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Preparation of Nanotextured VO_2[B] from Vanadium Oxide Aerogels

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Vanadium oxide aerogels were used as a precursor for preparing nanotextured VO_2[B] by low-temperature heat treatment under vacuum. The VO_2[B] material retains the fibrous morphology and high surface area of the aerogel. Evolution of the VO_2[B] phase, as studied by FTIR and X-ray diffraction, indicates that the local structure of the vanadium oxide aerogel is close to that of VO_2[B], in agreement with the bilayer-type structure previously proposed for vanadium oxide aerogels/xerogels. The electrochemical behavior of VO_2[B] also bears similarity to that of vanadium oxide aerogels. Specific capacities for lithium as high as 500 mA•h/g are obtained for nanocrystalline VO_2[B], and stable electrochemical response is obtained when cycled between 4 and 2.4 V vs Li^+/Li^0.

Introduction

One of the emerging directions in the search for electrode materials for use in high-performance lithium ion batteries is the identification of nanostructured materials.[1,2] This approach represents a significant departure from the more traditional investigations associated with micrometer-sized solids. Moreover, there are indications that the use of nanostructured materials may lead to advantages in both discharge rates and cycle life. Poizot et al. showed that the reduction at low voltage by lithium of MO transition metal oxides (M = Co, Ni, Cu, Fe) led to the formation of metal nanoparticles embedded in a Li_2O matrix.[2] The excellent reversibility of this reaction was attributed to in situ nanotexturation that was obtained during the first discharge. Subsequently, various binary and ternary transition metal oxides, sulfides, fluorides, and nitrides have been shown to exhibit similar conversion reactions and have been tested as anode materials for lithium cells.[3] Research on cathode materials is just beginning to re-examine the properties of nanotextured oxides.[4] Among the systems which have been investigated to date are vanadium oxides,[5] $Li_4Ti_5O_{12}$,[6] and anatase-type TiO_2.[7] For the latter, we showed that a decrease in crystallite size extends the solid solution domain and leads to improved reversibility because of better accommodation of the structural changes which occur upon lithium insertion/de-insertion. The use of V_2O_5 as a cathode material in secondary lithium batteries has been well-documented but the real starting point related to nanodimensional materials is the in situ formation of the ω-$Li_xV_2O_5$ phase reported by Delmas's group.[8] The reduction of α-V_2O_5 by lithium down to 1.5 V vs Li^+/Li^0 is characterized by a series of voltage plateaus linked to phase transitions that lead to a badly crystallized rock-salt-type ω-$Li_3V_2O_5$ phase. Upon subsequent cycles, this divided ω-$Li_xV_2O_5$ phase can be cycled between 1.5 and 3 V vs Li^+/Li^0 with good capacity retention. Related to this work has been an effort to prepare nanotextured vanadium oxide materials directly from "chimie douce" processes so as to avoid the electrochemical formation step during the first discharge. The use of the sol−gel method and careful control of the gel drying step (by supercritical drying[9,10] or freeze-drying[11]) has led to highly porous vanadium oxide aerogels with high surface areas (300 m^2/g). These materials exhibit large specific capacities for lithium of about 350 mA•h/g, above the values obtained for crystalline V_2O_5 or vanadium oxide xerogels.[8,12] By controlling the crystallite size of the vanadium oxide through heat treatments, it is possible to improve the electrochemical characteristics in terms of reversibility and rate capabilities.[11]

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(1) Tarascon, J.-M.; Armand, M. *Nature* **2003**, *414*, 359.

(2) Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J.-M. *Nature* **2000**, *407*, 496.

(3) Poizot, P.; Laruelle, S.; Grugeon, S.; Tarascon, J.-M. *J. Electrochem. Soc.* **2002**, *149*, A1212.

(4) Baudrin, E.; Sudant, G.; Cheng, W.; Dunn, B.; Tarascon, J.-M. *Proc.-Electrochem. Soc.* **2003**, *20*, 335.

(5) Sakamoto, J. S.; Dunn, B. *J. Electrochem. Soc.* **2002**, *149* (1), A26.

(6) Drago, D.; Kavan, L.; Drezen, T.; Crouzet, M.; Legagneur, V.; De Chambrier, E.; Exnar, I. 203rd ECS Meeting, Paris, May 2003, Abstract 219; Ohzuku, T.; Ueda, A.; Yamamoto, N. *J. Electrochem. Soc.* **1995**, *142*, 1431.

