Preparation, Structure Study and Electrochemistry of Layered $\text{H}_2\text{V}_3\text{O}_8$ Materials: High Capacity Lithium-ion Battery Cathode

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Abstract

The present study explores $\text{H}_2\text{V}_3\text{O}_8$ as high capacity cathode material for lithium-ion batteries (LIB's). Despite having high discharge capacity, $\text{H}_2\text{V}_3\text{O}_8$ material suffers from poor electrochemical stability for prolonged cycle life. Ultra-long $\text{H}_2\text{V}_3\text{O}_8$ nanobelts with ordered crystallographic patterns are synthesized via a hydrothermal process to mitigate this problem. The growth of the crystal is facile along [001] direction, and the most common surface is (001) as suggested by Wulff construction study. Electrochemical performance of $\text{H}_2\text{V}_3\text{O}_8$ cathode is tested against Li/Li^+ at various current rates. At 50 mA g^{-1} current rate, it delivers a discharge capacity of 308 mAh g^{-1} , whereas, at 3000 mA g^{-1} , an initial discharge capacity of 144 mAh g^{-1} is observed and stabilized at 100 mAh g^{-1} till 500 cycles. Further, the density functional theory (DFT) based simulations study of both the pristine and lithiated phase of $\text{H}_2\text{V}_3\text{O}_8$ cathode materials is undertaken. DFT study reveals the presence of hydrogen as hydroxyl unit in the framework of the host. In correlation, the magnetic property of vanadium atoms is examined in detail with through partial density of states (PDOS) calculation during three stage lithiation processes and evaluating various potential steps involved in lithium insertion.

Keywords: *Ab-initio* calculations, Lithium-ion battery, $\text{H}_2\text{V}_3\text{O}_8$ cathode, Hydrothermal synthesis, Nano-belt morphology

1. Introduction

Recent studies in lithium-ion batteries (LIB's) are directed towards the replacement of LiCoO_2 which has low energy density with vanadium based cathode material [1-3]. Other than the V_2O_5 cathode material, quasi 1-dimensional (1D) structured materials like $\text{Li}_x\text{V}_3\text{O}_8$, $\text{NH}_4\text{V}_4\text{O}_{10}$ and $\text{H}_2\text{V}_3\text{O}_8$ with high aspect ratio materials have been considered as potential cathode due to high energy density compared to existing materials [1,2,4, 5]. In literature, most of such cathode materials are prepared by the surfactant-assisted hydrothermal process [4-11]. Though synthesis of $\text{H}_2\text{V}_3\text{O}_8$ material is well studied in the literature [12], its electrochemical properties as cathode material in LIBs is rarely presented. As an example, the crystallography studies were carried out by Oka et al.[13]concluded the orthorhombic symmetry (space group: Pnam) for $\text{H}_2\text{V}_3\text{O}_8$, where V^{5+} and V^{4+} are in the ratio of 2:1 [13]. Li et al. reported the $\text{H}_2\text{V}_3\text{O}_8$ nanobelts morphology using HCl and V_2O_5 [14]. Zhang et al. reported the electrochemical properties of $\text{H}_2\text{V}_3\text{O}_8$ nanobelts which exhibited an initial discharge capacity of 373 mAh g^{-1} at a very low current rate of 0.2 mA cm^{-2} [15]. Similarly, Qiao et al. have reported nanobelts morphology of $\text{H}_2\text{V}_3\text{O}_8$ with an initial capacity of 253 mAh g^{-1} and a capacity of 228.6 mAh g^{-1} that couldretainits capacity till 50 cycles at a current density of 30 mA g^{-1} [16]. Further, Prado-Gonjal et al. have shown the electrochemical performances of $\text{H}_2\text{V}_3\text{O}_8$ cathode, where 5 Li^+ -ion were allowed to intercalate in the host matrix by allowing discharge potential down to 1 V against Li/Li^+ [17]. Due to an intake of 5 Li^+ , vanadium in $\text{V}^{5+/4+}$ states reduces to V^{3+} state in the host material [17]. More recently, Simões et al. have considered the traces of weakly bonded water in a V_3O_7 layer which is a major concern as it can react with fluoride based salt and form hydrogen fluoride (HF) [18]. To restrict such side reaction in $\text{H}_2\text{V}_3\text{O}_8$ cathode, surface coating of $\text{AlO}_x(\text{OH})_y$ with varying

concentration was suggested as a remedy. The result showed much improvement with 3 % of $\text{AlO}_x(\text{OH})_y$ coating and the $\text{H}_2\text{V}_3\text{O}_8$ cathode delivered 203 mAh g^{-1} discharge capacity at 100 mA g^{-1} current rate for 20 cycles and retained 89 % capacity after 200 cycles [18].

As it was observed that surface coating of $\text{H}_2\text{V}_3\text{O}_8$ cathode material could improve the electrochemical performance; however, the coating technology could add other extra steps in the electrode manufacturing process. To prevent such additional steps, the present study will explore the possibilities for (i) improving the electrochemical performances and stability without any coating, (ii) investigating the structural stability, (iii) involvement of water molecule in V_3O_7 layer using theoretical modelling study, and (iv) improving charge/discharge performance at high current rates.

