)</td>
<td>38.8</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.1</td>
</tr>
<tr>
<td>Electronic Conductivity ((\times 10^{6}) Ω⁻¹ m⁻¹)</td>
<td>82.3</td>
</tr>
<tr>
<td>V content (wt%)</td>
<td>75.01</td>
</tr>
<tr>
<td>Composition</td>
<td>VN₃ClₓCl₄−x</td>
</tr>
</tbody>
</table>

---

*a Specific capacitance measured for loading 0.02 mg/cm² and potential window, 0–1.2 V at pH 14.

*b Determined by XRD analysis using Scherrer equation of full width at half maximum (FWHM) of (2 0 0) Bragg peak.

*c BET surface area measured using N₂ adsorption.

*d Lattice constant measured through Rietveld refinement of the XRD peaks [13].

*e Mass density measured using pycnometer in micro-cell.

*f Determined by four-point probe measurement of a VN pellet.

*g Determined by atomic absorption of vanadium (stoichiometric VN has 78.43 wt% of vanadium).

h Elements were analyzed by EDX and amount by TGA analysis in Ar and Air.
obtaining these two species. From the 57.21 wt% weight change corresponding to the NH$_4$Cl shown in the TGA plot, it is most likely that the as-prepared powder is V(NH$_2$)$_3$Cl since the weight percent of NH$_4$Cl in the precursors of V(NH$_2$)$_3$Cl and V(NH)$_2$ product is 54.41 wt% and 72.55 wt%, respectively. The slightly higher weight percent of NH$_4$Cl released compared to the calculated value of V(NH$_2$)$_3$Cl is probably due to vanadium amido-chloride still undergoing nitridation up to 400 °C which coincides with the results reported by Fowles et al.[58]. Since the amido-chloride has been confirmed as V(NH$_2$)$_3$Cl, the nitridation mechanism into VN was investigated by using mass spectroscopy (MS) on the gas species released during the heat-treatment in NH$_3$.

Fig. 4 shows the MS spectra of the gas species released in the different temperature regions. Between 71 and 133 °C (region I), only NH$_3$ is present wherein no apparent weight changes are observed. The reaction between the vanadium chloroamide begins around 210 and 230 °C (region II) wherein the gas species related to NH$_2^-$ increased with release of N$_2$ gas and traces hydrazine (N$_2$H$_4$) accompanied by weight decrease which is not from NH$_4$Cl. These amide groups are likely released from the V(NH$_2$)$_3$Cl forming N$_2$ and/or N$_2$H$_4$. Above region II up to 590 °C (region III to IV), only NH$_3$ gas is observed. Between 590 °C and 650 °C (region V), more N$_2$ gas is detected due to the excess nitrogen released from VN$_{1+x}$. It is to be noted that throughout the heat-treatment, HCl is not detected since the HCl gas reacts immediately with NH$_3$ gas depositing NH$_4$Cl at the lower temperature cooler regions of the tube. These results indeed show that the NH$_4$Cl does not play a significant role in the nitridation since the nitridation commences at 150 °C wherein the first weight drop observed is lower than the decomposition temperature of NH$_4$Cl. Therefore, the proposed nitridation sequence is as follows.

First, at the temperature around 200 °C, V(NH$_2$)$_3$Cl loses one of the amide group accompanied by change in valance state of vanadium from V$^{4+}$ to V$^{3+}$ state. (The oxidation state of vanadium has been expressed as V$^{x+}$ where x is the oxidation state). The calculated weight change due to the release of one amide group is 5.4 wt% which is close to 4.5 wt% weight drop observed as a small step up to 202 °C in the TGA plot. This is also confirmed by the release of the amide (NH$_2^-$), hydrazine (N$_2$H$_4$) and nitrogen (N$_2$). Subsequently, the V(NH$_2$)$_3$Cl transforms into VN by giving up one ammonia (NH$_3$) and one hydrochloric acid (HCl). The overall reactions are further summarized below.

