Structure and Capacitive Properties of Porous Nanocrystalline VN Prepared by Temperature-Programmed Ammonia Reduction of V₂O₅[†]

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Vanadium nitride (VN) is currently one of the most promising materials for electrodes of supercapacitors. The structure and electrochemical properties of VN synthesized by temperature-programmed NH₃ reduction of V₂O₅ are analyzed in this paper. Vanadium nitride produced via this route has distinctive structural characteristics. VN mimics the shape of the initial V₂O₅ precursor indicating a pronounced direct attachment of nitride grains. The particles have domains of grains with a preferential orientation (texture). The large volume of pores in VN is represented by the range of 15–110 nm. VN demonstrates capacitive properties in three different types of aqueous electrolytes, 1 M KOH, 1 M H₂SO₄, and 3 M NaCl. The material has an acceptable rate capability in all electrolytes, showing about 80% of its maximal capacitance at a current load of 1 A/g in galvanostatic charging/discharging experiments. The capacitance of 186 F/g is observed in 1 M KOH electrolyte at 1 A/g. The previously reported negative effect of material loading on the capacitance is significantly suppressed. The observed electrochemical characteristics related to the application of this material in supercapacitors can be correlated with the crystalline structure of the nitride and the composition of its surface layer.

Introduction

Supercapacitors (also known as electrochemical capacitors and ultracapacitors) are a class of electrochemical energy storage devices that complement batteries. They are capable of providing quick charge release when it is needed and normally have a much longer cycle life than batteries.^{1,2} The current areas of applications of supercapacitors include power back-up devices, portable electronics, emergency doors of aircrafts, and hybrid and electric cars.^{3–5} Conventional electrochemical electric double layer capacitors (EDLC) utilize the charge storage by adsorption of ions at the surface of electrodes composed of graphitic carbons with huge surface areas.^{1,2,6}

A novel class of materials (including some inorganic compounds and conductive polymers) has been proposed

in the past decade for the applications in electrodes of supercapacitors.^{1,2} These materials possess the so-called pseudocapacitance, that is, most of the charge is stored not by the conventional EDL mechanism but is due to the presence of fast redox reactions on the surface of these materials. The use of pseudocapacitive nanoscale transition metal oxides and nitrides has been named one of the three greatest achievements in the field of supercapacitors in the most recent review paper². Hydrous RuO₂ is currently a benchmark pseudocapacitive material.^{1,7} It is capable of demonstrating capacitances exceeding 1000 F/g but is extremely expensive. Research in the area of pseudocapacitors is focused on finding a cheaper alternative to ruthenium oxide. Among other possible materials, vanadium nitride (VN) is currently one of the most promising candidates.

VN has been found to deliver a specific capacitance of up to 1340 F/g in 1 M KOH aqueous electrolyte when a thin film of this material (0.25 mg/cm²) was assessed by cyclic voltammetry at a sweep rate of 2 mV/s.^{8,9} The impressive performance has been attributed to the

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combination of high electronic conductivity of vanadium nitride and redox reactions provided by few layers of vanadium oxides or oxynitrides on the surface. The material acts as a core-shell composite, in which the surface layer is responsible for high pseudocapacitance and the nitride core is responsible for quick electron transport.

Vanadium nitrides for testing in supercapacitor cells were prepared by a chemical route based on a two-step ammonolysis reaction of VCl_4 in anhydrous chloroform.^{8,9} A disadvantage of VN materials prepared in this way is their limited rate capability. The initially impressive capacitance (at low sweep rates in cyclic voltammetry) has been observed to fade significantly when the sweep rate is increased. The effect of material loading, which is possibly related to the poor rate capability, was also reported.⁹ The essence of this effect is that when the amount of material per unit of area of the current collector is increased the capacitances decrease dramatically. Only thin films (with VN densities below 1 mg/cm^2) could deliver attractive capacitances.

The primary explanation is a decreased electronic conductivity of nanocrystalline VN which consists of weakly interconnected nanoparticles and a limited ionic conductivity of the electrolyte due to the porous structure of the electrode with small pores. The estimated conductivity of nanocrystalline VN was two- to threefold smaller than that of a bulk material.⁸ To achieve an improved rate capability for a nanostructured VN and suppress the dramatic dependence of its capacitance on material loading, an appropriate crystalline structure of a nanostructured vanadium nitride involving well-connected nanoparticles and optimized porosity has to be designed.