(7) Sudant, G.; Baudrin, E.; Larcher, D.; Tarascon, J.-M. *J. Mater. Chem.* **2005**, *15* (2), 1263.

(8) Delmas, C.; Cognac-Auradou, H.; Cocciantelli, J.-M.; Ménétrier, M.; Doumerc, J.-M. *Solid State Ionics* **1994**, *69* (3−4), 257.

(9) Le, D. B.; Passerini, S.; Guo, J.; Ressler, J.; Owens, B. B.; Smyrl, W. H. *J. Electrochem. Soc.* **1996**, *143*, 2099.

(10) Chaput, F.; Dunn, B.; Fuqua, P.; Salloux, K. *J. Non-Cryst. Solids* **1995**, *188*, 11.

(11) Sudant, G.; Baudrin, E.; Dunn, B.; Tarascon, J.-M. *J. Electrochem. Soc.* **2004**, *161*, A666.

(12) Tipton, A. L.; Passerini, S.; Owens, B. B.; Smyrl, W. H. *J. Electrochem. Soc.* **1996**, *143* (11), 3473.

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Although the reaction of lithium with these materials is now known to be unambiguously Faradaic, there are still intriguing questions related to their structure and reactivity.

The present paper represents an interesting direction for nanotextured materials, that of serving as a precursor for achieving other nanodimensional phases. Specifically, we use the high reactivity associated with the vanadium oxide aerogel texture to access a metastable phase, $VO_2[B]$, which can be difficult to obtain by traditional synthesis methods. The high specific capacity observed for the aerogel-prepared $VO_2[B]$, in excess of 500 mA•h/g, provides yet another example of how nanotextured materials exhibit enhanced electrochemical properties.

Experimental Section

Synthesis. The vanadium oxide aerogels were synthesized using the freeze-drying method.[11] The solvent-filled gels were prepared by the hydrolysis of the precursor, vanadyl triisopropoxide (VO(Oipr)$_3$), in a water/acetone solution. A typical gel composition consisted of 0.6 mL of alkoxide, 1.8 mL of water, and 3.75 mL of acetone, for a molar ratio of alkoxide/water/acetone $= 1/40/20$. To reduce the rate of hydrolysis, prior to mixing, both alkoxide and a water/acetone mixture were cooled separately in an ice bath for 15 min. After they were mixed vigorously for about 30 s, gel formation occurred within approximately 1 min. The wet gel was aged for 1 day at room temperature in a sealed tube. After the aging treatment, the sample was removed from the tube and washed once daily for the following 6 days and in anhydrous acetone for 3 days, followed by cyclohexane for another 3 days. For the freeze-drying treatment, the gel was cooled in liquid nitrogen and then put under primary vacuum to sublime the cyclohexane.[11] This route lead to a very porous material with a fibrous morphology and a high specific surface area. The $VO_2[B]$ phase was prepared by heating the freeze-dried vanadium oxide aerogel under primary vacuum (10^{-4} mbar) for 4 h at temperatures between 280 and 400 °C. Samples were typically heated at a rate of 5 °C/min up to the desired temperature.

Characterization. Powder X-ray diffraction (XRD) was used to characterize the development of the $VO_2[B]$ phase and its crystallite size for a series of samples heated to different temperatures under vacuum (labeled $VO_2[B]_{(T°C)}$). These patterns were obtained at room temperature using a Philips PW1710 diffractometer with Cu Kα ($\lambda = 1.54957$ Å) radiation with a specific sample holder that enabled us to avoid contact with ambient atmosphere. Infrared spectra for the same series of samples were recorded with a Nicolet FT-IR 510 spectrophotometer using the KBr pellet method. Specific surface areas of the different powders were evaluated using the Brunauer, Emmett, Teller (BET) multipoint method from results of N_2 physisorption at 77 K with a Micromeritics ASAP 2020 analyzer. Prior to these measurements, the samples were degassed for 2 h under flowing nitrogen at 110 °C, well below the temperature where aerogels crystallize. Although not shown here, thermogravimetric analysis (TGA) was used to determine the composition of the as-prepared aerogels.