Moreover, it is known that the electrochemical performance of V_3O_7 based electrode depends on the synthesis process. A detailed study to understand the growth of the $\text{H}_2\text{V}_3\text{O}_8$ nanobelts morphology was carried out with the help of Wulff construction [19]. As the molecular level understanding of this material is non-existent in the literature; so, we have undertaken a detailed *ab-initio* based DFT studies to complement the experimental results which can locate the lithium insertion site during lithiation process. Mixed valence states of vanadium and resulting magnetic structures were evaluated from our simulation studies. Unique structural aspects are captured through electronic structure evaluation and correlated with the studies on electrochemical charge transfer process during the three stage de-lithiation in this material. We believe that the present study should provide a deeper insight into the electrode materials design based on vanadate electrodes that will capture maximum capacity at a high rate and provide means to predict the electrochemical redox activity.

2. Experimental section

2.1 Synthesis procedure

H₂V₃O₈ nano-belts were prepared by oxalic acid assisted hydrothermal synthesis process. At first, V₂O₅ (Sigma-Aldrich, 99 %) was added to the solution of oxalic acid (Fisher Scientific, 98 %) (50 mL solution). The solution was stirred at 400 rpm for 3 h at 120 °C, where yellow precipitate of V₂O₅ completely turns to a blue color solution, indicating the formation of vanadium complex with oxalate anion where the charge state of vanadium changes from + 5 to + 4 state [20, 21]. The possible reaction is as follows[20, 21]:

Further, vanadium oxide (V₂O₅) was added to the above solution which contains vanadium oxalate complex. After stirring for 2 h, the color of the solution turned into bluish-green. The possible reaction is as follows:

The solution was transferred to Teflon-lined autoclave. The autoclave was maintained at various temperatures from 180 °C to 200 °C for 1 h to 7 h.

2.2 Material characterization

Phase analyses were systematically carried out by powder X-ray diffraction (XRD, Philips X'pert X-ray diffractometer) using Cu K α source in the 10°-50° (2 θ) range. Different vibrational modes of M-O were analyzed by a Fourier transform infrared (FTIR, Transmittance mode, MAGNA 550, Nicolet Instrument Co.) spectrometer. Field emission gun scanning electron microscope (FEG-SEM, Carl Zeiss, Ultra-55) and field emission gun transmission electron

microscopy (FEG-TEM, Jeol 2100F) were employed to obtain information on the microstructure. X-ray photoelectron spectroscopy (XPS) (CLAMP 2, Analyzer) was used to confirm the oxidation state of vanadium.

2.3 Theoretical study

In this study, the first-principles calculations for the total energy[22, 23]of different structures were performed using projector augmented wave method as implemented in Vienna ab-initio simulation package[24]. Generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof type (PBE) [25] was used for the exchange-correlation energy functional. An energy cut-off at 450 eV for wave functions and k-mesh grids (Monkhorst-Pack) of $1 \times 2 \times 5$ were used for these calculations. The correction for electronic correlation at transition metal site was included through Hubbard U parameter. U-value of 5 eV was used for the vanadium d-orbitals[26]. V_3O_7 exhibits magnetic anisotropy in the form of antiferromagnetic interaction between $(10\bar{1})$ layers and ferromagnetic interaction layers below[27]. The available reports on the magnetic nature of $H_2V_3O_8$ are highly contradicting and claimed to show ferromagnetic [28] or antiferromagnetic [29, 30] interaction perhaps depending on the presence of impurity/vacancy in the system. For this study we used ferromagnetic $H_2V_3O_8$ because of its structural simplicity and computational efficiency compare to the complex antiferromagnetic spin order [31].

The surfaces energies of all facets (seven) with low index surfaces of $H_2V_3O_8$ morphology was calculated for the Wulff construction. To avoid image effects, 10 Å vacuum between repetitive slabs under periodic boundary condition was used. Both the sides of the slabs were relaxed until all forces on atoms are less than $0.01 \text{ eV } \text{\AA}^{-1}$. For an accurate representation of surfaces, slab thickness was taken as at least 20 Å.

To quantify the charge-transfer process during lithium insertion, we calculated electron transfer using Bader's method of topological charge analysis [32]. The unit cell was partitioned into atomic volumes such that the flux of electron density (ρ) gradient is zero ($\nabla\rho=0$) on the surfaces of partitions. A grid-based code for Bader analysis was used in estimating Bader charges. An average equilibrium voltage was determined by using Nernst equation:

$$V = \frac{-\Delta G}{nF} \dots\dots\dots(1)$$

where, V is the electrochemical potential, ΔG is the change in Gibbs free energy, n is the moles of charge transferred and F is Faraday constant.

From the ground state energies of $\text{Li}_x\text{H}_2\text{V}_3\text{O}_8$ with different x (where x = 0-4), one can calculate the electrochemical potential against standard lithium electrode with few realistic assumptions. Neglecting entropic and volume changes, the Gibbs free energy difference is approximately the ground state energy difference. Thus, assuming linearity in discharge state to electrochemical potential curve, the electrochemical potential at a particular lithiation level x is given by

$$\dots\dots\dots V = \frac{E_{\text{Li}_x\text{H}_2\text{V}_3\text{O}_8} + (x'-x)E_{\text{Li}} - E_{\text{Li}_x\text{H}_2\text{V}_3\text{O}_8}}{nF} \dots\dots\dots(2)$$

where, V is electrochemical potential, E_{Species} are total energy of concerned materials, F is Faraday constant, n is a number of moles of electron transferred. An average electrochemical potential of $\text{H}_2\text{V}_3\text{O}_8$ was evaluated at varying level of lithiation. The partial density of states (PDOS) based on spherical projections to correlate to the change in V-O framework, as lithiation process progress, were evaluated.