Temperature-programmed ammonia reduction of V_2O_5 is a simpler alternative procedure to produce porous VN. It has been previously used for the preparation of vanadium nitride catalysts with high surface areas.^{10–12} Unlike an approach used in refs 8 and 9, this procedure involves only one step and does not require special equipment (a glovebox and a glovebag). Kwon et al.¹⁰ observed that the conversion of V_2O_5 into VN materials is pseudomorphic; that is, the resulting porous nitride retains the morphology of the initial V_2O_5 . It may be anticipated that the excellent interconnection of grains in such a material would favor better rate capabilities of VN.

In this article, we study the structure and capacitive behavior of VN materials produced by temperature-programmed ammonia reduction of V_2O_5 . It is shown that these porous textured nitrides demonstrate acceptable rate capabilities in three types of aqueous electrolytes (1 M KOH, 1 M H_2SO_4 , and 1 M NaCl). The observed performance of VN is linked to its crystalline structure and the composition of the surface layer.

During the final stages of the manuscript preparation, we have encountered another recently published article

on VN materials for supercapacitors.¹³ The VN materials have been prepared by calcining vanadium oxide xerogel under NH_3 atmosphere at 400°C . We have incorporated a discussion of these recent results into the current paper.

Experimental Section

The starting material for the synthesis was a commercial V_2O_5 powder from Sigma-Aldrich (99.6% purity). It consisted of relatively large particles (which were, in fact, aggregates of smaller submicrometer particles) with sizes of $200\text{--}500 \mu\text{m}$. Temperature-programmed reduction of V_2O_5 by ammonia gas was performed in a tube furnace (Jetflow furnaces, Melbourne, Australia). The NH_3 flow of 0.7 L/min was passing through the furnace tube. A total of 600 mg of the V_2O_5 precursor were loaded inside of the tube. The sample was heated up to 700°C at the rate of 2.8°C/min and kept at 700°C for 1 h. After that, the furnace cooled down naturally overnight in NH_3 flow. The as-prepared sample was normally passivated by passing the mixture of $0.1\% \text{ O}_2$ and high purity Ar gas over the sample for 2 h.

The original and resulting materials were analyzed by X-ray diffraction (XRD, Philips analytical X-ray spectrometer with Co radiation $\lambda = 0.1789 \text{ nm}$), scanning electron microscopy (SEM, Hitachi S-4500), and transmission electron microscopy (TEM, Phillips CM300). Surface area and pore size distribution were evaluated using N_2 adsorption (Quantachrome instruments Quadrasorb SI). The specific surface area was calculated from the N_2 adsorption isotherm using the Branauer–Emmett–Teller (BET) equation, and the pore size distribution was obtained from Barrett–Joiner–Helenda (BJH) method.

A special sample of VN was prepared specifically for TEM characterization to study the preferred orientation of grains in the material. The V_2O_5 precursor for this sample was different and represented single-crystalline nanorods. The morphology of the nanorods is described in detail elsewhere.¹⁴ Each single-crystalline nanorod had a rectangular cross section and was elongated along the $[010]$ crystallographic direction of V_2O_5 (see Figure 3 in ref 14).

The X-ray photoelectron spectroscopy (XPS) measurements were performed on ESCALAB220i-XL (VG Scientific, U.K.) using the Al $K\alpha$ source. The binding energy scale in the XPS measurements was corrected for the charging effect by assigning a value of 284.6 eV to the C 1s peak of adventitious carbon. O 1s and V $2p^3$ lines in the XPS spectra were fitted with several peaks using free XPSPeak 4.1 software. Initial peak positions of 514.1 , 515.6 , 516.5 , and 517.3 eV were used for fitting the V $2p^3$ line (these values correspond to typical positions of the V $2p^3$ line in VN, V_2O_3 , VO_2 , and V_2O_5 , see main text of the article for more details). The number of peaks, shapes, and positions of them were optimized for the best fit.

Three-electrode cells were assembled to assess the electrochemical properties of vanadium nitride. The working electrode was prepared by mixing the VN (80 wt %), carbon black (Mitsubishi #32, 10 wt %), and polyvinylidene fluoride (PVDF, 10 wt %) in *N*-methyl-2-pyrrolidone (NMP). The resulting slurry was spread onto pieces of titanium foil. Pt electrode was used as a counter electrode and Ag/AgCl as a reference electrode. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GC) tests were performed in 3 M NaCl, 1 M KOH, and 1 M H_2SO_4 aqueous electrolytes. Capacitances

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Figure 1. XRD pattern of VN produced by NH_3 reduction of V_2O_5 .