**Dissociation reaction:**

$$2\text{V(NH}_2\text{)}_3\text{Cl} \rightarrow 2\text{V(NH}_2\text{)}_2\text{Cl} + \text{N}_2\text{H}_4 + \text{N}_2$$  \hspace{1cm} (1)

**Polymerization and condensation reaction:**

$$\text{V-NH}_2 + \text{NH}_2\text{Cl} \rightarrow \text{V-NH}_2 + \text{NH}_2\text{Cl} + \text{N}_2$$

\hspace{1cm} (2)

**Overall reaction:**

$$2\text{V(NH}_2\text{)}_3\text{Cl} + 2\text{NH}_3\text{Cl} \rightarrow 2\text{V(NH}_4\text{)}_3\text{Cl} + 2\text{Cl}_2$$  \hspace{1cm} (3)

The NMR analyses were also conducted on the as-prepared powder as well as the powders heated to 200 °C, 300 °C and VN obtained following heat treatment at 400 °C under anhydrous NH$_3$ for 10 h. The $^1$H NMR spectra at room temperature of the four different samples are displayed in Fig. 5(a) in the collated spectra labeled $^1$H. The as-prepared powder gives two clearly resolved broad and narrow components
with line-width values of 4.3 and 47 kHz, respectively. There is significant reduction of the broad feature signature for the heat-treated samples as the annealing temperature is increased. It is tempting to assign the broad peak to crystalline NH$_4$Cl because of its intensity reduction after annealing. However, from the $^{35}$Cl results presented in Fig. 5(a)-(c) in the collated spectra labeled $^{35}$Cl, there is strong

Fig. 5. NMR spectra of $^1$H, $^{35}$Cl and $^{51}$V at 20 °C of the (a) as-prepared powder and those heat-treated at (b) 200 °C, (c) 300 °C and (d) VN synthesized at 400 °C under anhydrous NH$_3$ atmosphere for 10 h.

Fig. 6. HRTEM images of the VN nano-crystallites synthesized at 500 °C for 10 h under anhydrous NH$_3$ atmosphere.
evidence that this compound persists until the 400 °C anneal. It is hence, suggested here that VN sample obtained at 400 °C exhibits a narrow 1H NMR signal, obviously indicating significant presence of a hydrogen containing compound, though it is not possible to ascertain whether the hydrogen is directly bonded to the VN or if there is a mixture of pure VN and an ammonium compound. The 35Cl NMR spectra collected at room temperature of the same samples are also displayed in Fig. 5 under the collated spectra labeled 35Cl. The first three samples give a reasonably narrow peak with a similar line-width of 2.6 kHz, strongly suggesting the presence of a significant amount of NH4Cl at 300 °C. The large 35Cl nuclear quadruple moment renders its NMR signal very difficult to observe, especially at the 29.5 MHz utilized here, unless the Cl− ion is in a highly symmetric environment as would be the case of crystalline NH4Cl. Thus, even if there are any chloride species remaining after the 400 °C anneal, there is little if any NH4Cl detectable at that point. The 51V NMR spectra collected on the same sample are also shown in Fig. 5 in the column labeled 51V. The first three samples in the column Fig. 5(a-c) give weak and broad feature with the line width decreasing from 130 kHz to 100 kHz, as the heat-treatment temperature is increased. The VN sample obtained at 400 °C however, gives a relatively strong peak with a line-width of 80 kHz. It is usually difficult to observe 51V NMR signals for V oxidation states other than the diamagnetic one for the (+5) oxidation state, unless the electron spin density is not strongly localized near the V-ion. Although it is not possible to ascertain the oxidation state from the NMR spectra alone, the large change occurring between 300° and 400 °C does indicate new compound formation. The NMR results presented here thus strongly indicate that the nitrides obtained at 400 °C contain excess nitrogen making V5+ and the presence of H detected is probably arising from the imides formed during the polymerization of amino-chlorides especially at the surface of the crystallites. This can be the main reason why VN obtained at 400 °C is pyrophoric requiring surface oxidation as a passivation treatment to render it stable before exposure to air.