2.4 Electrochemical characterization

$\text{H}_2\text{V}_3\text{O}_8$ nanobelts were tested as cathode material against lithium using lab scale Swagelok-type cell assembly. The working electrode comprises of 70 % active material, 20 % carbon black (C-65, Timcal, Switzerland) and 10 % polyvinylidene fluoride (PVdF, Sigma-Aldrich) as a binder. Electrode material mentioned here was blended with N-Methyl-2-pyrrolidone (NMP) as a dispersant and spread onto aluminum foil using doctor blade. The electrode material on aluminum foil was then dried overnight at $65 \pm 2^\circ\text{C}$ and cut into a circular disc of 10 mm diameter with $\sim 2.0\text{-}2.4\text{ mg cm}^{-2}$ active mass loading. Charge/discharge tests were performed with Biologic VMP-3 battery testing unit in the potential range between 1.5-4 V at $20 \pm 2^\circ\text{C}$ accuracy range. The cells were assembled in an argon-filled dry box using the $\text{H}_2\text{V}_3\text{O}_8$ as the positive electrode and the Li metal as the negative electrode. Both positive and negative electrodes were electronically separated by a Whatman GF/D borosilicate glassfiber sheet saturated with 1 M LiPF_6 electrolyte solution (in EC: DMC/1:1 in mass ratio, LP-30, Merck, Germany). Electrochemical Impedance Spectroscopy (EIS) experiments were carried out at open circuit potential (OCP) of frequency ranges from 1 MHz-0.1 Hz in Bio-logic VMP-3 for various charge/discharge steps during cycling.

3. Results and discussion

Previous literature on $\text{H}_2\text{V}_3\text{O}_8$ shows poor electrode kinetics and electrochemical stability of $\text{H}_2\text{V}_3\text{O}_8$ electrode. Aware of such charge-transfer limitations; we embarked on a study of controlled morphology of $\text{H}_2\text{V}_3\text{O}_8$ by varying synthesis parameters. After preparing $\text{H}_2\text{V}_3\text{O}_8$ nanobelts, X-ray diffraction (XRD) experiment of $\text{H}_2\text{V}_3\text{O}_8$ samples is performed (Fig. 1a). All the peaks of $\text{H}_2\text{V}_3\text{O}_8$ samples designated as HVO_T (where T is temperature like 180, 190 and 200

°C) are indexed with an orthorhombic system (CIF Code # 80572) with impurity peaks observed at 15° and 25° for HVO_180 sample due to the presence of V_2O_5 . It is interesting to note that with increasing temperature from 180 °C to 200 °C, the impurity peaks disappeared which reveal the ordered and pure $H_2V_3O_8$ growth at a higher temperature. Further, FTIR confirms the presence of different metal-oxygen bonding in $H_2V_3O_8$ and the presence of water. Fig. 1b shows FTIR spectra of $H_2V_3O_8$ nanobelts prepared at varying temperatures. The peak at 532 cm^{-1} corresponds to the stretching vibration of V-O-V bridging bonds [33]. The bands at 925.7 cm^{-1} and 1006.7 cm^{-1} are attributed to symmetric stretching of $\nu_s(V^{4+}=O)$ and $\nu_s(V^{5+}=O)$ bonds; respectively, which signifies the presence of mixed valence state of vanadium in $H_2V_3O_8$ [33]. The peak at 3402 cm^{-1} and 1623.9 cm^{-1} indicates stretching and bending modes of O-H vibrations, respectively [34]. Further, our theoretical study suggests that hydrogen is present as hydroxyl group rather than a water molecule, which is in agreement with the FTIR analysis. The theoretical analysis is discussed in the later section.

Fig. 1. a) X-ray diffraction (XRD) pattern of $\text{H}_2\text{V}_3\text{O}_8$ prepared for 5 h at varying temperature and b) FTIR of $\text{H}_2\text{V}_3\text{O}_8$ prepared for 5 h at varying temperature.

3.1 Microstructure study (synthesis: 5 h with varying temperature)

The microstructure of $\text{H}_2\text{V}_3\text{O}_8$ prepared at varying temperature is shown in Fig. S1 and Fig. 2. It is evident from the microstructure analysis that at 180 °C (Fig. S1a-b) for 5 h synthesis time, short nanobelts of $\text{H}_2\text{V}_3\text{O}_8$ are formed, and the growth of ultra-long nanobelts are observed at 190 °C with the occasional presence of short nanobelts in Fig. S1c-e. Further increase in the temperature to 200 °C, ultra-long nanobelts grow with fewer traces of short nanobelts (Fig. S1f). Thus, it is well illustrated by the microstructure study that the ultra-long $\text{H}_2\text{V}_3\text{O}_8$ nanobelts grow a

few micrometers in length and develop further with an increase in the temperature beyond 180 °C. The selected area electron diffraction (SAED) analysis is carried out for $\text{H}_2\text{V}_3\text{O}_8$ nanobelts (Fig. 2a-f) at different reaction temperatures. The SAED patterns are simulated with Single Crystal software to index with a plane of $\text{H}_2\text{V}_3\text{O}_8$ with orthorhombic symmetry with space group Pnam as shown in Fig. 2b, 2d, and 2f. The well-resolved diffraction patterns demonstrate the high crystalline features of the $\text{H}_2\text{V}_3\text{O}_8$ structures.

