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Symmetric Aqueous Rechargeable Lithium Battery Using $\text{Na}_{1.16}\text{V}_3\text{O}_8$ Nanobelts Electrodes for Safe High Volume Energy Storage Applications

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Synthesis of bundled, single crystalline $\text{Na}_{1.16}\text{V}_3\text{O}_8$ nanobelts is done by a simple and novel cost-effective low-temperature hydrothermal method and further annealed at different temperatures. These nanobelts are applied as both cathode and anode material for aqueous rechargeable lithium ion battery. The morphologies and structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ nanobelts are studied via field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. The nanobelts are observed to have a large aspect ratio, with a diameter of $75(\pm 5)\text{nm}$ and an average length of $\sim 5\text{ }\mu\text{m}$. Electrochemical behavior of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ nanobelts were studied via cyclic voltammetry (CV) and galvanostatic studies. Systematic, comparative studies for $\text{Na}_{1.16}\text{V}_3\text{O}_8$ annealed at various temperatures showed a good reversible initial discharge capacity values, with a maximum of high-temperature-annealed symmetric $\text{Na}_{1.16}\text{V}_3\text{O}_8$ cell has an initial discharge capacity of $\sim 152.42\text{ mAhg}^{-1}$ and $>75\%$ retention of initial capacity over 100 charge/discharge cycles exhibiting excellent cyclic stability and rate performance at a current density of 5000 mA g^{-1} . The pseudocapacitive surface charging in $\text{Na}_{1.16}\text{V}_3\text{O}_8$ nanobelts which facilitate low energy Li^+ pathways from surface to the subsurface V_3O_8^- interlayer sites could be the main reason for its high rate performance capabilities observed.

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Global concerns over depleting fossil fuels and increase in global warming has resulted in extensive research in the area of renewable energy and, indisputably, energy storage plays a vital role in the conversion of energy obtained from renewable resources to energy grid.¹⁻⁷ One such energy storage system is the rechargeable battery, which plays a vital role in portable electronics such as computers, mobile phones and hybrid electric vehicles (HEVs). Existing rechargeable battery technologies include lead-acid, nickel-cadmium, nickel-metal hydride (Ni-MH) and lithium-ion batteries (LIBs). Most of these batteries have intrinsic problems:⁸⁻¹² for example, lead acid and nickel cadmium systems suffer from low energy density and environmental concerns owing to the use of toxic materials like lead and cadmium, while Ni-MH batteries have large self-discharge and LIBs have high safety risks due to the combustible nature of organic electrolytes and the vigorous reaction that electrode material has with the organic electrolyte during overcharging or short-circuiting. As a result, manufacturing of LIBs requires sophisticated cell assembly technologies: the importance of having a dry, air-tight environment to prevent premature oxidation / hydroxylation of lithium (Li) ions lead to the high cost of LIBs in general.¹³⁻¹⁶ Moreover, large-scale energy storage technologies lead to considerable concern regarding safety and toxicity, alongside electrochemical issues related to loss of energy density and efficiency. Four aircrafts from Boeing 787 dreamliner had electrical problems arising from its lithium ion battery. Thus, there is an pressing need for the development of a safe, low-cost, high-power LIBs for large scale applications like electric vehicles (EVs), aircrafts and renewable energy storage.

One such promising alternative is aqueous rechargeable lithium ion batteries (ARLB),¹⁷⁻²² first reported by Dahn and co-workers in 1994, which potentially could address both the safety problems of LIB and the low energy/power density and cycle life associated with commercialized aqueous based lead-acid and nickel-metal-hydride batteries. A voltage vs. capacity plot of potential cathode and anode materials that have been studied for ARLB are shown in Fig. 1. As can be seen, hydrogen and oxygen evolution is a critical factor in ARLB. Li et al have shown a full ARLB cell made up of LiMn_2O_4 as cathode and $\text{VO}_2(\text{B})$ as anode in an aqueous electrolyte of LiNO_3 with a capacity of $\sim 100\text{ mAh g}^{-1}$ and a cell potential of 1.5 V .²³ However, several critical challenges need to be addressed for successful practical realization of ARLB which includes optimization of the right anode/cathode/electrolyte material combination that can deliver high energy/power density and excellent cycleability.