The crystallite size, specific surface area, lattice constants and density of VN synthesized at different temperatures are further summarized in Table 2. The crystallite size is 6.33 nm and 57.98 nm for the nitrides obtained following heat-treatment at 400 °C and 1000 °C, respectively. Fig. 6 shows the HRTEM images of VN synthesized at 500 °C (The TEM images of the VN synthesized at 400 °C have been included in Fig. S2). The VN powders are mainly agglomerates of spherical nano-crystallites and the clearly delineated lattice fringes indicates the formation and presence of a well-crystallized phase. The lattice fringes from the HRTEM image were profiled into peaks wherein the distance between the 26 peaks is 53.04 nm with respect to the reference length bar giving a lattice constant of 2.04 nm, corresponding to the (2 0 0) plane where the ideal inter-planar spacing value is 2.063 nm. The highest specific surface area is 71.58 m2/g for the VN synthesized at 500 °C. The effective particle size ‘d’ is estimated from the specific surface area Sd assuming a spherical particle morphology using the following relation:

\[ d = 6/S_d \rho \]

Considering the theoretical density of VN = 6.04 g/cm3 for VN, a surface area Sd of 100 m2/g corresponds to a crystallite size of 9.93 nm in diameter. The theoretical surface area calculated assuming spherical particles of VN with particle size of 7.18 nm and 6.33 nm for the 500 °C and 400 °C ammonia heat treatments, is 138.35 m2/g and 156.93 m2/g, respectively. This discrepancy perceived between the calculated and measured surface area is expected due to the aggregation caused by sintering and the exothermic surface oxidation leading to coarsening of the nitride nano-crystallites resulting in loss of surface area.

The lattice parameters obtained from Rietveld refinement13 conducted on the VN powder synthesized at different temperatures is collated in Table 2. The lattice constant increased from 4.108 to 4.134 Å with the corresponding heat-treatment temperature, which coincides with the 4.13 Å lattice parameter indicated for the cubic VN (ICPDS Powder Diffraction File Card No.73-0528) (Table S1 provides refinement details and goodness of fit for various VN materials). This shows that the VN obtained at higher temperatures are closer to the stoichiometric VN since excess nitrogen abruptly decreases the lattice constant producing vanadium site defects. From the elemental analysis conducted using EDX, vanadium, nitrogen, oxygen and chlorine were present in the synthesized VN nano-crystallites obtained at lower temperatures. The compositions of VN nano-crystallites analyzed using the TGA following the method used by Saeki et al. are shown in Table 2 [59]. All the vanadium nitride obtained at the lower heat treatment temperatures lower than 900 °C indicate presence of excess nitrogen which is characteristic of the transition metal chloride-ammonia reaction [59]. The VN synthesized lower than 700 °C also indicate oxygen which must arise from the surface oxides of the VN nano-crystallites and the oxygen content expectedly increased with decrease in heat-treatment temperature with traces of chlorine impurities (< 0.1 at%).

The densities measured for the nitrides obtained are in the range of 5.1–5.72 g/cm3, which is slightly lower than the bulk density of 6.04 g/cm3 with no significant variation in density with respect to heat-treatment condition observed. The electrical conductivities measured on the synthesized VN were lower than that reported for the bulk electronic conductivity of 1.67 × 109 Ω−1 cm−1. Nevertheless, the electronic conductivity is observed to improve as the heat-treatment temperature is raised probably related to the stoichiometry, porosity and reduction in grain boundary due to sintering.