Fig. 2. HR-TEM image and SAED analysis of $\text{H}_2\text{V}_3\text{O}_8$ nanobelts prepared at various temperatures ($\text{H}_2\text{V}_3\text{O}_8$ prepared at Fig. a)-b) 180 °C; c)-d) 190 °C and e)-f) 200 °C).

3.2 Theoretical calculation of $\text{H}_2\text{V}_3\text{O}_8$

In this study, the experimental evidence to solve the crystal structure solution was inappropriate and that to resolve the position of hydrogen atoms in this material is almost impossible. The first-

principle based structural optimization calculation is a useful tool to pinpoint the hydrogen position in such situation [35]. The experiment captured the positions of all the oxygen in the $\text{H}_2\text{V}_3\text{O}_8$ crystal successfully but inept to identify the oxygen belonging to the intercalated water. So, we took a simple approach to locating the first intercalation sites in the experimentally obtained (Oka et al. [13]) crystal structure and the oxygen atoms next to these sites which might come from the intercalated water. In the experimentally obtained V_3O_8 structure, we detected that some oxygen atoms (marked with a green ring in Fig. S2a) have much longer V-O bond distance (2.056 Å) than other V-O bonds (1.73 -1.91 Å) due to higher coordination achieved through hydrogen atoms. We added H atoms to one of this oxygen (marked by a green circle in Fig. S2a) in different possible orientation, relaxed and perturbed the position before re-relaxing again (simulated annealing) to obtain final lowest energy structure. This procedure was repeated for all such symmetry equivalent oxygen atoms together. Among these relaxed configurations, we then choose the energetically lowest one as the final crystal structure of pristine $\text{H}_2\text{V}_3\text{O}_8$ (Fig. S2b) and used it for our next set of calculations. In the final $\text{H}_2\text{V}_3\text{O}_8$ structure, hydrogen stays as part of the intercalation framework itself as hydroxyl unit. The similar observation has been experimentally reported by Li et al. already. [36].

The morphology and growth mechanism of $\text{H}_2\text{V}_3\text{O}_8$ materials are primarily dictated by the crystal structure, which in turn governs the surface free energy and the defect formation. Crystal surfaces are composed of lattice planes, and the surface free energy of a lattice plane is inversely proportional to the directional atomic density i.e. the inter-planar spacing. Crystal growth occurs through the addition of layers of atoms to the existing surfaces. Thus, the closer the packed atoms are in that direction, the slower the growth of the crystal. This leads to an inverse relationship between density of a crystal and its growth rate in that direction. If there exist larger

ratio of anisotropy between low index surfaces of the material, the surface with the lowest energy dominates the open facets of the crystal and growth is much faster along that direction creating crystal shaped like nano-belts. If the two lowest energy surfaces are almost degenerate energetically, from Gibbs-Wulff theorem, the surfaces forming the sides of the nanobelt will have similar area/ distance from the center of the crystal. Due to anisotropy in a crystal structure of $\text{H}_2\text{V}_3\text{O}_8$, the surface energies vary significantly among low index surfaces (Table 1). This emanates from the differences in the stacking of atomic planes, which is visually understandable from Fig. 3a-c. Our representative Wulff construction of $\text{H}_2\text{V}_3\text{O}_8$ crystal (Fig. 3d) shows how large difference in surface energy leads to a plate-like crystal in equilibrium. This happens due to minimization of free energy by allowing the growths of crystal facile along [001] direction, and the most common surface is (001). The (100) Surface may host a large number of defects due to its low packing density and high surface energy. The presence of surface defects can greatly help new atom attachment and thus growth. Adding atoms to (100) surface have little energy penalty and thus leads to fast growth. This result agrees with experimental observations [14].

Table 1. Surface energies for low index surface.

Surface	Surface Energy (Jm^{-2})
(100)	4.51
(010)	2.52
(001)	0.78
(011)	1.55
(101)	1.29
(110)	1.95
(111)	1.14

Fig. 3. a) (100) plane-low atomic packing density; b) (001) plane-highest atomic packing density of all surfaces considered; c) (011) plane-moderate high atomic packing density of $\text{H}_2\text{V}_3\text{O}_8$

(Color scheme: grey for V, Red for O and White for H) and d) Wulff construction of $\text{H}_2\text{V}_3\text{O}_8$ crystal shape using $\{100\}$ and $\{011\}$ set of surfaces.