Figure 2. SEM characterization: a typical particle of the commercial V_2O_5 powder (a) and a particle in the resulting VN (b). Insets show high-magnification images of particles.

were calculated from the discharge branches of galvanostatic charge/discharge curves and areas enclosed by cyclic voltammetry curves. The used Ag/AgCl reference electrode could withstand the alkaline electrolyte since it was not the standard Ag/AgCl with the porous glass tip (that dissolves in concentrated KOH) but the special Ag/AgCl designed for acidic as well as basic electrolytes.

Results and Discussion

Structural Characterization. Figure 1 shows an XRD pattern of the sample obtained by temperature-programmed NH_3 reduction of the V_2O_5 powder. The positions of diffraction peaks in the pattern are close to those of cubic vanadium nitride (PDF file 73-0528). The peaks are broadened, indicating a small size of individual crystallites.

SEM images of the initial V_2O_5 powder and the resulting VN sample are shown in Figure 2. A typical particle of the commercial V_2O_5 powder is demonstrated in Figure 2a, and Figure 2b depicts a representative VN particle obtained by the NH_3 reduction. The high-magnification SEM images in the insets show that the VN particle has a porous nature with typical pore sizes below 100 nm while the initial V_2O_5 particle does not have a pronounced porous structure. It can be concluded from SEM analysis that the NH_3 reduction of V_2O_5 powders leads to the conservation of the overall particles' shapes and sizes while the interior of particles becomes porous. The conservation of the external shape is presumed to be due to a strong direct attachment of grains in the resulting nitrides. The VN particles can be interpreted as porous frameworks built with interconnected crystalline fragments.

Figure 3. Pore size distribution of the VN sample produced.

The pore size distribution of vanadium nitride is shown in Figure 3. It is dominated mostly by pores in the range of 15–110 nm (the broad peak on the right-hand side of the distribution), but some smaller pores are also present. The measured BET surface area of the sample was $22.9 \text{ m}^2/\text{g}$. It is smaller than some reported values,^{10,11} which can be correlated to the fact that vanadium nitrides were prepared using a “licked” bed of material (the gas flow was passing above the layer of the oxide powder in the furnace tube).

Figure 4 shows the results of TEM characterization of a fragment of a VN particle. The electron diffraction pattern is in the form of discontinuous rings (Figure 4a). The grainy contrast in the bright-field image (Figure 4b) confirms the nanocrystalline structure of the material. The dark-field image recorded using the diffracted beam (emphasized with a circle in Figure 4a) is depicted in Figure 4c. Specifically, it reveals the area in the nanocrystalline agglomerate consisting of the grains with similar orientations. These grains give a noticeable bright contrast in the dark-field image, and the corresponding area is shown with arrows.

To evaluate the nature of the preferential grain orientation, additional TEM work has been conducted. A special sample of VN has been prepared by NH_3 reduction of single-crystalline V_2O_5 nanorods. The detailed characterization of the crystalline structure of this V_2O_5 sample can be found in ref 14. Briefly, each V_2O_5 nanorod was elongated along the [010] crystallographic direction and had a rectangular cross section defined by {001} and {100} crystal planes (see Figure 3 in ref 14). The SEM image of the V_2O_5 nanorods is shown in Figure 5a. Porous VN nanorods obtained by NH_3 reduction of them are shown in Figure 5b. These VN nanorods are an ideal sample to investigate the internal structure of VN by TEM and relate it to the structure of initial V_2O_5 crystals.

The diffraction pattern of a VN nanorod (Figure 5c) is similar to that of a single crystal. However, each diffraction spot is converted into an arc, which is an evidence of texture in the polycrystalline structure. In other words, there exists a preferential orientation of grains (crystallites) in each nanorod of VN. It follows from the analysis of the diffraction pattern that the [110] direction of VN tends to be parallel to the [010] direction in the initial

Figure 4. TEM characterization: (a, b) SAED pattern and bright-field image of a piece of a VN particle; (c) dark-field image taken using the diffracted beam shown with a circle in (a). The arrows in (c) show the area consisting of grains with similar crystalline orientations.

V_2O_5 , and disorientation of grains happens mainly by a rotation around the [001] direction of the original V_2O_5 crystal. When the 200 diffracted beam was selected to form a dark-field image (Figure 5d), we could observe numerous groups of grains with contrast similar to that detected in VN particles (Figure 4c). Figure 5e is a high-resolution image taken from two adjacent crystallites in the nanorod. Two sets of (200) planes of VN are rotated slightly in respect to each other around the former [001] direction of V_2O_5 , and the FFT pattern of the image (Figure 2f) shows that even more clearly. Two pairs of spots can be seen, rotated in relation to each other by a small angle. The situation in the large VN particles (which we discuss in this article) is more complicated since the original V_2O_5 precursor is polycrystalline. However, it is likely that individual single-crystalline areas within each particle are converted into textured domains of grains in the course of NH_3 reduction.