These synthesized nanocrystalline VN powders were also tested as electrodes to evaluate their supercapacitor response. The cyclic voltammetry results of the nanocrystalline VN obtained are summarized in Table 3 where very high specific capacitance of 855 F/g was achieved at scan rate of 2 mV/s from VN synthesized at 400 °C with a loading density of 0.02 mg/cm2. Such a high capacitance cannot be attained solely by the electrical double layer formation since the general specific surface areas of these nitrides are much lower than other electrical double layer capacitors (EDLCs). It is thus natural to consider that the high value of capacitance is arising from an electrochemical redox contribution occurring at the electrode/electrolyte interface, which is responsible for the pseudocapacitance assigned to the transitions among the various ionizations states of vanadium. Since the ideal cubic VN is at III state, the only possible reaction from pure nitride is formation of hydroxyl bonding or if the nitride surface undergoes certain degree of oxidation. In aqueous solutions, many of these vanadium oxide compounds and ions undergo extensive hydrolysis. Furthermore, it is recently recognized that the vanadium at lower oxidation state can also exhibit marked hydrolysis and association. Therefore, the surface chemistries of the VN nanocrystals before and after electrochemical cycling for ten cycles in 1 M KOH electrolyte were further analyzed using FTIR and the results are shown in Fig. 7. The absorption bands at 970 cm−1 and 792 cm−1 due to V=O and V−O vibrations indicates the presence of vanadium oxide layer on the VN nanocrystal surface confirming the composition analysis shown in Table 1. However, the peaks have been shifted from that of crystalline phase where V=O and V−O appears at 1020 cm−1 and 840 cm−1, respectively, indicating amorphous nature of vanadium oxide layer [77]. The free −OH stretching vibration peak appears around 3650−3600 cm−1 whereas the hydrogen bonded −OH stretching vibration peak is 3200−3500 cm−1. When the

### Table 3

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<tr>
<th>Scan Rate (mV/s)</th>
<th>Specific Capacitance (F/g)</th>
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<tr>
<td>400</td>
<td>855</td>
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<td>500</td>
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*Materials Science & Engineering B 230 (2018) 8–19*
VN powders were electrochemically cycled for 10 cycles, the hydroxyl –OH peaks appeared in three different frequencies with one distinct peak at 3047 cm⁻¹ possibly related to the –OH stretching vibration of VO(OH)₂ phase related to surface chemical reaction (redox activity) [76,78–80].

XPS analysis was further conducted on the VN powder to elucidate the observations discussed above for the nitride before and after electrochemically cycling the nitride electrodes to 200 cycles to identify the oxidation states of surface VO₆ layers to deduce the possible redox activities within the electrochemical potential window applied. The presence of V, N, O, and C was confirmed in the full XPS spectra of the VN powder shown in Fig. 8(a and b). The carbon present is due to absorption of gaseous carbon dioxide molecules from the atmosphere and from the mold releaser used but no traces of chlorine residue has however, been detected. The N1s (396.8 eV) and O1s (529.6 eV) observed corresponds to a metal nitride (N1s: 396.8–398.9 eV) and a metal oxide (O1s: 529.5–531.3 eV), respectively. Fig. 8(c–h) shows the de-convoluted XPS peaks between 504 eV and 540 eV where O1s, V2p¹/² and V2p³/² peaks are observed. A vanadium V2p³/² binding energy of 513.2–513.7 eV observed for nitride (VN) is close to the reported binding energies of 513.3 eV for VN thin film deposited through gaseous VCl₄-NH₃ reaction [46]. However, the shifts in peaks are observed when VN nanocrystals have undergone the electrochemical cycling tests. Especially, it can be seen that the vanadium oxide V2p³/² peaks corresponding to V₂O₅ between 516.4 and 516.2 eV are shifted to 515.9–513.2 eV observed for nitride (VN) is close to the reported binding energies of 513.3 eV for VN thin film deposited through gaseous VCl₄-NH₃ reaction [46].