The electrochemical measurements were made using Swagelok-type cells. The active materials were mixed with 20 wt % carbon (Ketjen black) without any binder added. The carbon and $VO_2[B]$ were mixed in cyclohexane for 1 night, after which the solvent was evaporated. The resulting $VO_2[B]$/C powder mixture was heated for 1 h at 220 °C to remove adsorbed water prior to cell assembly in an argon-filled glovebox. The electrochemical cell consisted of about 10 mg of the $VO_2[B]$/C powder mixture as the positive electrode which was separated from a lithium foil (counter electrode) by two sheets of fiberglass that were soaked in a $LiClO_4$ (1 M) propylene carbonate solution. Galvanostatic tests were conducted at constant temperature (25 °C) with a MacPile controller (Biologic S.A., Claix, France) at constant discharge rates ranging from 1 Li/20 h (noted C/20 in the paper) to 1 Li/6 h (C/6).

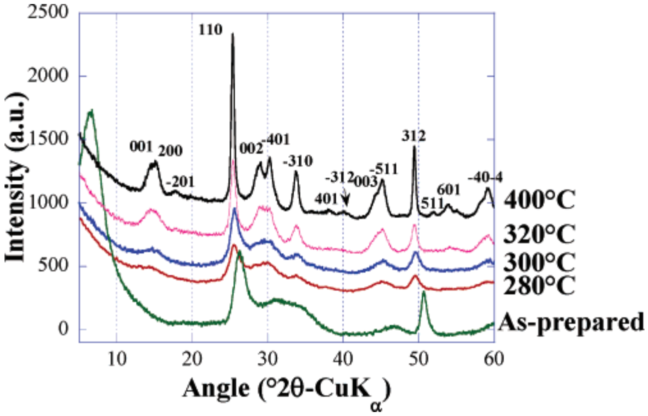

Figure 1. X-ray diffraction patterns for vanadium oxide aerogels heat-treated under vacuum at temperatures between 280 and 400 °C. The as-prepared vanadium oxide aerogel is shown for comparison.

Results and Discussion

Synthesis and Characterization of $VO_2[B]$. The synthesis of $VO_2[B]$ is based upon the reactivity of the vanadium oxide aerogels under vacuum. The precursor, vanadium oxide aerogel prepared by the freeze-drying process, possessed a surface area of nearly 300 m^2/g. From thermogravimetric experiments, we estimated the as-prepared aerogels to have the following composition: $V_{1.7}{}^{5+}V_{0.3}{}^{4+}O_{4.7}(OH)_{0.3}\cdot 1.55H_2O$ or $H_{0.3}V_2O_{4.85}\cdot 1.55H_2O$. This material contains about 15% V^{4+}. We showed previously[11] that heating the aerogel in air at temperatures higher than 250 °C for about 30 min leads to crystallization of the orthorhombic form of V_2O_5 and, by controlling the annealing temperature, it becomes a convenient process for preparing materials with controlled crystallite sizes. Here we performed heating experiments under vacuum between 280 and 400 °C. Upon heating of the aerogel to 280 °C for 4 h under a vacuum of 10^{-4} mbar, there are changes in the XRD pattern from that of the as-prepared aerogel (Figure 1). We observe the disappearance of the Bragg peak located at $2\theta = 6.52°$ simultaneously with a shift toward lower angles of all the other reflections. A small bump also appears around $2\theta = 15°$. When the temperature is further increased, the XRD reflections become sharper and the scan at 400 °C can be identified as $VO_2[B]$ (JCPDS 31-1438). This material is normally obtained by heating α-V_2O_5 under hydrogen between 210 and 400 °C.[13] It is significant to note that this method is not always straightforward and can lead to the formation of V_2O_3 if the temperature is too high. In comparison, the use of aerogel as the precursor leads easily to the $VO_2[B]$ phase with no evidence of V_2O_3.

We have noticed some reversibility of the transition between the $VO_2[B]$ phase and the vanadium oxide aerogel precursor. For the $VO_2[B]$ materials heated to either 280 or

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(13) Theobald, F. R.; Cabala, R.; Bernard, J. *J. Solid State Chem.* **1976**, *17*, 431.