The remarkable structural flexibility, high discharge capacity, abundance and low cost of vanadium oxides amongst the numerous transition metal oxides have spurred immense interest amongst the research community to explore the possibility of using this vanadium oxides and its derivatives for large scale grid storage-application.²⁴⁻²⁸

Studies on lithiated vanadium oxide materials show the instability of $\text{Li}_x\text{V}_2\text{O}_5$ upon electrochemical cycling. Fully-lithiated $\text{Li}_3\text{V}_2\text{O}_5$ exhibits rock-salt structure and the lithium insertion/ de-insertion process results in multiple redox reactions resulting in crystal structural collapse, eventually leading to amorphization and capacity loss upon further cycling.²⁹⁻³² Layered LiV_3O_8 structure comprises of VO_6 octahedra and VO_5 tetrahedra held together by lithium ions situated at the interlayer octahedral sites that are immobile and cannot participate in intercalation / deintercalation processes. Lithium ions in the tetrahedral sites can enable insertion of two Li ions contributing to a high specific capacity of $\sim 200\text{ mAh g}^{-1}$. Recent studies on LiV_3O_8 shows poor cycling behavior of this material in aqueous electrolyte attributed to crystal structure collapse and vanadium dissolution.³³ One way to alleviate this issue is to replace Li ions in LiV_3O_8 with sodium (Na) ions giving rise to sodium vanadate ($\text{Na}_{1.16}\text{V}_3\text{O}_8$, NVO) structure. Recent studies on lithium ion organic electrolytes based batteries (LIB) on NaV_3O_8 showed that this structure is more resilient to lithium intercalation/deintercalation with decreased vanadium dissolution than LiV_3O_8 .³⁴⁻³⁶

As such, solid state synthesis of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ using V_2O_5 and Na_2CO_3 has been previously reported by M. Onoda³⁷ while the effect on crystallinity of $\text{Na}_{1+x}\text{V}_3\text{O}_8$ during the electrochemical lithium insertion / deinsertion processes has been studied by Kawakita et al.³⁵ Wang et al.³⁸ has studied the use of $\text{Na}_2\text{V}_6\text{O}_{16}$ nanowire for LIBs, which gave a initial specific discharge capacity of 268 mAh g^{-1} and improved cycling stability upon heat-treatment of the compound. According Wang et al, $\text{Na}_2\text{V}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$ shows a different crystal structure from NaV_3O_8 , thereby different electrochemical performance.^{35,36} However, based on our knowledge there are no reported studies on the electrochemical performance of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (NVO) nanobelts as electrodes for aqueous rechargeable lithium ion batteries. In this work, electrochemical performance of the $\text{Na}_{1.16}\text{V}_3\text{O}_8$ nanobelts synthesized by hydrothermal method is studied in aqueous rechargeable lithium batteries (ARLB). Considering the wide operating potential window for $\text{Na}_{1.16}\text{V}_3\text{O}_8$ in aqueous electrolyte, we report for the first time its applicability as both cathode and anode material, thereby resulting in a symmetric (NVO/NVO) aqueous rechargeable lithium ion battery (ARLB) with excellent cycling stability and rate capabilities.

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Figure 1. Voltage vs capacity for cathode and anode materials presently used or under serious consideration for next generation of aqueous rechargeable lithium-ion batteries.

Experimental

Synthesis and characterization of $\text{Na}_{1.16}\text{V}_3\text{O}_8$.— Analytically-pure vanadium pentoxide (V_2O_5 , 98%, Sigma Aldrich) and sodium hydroxide (NaOH , Sigma Aldrich) was used as received. 0.01 moles NaOH was mixed with 0.01 moles of V_2O_5 in deionized (DI) water and stirred overnight to obtain an orange brown solution which was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 180°C for 48 h. Resulting precipitate mixture was filtered, washed, and dried at 80°C for 4 h to obtain the as-synthesized $\text{Na}_{1.16}\text{V}_3\text{O}_8$ powder (NVO). To study the effect of heat-treatment on the structural and electrochemical properties of NVO, further heat-treatment was carried out for 2 h at 200°C , 300°C and 400°C and the respective samples are denoted as NVO-200, NVO-300 and NVO-400 respectively.

Morphological studies were conducted using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6340F) at an accelerating voltage of 5 kV and transmission electron microscopy (TEM, JEOL 2100F) at an accelerating voltage of 200 kV. Phase purity and crystal structure of NVOs were examined by a Bruker X-ray diffractometer D8 Powder ($\text{Cu-K}\alpha$ radiation, with step scanning (0.01° , 0.6s dwell time, 40 kV). The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld phase analysis within the Topas V3 (Bruker-AXS), using fundamental parameters approach. Thermal gravimetric (TG) analysis was done using TA-TGA Q500 instrument under N_2 atmosphere.

