Synthesis and characterization of a new vanadium oxide, $TMAV_8O_{20}$

Thomas Chirayil, Peter Y. Zavalij and M. Stanley Whittingham†

Chemistry Department and Materials Research Center, State University of New York at Binghamton, Binghamton, NY 13902–6000, USA

Hydrothermal synthesis of $V_2O_5 + TMA + LiOH$ in a 1 : 2 : 1 molar ratio after adjusting the pH with acetic acid to pH 3.3 resulted in the formation of a new vanadium oxide, $TMAV_8O_{20}$. The new vanadium oxide has a monoclinic structure with space group $C2/m$ and lattice parameters: $a = 23.655(2)$, $b = 3.5931(3)$, $c = 6.3175(5)$ Å and $\beta = 103.060(4)$°. $TMAV_8O_{20}$ has a layered structure with the vanadium atom in the octahedral sites and tetramethylammonium ions residing in between the vanadium layers.

The hydrothermal technique has been shown to be a very rich method in the synthesis of many vanadium oxides.[1–15] This low temperature synthesis method is actively pursued in order to form new layered vanadium oxides. Intense research is currently being applied to these newly formed vanadium oxides to test their behavior as potential cathodes in lithium secondary batteries.[16] Previously, we have reported how the pH can affect the formation of different types of vanadium oxides.[14] Lowering the pH of the reaction medium with acetic acid is beneficial in that it also behaves as a buffer. The change in pH of the reaction medium before and after hydrothermal synthesis is minimal when using this acid. In our research, this is not the case when a mineral acid is used instead of acetic acid.

Here we report a new compound we synthesized hydrothermally‡ in a controlled pH acidic medium with acetic acid at pH 3.3. This is a layered vanadium oxide with a new monoclinic structure in which the tetramethylammonium ions reside between the vanadium oxide layers. An electron microscope image, Fig. 1, showed long thin ‘fettuccini’ type crystals that have a tendency to lie flat. These crystals can be anywhere from 15 to 50 µm long but only *ca.* 1 µm wide. Their density, measured pycnometrically, was found to be 2.54 g cm^{-3}. The thermogravimetric analysis (Perkin-Elmer Model TGA 7), Fig. 2, of this new vanadium compound under oxygen indicates a mass loss of *ca.* 10.8% at 350 °C. The mass change is characteristic of loss of the TMA. The product after the thermal treatment was orange and an X-ray pattern confirmed that it was pure V_2O_5. This indicated that no lithium was present in the initial compound. From the TG and the X-ray data, the general formula of the compound can be designated as $TMA_{1.2}V_8O_{20}$; however, the presence of some strongly bound water cannot be ruled out, giving the formula $TMA_{1.2-\delta}V_8O_{20} \cdot 5\delta H_2O$ with the same mass loss. The removal of TMA by thermal treatment under N_2 resulted in collapse of the structure and the formation of a reduced vanadium oxide.

The FTIR spectrum supports the presence of the TMA ion with the three characteristic bands at 1483, 1383 and 949 cm^{-1}.[17] The other four major bands at 996, 924, 776 and 533 cm^{-1} belong to the different types of V—O bonds. The band at 996 cm^{-1} is characteristic of the V=O bond. The band at 924 cm^{-1} may be associated with the corner-sharing V=O—. The band at 776 cm^{-1} is due to the oxygens between

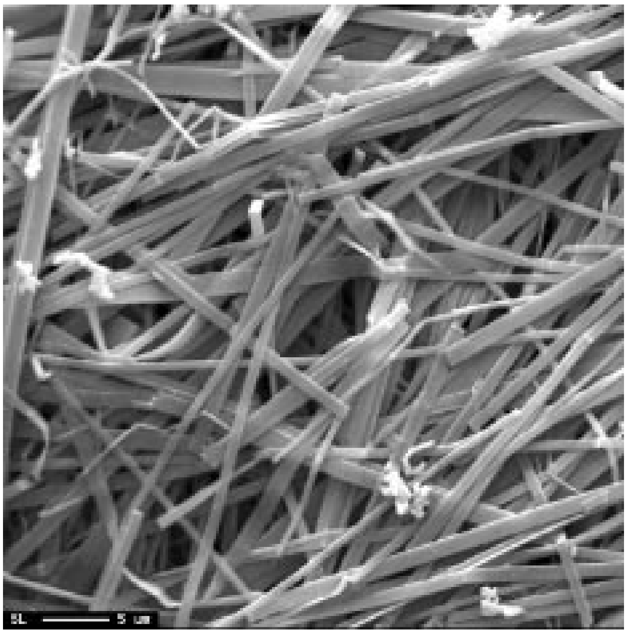

Fig. 1 Electron microscope image of $TMAV_8O_{20}$ microcrystallites, using a JEOL 8900 instrument