Moreover, intercalation chemistry of V_3O_7 based compound (vs. Li/Li^+) depends on and varies with the cation or the kind of molecule attached/intercalated in the layers. Further, with the presence of the molecule in the host structure, the intercalation process, and potential varies; thus, the DFT-based theoretical calculation is employed for the first time to evaluate intercalation chemistry of $\text{H}_2\text{V}_3\text{O}_8$. Structural parameters of an orthorhombic $\text{H}_2\text{V}_3\text{O}_8$ unit cell obtained from DFT calculations match closely with that reported in previous experimental work [13]. During lithiation, Li ions can occupy various positions inside the layered structure of $\text{H}_2\text{V}_3\text{O}_8$. Following symmetry-allowed sites in the crystal, we generated all possible configurations for each stage of lithiation. First-principles-based structural relaxation method then used to optimize each configuration, and the lowest energy among these structures is taken as the ground state structure for charge transfer and electrochemical potential calculation. The final ground state configurations for each stage of lithiation are demonstrated in Supplementary fig. S3. Lattice parameters and cell volume increase progressively as lithium gets inserted into the framework (Table 2). Volume increase predicted from the theoretical analysis (+12 %) is quite significant at fully lithiated state (four lithium atoms per formula unit). As predicted by DFT calculation, with the insertion of Li^+ in the host structure, the basic model (orthorhombic structure) remains intact without a change in the structure. Thus, it is necessary to validate DFT with the help of ex-situ XRD experiments during various stages of the insertion process. Fig. S4 shows the XRD of $\text{H}_2\text{V}_3\text{O}_8$ material, with the insertion of lithium into the host structure there is a slight shift in 10.75° (2θ value, (200)) towards lower angle, which signifies the increase in the d-spacing due to lithiation in $\text{H}_2\text{V}_3\text{O}_8$ host.

However, as illustrated by Fig. S4, the basic structure of $\text{H}_2\text{V}_3\text{O}_8$ remains intact during various onset potentials during the discharge process. The crystallography parameter of $\text{Li}_x\text{H}_2\text{V}_3\text{O}_8$ during various lithiated states are shown in Table S1.

Table 2. Cell parameter and unit cell volume of $\text{H}_2\text{V}_3\text{O}_8$ with different level of lithiation.

Material	a (Å)	b (Å)	c (Å)	Vol (Å ³)
$\text{H}_2\text{V}_3\text{O}_8$	16.76	9.24	3.75	581.03
$\text{H}_2\text{V}_3\text{O}_8$ [13]	16.93	9.36	3.64	577.42
$\text{Li}_1\text{H}_2\text{V}_3\text{O}_8$	16.47	9.32	3.81	584.55
$\text{Li}_3\text{HV}_3\text{O}_8$	16.73	9.56	3.99	638.73
$\text{Li}_4\text{HV}_3\text{O}_8$	16.65	9.80	4.00	651.70

Besides, the study on volume change, theoretical calculation predicts H atoms indeed are attached with O6 atoms rather than the intercalated water molecule. In fact, it is interesting here to mention that H atoms play a vital role in stabilization of $\text{H}_2\text{V}_3\text{O}_8$ framework which helps in the better electrochemistry of the system (discussed later section). Our simulations exhibited that lithiation in the $\text{H}_2\text{V}_3\text{O}_8$ system happened in three distinct stages. First, one lithium atom per formula unit (four atoms per unit cell) intercalated and thus formed $\text{LiH}_2\text{V}_3\text{O}_8$. In the next stage, two more lithium atoms occupied the framework. In the final stage, one more lithium atom entered in the system (unit cell with sixteen lithium atoms). The intercalation process leads to delocalization of lithium valence electrons in the intercalated framework. Extra electrons coming from these intercalated Li atoms get distributed between O, V and H valance orbitals in the system. The Bader charge analysis (Table 3) quantified the charge transferred to O, V, and H in

different stages of lithiation. The changes in valence charge of different ions due to lithiation not only altered the electronic environment of the system but also affected the magnetic spin distribution considerably. Our results demonstrated that the magnetic moment of each V ion increases prominently with intercalating Li atoms in the system (Table 4). Although oxygen ions received a major portion of the transferred charge during the lithium intercalation process, strong covalency in the system arising from the molecular orbital formation and that may have resulted in the striking change observed in the magnetic moment. Vanadium ions are in a high spin state in $\text{H}_2\text{V}_3\text{O}_8$ and the extra electron from intercalated Li-ion may occupy the molecular orbitals formed by t_{2g} d-orbitals of vanadium atoms to increase the ferromagnetic moment of the system. We propose a simplified model to explain the relationship between lithiation and magnetic moment of V ion as initially; $\text{H}_2\text{V}_3\text{O}_8$ unit cell has eight vanadium ions (V^{5+}) with d^0 electronic configuration and four vanadium ions (V^{4+}) with $d1$ electronic configuration. After the first stage of lithiation, the system had four vanadium ions with $d0$ electronic configuration and eight vanadium ions with $d1$ configuration. As a result, the net magnetic moment of the unit cell became double compared to the de-lithiated stage. Further, the addition of eight valence electrons (from eight lithium atoms) in the 2nd stage makes eight V^{4+} ($d1$) and four V^{3+} ($d2$) ions in the system. When all sixteen lithium atoms get intercalated in the final stage of lithiation, four V^{4+} ($d1$) and eight V^{3+} ($d2$) ions in the unit cell lead to a high ferromagnetic moment of over 20 μB per unit cell (Table 4).

Table 3. Lithium valence charge transfers characteristics and the electrochemical potential for all lithiation steps.

Lithiation stage	Initial composition	Final composition	Charge transfer to V (%)	Charge transfer to O (%)	Charge transfer to H (%)	Voltage (V)
1	$\text{H}_2\text{V}_3\text{O}_8$	$\text{Li}_1\text{H}_2\text{V}_3\text{O}_8$	2.1	87.5	10.4	3.86
2	$\text{Li}_1\text{H}_2\text{V}_3\text{O}_8$	$\text{Li}_3\text{H}_2\text{V}_3\text{O}_8$	19.0	77.9	3.1	2.92
3	$\text{Li}_3\text{H}_2\text{V}_3\text{O}_8$	$\text{Li}_4\text{H}_2\text{V}_3\text{O}_8$	20.4	76.8	2.8	2.39

Table 4. Magnetic moments of vanadium atoms at different lithiation levels.