To obtain the accurate redox potentials among these oxides, cyclic voltammetry was performed at a scan rate of 2 mV/s for VN synthesized at 600 °C shown in Fig. 9. (The impedance behavior of the various nitrides are identical at various synthesis temperatures. Figs. S3–S6 demonstrate the EIS behavior at various temperatures and this can be seen therein.) The charge observed under the voltammetric curves are due to the double layer formation and a series of redox processes involving formation of surface vanadium oxides on the nitride undergoing successive electron transfers as manifested by the current peaks observed. The distinguishable peaks appeared at three different regions in the CV plot at −0.86 V, −0.61 V and −0.23 V during charge and at −0.89 V, −0.68 V and −0.3 V during discharge confirming that the redox reaction is reversible. The possible reactions related to these observed peaks are deducted by calculating the potentials using electrochemical data provided by Kelsall et al. [53]. Even though dissolution of vanadium into highly basic KOH solution forming some ionic species is possible, due to its complexity, the calculations were confined only among the solid vanadium oxides formed. The standard electrode potential of Hg/HgO half-cell is +0.098 V vs. the standard hydrogen electrode (SHE) in basic KOH solution. When limiting the potential window between 0 and −1.2 V at pH = 14, the possible redox reaction is likely to be among VO, V₂O₃, V₃O₅ and VO₂. The calculated reaction potentials (vs. SHE) are summarized below:

\[ E/\text{V} = -0.0591 \times \text{pH} \]

\[ 3\text{V}_2\text{O}_5(s) + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{V}_2\text{O}_3(s) + 4\text{OH}^- \quad E^0/\text{V} = -0.437 \]

This also explains the ⁵¹V NMR signals where V⁵⁺ is observed for VN synthesized at 400 °C due to presence of surface V₂O₅. Among the four vanadium oxide phases V₂O₅ (2 ≤ x ≤ 5), V₂O₄ has the greatest stability from the oxidation and reduction points of view since its stability domain lies entirely within the limits of water (at neutral pH region) [88]. V₂O₅ is unstable in the presence of water, as the stability domain lies clearly below 0 V whereas the V₂O₄ is stable in the presence of solutions free from oxidizing agent and reacts with the oxygen in the air, converting to V₂O₄. Concerning acidic-basic character, it is seen that the almost exclusively basic properties corresponding to the divalent and trivalent states: V₂O₅ and V₂O₇ render it soluble in acids but not in bases. From the pH-potential (vs. SHE) diagram, it is most likely that the redox reaction and stable vanadium oxides in 1 M KOH solution (pH ≈ 14) within the potential window between 0 V and −1.2 V are among V₂O₅, V₃O₅ or VO with little possibility of VO₂ in accordance with the XPS results [88,89]. Such a phenomenon has also been exhaustively analyzed by Hanumantha et al. [10] and the fade in capacity is most prominently observed in the smaller nanoparticles due to the more pronounced surface oxide coating.

Fig. 7. FTIR spectra of the VN nano-crystallites synthesized at 500 °C for 10 h under anhydrous NH₃ atmosphere before electrochemical cycling (a) and after electrochemical cycling for 10 cycles (b). The spectra are shown corresponding to the various specific wavenumbers to depict the corresponding regions of interest.
Although VO₂ is unstable in such a high pH environment, it can be considered to form during the non-equilibrium charging process. The XPS results show presence of either V₂O₃ or VO₂ (Fig. 8) because VO will undergo oxidation when exposed to air. These oxides are in the amorphous state as the XRD taken on VN nanocrystals after electrochemical cycling showed no traces of crystalline oxide phases. Also, the pH value at the electrode surface can be quite different from the electrolyte due to the higher ion (OH⁻) concentration near the surface of the electrode as a result of electrical double layer effect (dE/dpH = 0.0591). Consequently, the calculated redox potentials do not exactly match with that of CV peaks seen in Fig. 9. This is expected

\[ 2\text{V}_2\text{O}_3(s) + \text{H}_2 \text{O} + 2e^- \rightarrow 3\text{V}_2\text{O}_5(s) + 2\text{OH}^- \quad E^\circ / V = -0.713 \]

\[ \text{V}_2\text{O}_4(s) + 2\text{H}_2 \text{O} + 4e^- \rightarrow 2\text{VO}_2(s) + 4\text{OH}^- \quad E^\circ / V = -0.807 \]
since the overpotential of the oxidation/reduction reactions can vary based on the local concentrations and local ohmic effects i.e. nano-level electron conductivity/ohmic factors inducing shift from equilibrium potentials. However, it can be deduced from the above analysis that the ionization of the vanadium is indeed among the II, III, and IV states of V.