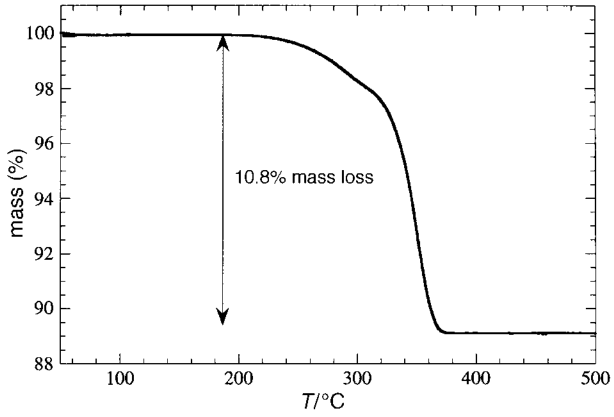

Fig. 2 TG trace of the new vanadium oxide under oxygen. Heating the compound to 500 °C at 3 °C min^{-1} shows a 10.8% mass loss at 350 °C due to TMA loss.

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† E-mail: stanwhit@binghamton.edu

‡ *Experimental procedure:* V_2O_5 powder (1.25 g; Alfa) was mixed with tetramethylammonium (TMA) hydroxide (5 g; Alfa) and LiOH (Fisher Scientific) in a 1 : 2 : 1 molar ratio, then acidified to pH 3.3 with 3 M acetic acid (Fisher). About 80 ml of this reaction mixture was placed in a 125 ml Parr bomb, sealed, and reacted hydrothermally for 3 days at 185 °C under autogeneous pressure. The resulting green powder was filtered, washed with water, and dried.

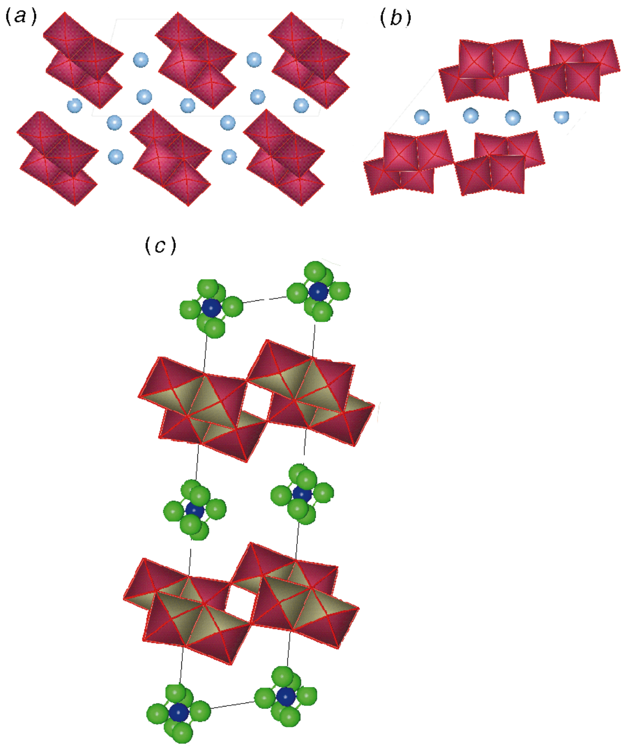

Fig. 3 The structure of (*a*) β-$Ag_4V_4O_{12}$, (*b*) $Ag_2V_4O_{11}$, and (*c*) $TMAV_8O_{20}$. The building block in all three structures consists of a quadruple unit. In (*a*) these units are not joined together, whereas in (*b*) they share one corner leading to a layered structure, and in (*c*) they share two corners.

two vanadium atoms and the other at 533 cm^{-1} is due to the oxygens in chain positions between three vanadiums.[18,19]

The powder X-ray diffraction pattern[§] indicated that this new vanadium oxide has an interlayer spacing of 11.5 Å. The pattern could be indexed with a monoclinic symmetry and space group *C*2/*m*. The TMA cations are located between the V_8O_{20} vanadium oxide layers. Initially, it was assumed that the TMA cation could not fit into the unit cell we had indexed. The TMA ion is *ca.* 7 Å in diameter and it seemed that the unit cell length, 3.593 Å, along the *b* direction was too small for the TMA ion, but the TG pattern showed the definite presence of TMA. After solving the structure, we found that the TMA ions are situated in the layers in a disordered fashion around the 000 site. The inorganic framework of this compound can be viewed with the vanadium atom coordinated by six oxygens forming an octahedron, [Fig. 3(*a*)]. The building block of the framework consists of a quadruple unit, of composition V_4O_{12}, first reported in the structure of β-$Ag_4V_4O_{12}$.[20] The quadruple unit consists of four octahedra joined together by sharing edges. A layered structure with this type of building block but sharing one corner with an adjacent V_4O_{12} block [Fig. 3(b)], was seen in $Cu_xV_4O_{11}$[21] and $Ag_2V_4O_{11}$.[22] Galy and coworkers[20] hypothesized that a structure with the V_4O_{12} quadruple unit sharing two corners ought to exist and $TMAV_8O_{20}$ is the first experimental report of the quadruple unit sharing two corners [Fig. 3(*c*)]. Even though the structure can be described as being built from VO_6 octahedra, these octahedra are highly distorted as is common with vanadium, with short V—O bonds of length 1.56 and 1.5 Å and long V—O bonds of 2.31 and 2.33 Å.