Composition ($\text{Li}_x\text{H}_2\text{V}_3\text{O}_8$)	V atoms with high magnetic moment	Magnetic moment (μB)	V atoms with low magnetic moment	Magnetic moment (μB)
$\text{Li}_4\text{H}_2\text{V}_3\text{O}_8$	8	2.03	4	1.16
$\text{Li}_3\text{H}_2\text{V}_3\text{O}_8$	4	2.03	8	1.16
$\text{Li}_1\text{H}_2\text{V}_3\text{O}_8$	8	1.14	4	0.13
$\text{H}_2\text{V}_3\text{O}_8$	4	1.16	8	0.02

3.3 Theoretical prediction of intercalation process

The theoretical study is particularly important in understanding the intercalation process which occurs during various stages. The first set of lithium atoms releases up to 3.86 eV of energy

when lithium-ion is intercalating into $\text{H}_2\text{V}_3\text{O}_8$ framework providing with a theoretical capacity of 86 mAh g^{-1} . The next set of lithium intercalation happens at a significantly lower potential at 2.92 V , and the electrochemical potential for the last stage even lower at 2.39 V . However, the observed potential for $\text{H}_2\text{V}_3\text{O}_8$ lithiated state was lower compared to calculated potential and the plateau arising from any stage is expected to be 0.3 to 0.5 V lower than the calculated electrochemical potential. This phenomenon is familiar with the LiCoO_2 system. Though DFT derived intercalation potential for LiCoO_2 is 4.26 V , experimentally it is observed at 3.95 V [37, 38]. Further, various studies have concluded that higher electrochemical potential is expected if the charge of lithium gets preferentially transferred to oxygen atoms instead of V-metal ions [37-40]. This simple electrostatics based argument holds true in layered crystal structure and if the composition is very close, as is the present case. Participation of oxygen in charge transfer gradually decreases as (Table 3) for the three lithiation steps and that of vanadium increases and voltage drops (Fig. S5). Hydrogen is found to be present in all the stages of lithiation and play an active role in the charge transfer process (Table 4). This further establishes the fact that $\text{H}_2\text{V}_3\text{O}_8$ crystal structure cannot be considered as water intercalated species $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{V}_3\text{O}_8$ has three types of ions: 1) vanadium cation, 2) oxygens anion and 3) hydroxyl anion. O (both as oxygen ion and in hydroxyl ion) is the most electronegative element in this system and hence occupies the major chunk of the transferred charge from intercalating Li in every stage of lithiation. However, after each stage of lithiation, the electronegativity of O ion gets suppressed due to increasing level of saturation of its valance 3p-orbitals. Hence, charge transferred ratio to O ions decreases with each stage of lithiation. H in the hydroxyl ion probably gets its share of transferred charge via partial covalent nature of its bonding with oxygen ion. So, with the decrease in the charge transferred rate to O ion with lithiation also results in the decrease of the

charge transferred to H. V as a transition metal has variable oxidation state and can accommodate the extra charge in its 3d-orbitals more comfortably than O-3p and H-1s orbitals. Hence, after each stage of lithiation when charge transferred rate to anions decreases, V-3d orbital accommodates more transferred charge. Therefore, the opposite trend in the transferred charges to anions and cations during lithiation can be considered as a result of the interplay between the electronegativity of O and the variable nature of the oxidation state of the V-3d orbital.

The modification of electronic structure during the lithiation process is illustrated through our PDOS results which are shown in Fig. 4a-d. From Fig. 4a-d, the presence of V^{4+} and V^{5+} in the initial compositions and V^{3+} and V^{4+} in the latter two is clearly observed. The electronic states just below (1 eV) Fermi energies are contributed from up spin t_{2g} orbitals of vanadium. However, all other states up to 6 eV below Fermi energy come from mainly O orbitals. On complete lithiation, the contribution of vanadium d-orbitals increases significantly but remains confined up to 1 eV below Fermi energy. It is noticeable here that due to strong Hund's coupling, majority spin, e.g., orbitals and minority spin t_{2g}/e_g , orbitals are at significantly higher energy level than majority spin t_{2g} orbitals leading to high magnetic moment. A large amount of charge transfer occurring to O orbitals on lithiation is clearly evident in PDOS of $H_2V_3O_8$ and $LiH_2V_3O_8$. It is also observed that the O_2 oxygen atoms attached to hydrogen atoms are appeared to be slightly more ionic than other oxygen atoms.

Fig. 4. PDOS plots for different types of atom present in a) $H_2V_3O_8$; b) $LiH_2V_3O_8$; c) $Li_3H_2V_3O_8$ and d) $Li_4H_2V_3O_8$.

3.4 Electrochemical study (nanobelts prepared for 5 h at various temperatures)

The galvanostatic charge/discharge experiments are carried out between 1.5-4.0 V vs. Li/Li⁺ at 200 mA g⁻¹ current rate. Fig. 5a illustrates the first discharge capacity of H₂V₃O₈ prepared for 5 h at various temperatures. The multiple plateaus suggest that the insertion of Li⁺ occurs in various vacant sites of the host in multiple steps (Fig. 5a). The steep potential from 3.5 V to 2.6 V region indicates a single phase insertion reaction, whereas unique plateau at 2.6 V indicates the two-phase insertion reaction. With further increase in lithium insertion, a sloppy curve arises between 2.5 to 2.0 V region, whereas a well-defined plateau occurs at 1.9 V region, indicating a two-phase reaction in H₂V₃O₈ and Li_xH₂V₃O₈ (where x=2.20 for H₂V₃O₈ prepared at 180 °C).