Electrochemical measurements.— Electrodes were prepared by mixing the active material, binder (Kynar 2801), and Super P Li carbon (Timcal) in the weight ratio of 75:15:10, using 1-methyl-2-pyrrolidinone (NMP, anhydrous) as solvent to form slurry. This viscous slurry was coated onto a 1 cm^2 area of graphite paper and dried in a convection oven at 80°C to form the electrodes. To elucidate the electrochemical processes of the aqueous LIB, cyclic voltammetry (CV) and galvanostatic charge / discharge of the half cells were carried out in a three-electrode configuration, using 4 M lithium chloride (LiCl) aqueous solution, with platinum foil and a standard calomel electrode (SCE) as the counter and reference electrodes. Full cell cyclic voltammetry and galvanostatic charge / discharge was performed in three-electrode configuration in 4 M lithium chloride (LiCl) aqueous solution, with $\text{Na}_{1.16}\text{V}_3\text{O}_8$ coated over graphite paper as the working and counter electrode and standard calomel electrode (SCE) as reference electrode, using a computer-controlled potentiostat (Solartron, 1470E) at room temperature, in the voltage range of 0 to 1.9 V vs. SCE.

Results and Discussion

Morphological and structural characterization.— Following sequential reactions occur when NaOH and V_2O_5 are mixed and autoclaved to yield $\text{Na}_{1.16}\text{V}_3\text{O}_8$ hydrothermally: Na^+ inserts into the V_3O_8^- layers forming the $\text{Na}_{1.16}\text{V}_3\text{O}_8$.⁵¹

FE-SEM was carried out to observe NVO morphologies, as shown in Fig. 2. NVO-200 shows well-bundled nanobelt morphology with aspect ratio ~ 20 (average diameter of $\sim 100\text{ nm}$ and length $\leq 2\text{ }\mu\text{m}$). On the other hand, NVO-300 possesses nanobelt morphology, which may indicate better crystallinity than NVO-200, with particle size in submicron range of 80–100 nm. Finally NVO-400 exhibits high aspect ratio (> 50) nanobelts with average diameter of ~ 50 –100 nm.

Further, observations of NVOs under bright-field TEM (Fig. 3) shows the presence of several layers of lamellar crystals, giving rise to the belt-like morphology. In general, the crystals of NVO sintered at 400°C , (NVO-400, Fig. 3c) show the formation of larger and thicker crystals as compared to those in NVO-200 (Fig. 3a) and NVO-300 (Fig. 3b). High resolution image of NVO-400 (Fig. 3d) with diffraction pattern (inset) of a single NVO-400 crystal oriented along the $[-132]$ zone axis is obtained. The diffraction pattern can be indexed, within reasonable agreement with the XRD data of NVO-400.

The powder XRD patterns of NVOs (Fig. 4) are collected to elucidate the crystal structures, and evaluated using the Rietveld refinement method. The XRD patterns (Fig. 4) can be fully indexed to the crystal structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ ($P12_1/m1$, PDF 16-4514) via Rietveld refinement, without the presence of any impurity peaks. As presented in Table I, the lattice parameters calculated by the Topas software for NVO-200 are $a = 7.10(2)\text{ }\text{\AA}$, $b = 3.45(5)\text{ }\text{\AA}$ and $c = 11.84(2)\text{ }\text{\AA}$, with average crystal size $\sim 7\text{ nm}$. Upon further heat-treatment at 300°C and 400°C , lattice parameters and average crystal size increases, which can be observed through the sharpening of XRD peaks from NVO-200 through NVO-400 ($a = 7.31(2)\text{ }\text{\AA}$, $b = 3.61(6)\text{ }\text{\AA}$ and $c = 12.16(2)\text{ }\text{\AA}$, with average crystal size $\sim 28\text{ nm}$). Increase in heat-treatment temperature from 200 to 400°C seemingly leads to the increase in cell volume, and the lattice parameters are very close to that of the calculated pattern. It is probable that, higher heating temperature could enable the better formation of a stable super-cell structure, resulting

Figure 2. Field-emission scanning electron microscopy images of (a) NVO-200, (b) NVO-300 and (c) NVO-400.

in $\text{Na}_{2.32}\text{V}_6\text{O}_{16}$. Also, the lattice parameters have similar values to those reported in the papers by M. Onoda,³⁷ therefore the formation of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ can thus be confirmed. The increase in crystal size is very much in agreement with the observations under the TEM.