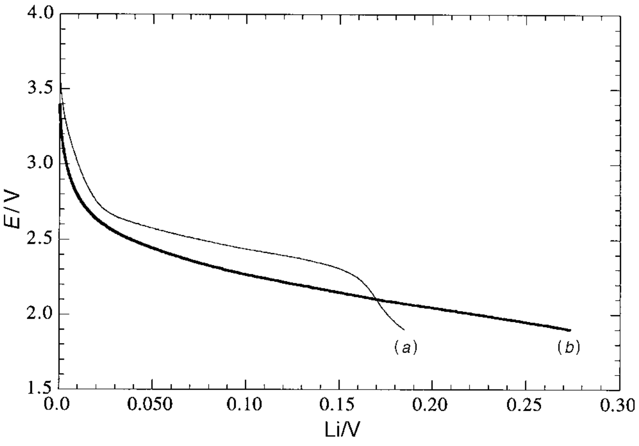

Fig. 4 Electrochemical behavior of $TMAV_8O_{20}$: (*a*) the first discharge of the pure compound, and (*b*) discharge after the TMA was driven off by thermal treatment under nitrogen.

Initial electrochemical studies[¶] on this compound indicate that Li insertion is hindered due to the TMA ions between the layers. The electrochemical reduction at 0.1 mA of pure $TMAV_8O_{20}$ and after the removal of the organic cation is shown in Fig. 4. The Li/$TMAV_8O_{20}$ cell has an initial emf of 3.7 V. The first discharge cycle of $TMAV_8O_{20}$ shows an uptake of 0.19Li V above a cut-off of 1.9 V. After removal of the TMA under N_2, which leads to an overall composition of $VO_{1.6}$ the capacity increases slightly to 0.27Li/V. This result is consistent with other reports[7] that the presence of an organic cation between the vanadium layers limits lithium uptake.

Initial magnetic susceptibility results indicate Curie–Weiss behavior with an anomaly at 10 K. The fitting of the $\chi^{-1} = f(T)$ curve allows us to determine $C = 1.18$ emu K $mole^{-1}$ and $\theta = 145$ K. A more complete study and comparison of the magnetic properties of these layered vanadates will be presented elsewhere.[23]

In conclusion, $TMAV_8O_{20}$ is one of several vanadium oxides we have synthesized hydrothermally by using the tetramethylammonium ion. This new vanadium oxide has a monoclinic symmetry with vanadium double layers that can be viewed as being built from distorted octahedra. The TMA ions that reside between the layers are disordered, as noted in the related compound, $TMA_xFe_yV_2O_5$.[15] The electrochemical behavior of this compound does not seem promising due to the presence of organic cations. Work is currently underway to attempt to ion exchange the TMA ion that might increase its electrochemical behavior.

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[§] *Crystal data* for $TMAV_8O_{20}$: monoclinic, space group *C*2/*m*, $a = 23.655(2)$, $b = 3.5931(3)$, $c = 6.3175(5)$, $\beta = 103.060(4)°$, $V = 523.05(8)$ Å^3, $Z = 1$, $M_w = 814.56$, $D_c = 2.586$ g cm^{-3}. The powder data were collected from 7 to 73° 2θ with 0.03° 2θ steps and 50 s per point using Cu-Kα radiation on a Scintag θ–θ diffractometer. The total number of reflections in the range 7–66° 2θ was 127; the first reflection at 7.6° 2θ was excluded from the final refinement owing to its high intensity. The profile fitting program from the crystallographic programs package CSD[24] was used to obtain 97 integrated intensities. The integrated intensities were used in the direct method to solve the structure with the CSD program. The final refinement using the GSAS program, converged with $R(F^2) = 0.068$ and R(profile) = 0.067. CCDC reference no. 1145/53.

[¶] *Electrochemical studies:* The cathode was prepared by mixing 80% vanadium oxide with 10% carbon black and 10% Teflon binder, then hot pressing at 200 °C onto a stainless-steel Exmet grid. The cathode was then wrapped in Celgard™ followed by a sheet of lithium foil, which served as anode and reference. The electrolyte was a solution of $LiAsF_6$ in 1 : 1 propylene carbonate (PC): 1,2-dimethoxyethane (DME). A Biologic potentiostat was used to cycle the cells in a helium-filled glove box.

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