The discharge capacity contribution of H₂V₃O₈ prepared at various temperatures at a constant current of 200 mA g⁻¹ is illustrated in Fig. 5a, where first discharge capacity of samples prepared at 180 °C, 190 °C, and 200 °C, are observed to be 238 mAh g⁻¹, 249 mAh g⁻¹, and 212 mAh g⁻¹, respectively. Long cycling tests are performed (Fig. 5b) for various samples prepared at different reaction temperatures, cycled under constant cycling rate (200 mA g⁻¹) between 1.5 V-4 V. Though all samples exhibit initial capacities exceeding 200 mAh g⁻¹ however the sample prepared at 200 °C shows the highest capacity retention of 90 % after 50 cycles. Moreover, as seen from the Fig. 5b, the discharge capacity of H₂V₃O₈ remains more or less similar at the end of the cycle number.

After qualifying the constant current tests, all the samples have undergone the rate capability tests as shown in Fig. 5c. The power tests exhibit a superior cathode performance of H₂V₃O₈, which is scarce in the literature. The initial discharge capacity of 288 mAh g⁻¹ at 100 mA g⁻¹ is achieved for a sample prepared at 190 °C. The same material withstands high current rates and

delivers a discharge capacity of $\sim 180 \text{ mAh g}^{-1}$ and $\sim 150 \text{ mAh g}^{-1}$ at 500 mA g^{-1} and 1000 mA g^{-1} , respectively. It is noteworthy to mention here that there is a slight variation in the capacity in the samples prepared at various temperatures as observed from Fig. 5c. Though the above result shows the insertion of three Li^+ (equivalent to $\sim 288 \text{ mAh g}^{-1}$) in the cathode matrix, however, the electrochemical storage property of $\text{H}_2\text{V}_3\text{O}_8$ vs. Li/Li^+ depends on the synthesis temperature and time, which significantly affects the lithium insertion in the host as seen from the results.

Fig.5. a) First discharge voltage-capacity profile of $\text{H}_2\text{V}_3\text{O}_8$; b) Discharge capacity against cycle number of $\text{H}_2\text{V}_3\text{O}_8$ prepared at varying temperature (synthesis time: 5 h) at 200 mA g^{-1} current rate at $20 \pm 2^\circ \text{C}$ and c) Power performance tests of $\text{H}_2\text{V}_3\text{O}_8$ nanobelts prepared at different reaction temperature at varying current rates (all the tests were performed at $20 \pm 2^\circ \text{C}$ temperature and controlled humidity condition).

3.5 Study with samples synthesized at 190 °C with varying time of reaction

As observed from the charge/discharge performance of samples synthesized at various temperatures which show electrochemical property of V_3O_7 layered material that strongly depends on synthesis parameters. Moreover, pristine and phase pure $H_2V_3O_8$ nanobelts are formed at 190 °C; thus, by fixing the synthesis temperature at 190 °C and varying the time (1-7 h), the effect of variation of synthesis time in electrochemical performance is evaluated. Fig. 6a shows the XRD pattern of as-synthesized $H_2V_3O_8$ nanobelts, which resembles orthorhombic symmetry with impurity peak $\sim 15^\circ$ (2θ value) assigned to the sample prepared for 3 h due to the presence of V_2O_5 . However, it is seen from Fig. 6a that at 1 h synthesis time, the XRD pattern is different from rest of $H_2V_3O_8$. To investigate the formation of phase at 1 h synthesis time, XRD at a lower angle was performed which suggests the formation of $V_2O_5 \cdot nH_2O$ (Supplementary Information, Fig. S6). Further, FTIR study of $H_2V_3O_8$ material is shown in Fig. 6b. The peak at 532 cm^{-1} , 925.7 cm^{-1} and 1006.7 cm^{-1} corresponds to the stretching vibration $\nu_s(V-O-V)$ bridging bonds and symmetric stretching of $\nu_s(V^{4+}=O)$ and $\nu_s(V^{5+}=O)$ bonds, respectively [33]. The minute peak at 3402 cm^{-1} and 1623.9 cm^{-1} signifies the stretching and bending modes of O–H vibrations, respectively [34]. Thus, from XRD and FTIR analysis it can be concluded that the formation of pristine $H_2V_3O_8$ nanobelts takes place at 5 h synthesis time and 190 °C.

Fig.6. a) X-ray diffraction patterns of $\text{H}_2\text{V}_3\text{O}_8$ prepared at 190 °C with varying reaction time and b) FTIR of $\text{H}_2\text{V}_3\text{O}_8$ prepared at 190 °C as a function of reaction time.

