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

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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 ($\approx 6 \times 10^9 \Omega m$) [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 dimensionalities 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 N_2 and direct nitridation of vanadium metal in H_2/N_2 , NH_3 and N_2H_4 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 $N \equiv N$

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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 pseudocapacitance mechanism leading to high specific capacitance has been observed [10,13-34,61]. 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, \geq 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 NH_3 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 = $154 \,^{\circ}$ 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-tight liquid FTIR cell. The asprepared 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 CuK α radiation ($\lambda = 1.5418$ Å) with detector (X'celerator, Philips) and $\theta/2\theta$ 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 crystallite size 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), ⁵¹V (I = 7/2) and ³⁵Cl (I = 3/2) NMR spectra were collected at B₀ = 7.05 T ¹H, 301 MHz; ⁵¹V, 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 ⁵¹V 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 used 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 NH_3 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 NH_3 atmosphere was analyzed using mass spectroscopy (MS, Automass) starting from 50 °C to 650 °C.

Scanning electron microscopy (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 microscopy (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 $\pm 5 \,\mu$ V (sourcing) and $\pm 1 \,\mu$ V (measuring) to $\pm 200 \,\text{V}$ DC and current ranging from $\pm 10 \,\text{PA}$ to $\pm 1 \,\text{A}$). 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:

Capacitance C (in F/g) =
$$\frac{\int I \, dV}{s*2*V*m}$$

where

 $\int I \, dV$ = Area of the cyclic voltammogram s = scan rate in V/s

V = voltage window

m = 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 $\nu_1 + \nu_2$, ν_1 and $\nu_1 - \nu_2$ peaks of C-H stretching have shifted close to 2898 cm⁻¹ [62–65]. The significant shifts of $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ peaks are due to disappearance of the ν_2 mode of CHCl₃ at 675 cm⁻¹ when chloroform 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. 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 (\sim 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 ν_2 mode (C-Cl₃ 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).

Table 1

Characteristic IR spectra modes of CH₃Cl, NH₄Cl and as-prepared powder.

	Mode	Description	Frequency (cm ⁻¹)	Reference
CHCl ₃	ν_1	C–H s stretching	3021	[16,26,27]
	ν_2	C-Cl ₃ s stretching	680	[16,26,27]
	ν_3	C-Cl ₃ s deformation	363	[26,27]
	ν_4	C-H d bending	1220	[26,27]
	ν_5	C-Cl ₃ d stretching	774	[26,27]
	ν_6	$C-Cl_3 d$ deformation	261	[26,27]
NH ₄ Cl	ν_1	N-H s stretching	3048	[21,30–33]
	ν_2	N-H ₄ d bending	1716	[30-33]
	ν_3	N-H ₄ t stretching	3126	[21,30-33]
	ν_4	N–H t bending	1403	[21,30-33]
	ν_5^*	N-H ₄ z-c trans-optic	186	[31,32]
	ν_6^*	N–H ₄ t librational	389	[30–32]
As-prepared		N-H stretching	3000-3300	[34–38]
powder		N-H bending	1604	[34–38]
		N-H ₂ wagging or	1270/974	[35-38]
		twisting	696	[34–38]
		N–H ₂ rocking	433	[32,34]
		V-Cl stretching		

(s: 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 ν_3 , ν_4 , and ν_5 modes of which strong absorption bands at $3139 \,\mathrm{cm}^{-1}$ and $1402 \,\mathrm{cm}^{-1}$ are obviously from the ν_3 and ν_4 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 $2\nu_4$, $\nu_2 + \nu_6$, $\nu_4 + \nu_6$, and $\nu_4 - \nu_6$ 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 chlorine groups are replaced during the ammonolysis of VCl₄ and the characteristic IR modes are summarized in Table 1. The broad peak around $3000-3300 \text{ cm}^{-1}$ 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 $V(NH_2)_x Cl_{4-x}$ $(1 \leq x \leq 3)$ 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]:

$$VCl_4 + NH_3(excess) \xrightarrow{K.T.} V(NH_2)_x Cl_{4-x} + xNH_4Cl(1 \le x \le 4)$$