Figure 3. Bright-field transmission electron microscopy images of (a) NVO-200, (b) NVO-300, (c) NVO-400 and (d) high-resolution image with corresponding indexed selected-area diffraction pattern (SAED) (inset) of NVO-400.

Electrochemical characterizations.—Cyclic voltammetry (CV) of the three annealed NVOs as anode and cathode was carried out in three-electrode configuration within the potential range of -1.0 to 0.0 V and 0.0 to 1.0 V vs. SCE respectively, at a scan rate of 1 mVs^{-1} , to elucidate the phase transformations occurring during the electrochemical processes and presented in Fig. 5. In the anodic CV of NVO-200, one main reduction peak can be observed at -0.58 V and a faint reduction peak at -0.28 V vs. SCE and two main oxidation peak at -0.49 V and -0.2 V vs. SCE respectively (Fig. 5a). In the cathodic CV of NVO-200, one main oxidation peak can be observed at 0.6 V vs. SCE and a reduction peak at 0.45 V vs. SCE (Fig. 5b). These peaks indicate redox processes occurring during electrochemical charging / discharging. Similarly, these redox peaks^{39,40} are also observed in the CV of NVO-300 (Fig. 5) and NVO-400 (Fig. 5). Upon subsequent cycling, it can be observed that the current density of NVO-200 reduces drastically, whereas the current density fades less in the cases of NVO-300 and NVO-400. This could indicate that the higher heat-treatment temperature helped to improve the electrochemical properties and cyclic stability of the $\text{Na}_{1.16}\text{V}_3\text{O}_8$ active material.

To further investigate the electrochemical performance of NVO as cathode, anode and symmetric full cell, cyclic voltammetric (CV) of NVO-400 was carried out in three-electrode configuration within the potential range of -1.0 to 0 V, 0 to 1.0 V and 0 to 2.0 V vs. SCE respectively, at a scan rate of 5 mVs^{-1} as shown in Fig. 6. The redox peak at ~ -0.5 V might correspond to $\text{V}^{2+}/\text{V}^{3+}$ redox reaction.⁴¹

The redox peaks at ~ 0.5 V & ~ 0.7 V correspond to redox reaction 2 and 3.^{42,43}

The CV curve of NVO/NVO symmetric full ARLB fabricated using 4M LiCl in aqueous electrolyte studied between 0 to 2.0 V vs.

Figure 4. (a) Rietveld refinement of X-ray diffraction (XRD) pattern of NVO-400 and (b) XRD patterns of NVO-200, NVO-300 and NVO-400 respectively.

SCE showed 3 distinct redox couples with oxidation peaks at 0.52 V, 0.8 V, 1.6 V and corresponding reduction peaks at 0.14 V, 0.5 V, 1.32 V vs. SCE respectively.

Complete full cell reaction can be written as follows :

As shown in Fig. 7, half cell electrochemical performance of NVO as cathode and anode was further studied using galvanostatic charge/discharge cycles, in three electrode configuration, at a current density of 5 Ag^{-1} . NVO-200 as anode gave an initial charge capacity of 100 mAhg^{-1} and discharge capacity of 98 mAhg^{-1} , while NVO-300 and NVO-400 as anode gave an initial charge capacity of $\sim 120 \text{ mAhg}^{-1}$ and discharge capacity of $\sim 121 \text{ mAhg}^{-1}$. All the specific capacity values are calculated with respect to the mass of the active material. Apparently, NVO as anode displays higher reversible capacity in aqueous solution than other commonly used anode materials. LiV_3O_8 , $\text{LiT}_2(\text{PO}_4)_3$ and TiP_2O_7 , which delivered a discharge capacity of 40 mAhg^{-1} , 80 mAh g^{-1} and 100 mAhg^{-1} respectively.⁴⁴⁻⁴⁶ NVO-200 as cathode gave an initial charge capacity of $\sim 80 \text{ mAhg}^{-1}$ and discharge capacity of $\sim 80 \text{ mAhg}^{-1}$, while NVO-300 and NVO-400 as cathode gave an initial charge capacity of $\sim 80 \text{ mAhg}^{-1}$ and discharge capacity of $\sim 80 \text{ mAhg}^{-1}$. NVO as cathode shows slightly lower reversible capacity of $\sim 80 \text{ mAhg}^{-1}$ in aqueous solution compared to traditional ARLB based cathode materials, LiMn_2O_4 , LiCoO_2 and LiMnO_2 , which delivered a discharge capacity of 84 mAhg^{-1} , 100 mAhg^{-1} and 60 mAhg^{-1} respectively.⁴⁷⁻⁴⁹ Absence of real dis-