In summary, the VN material produced by NH_3 reduction of V_2O_5 possesses the following structural characteristics: (1) individual grains in each particle are directly attached to each other; (2) the particles have crystalline domains with a preferential orientation of grains (texture); and (3) a large volume of pores is in the range of 15–110 nm.

Electrochemical Properties. Vanadium nitride has shown capacitive properties in all electrolytes tested—1 M H_2SO_4 , 1 M KOH, and 3 M NaCl. The corresponding CV curves of VN at the sweep rates of 5 and 100 mV/s are depicted in Figure 6. The suitable voltage windows are defined as –0.2 to 0.6 V for 1 M H_2SO_4 and 3 M NaCl and –1.2 to 0 V for 1 M KOH vs Ag/AgCl reference electrode. The voltage window of 1.2 V in 1 M KOH solution is the same as was previously reported.^{8,9} The ordinate axes in Figure 6 represent differential capacitances (specific currents divided by the sweep rates), and such a representation visualizes directly the comparison of capacitances at various sweep rates.

The capacitive properties in 1 M H_2SO_4 and 3 M NaCl aqueous solutions are evaluated for the first time. The presence of significant redox peaks in cyclic voltammograms undoubtedly confirms pseudocapacitance in both the acidic and neutral electrolytes. However, the investigation of the exact pseudocapacitive interactions in 3 M

NaCl and 1 M H_2SO_4 is beyond the scope of the current paper, and we plan to address that in a future publication. It is obvious that VNs have reasonably good rate capabilities in 1 M KOH since the area enclosed by the CV curve does not fall dramatically when the sweep rate is increased from 5 to 100 mV/s. Poor rate capabilities were found to be a disadvantage of VN electrodes for supercapacitors,⁸ and it is apparent that VN materials produced by NH_3 reduction of V_2O_5 can improve the high rate performance.

It has been indicated previously⁹ that the performance of vanadium nitrides in 1 M KOH in CV experiments was also dependent strongly on the material density on the current collector. When the material loading per unit of area of the current collector was increased, the capacitance of VN dropped and rate capabilities degraded noticeably. For example, the capacitance of vanadium nitride with the density of 0.99 mg/cm² was almost twice smaller than that of VN with the density of 0.25 mg/cm² at the CV scan rate of 2 mV/s and became 5 times smaller at the sweep rate of 100 mV/s.⁹ In the present study, vanadium nitride is prepared by a different approach, NH_3 reduction of V_2O_5 , and the dependence of the capacitances and rate capabilities on the material loading is weak and does not demonstrate a dramatic decrease with the increase in the material's density. For example, electrodes with densities of 1.1 and 0.55 mg/cm² demonstrated similar capacitances in 1 M KOH (101 and 105 F/g at the CV sweep rate of 5 mV/s). Furthermore, the vanadium nitrides in this study can retain acceptable rate capabilities at high material loadings on a current collector. The rate capabilities shown in Figure 6, for example, were measured using thick films of VN (with densities of about 4–6 mg/cm²).

The improved rate capability and the minimized dependence of capacitance on the density of the material on a current collector is likely to be due to the structural features of VN synthesized by NH_3 reduction of V_2O_5 . These features are clearly different from those in nitrides synthesized by Choi et al.,^{8,9} whose material consisted of rather weakly connected nanoparticles with no preferential orientation and the typical pore sizes of 3–40 nm. The

Figure 5. Electron microscopy study of the preferred grain orientation in vanadium nitride. A special sample of VN is produced from single-crystalline nanorods of V_2O_5 . (a, b) SEM images of the initial V_2O_5 nanorods and the resulting porous nanorods of VN. (c, d) SAED pattern and dark-field image of a VN nanorod. (e, f) High-resolution image of two adjacent grains and its FFT pattern.