When the amido-chlorides obtained were subjected to further heattreatment in vacuum at 200 °C and 400 °C, compositions leading to VN₃Cl₃ 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 amidochloride and crystalline NH₄Cl, verified by both FTIR and XRD. The asprepared precursor transforms into cubic VN at temperature as low as 400 °C wherein the broad XRD peaks indicate the formation of nanosized crystallites. The stoichiometry of the nitrides 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 $(-NH_2)$ in vanadium amido-chloride is difficult to analyze due to the presence of NH_4Cl by-product. However, the number of amides replacing chlorines are calculated from the amount of NH_4Cl present, measured by the TGA if the decomposition of NH_4Cl and nitridation of vanadium amido-chloride occurs at different temperatures. In addition, the possible chemical species of the as-prepared powder other than NH_4Cl 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 NH_3 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(NH)₂ but the amount of NH₄Cl produced by the VCl₄-NH₃ reaction is different when



Fig. 2. XRD patterns of as-prepared powder and VN synthesized at various temperatures under NH_3 environment (flow rate 130 cc/min). (* – NH_4Cl). VN was indexed to JCPDS Powder Diffraction File Card No.73-0528.

Table 2

Crystallite size, specific surface area, lattice constants, density, and composition of cubic VN powders synthesized at different temperatures under anhydrous $\rm NH_3$ gas including specific capacitance.

Material Property	Heat-Treatment Temperature (°C)						
	400	500	600	700	800	900	1000
Crystallite Size $(nm)^a$ Spec. Surf. Area $(m^2/g)^b$ Lattice Constant a $(Å)^c$ Density $(g/cm^3)^d$ Electronic Conductivity $(\times 10^2 \Omega^{-1}m^{-1})^e$ V content $(vt\%)^f$	6.3 38.8 4.108 5.1 82.3 75.01	7.2 71.6 4.118 5.2 92.8 75.42	16.9 29.2 4.129 5.5 94.5 75.8	30.6 12.3 4.133 5.6 97.3 78.1	42.3 12.0 4.135 5.7 109.6 78.2	55.0 3.4 4.138 5.4 152.3 78.3	57.9 2.4 4.134 5.6 282.8 78.4
Composition	$VN_XO_yCl_z$ ^g						
X Y Z	1.080 0.363 0.103	1.132 0.084 0.09	1.151 0.053 0.062	1.137 - 0.04	1.113 - 0.017	1.094 - -	1.068 - -

 $^hSpecific capacitance measured for loading <math display="inline">0.02\,mg/cm^2$ and potential window, 0–1.2 V at pH \sim 14.

^a Determined by XRD analysis using Scherrer equation of full width at half maximum (FWHM) of (200) Bragg peak.

^b BET surface area measured using N₂ adsorption.

^c Lattice constant measured through Rietveld refinement of the XRD peaks [13].

^d Mass density measured using pycnometer in micro-cell.

^e Determined by four-point probe measurement of a VN pellet.

 $^{\rm f}$ Determined by atomic absorption of vanadium (stoichiometric VN has 78.43 wt% of vanadium).

^g Elements were analyzed by EDX and amount by TGA analysis in Ar and Air.



Fig. 3. TGA evolution on the (a) $\rm NH_4Cl$ and (b) as-prepared powder under $\rm NH_3$ atmosphere (flow rate 130 cc/min).

obtaining these two species. From the 57.21 wt% weight change corresponding to the NH₄Cl shown in the TGA plot, it is most likely that the as-prepared powder is V(NH₂)₃Cl since the weight percent of NH₄Cl in the precursors of V(NH₂)₃Cl and V(NH)₂ product is 54.41 wt% and 72.55 wt%, respectively. The slightly higher weight percent of NH₄Cl released compared to the calculated value of V(NH₂)₃Cl 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(NH₂)₃Cl, the nitridation mechanism into VN was investigated by using mass spectroscopy (MS) on the gas species released during the heat-treatment in NH₃.

Fig. 4 shows the MS spectra of the gas species released in the different temperature regions. Between 71 and 133 °C (region I), only NH₃ 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 NH2⁻ increased with release of N2 gas and traces hydrazine (N2H4) accompanied by weight decrease which is not from NH₄Cl. These amide groups are likely released from the V(NH₂)₃Cl forming N₂ and/or N₂H₄. Above region II up to 590 °C (region III to IV), only NH₃ gas is observed. Between 590 °C and 650 °C (region V), more N_2 gas is detected due to the excess nitrogen released from $\text{VN}_{1\,+\,\text{x}}.$ It is to be noted that throughout the heat-treatment, HCl is not detected since the HCl gas reacts immediately with NH₃ gas depositing NH₄Cl at the lower temperature cooler regions of the tube. These results indeed show that the NH₄Cl 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 NH₄Cl. Therefore, the proposed nitridation sequence is as follows.