charge plateau is attributed to multi-lithium ion intercalation/de-intercalation process.⁴⁰ The electrochemical properties of all the NVO electrodes in NVO/NVO full symmetric cell configuration (ratio of anode and cathode used is 1:1.5) were evaluated via galvanostatic cycling, in three electrode configuration, at a high current density of 5 Ag^{-1} between 0 and 1.9 V vs. SCE respectively, and the galvanostatic traces are presented in Fig. 8. The initial charge capacity is $\sim 156.18 \text{ mAhg}^{-1}$ and discharge capacity $\sim 152.42 \text{ mAhg}^{-1}$ can be observed in almost all the NVO samples. (All the specific capacity values are calculated with respect to the limiting electrode which is anode in this case.) In the above mentioned equations 1–4, Vanadium in NVO undergoes redox reaction from V^{5+} to V^{2+} during the charge/discharge cycle thereby inserting 3 moles of lithium. Therefore, one redox change is accompanied by insertion of 3 moles of lithium per formula unit of $\text{Na}_{1.16}\text{V}_3\text{O}_8$, which is in accordance with the structural similarity and lithium insertion observed in LiV_3O_8 .^{34,35} According to the potential of both the cathode and anode, the terminal voltage of the symmetric cell is around $1.8(\pm 0.5) \text{ V}$ as seen in Fig. 8, which has an energy density of $\sim 120 \text{ Whkg}^{-1}$, the highest energy density reported by any symmetric ARLB so far.⁵⁰ Charging above 1.9 V leads to side reactions and hence the full cell potential of the symmetric cell architecture has been limited to 1.9 V. From the charge/discharge curve observed in Fig. 8, one can conclude that the charge storage in $\text{Na}_{1.16}\text{V}_3\text{O}_8$ is dominated by pseudocapacitive energy storage mechanism compared to the normal faradaic diffusion-controlled insertion process.⁵³ Lithium ion insertion via pseudocapacitance is not

Table I. Calculated lattice parameters and volume of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ heat treated at 200°C , 300°C and 400°C for 2h.

$\text{Na}_{1.16}\text{V}_3\text{O}_8$ (annealing temperature in $^\circ\text{C}$)	a (Å)	b (Å)	c (Å)	Crystal size (nm)	Volume (Å ³)
200	7.10(2)	3.45(5)	11.84(2)	$\sim 7(3)$	277.9(10)
300	7.28(1)	3.591(4)	12.12(1)	9(4)	301.76(49)
400	7.306(2)	3.607(6)	12.160(2)	$\sim 28(5)$	305.22(11)

Figure 5. Cyclic voltammograms (CV) of NVO-200, NVO-300 and NVO-400 as (a)Anode and (b)Cathode in three-electrode configuration (vs. SCE) from -1.0 to 0 V and 0 to 1.0 V respectively, at scan rate of 5 mV s^{-1} .

diffusion limited like battery even though both the processes require redox reaction for charge storage.

The cyclic stability of these active materials was further evaluated by prolonged cycling, up to 100 cycles, at 5 Ag^{-1} (Fig. 9). The discharge capacity at the end of 100 cycles for NVO-200 was 70.33 mAh g^{-1} , equivalent to $\sim 50\%$ retention of initial capacity, while NVO-300 and NVO-400 retained $>60\%$ and $\sim 80\%$ of the initial capacity respectively. The initial rapid fading of the capacity observed in NVO-200 and NVO-300 can be attributed to their poorer crystallinity. From the TG curves (Fig. 11), it can be clearly seen that heat-treatment at 400°C is extremely efficient to remove the water content from the NVO completely while, NVO-200 and NVO-300 has $5.59 \text{ wt\%}$ and $2.94 \text{ wt\%}$ water content in them. Absence of water molecule from the crystal due to annealing at high temperature can also increase the capacity and also help in the cycling stability.^{52,39} Wang et al.³⁸ has observed reduction in crystal volume with heat-treatment due to the loss of water molecules from the crystal which he has confirmed using TGA and XRD. Annealing at higher temperatures increases the

crystallinity and thereby the crystal size of a material. So, in materials where there is loss of water of crystallization due to heat-treatment, the overall crystal volume is dependent on the phenomena which dominates the most. Wang et al., observed higher loss of water molecules and decrease in crystallinity at higher annealing temperatures, hence the crystal volumes for $\text{Na}_2\text{V}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$ decreases with increase in the annealing temperatures.