VN particles synthesized in our study are well-connected polycrystalline porous frameworks, and this leads to their higher electronic conductivity. The conductivity is possi-

bly further improved by the presence of textured domains (i.e., areas with preferential grain orientations) in the particles. As a result of the better electrical conductivity,

Figure 6. CV curves of vanadium nitride in 1 M H_2SO_4 (a), 1 M KOH (b), and 3 M NaCl (c) aqueous electrolytes at the sweep rate of 5 mV/s (colored solid symbols) and 100 mV/s (gray open symbols).

the VN performs reasonably well at higher sweep rates or charging/discharging rates. The thickness of the film is also no longer a critical parameter limiting the use of larger amounts of the active material in an electrode.

Generally, our results are in a good agreement with the results of a recent publication by Zhou et al.¹³ who produced vanadium nitrides by calcining vanadium oxide xerogel under NH_3 atmosphere at 400 °C. The capacitance of 161 F/g has been measured at 30 mV/s by cyclic voltammetry. The ammonia reduction of hydrous vanadium oxide is a process similar to ours, and somewhat similar structural characteristics of vanadium nitride can be expected. The authors, however, have brought forward a different explanation of the good capacitance retention

Figure 7. Rate capability of vanadium nitride. (a) Capacitance retention at various current loads. (b, c) Charge/discharge curves at the current loads of 50 mA/g and 1 A/g, respectively. Red curves (rhombs) correspond to 1 M H_2SO_4 electrolyte and green curves (squares) correspond to 3 M NaCl electrolyte.

at high current loads or voltage sweep rates. According to their interpretation, the good capacitance retention should be explained by the dominance of fast, reversible redox reactions at the surface with only small contribution from slow or irreversible processes. Meanwhile, we believe that the improvement in rate capability is mainly due to the crystalline structure of the nitride.

The capacitance retention by our VN material acceptable for applications in supercapacitors is confirmed by galvanostatic charge/discharge experiments (Figure 7a). When it is charged and discharged at the current load of 1 A/g, the VN sample demonstrates 79% of the capacitance measured at 50 mA/g in 1 M H_2SO_4 and 84% of the initial capacitance in 3 M NaCl electrolyte. Figure 7b,c shows the charge/discharge curves of VN in 1 M H_2SO_4 and 3 M NaCl electrolytes at the current loads of 50 mA/g and 1 A/g. The curves have a triangular shape close to an

Figure 8. Charge/discharge curve of VN at the current of 1 A/g in 1 M KOH electrolyte.

ideal one at both current rates, and only a minor IR drop is detected in the GC curves when the current of 1 A/g is switched to the opposite value. The time of charge and discharge is longer in 1 M H_2SO_4 since vanadium nitride demonstrates higher capacitances in this electrolyte.

The highest capacitance measured at 1 A/g was 186 F/g (82% of the maximal capacitance) in 1 M KOH electrolyte (the charge/discharge profile is given in Figure 8). To obtain this value, the sample was additionally annealed in air at 200 °C after the synthesis to modify the composition of the surface layer. The corresponding maximal capacitance (225 F/g) has been achieved at 500 mA/g and correlates well with the value of capacitance (221 F/g) measured by CV at a slow sweep rate of 5 mV/s. It has been observed that the VN electrodes fail to charge and discharge in 1 M KOH at low current densities (50 and, in some cases, 100 mA/g). This phenomenon manifests itself as extremely long charge or discharge branches in GC curves. At this stage, we do not have a convincing explanation for such behavior.

The observed maximal capacitances of vanadium nitrides in our paper and in recent publication of Zhou et al.¹³ are lower than those reported previously by Choi et al.^{8,9} and can be related to a different composition of the surface layer. The amount of oxygen at the surface of vanadium nitride is likely to be an important parameter affecting the capacitance of the material. X-ray photoelectron spectroscopy was applied to probe the surface chemistry of vanadium nitride. The XPS technique is an effective tool to study the composition of a surface layer of materials (2–4 nm in depth). It allows one to determine the presence of elements at the surface, estimate their content quantitatively, and in some cases, study the depth profile of elemental composition at the surface of the samples.¹⁵ If a particular element exhibits different oxidation states, the XPS technique is capable of distinguishing between them. Great care, however, has to be exercised to determine the presence of vanadium in different oxidation states since the binding energies (BE) of V 2p³ line (which is normally used) for vanadium oxides with various oxidation states of vanadium (V_2O_5 , VO_2 , and V_2O_3 , corresponding to

Figure 9. XPS spectrum of the surface of VN.