First, at the temperature around 200 °C, V(NH₂)₃Cl loses one of the amide group accompanied by change in valance state of vanadium from V⁴⁺ to V³⁺ state. (The oxidation state of vanadium has been expressed



Fig. 4. Mass spectroscopy at different temperature during heat-treatment of the as prepared powder under NH_3 atmosphere (flow rate 130 cc/min).

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 (NH₂⁻), hydrazine (N₂H₄) and nitrogen (N₂). Subsequently, the V(NH₂)₂Cl transforms into VN by giving up one ammonia (NH₃) and one hydrochloric acid (HCl). The overall reactions are further summarized below.

Dissociation reaction:

$$2V(NH_2)_3Cl \rightarrow 2V(NH_2)_2Cl + N_2H_4 \text{ or } N_2 + 2H_2$$
 (1)

Polymerization and condensation reaction:

Overall reaction:

 $2V(NH_2)_3Cl \rightarrow 2VN + 2NH_3(g) + 2HCl(g) + N_2H_4 \text{ or } N_2 + 2H_2$ (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 ¹H NMR spectra at room temperature of the four different samples are displayed in Fig. 5(a) in the collated spectra labeled ¹H. The as-prepared powder gives two clearly resolved broad and narrow components



Fig. 5. NMR spectra of ¹H, ³⁵Cl and ⁵¹V 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 NH₃ atmosphere for 10 h.





Fig. 6. HRTEM images of the VN nano-crystallites synthesized at 500 $^{\circ}\text{C}$ for 10 h under anhydrous NH_3 atmosphere.

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_4Cl because of its intensity reduction after annealing. However, from the ³⁵Cl results presented in Fig. 5(a)–(c) in the collated spectra labeled ³⁵Cl, there is strong

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 heattreatment 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 amido-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 nanocrystallites 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 respect to the reference length bar giving a lattice constant of 2.04 nm, corresponding to the (200) plane where the ideal inter-planar spacing value is 2.063 nm. The highest specific surface area is $71.58 \text{ m}^2/\text{g}$ for the VN synthesized at 500 °C. The effective particle size 'd' is estimated from the specific surface area S_g assuming a spherical particle morphology using the following relation:

$d = 6/S_g \rho$

Considering the theoretical density of $\rho_{VN} = 6.04 \text{ g/cm}^3$ for VN, a surface area S_g of $100 \text{ m}^2/\text{g}$ 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 $138.35 \text{ m}^2/\text{g}$ and $156.93 \text{ m}^2/\text{g}$, respectively. This discrepancy perceived between the calculated and measured surface area is expectedly 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 (JCPDS 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 $1.67 \times 10^6 \Omega^{-1} m^{-1}$. 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	
Specific capacitance of VN derived at various temperature	res.

Scan Rate (mV/s)	Specific Capacitance (F/g) ^h						
Synthesis temperature of VN	400	500	600	700	800	900	1000
2 10 25 50 100	855 497 296 190 110	538 443 265 173 108	348 258 157 102 63	162 93 67 58 46	141 78 60 50 41	74 36 27 23 15	58 26 19 15 12



Fig. 7. FTIR spectra of the VN nano-crystallites synthesized at 500 °C for 10 h under anhydrous NH_3 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.

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 VO_x 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, $V2p^{1/2}$ ² and $V2p^{3/2}$ peaks are observed. A vanadium $V2p^{3/2}$ 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 $V2p^{3/2}$ peaks corresponding to V₂O₅ between 516.4 and 516.2 eV are shifted to 515.9 and 515.7 eV closer to either VO2 or V2O3 [81-85]. From these XPS results, it appears that the initial V2O5 that is present on the surface of the VN nanocrystals undergoes reduction to lower oxidation states after the electrochemical process. The change in the oxidation state coincides with the equilibrium pH-potential diagram of vanadium oxide in high alkaline solution examination reported by Pourbaix et al. and Kelsall et al. [86,87].