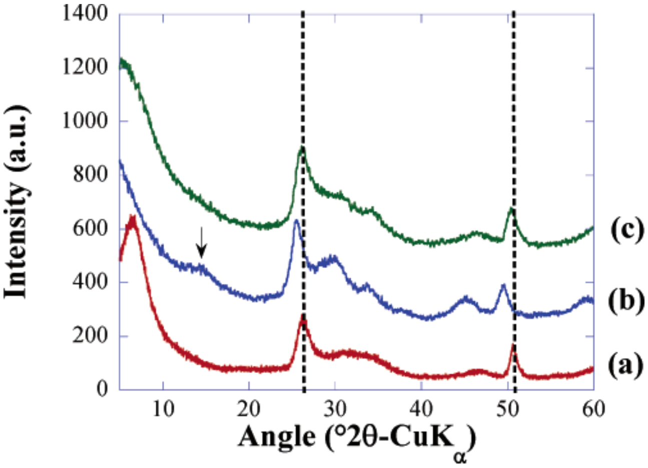

Figure 2. X-ray diffraction patterns comparing (a) the freeze-dried vanadium oxide aerogel, (b) a sample heated under vacuum at 280 °C (the arrow indicates the 001 and 200 broad reflections of VO_2[B]), and (c) the same sample after equilibration in air at room temperature.

Table 1. Variation in BET Specific Surface Area and Crystallite Size for VO_2[B] Heated to Different Temperatures

samples	specific surface area (m^2/g)	crystallite size [110] (nm)	crystallite size [312] (nm)
$VO_2[B]_{(280°C)}$	185	6.1	7.6
$VO_2[B]_{(300°C)}$	170	7.1	7.8
$VO_2[B]_{(320°C)}$	155	11.2	11.7
$VO_2[B]_{(400°C)}$	122	19.9	25.5

320 °C, if they are exposed to ambient atmosphere conditions for 24 h, the XRD pattern for the aerogel is recovered, although the peaks are shifted slightly to higher angles (Figure 2). However, the VO_2[B] transformation is irreversible for samples heated above 400 °C.

The use of different heat treatment conditions leads to VO_2[B] samples with different textures. The BET surface area decreases by about one-third, from 185 to 122 m^2/g, when the annealing temperature increases from 280 to 400 °C (Table 1). Use of the Scherrer method[14] enables us to determine the crystallite size for the VO_2[B] from the (110) and (312) planes at $2\theta = 25.34°$ and 49.40°, respectively. We find that the crystallite size increases from about 6 to 20 nm over this same temperature range. The fact that the crystallite size for the two directions is comparable indicates that crystallite growth is nominally isotropic. Interestingly, we find that the texture of the VO_2[B] phase prepared from the aerogel consists of a three-dimensional network of filaments of about 50 nm thickness (Figure 3). The fact that the fibrous morphology of the vanadium oxide aerogel is retained suggests that the VO_2[B] is formed by a topotactic reaction. Furthermore, even for the samples prepared at 400 °C, these filaments are polycrystalline as the crystallite sizes remain lower than the particle size, consistent with HRTEM images (not shown here).

FTIR has been used to characterize the local environment of vanadium and the changes which occur upon heat treatment. The results shown in Figure 4 include aerogel and α-V_2O_5 spectra for comparison. The band situated at 1004 cm^{-1} for all the VO_2[B] samples can be attributed to the vanadyl ν-(V=O) vibration. The shift in this band compared to that for α-V_2O_5 (1025 cm^{-1}) is consistent with the reduced state of vanadium in VO_2[B]. The vibrational bands observed at 530 cm^{-1} and in the 720−850 cm^{-1} region can be attributed to δ-(V−O−V) and ν-(V−O), respectively, as reported for vanadium pentoxide.[15] In general, the relatively smooth progression in vibrational spectra, from the aerogel to VO_2[B], suggests that structurally the aerogel is closer to VO_2[B] than α-V_2O_5. One feature in the VO_2[B] spectra which has yet to be identified is the band that grows in at around 900 cm^{-1}.

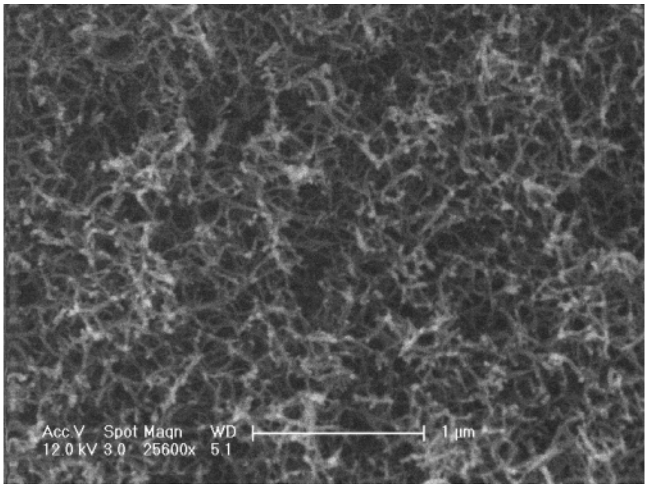

Figure 3. SEM image of the VO_2[B] material prepared by heat treating the vanadium oxide aerogel precursor at 300 °C under vacuum.