V^{5+} , V^{4+} , and V^{3+}) are in a narrow range of about 515.5–517.5 eV.¹⁶ The situation is further complicated since a range of BE values is reported for each oxidation state of vanadium possibly because of equipment calibration differences and inaccuracy of the correction for sample charging.¹⁷

Bondarenka et al.¹⁷ have conducted a useful statistical analysis of XPS literature data on the binding energies of V 2p³ lines for vanadium in different oxidation states. The reported binding energies for V^{5+} , V^{4+} , and V^{3+} species were found to correspond to three Gaussian distributions centered at 517.3, 516.5, and 515.6 eV, respectively, with the statistical deviation $W_{\text{BE}} = 0.25$ eV. In other words, the reported binding energies for V^{5+} , V^{4+} , and V^{3+} species are in the ranges 517.3 ± 0.25 , 516.5 ± 0.25 , and 515.6 ± 0.25 eV with a probability of 70% and within the ranges 517.3 ± 0.5 , 516.5 ± 0.5 , and 515.6 ± 0.5 eV with a probability of 95%.¹⁷ A careful data analysis is therefore possible for the reliable qualitative separation of vanadium species in different oxidation states.

The XPS spectrum of VN passivated with 0.1% O_2 in Ar gas is shown in Figure 9. A clear O 1s line confirms that a thin oxide layer exists on the surface of VN. The oxygen signal is fitted with two peaks. The main component is centered at 530.3 eV and is typical for oxygen in a metal oxide. The second small peak is at about 531.8 eV and can be attributed to the signal from –OH groups chemisorbed at the surface. The BE of such a feature is typically 1.3–1.6 eV higher than that of an oxide in an XPS spectrum. The V 2p³ line was fitted with three peaks. The peak at 513.9 eV belongs to vanadium in the vanadium nitride structure. Two other features composing the V 2p³ line are centered at 515.0 and 517.2 eV and, most likely, correspond to V^{3+} and V^{5+} oxidation states of vanadium in surface oxides. The composition of the surface oxides is different from that in the previous study⁹ where the V 2p³ line was a combination of the nitride peak at 514.1 eV and the second feature centered at 516.3 eV. The latter is likely to be related to the V^{4+}

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oxidation state of vanadium. The value 516.3 eV fits well into the typical range of binding energies for V^{4+} (515.6 ± 0.5 eV¹⁷).

The passivation with an inert gas containing a small amount of O_2 (0.1–2%) is an established procedure for VN materials in the field of catalysis.^{10–12} Choi et al. used this approach (particularly, a gas mixture of 0.1% O_2 in Ar) for passivation of VN supercapacitors in ref 9. The same procedure is intentionally applied in this study to control the surface functionalities of vanadium nitrides. However, according to the XPS data and lower values of capacitances achieved, the composition of the surface layer of VN is different. The V^{5+} and V^{3+} states are dominant at the surface of nitride in the current study while V^{4+} is the most likely oxidation state observed for vanadium in the previous publication.⁹ The surface chemistry can be sensitive to a number of parameters such as the temperature of passivation, oxygen content in the gas, surface area, and pore structure of a nitride. Further research is needed to find reliable methods to control the surface composition of vanadium nitrides and, as a consequence, their capacitances. The prospective VN material for electrochemical capacitors should combine a fine-tuned nitride crystalline structure (for a good high-rate performance) and a fine-tuned composition of the surface oxygen-containing layer.

Conclusions

We have evaluated the structural characteristics and electrochemical properties of vanadium nitride synthesized by NH_3 reduction of a V_2O_5 powder for its

potential application in supercapacitors. VN material forms via a pseudomorphic process: its morphology mimics the shape of the initial V_2O_5 precursor, indicating the direct attachment of grains in the polycrystalline structure formed. Crystalline domains with texture (preferential grain orientation) are detected in VN; the [110] crystallographic direction tends to be parallel to the [010] direction in the initial precursor. A large volume of pores within a range of 15–110 nm is observed.

Vanadium nitride produced by NH_3 reduction of V_2O_5 has an acceptable rate capability in three aqueous electrolytes—1 M H_2SO_4 , 1 M KOH, and 3 M NaCl solutions. VN demonstrates about 80% of its maximal capacitance at the current rate of 1 A/g in galvanostatic charging/discharging experiments in all electrolytes. The negative effect of material loading on the value of capacitance of VN is suppressed: thick films of VN can retain high capacitances. The capacitance of 186 F/g is achieved at the rate of 1 A/g in 1 M KOH electrolyte. The values of capacitance are believed to be limited by the structure and composition of the surface oxide layer of vanadium nitride. The fine-tuning of both the crystalline structure of the nitride and the surface composition of the oxygen-containing layer is important for the creation of an efficient nanostructured VN material for supercapacitors.

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