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 V₂O_x ($2 \le x \le 5$), 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]. V₂O₂ is unstable in the presence of water, as the stability domain lies clearly below 0 V whereas the V₂O₃ 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: V₂O₂ and V₂O₃ 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 \approx 14) within the potential window between 0 V and -1.2 V are among V₂O₃, 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.

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 \approx 14, the possible redox reaction is likely to be among VO, V2O3, V3O5 and VO2. The calculated reaction potentials (vs. SHE) are summarized below:

 $E/V = E^{o}/V - 0.0591 \times pH$

 $V_2O_4(s) + H_2 O+ 2e^- \leftrightarrow V_2O_3(s) + 2OH^- E^0/V = -0.322$

 $3V_2O_4(s) + 2H_2 \ O+ \ 4e^- \leftrightarrow \ 2V_3O_5(s) + \ 4OH^- \quad E^o/ \ V= -0.437$



Fig. 8. XPS spectra of VN obtained at 400 °C (a) before and (b) after cycling, Deconvoluted peaks of VN obtained at 400 °C (c) before and (d) after cycling; VN obtained at 500 °C (e) before and (f) after cycling, VN obtained at 600 °C (g) before and (h) after 200 cycles.

 $2V_3O_5(s) + H_2 \text{ O}+ 2e^- \leftrightarrow 3V_2O_3(s) + 2OH^- \quad E^o/\text{ V}=-0.713$

 $V_2O_4(s) + 2H_2 O+ 4e^- \leftrightarrow 2VO(s) + 4OH^- E^0/V = -0.807$

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 V_2O_3 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 ($\partial E/\partial pH = -0.0591$). Consequently, the calculated redox potentials do not exactly match with that of CV peaks seen in Fig. 9. This is expected



Fig. 9. Cyclic voltammetry plot of VN synthesized at 600 °C scanned at (a) 2 mV/s and (b) 1 mV/s for six cycles. (Active material loading ~0.02 mg/cm²). See Table S2 for peak values and reactions.

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 attributed to the redox reaction between V3O5 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 valance 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 fade behavior discussed above occurring through 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 $C_{\rm dl}$, a Faradaic resistance $R_{\rm F}$ (or electron charge transfer resistance $R_{\rm ct}$) corresponding to the potential-dependent pseudocapacitance $C_{\rm p}$ associated with the coverage of electrodeposited species, or



Fig. 10. Impedance spectra of the VN synthesized at 400 °C tested at different potentials (-0.2, -0.7, -1.2 V) and circuit models for under potential deposition (UPD) and over potential deposition (OPD).

that of Ox and Red species concentrations. A solution resistance R_S is usually combined in series with the Faradaic impedance involving C_{dl}, R_F and C_p. However, when the simulated circuit model is fitted to the experimental impedance data, alterations of C_{dl} and C_p circuit elements were necessary since depressed semicircles were observed which relates to the fractal character of the electrode material, porosity, roughness and inhomogeneity of crystallographic reaction sites resulting in a non-ideally polarized interface. Therefore, a constant phase element (CPE:))_{CPE} an empirical function needs to replace the capacitor (¬¬) in the equivalent circuit representing its impedance spectra [92,93]. The impedance of a CPE is given by a power law frequency dependence as $Z_{CPE} = 1/[T(j\omega)^{\phi}]$, where T and ϕ are constants, $j = \sqrt{-1}$, and ω is the angular frequency ($\omega = 2\pi f, f$: frequency) [94,95]. Note that the CPE is a capacitor when $\phi = 1$ and relates to the constant phase angle $\alpha = 90^{\circ}(1 - \phi)$ [94,96]. The combined circuit elements are shown in

Table 4

Equivalent-circuit model values obtained by fitting experimental impedance spectra.

v	R_S/Ω	R_F/Ω	R_F^{\prime}/Ω	CPE-DL		CPE-P	
				$T\times 10^{-5}$	φ	$T\times 10^{-5}$	φ
-0.2	111.5 105.1	48.5 41.7	-	2.6 10.6	0.79 0.65	6.7 40 4	0.88 0.87
-1.2	106.7	44.9	58.74	6.4	0.65	142.9	0.72

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 Faradiac 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-Hevrovský or Volmer-Tafel mechanism, which proceeds through oxide reduction 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 ϕ 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 nitrides 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(NH₂)₃Cl 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 NH3 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 V₂O₅ 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.

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