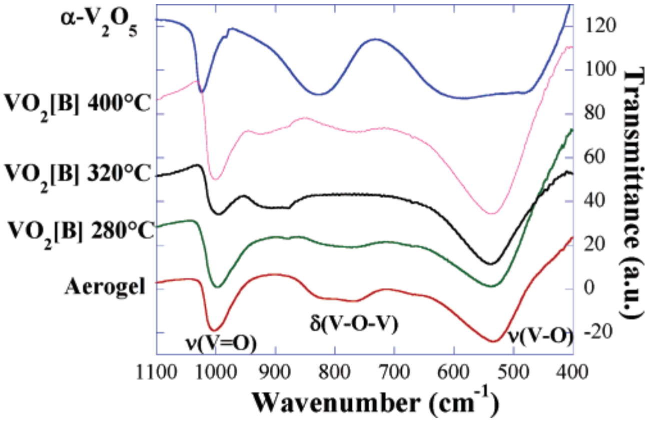

Figure 4. FTIR spectra for the VO_2[B] materials prepared from vanadium oxide aerogels. The spectra for the as-prepared aerogel and α-V_2O_5 are included for comparison.

Electrochemical Properties. Our electrochemical studies were directed at determining the effect of crystallite size on lithium capacity and understanding the relationship between the precursor aerogel and the resulting VO_2[B] phase. One series of experiments involved characterizing the voltage−capacity behavior for the various VO_2[B] materials. The results shown in Figure 5 were obtained under galvanostatic conditions at a C/20 rate. The vanadium oxide aerogel (Figure 5a) exhibits a relatively smooth characteristic with only a pseudo-plateau at 2.5 V vs Li^+/Li^0 in reduction. The lithium capacity of about 400 mA·h/g is analogous to what we reported previously.[11] Among the different VO_2[B]

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[14] Scherrer, P. *Nachr. Gotting. Ges.* **1918**, *2*, 98.

[15] Claws, P.; Broeckx, J.; Vennik, J. *Phys. Status Solidi B* **1985**, *131*, 459.

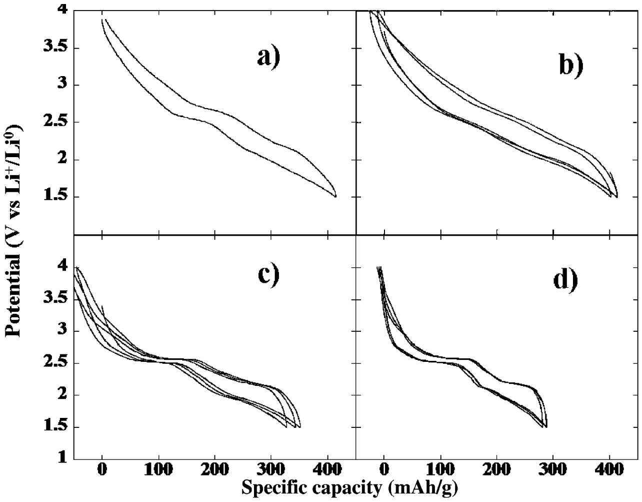

Figure 5. Voltage vs capacity curves comparing (a) the vanadium oxide aerogel with the VO_2[B] materials prepared by vacuum heating to (b) 280 °C, (c) 320 °C, and (d) 400 °C. Measurements were made galvanostatically at the C/20 rate.

samples, the least crystalline material (heated to 280 °C, Figure 5b) has approximately the same capacity as that of the aerogel, although the voltage profile is essentially featureless, without any plateau regions. Higher heat treatment temperatures lead to the appearance of two well-defined features at 2.5 and 2.1 V vs Li^+/Li^0 which are especially noticeable in the material heated to 400 °C (Figure 5d). These results are consistent with those reported by Zachau-Christiansen et al.[16] We have noticed that, for the materials prepared at 280 and 320 °C, the capacity observed on the first oxidation is higher than that of the first reduction. We observed a similar response for the α-V_2O_5 materials[11] and, based on that work, we can attribute this behavior to the incomplete transformation from the aerogel to VO_2[B] phase and the presence of residual protons.