While in $\text{Na}_{1.16}\text{V}_3\text{O}_8$, we observe an increase in crystallinity along with higher loss of water molecule within the crystal with increase in the annealing temperature. Hence NVO-400 shows higher crystal volume compared to NVO-200 and NVO-300 (Table I). Therefore, crystal structure of a material plays a very important role in the thermodynamic and crystalline nature of a material, which in-turn plays a key role in its electrochemical performance.

The cyclic stability of NVO-400, compared to NVO-200 and NVO-300 is superior and this can be attributed to the higher crystallinity (larger crystal size) as observed from the TEM (Fig. 3) and XRD (Fig. 4). Apparently, NVO symmetric cell shows a higher capacity

Figure 6. Cyclic voltammograms (CV) of NVO-400 as Cathode, full cell, Anode in three-electrode configuration (vs. SCE) from -1.0 to 0 V, 0 to 2.0 V and 0 to 1.0 V respectively, at scan rate of 5 mV s^{-1} .

Figure 7. Galvanostatic charge-discharge profiles of NVO-200, NVO-300 and NVO-400 respectively, as (a) Anode in three-electrode configuration (vs SCE) from -1 to 0 V and (b) Cathode in three-electrode configuration (vs SCE) from 0 to 1 V, in 4M aqueous solution of LiCl , at current density of 5 Ag^{-1} .

retention of $\sim 80\%$ at the end of 100 cycles compared to the 55% capacity retention shown by LiMn_2O_4 symmetric cell reported by Sun et al. at the end of 30 cycles.⁵⁰ Capacity fading can be further slowed down by adjusting the electrolyte composition, for example, by the addition of different additive, modification of electrode surface or modulation of pH, which will be the object of future research.

In general, the increase in annealing temperature leads to increase in the diameter of the nanobelt, which in turn leads to higher electroactive surface area and reduced ion diffusion path, due to the higher aspect ratio. This, in turn, improves the mobility of lithium ions within the active material, enabling a larger number of lithium ions to intercalate into the active electrode material and occupy the vacant tetrahedral sites in the crystal structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (Fig. 10). High-rate capability of materials depends not only on the miniaturization of the particle size of active materials, but also on the structure, electrode

porosity and composition of the materials.⁵¹ Therefore, electronic and ionic wirings of the active mass which allows faster pathways to conduct ions and electrons are crucial for high-rate capabilities. The layered crystal structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ facilitates the lithium insertion / de-insertion into and from the layers via the diffusion, while presence of sodium ions (Na^+) residing in the octahedral sites^{37–39} aids in maintaining the layered structure, by supporting the V_3O_8^- puckered layers, during the electrochemical lithiation / de-lithiation processes, resulting in excellent electrochemical performance in terms of rate capability and cyclic stability.^{28,39} The superior electrochemical performance of NVO-400, among NVO-200 and NVO-300, can be attributed to the larger cell volume and crystal size. The expansion of the a , b and c lattice parameters indicate that the tetrahedral voids are larger than those in NVO-200 and NVO-300, thereby facilitating the entry of lithium ions into the crystal structure. Good Coulombic efficiency in the range of $98\text{--}100\%$ was achieved over the cycles at a high current density of 5 Ag^{-1} .

Figure 8. Galvanostatic charge-discharge profiles of NVO-200/NVO-200, NVO-300/NVO-300 and NVO-400/NVO-400 respectively in a 4M LiCl aqueous solution, in three-electrode configuration (vs SCE) from 0 to 1.9 V, at current density of 5 Ag^{-1} .

Figure 9. Specific capacity vs. cycle no. and Coulombic efficiency of NVO-200/NVO-200, NVO-300/NVO-300 and NVO-400/NVO-400 respectively, in three-electrode configuration from 0 to 1.9 V, at current density of 5 Ag^{-1} .

Figure 10. Crystal structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$.

Figure 11. TG curves of NVO-200, NVO-300 and NVO-400.