Since the vanadium oxides at the VN surface before and after electrochemical process are different as confirmed by XPS analyses, the shape of the CV curves should change during cycling wherein the redox reaction related to more stable phase will appear and unstable phase will disappear. Fig. 9(b) shows the CV curves of VN synthesized at 600 °C cycled six times at scan rate of 1 mV/s. At higher cycle number, more intense peaks related to the new process appeared which is similar to the voltammetric profile of the electrochemically grown vanadium oxide film on nitride. The first cycle shows only a peak at −0.61 V but the peak at −0.86 V appears beginning of the second cycle and becomes sharper as the cycle number increases reaching a maximum at the sixth cycle with no further increase. Our previous XPS analyses (Fig. 8) and CV cycling results (Fig. 9) confirm that the initial V2O5 will undergo reduction to lower oxidation states among VO, V3O5 or V2O3 in 1 M KOH electrolyte. According to the potential calculated, the CV peak near −0.875 V is closest to the redox reaction between V3O5 and V2O3 or VO and VO2. The increase in this peak intensity indicates the increase in the VO, V3O5 or V2O3 oxide phases as the V2O5 undergoes reduction during cycling resulting in the formation of the more stable phases during repeated cycles. The peak near −0.645 V can be attributed to the redox reaction between V2O5 and V2O4 whereas redox peak near −0.265 V can be ascribed to the reaction between V2O3 and VO2.

The cyclic voltammogram up to six cycles shows that the peaks near −0.265 V and −0.645 V decreases as the cycle number increases indicating that these redox reactions occur between the unstable valence state of the vanadium. The post-cycled ICP analysis revealed the presence of dissolved vanadium species (~14.3 ppm) after 100 cycles. This is indicative of the dissolution of V5+ species. Work by Hanumantha et al. has also further highlighted the conditions responsible for charge-storage in VN [9,10]. Nevertheless, other type of charging mechanisms involving vanadium ionization among II, III and IV states cannot be discounted [90,91].

To understand the electrochemical kinetics contributing to the overall charge storage mechanism, impedance analyses was performed at −0.2 V, −0.7 V and −1.2 V for the VN nanocrystals synthesized at 400 °C and shown in Fig. 10. The ideal equivalent circuit for a typical supercapacitor involves the circuit elements including a double layer capacitance Cdl, a Faradaic resistance RF (or electron charge transfer resistance Rct) corresponding to the potential-dependent pseudocapacitance Cp associated with the coverage of electrodeposited species, or that of Ox and Red species concentrations. Work by Hanumantha et al. has also further highlighted the conditions responsible for charge-storage in VN [9,10]. Nevertheless, other type of charging mechanisms involving vanadium ionization among II, III and IV states cannot be discounted [90,91].

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Fig. 10 [97] where two CPE model produces two semicircles on the complex-plane plot with generally high frequency semicircle related to the surface porosity and the low frequency semicircle related to the charge-transfer process (redox reaction) [98]. The first circuit model applies to the under potential deposition (UPD) process which represents ion deposition in the sub-monolayer regime where new phase is being deposited (redox reaction) [95,97]. Whereas when potential is beyond the UPD range, another Faradaic or chemical potential-dependent $R_F'$ arises in parallel with CPE$_P$, in the equivalent circuit as shown in Fig. 10 corresponding to over potential deposition (OPD) [94,97]. The OPD represents conditions above monolayer regime where the identical ion is being deposited and the potential depends on the bulk corresponding to the deposited species, which is different from the UPD where reaction potential depends on the interaction between the surface and the deposited species. This situation corresponds to the overcharge state of the pseudocapacitance wherein a continuous Faradaic reaction takes place (current leakage across CPE$_{p}$) in the over-potential region. Mechanisms and kinetics of the OPD usually accompanies hydrogen evolution reaction (HER) at the electrode. From the previous XPS and FTIR results, the presence of an oxide layer and hydroxyl groups at the surface of the VN nanocrystals is indeed confirmed and is widely accepted that the HER in aqueous electrolytes proceeds via the Volmer-Heyrovský or Volmer-Tafel mechanism, which proceeds through oxidation on the electrode surface in alkaline solution at the lower potential limit [98].