The derivative of the voltage−capacity curves shows that the electrochemical properties for the as-prepared aerogels and the VO_2[B] phase are actually quite similar. The two redox couples observed in the vanadium oxide aerogels are also present, at the same potentials, in the VO_2[B] material prepared at 400 °C (compare Figures 6a and 6b). However, the α-V_2O_5 phase prepared by heating the aerogel in air is quite different (Figure 6c). On reduction, four peaks are observed in this material, none of which occur at 2.5 V vs Li^+/Li^0. Whereas the FTIR results underscored the similarities in local structure between vanadium oxide aerogels and the VO_2[B] phase, the results shown in Figure 6 indicate that there is considerable similarity in the electrochemical behavior for these two different materials.

We also investigated the cycling behavior for two of the VO_2[B] materials (280 and 400 °C). These experiments were carried out at a specific current of 50 mA/g, which corresponds to a discharge rate of 1 Li/6 h. The results are shown in Figure 7. When these materials are cycled between 4 and 1.5 V vs Li^+/Li^0, the nanodimensional VO_2[B] phase (heated to 280 °C) exhibits a rather high capacity for lithium; after 10 cycles, the specific capacity is in the range of 500 mA·h/g. The material heated to 400 °C also exhibits good capacity on cycling, in excess of 350 mA·h/g. The ability of nanocrystalline materials to display higher capacities for lithium as compared to traditional micrometer-sized materials has been noted with various material systems. Unfortunately,

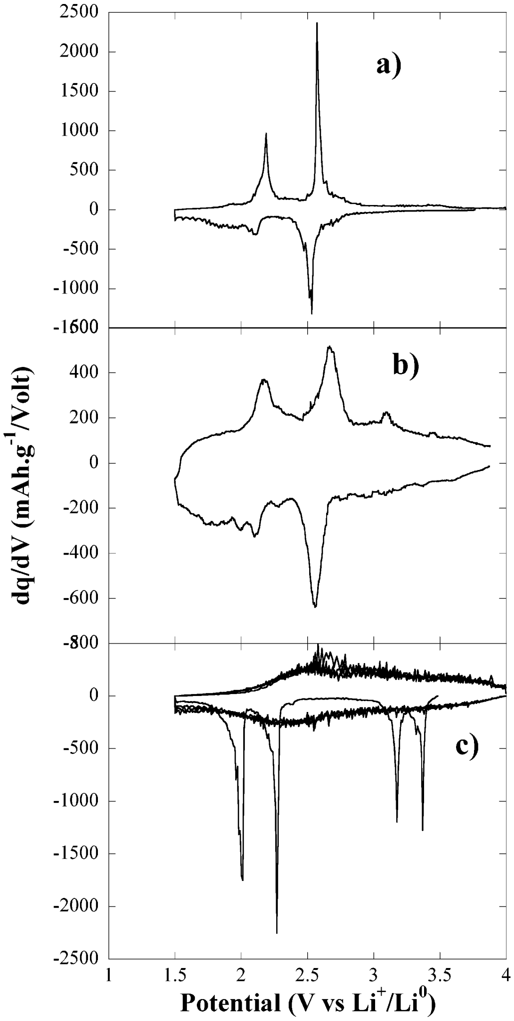

Figure 6. Comparison of the derivative of the voltage vs capacity curves for (a) VO_2[B] prepared at 400 °C, (b) vanadium oxide aerogel, and (c) α-V_2O_5.

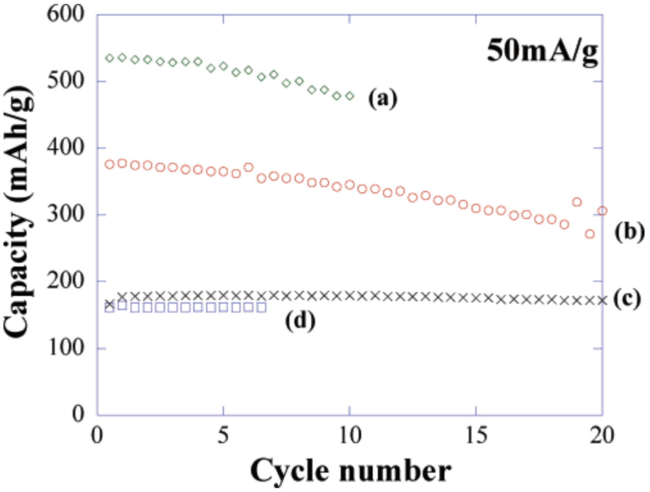

Figure 7. Electrochemical cycling behavior for VO_2[B] materials vacuum-heated to 280 °C (curves a and c) and 400 °C (curves b and d). The voltage range for (a) and (b) is 4 to 1.5 V; the voltage range for (c) and (d) is 4 to 2.4 V.