Conclusions

Nanobelt $\text{Na}_{1.16}\text{V}_3\text{O}_8$ has been synthesized by a facile hydrothermal method, followed by subsequent heat-treatment at different temperatures (200°C, 300°C and 400°C). Characterization via field-emission scanning electron and transmission electron microscopes showed the formation of belt-like structures with high aspect ratio >20. X-ray diffraction confirmed the formation of 100% phase pure sodium vanadate $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (NVO). The application of NVO both as cathode and anode material in an aqueous lithium ion battery was demonstrated and the electrochemical properties were studied via

cyclic voltammetry and galvanostatic charge/discharge. High initial capacity of $>150 \text{ mAhg}^{-1}$ at high current rate was achieved. Upon cycling to 100 cycles, $\sim 75\%$ of initial capacity was retained, exhibiting the superior rate performance and cycling stability of NVO. More importantly, it can be deduced that the layered structure of NVO, coupled with the presence of sodium ions, resulted in a stable structure, enabling the ease of lithium intercalation/deintercalation, leading to future applications of NVO as potential electrode material for aqueous lithium ion batteries. Further studies on NVO could target to improve its volumetric energy density by enhancing the diffusion controlled lithium insertion along with the pseudocapacitive charging by tailoring different nanoarchitectures and alkali-metal ion replacement.

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References

1. M. Winter and R. J. Brodd, *Chem. Rev.*, **104**, 4245 (2004).
2. M. S. Whittingham, *Chem. Rev.*, **104**, 4271 (2004).
3. Y.-M. Chiang, *Science*, **330**, 1485 (2010).
4. M. Duduta, B. Ho, V. C. Wood, P. Limthongkul, V. E. Brunini, W. C. Carter, and Y.-M. Chiang, *Adv. Energy Mater.*, **1**, 511 (2010).
5. M. D. Slater, D. Kim, E. Lee, and C. S. Johnson, *Adv. Funct. Mater.*, **23**, 947 (2013).
6. N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, and S. Komaba, *Nat. Mater.*, **11**, 512 (2012).
7. Z. Peng, S. A. Freunberger, Y. Chen, and P. G. Bruce, *Science*, **337**, 563 (2012).
8. W. A. O'Brien, R. B. Stickel, and G. J. May, *J. Power Sources*, **67**, 151 (1997).
9. M. Broussely, J. P. Planchat, G. Rigobert, D. Virey, and G. Sarre, *J. Power Sources*, **68**, 8 (1997).
10. P. C. Frost, *J. Power Sources*, **78**, 256 (1999).