Table 4 shows the values of the circuit components obtained through the data fitting. From the circuit model indicated requiring introduction of the two CPE component, accurate double layer and pseudo capacitance values cannot be assessed due to the dispersion effect. The solution resistance $R_S$ and Faradaic resistance $R_F$ is observed to decrease at lower potentials. Furthermore, it is seen that the resistance values are the lowest at $-0.7$ V indicating that a majority of the redox reaction is occurring near this potential region. At $-1.2$ V, appearance of desorption equivalent resistance $R_F$ (OPD) indicates that further reduction is deterred. The $\varphi$ values decreased from 0.79 to 0.65 and 0.88 to 0.72 for CPE-DL and CPE-P, respectively, as the potential decreased from $-0.2$ V to $-1.2$ V showing large deviations from the ideal capacitive characteristics. This could be attributed to many aspects such as loading, the electronic conductivity of the synthesized material and the corresponding electrode, the microporosity as well as permeability and wetting of the electrolyte over and within the synthesized material and also its electrochemical stability as outlined above and also detailed recently by Hanumantha et al. [9].

The current study on the surface modified VN nanocrystals indeed shows the occurrence of the surface redox activity, which gives rise to the high specific capacitance. These redox activities can indeed be optimized for stability and reversibility by adjusting the potential window applied [61]. Subsequent reports in the literature have indeed demonstrated the electrochemical activity and similar response that is demonstrated by other transition metal nitrades and oxides as well as the influence of loading and electrode thickness [9,10,15,16,24,61,99]. Further work outlining the subtle nuances of the nanocrystalline state of the nitride, the distribution of the surface oxide, microstructure of the various phases formed during electrochemical cycling and the microporous nature of the electrode and their combined influence on the charge transfer and stability of the system are all topics of additional research. It is anticipated however, that these studies will likely further shed light into these novel class of transition metal nitride supercapacitor systems. The aim of this work was to study the ammonolysis procedure to prepare ultra-fine nitride nanoparticles with a very thin surface oxide layer. Oxide materials have been explored extensively for electrochemical applications and though they exhibit faradaic response, the unique morphology afforded by the ammonolysis procedure discussed herein wherein the nitride acts as a conductive substrate and accordingly affording possible charge-transfer enhancement. This makes the exploration of the mechanism of nitridation of critical relevance. Additionally, nitride materials are being used for several other catalytic applications and the mechanistic insight offered by this work will facilitate further nitride materials development in such parallel fields.

4. Conclusions

Nanocrystalline VN powders were synthesized by a two-step ammonolysis reaction of vanadium tetra-chloride and chloroform solvent that is inert to the nitridation of vanadium tetrachloride. Nitridation of V(NH$_2$)$_3$Cl in the as-prepared powder is initiated through polymerization and condensation during heat-treatment and cubic VN formed at temperatures as low as 400°C in anhydrous NH$_3$ atmosphere. The specific surface area was however, lower than the corresponding nitride synthesized from organic precursors or complex adducts formed by using polar aprotic or protic solvents. The VN formed at temperatures as low as 400°C contained surface oxides giving rise to pseudocapacitance behavior. The stoichiometry of the initial amorphous vanadium oxide formed was close to V$_2$O$_5$ in stoichiometry, which is stable in air. During electrochemical cycling however, these oxides undergo reduction to lower oxidation states of vanadium wherein the redox reaction occur between the oxidation states of II to IV generating the observed and previously reported large pseudocapacitance values for nanostructured VN.

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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.mseb.2017.12.017.

References