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(16) Zachau-Chistiansen, B.; West, K.; Jacobsen, T.; Skaarup, S. *Solid State Ionics* **1992**, *53*−*56*, 364.

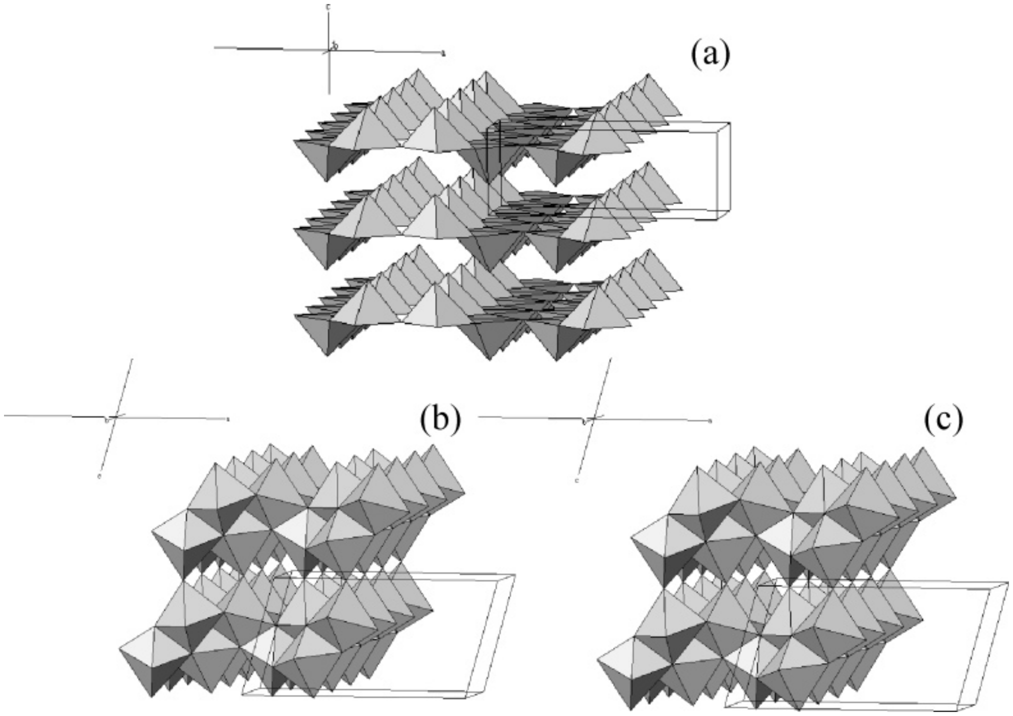

Figure 8. Structures of (a) V_2O_5, (b) $V_2O_5 \cdot nH_2O$, and (c) VO_2[B].

these nanotextured materials also exhibit a significant capacity loss, consistent with the dissolution of vanadium which occurs at low voltage.[11] By cycling between 4 and 2.4 V, however, it is possible to have good capacity retention as shown by both materials in Figure 7 (curves c and d). The stable response of 175 mA·h/g for the first 20 cycles corresponds to reversible insertion of 0.5 lithium ion per vanadium atom.

Discussion

Although the ability of vanadium oxide aerogels to serve as a precursor material for nanodimensional VO_2[B] has been established, our understanding of how this transformation occurs is incomplete. There is a lack of structural details for the vanadium oxide aerogels as the XRD shows the material to be poorly crystallized. In contrast, V_2O_5 xerogels have received considerably more study[17] and various structural models have been proposed. It is tempting to assume that the vanadium oxide xerogels and aerogels possess comparable structures. After all, both are formed through similar hydrolysis/condensation processes, the most significant difference being in how the solvent phase is removed at low temperature. Moreover, V_2O_5 xerogels have also shown the ability to transform to the VO_2[B] phase, albeit by heat treatment in a hydrogen-containing atmosphere.[18] Thus, while the aerogel is more reactive than the corresponding xerogel and differs in terms of morphology and surface area, in the discussion below we assume that the fundamental oxide framework for the two materials is similar. In this way, we are able to understand the relationship between the precursor and the resulting VO_2[B] phase.