11. P. Gifford, J. Adams, D. Corrigan, and S. Venkatesan, *J. Power Sources*, **80**, 157 (1999).
12. A. N. Jansen, A. J. Kahaian, K. D. Kepler, P. A. Nelson, K. Amine, D. W. Dees, D. R. Vissers, and M. M. Thackeray, *J. Power Sources*, **81**, 902 (1999).
13. W. Li, J. R. Dahn, and D. Wainwright, *Science*, **264**, 1115 (1994).
14. J. Kohler, H. Makihara, H. Uegaito, H. Inoue, and M. Toki, *Electrochim. Acta*, **46**, 59 (2000).
15. G. J. Wang, L. J. Fu, N. H. Zhao, L. C. Yang, Y. P. Wu, and H. Q. Wu, *Angew. Chem. Int. Ed.*, **46**, 295 (2007).
16. H. B. Wang, K. L. Huang, Y. Q. Zeng, S. Yang, and L. Q. Chen, *Electrochim. Acta*, **52**, 3280 (2007).
17. B. Dunn, H. Kamath, and J.-M. Tarascon, *Science*, **334**, 928 (2011).
18. J.-Y. Luo, W.-J. Cui, P. He, and Y.-Y. Xia, *Nat. Chem.*, **2**, 760 (2010).
19. J. F. Whitacre, A. Tevar, and S. Sharma, *Electrochem. Commun.*, **12**, 463 (2010).
20. C. D. Wessells, R. A. Huggins, and Y. Cui, *Nat. Commun.*, **2**, 550 (2011).
21. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, and J. Liu, *Chem. Rev.*, **111**, 3577 (2011).
22. G. L. Soloveichik, *Annu. Rev. Chem. Biomol. Eng.*, **2**, 503 (2011).
23. W. Li, J. R. Dahn, and D. S. Wainwright, *Science*, **264**, 1115 (1994).
24. J. Jiang, Z. X. Wang, and L. Q. Chen, *J. Phys. Chem. C*, **111**, 10707 (2007).
25. H. M. Liu, Y. G. Wang, K. X. Wang, Y. R. Wang, and H. S. Zhou, *J. Power Sources*, **192**, 668 (2009).
26. N. A. Chernova, M. Roppolo, A. C. Dillon, and M. S. Whittingham, *J. Mater. Chem.*, **19**, 2526 (2009).
27. H. M. Liu, Y. G. Wang, L. Li, K. X. Wang, E. Hosono, and H. S. Zhou, *J. Mater. Chem.*, **19**, 7885 (2009).
28. G. Q. Liu, C. L. Zeng, and K. Yang, *Electrochim. Acta*, **47**, 3239 (2002).
29. Y. L. Cheah, N. Gupta, S. S. Pramana, V. Aravindan, G. Wee, and M. Srinivasan, *J. Power Sources*, **196**, 6465 (2011).
30. C. M. Ban, N. A. Chernova, and M. S. Whittingham, *Electrochemistry Communications*, **11**, 522 (2009).
31. R. Pitchai, S. Shivakumara, H. N. Vasan, and N. Munichandraiah, *Journal of Physical Chemistry C*, **112**, 16700 (2008).
32. R. Pitchai, V. Thavasi, S. G. Mhaisalkar, and S. Ramakrishna, *Journal of Materials Chemistry*, **21**, 11040 (2008).
33. S. Jouanneau, A. Verbaere, S. Lascaud, and D. Guyomard, *Solid State Ionics*, **177**, 311 (2006).
34. J. Kawakita, T. Miura, and T. Kishi, *Solid State Ionics*, **124**, 21 (1999).
35. J. Kawakita, T. Miura, and T. Kishi, *Solid State Ionics*, **124**, 29 (1999).
36. M. E. Spahr, P. Novák, W. Scheifele, O. Haas, and R. Nesper, *J. Electrochem. Soc.*, **145**, 421 (1998).
37. M. Onoda, *J. Phys.: Condens. Matter*, **16**, 8957 (2004).
38. H. Wang et al. *Journal of Power Sources*, **199**, 263 (2012).
39. H. Y. Wang, K. L. Huang, S. Q. Liu, C. H. Huang, W. J. Wang, and Y. Ren, *J. Power Sources*, **196**, 788 (2011).
40. D. Zhou et al. *Journal of Power Sources*, **227**, 111 (2013).
41. Michel Fiore, Santino Orecchio, Vincenzo Romano, and Roberto Zingales, *J. CHEM. soc. DALTON TRANS.*, 799 (1993).
42. Part 1. S. Orecchio, V. Romano, and R. Zingales, *J. Chem. Res.*, (S), **14**, (M), 214 (1989).
43. Part 2. S. Orecchio, V. Romano, and R. Zingales, *J. Chem. Res.*, (S) **335**; (M) 2701 (1989).
44. J. Kohler, H. Makihara, H. Uegaito, H. Inoue, and M. Toki, *Electrochim. Acta*, **46**, 59 (2000).
45. X.-H. Liu, T. Saito, T. Doi, S. Okada, and J.-I. Yamaki, *J. Power Sources*, **189**, 706 (2009).
46. H. Wang, K. Huang, Y. Zeng, S. Yang, and L. Chena, *Electrochim. Acta*, **52**, 3280 (2007).
47. S. Chen, C. Mi, L. Su, B. Gao, Q. Fu, and X. Zhang, *J. Appl. Electrochem.*, **39**, 1943 (2009).
48. R. Ruffo, C. Wessells, R. A. Huggins, and Y. Cui, *Electrochem. Commun.*, **11**, 247 (2009).
49. M.-S. Wu and R.-H. Lee, *J. Power Sources*, **176**, 363 (2008).
50. S. I. Park, I. Gocheva, S. Okada, and J.-I. Yamaki, *J. Electrochem. Soc.*, **158**, A1067 (2011).
51. C. Fongy, A.-C. Gaillot, S. Jouanneau, D. Guyomard, and B. Lestriez, *Journal of The Electrochemical Society*, **157**, A885 (2010).
52. Y. M. Liu, X. C. Zhou, and Y. L. Guo, *Electrochim. Acta*, **54**, 3184 (2009).
53. Y. L. Dylla et al., *Accounts of chemical research*, **45**, 1104 (2013).