Two different structural models for vanadium oxide xerogels have emerged. The model proposed by Livage et al.[17] is based on corrugated single layers of VO_5 units, similar to those encountered in crystalline V_2O_5 (Figure 8a). The model from Oka et al.[19] is based on the presence of double-layer structures similar to the $[V_2O_5]_n$ bilayers found in δ-$Ag_xV_2O_5$.[20,21] Polarized X-ray absorption spectroscopy experiments[22] and DFT calculations[23] are consistent with this second model. In the xerogel, the water molecules are accommodated between these bilayers, leading to a 11.5 Å interlayer distance (Figure 8b). In the present work, we have shown that vacuum annealing at a temperature as low as 280 °C led to the synthesis of the VO_2[B] phase. Such low temperature and the observed reversibility indicate that the energy required to induce the transformation is relatively small and thus there should be a close relationship between the aerogel framework and the VO_2[B] structure. It is not surprising then that the structure of VO_2[B] can be described by bilayers formed from edge-sharing VO_6 octahedra, similar to the bilayer model proposed by Oka and co-workers.[19] The 3D structure is obtained by simply bridging oxygen atoms between these layers (Figure 8c). When the reaction occurs below 400 °C, only a few fragile linking bonds can be established and thus the materials can be rehydrated and oxidized to form aerogel-like solids. In a comparison of Figures 8b and 8c, it is evident that the phases are structurally related and the formation of VO_2[B] could simply result from the condensation of the bilayers during the dehydration process. This mechanism parallels the work described by

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(17) Livage, J. *Chem. Mater.* **1991**, *3*, 578.
(18) Soudan, P.; Pereira-Ramos, J.-P.; Farcy, J.; Grégoire, G.; Baffier, N. *Solid State Ionics* **2000**, *135*, 291.
(19) Yao, T.; Oka, Y.; Yamamoto, N. *Mater. Res. Bull*. **1992**, *116*, 279.
(20) Galy, J. *J. Solid State Chem.* **1992**, *100*, 229.
(21) Andersson, S. *Acta Chem. Scand.* **1965**, *19*, 1371.
(22) Giorgetti, M.; Passerini, S.; Smyrl, W. H.; Berrettoni, M. *Inorg. Chem.* **2000**, *39*, 1514.
(23) Petkov, V.; Trikalitis, P. N.; Bozin, E. S.; Billinge, S. J. L.; Vogt, T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *124*, 10157.

Tournoux et al. on the preparation of TiO_2[B],[24] which is isostructural to VO_2[B]. The TiO_2[B] phase is prepared from the dehydration of $Ti_4O_7(OH)_2$ at 500 °C. In that case, the transformation is reconstructive and consists of an oriented daughter/mother nucleation based on common structural building blocks. For the vanadium phases described in this paper, we can propose a similar process for the transformation of $H_{0.3.}V_2O_{4.85}\cdot 1.55\ H_2O$ to VO_2[B] through both dehydration and reduction of the nanostructured aerogels. The similar electrochemical properties exhibited by the derivative of the galvanostatic measurements (Figure 6) support the contention that the vanadium oxide aerogel and the VO_2[B] phase offer closely related structural environments.

Conclusions

We have shown that the reactivity of nanostructured vanadium oxide aerogels enables these materials to serve as a precursor for VO_2[B] by low-temperature vacuum annealing. The nature of the heat treatment leads to materials with different crystallite sizes and we have investigated how their electrochemical properties vary accordingly. Nanodimensional VO_2[B] materials exhibited specific capacities for lithium in excess of 500 mA·h/g, and although these materials are susceptible to capacity fade, stable performance at 175 mA·h/g is obtained by cycling between 4 and 2.4 V (vs lithium). The good reversibility shown here demonstrates the promise of using nanodimensional electrode materials provided their side reactions are avoided. The electrochemical results also indicate that the vanadium oxide aerogels are more similar to the VO_2[B] phase than α-V_2O_5, a result which is also reached from characterizing the infrared spectra and comparisons with the local structure of V_2O_5 xerogels.

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(24) Tournoux, M.; Marchand, R.; Brohan, L. *Prog. Solid State Chem.* **1986**, *17*, 33.