Further, it will be interesting to study the morphological change happening during the synthesis time. Fig. S7a-i shows the FEG-TEM micrograph of $\text{H}_2\text{V}_3\text{O}_8$ nanobelts prepared at 190 °C with varying reaction times. As evident from the FEG-TEM that at 1h, shorter nanobelts of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ are present, whereas, with further increase in the reaction time, $\text{H}_2\text{V}_3\text{O}_8$ nanobelts with ultra-long morphology (with the occasional presence of shorter nanobelts) are observed. However, with further increase in the reaction time, uniform growth of ultra-long $\text{H}_2\text{V}_3\text{O}_8$ nanobelts is observed. Thus, we can conclude from our study that morphology of ultra-long $\text{H}_2\text{V}_3\text{O}_8$ nanobelts occurs at 190 °C of synthesis time of 5 h and slightly higher temperature.

As we observed from the XRD data and the microscopy study that the reaction temperature and minimum time required to form well-aligned nanobelts are 190 °C and 3 h. Therefore all further electrochemical performance of $\text{H}_2\text{V}_3\text{O}_8$ nanobelt samples (at 190° C and 3h) are tested using galvanostatically charge/discharge experiments at varying current density (electrochemical performance of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was not carried out because our goal was to synthesize $\text{H}_2\text{V}_3\text{O}_8$ and evaluate electrochemical performances of $\text{H}_2\text{V}_3\text{O}_8$). The discharge capacity of each sample with

varying synthesis time is shown in Fig. 7. As observed from Fig. 7, the discharge capacity of a sample prepared at 190 °C for 3 h performs better compared to all other samples at various current rates. The particular sample delivered a discharge capacity of 177 mAh g⁻¹ at 1000 mA g⁻¹ current rate, which indicates the capacity retention of about 57.4 % of initial capacity (308 mAh g⁻¹) observed at 50 mA g⁻¹ current rate. Other samples performance is slightly less compared to sample prepared at 190 °C for 3 h; however, all of them withstand high current rates and attain initial state at the end of the tested cycles.

It is always recommended that the best-performed sample should be tested rigorously. To do so, the sample prepared at 190 °C for 3 h was further tested at higher current rates for a prolonged cycle which are presented in Fig. 8a-b. The first discharge capacity of H₂V₃O₈ nanobelts is observed to be 180 mAh g⁻¹, 168 mAh g⁻¹ and 144 mAh g⁻¹ at 1000 mA g⁻¹, 2000 mA g⁻¹ and 3000 mA g⁻¹ current rates, respectively. The current rate as high as 3000 mA g⁻¹, the material lost its initial discharge capacity and stabilized at 100 mAh g⁻¹ capacity till 500 cycles.

Fig. 7. Rate performance tests of H₂V₃O₈ nanobelts prepared at 190°C at various time of synthesis.

Further increase in cycle number, the discharge capacity sacrifices substantially and reached ~ 75 mAh g⁻¹ at the end of 1000 cycles (Fig. 8b).

Fig. 8. a) First discharge voltage-capacity curve; b) Discharge capacity against cycle number at high current rates for H₂V₃O₈ nanobelts (HVO_190, synthesis time: 3h); c) Potentiodynamic plot of H₂V₃O₈ electrode, the charge/discharge was carried out at 50 mA g⁻¹ for sample prepared at 190 °C (synthesis time: 3h) and d) XPS spectrum for vanadium of H₂V₃O₈ electrode before cycling and after 50th cycle (charge/discharge at current rate of 50 mA g⁻¹ for sample prepared HVO_190 for 3 h).

In the present report, the H₂V₃O₈ nanobelts showed stable cycling data without capacity fading; moreover, discharge profile shows multiple plateaus which resemble multiple step insertion reactions of Li⁺ in the host matrix. To understand the lithium insertion process better, a potentiodynamic plot of initial charge/discharge at 50 mA g⁻¹ is plotted which is shown in Fig. 8c.

From Fig. 8c, it is revealed that the insertion reaction at ~ 2.6 V peak/plateau is accompanied by two phase region, where $\text{H}_2\text{V}_3\text{O}_8$ and $\text{Li}_x\text{H}_2\text{V}_3\text{O}_8$ co-exist, which is not visualized during our previous charge/discharge processes (Fig. 5a) due to the high rate of cycling. The insertion of lithium is maximum in this region followed by further single phase region from 2.4 V to 2.0 V. With further insertion of lithium; plateau arises at 1.9 V, which is minimum compared to 2.6 V plateau and resembles two-phase region. In the present study, we report a maximum of 3.2 lithium insertion (the equivalent of 308 mAh g^{-1} capacity) in the sample prepared at 190°C for 3 h synthesis time; thus, it is possible that mixed state of V^{5+} and V^{3+} still exist in the material and facilitate the redox mechanism.

To elucidate the reaction process with lithium, X-ray Photoelectron spectroscopy (XPS) study of the electrodes was investigated before and after completion of 50th charge/discharge cycle which is shown in Fig. 8d and S8a. Fig. 8d shows the XPS of $\text{H}_2\text{V}_3\text{O}_8$ and $\text{Li}_x\text{H}_2\text{V}_3\text{O}_8$ (100 % depth of discharge (DOD) and, 100 % state of charge (SOC)). The individual spectrum for vanadium V2p exhibited two representative peaks corresponding to V2p3/2 and V2p1/2. However, the spectrum for V2p3/2 is deconvoluted into two ~ 515 eV and 516.7 eV which corresponds to V^{4+} and V^{5+} , respectively. However, at 100 % DOD (after 50th cycle), the spectrum resembles with the pristine material (before cycling). Though, at 100 % DOD, V^{3+} should exist due to the reduction of $\text{V}^{5+}/\text{V}^{4+}$ during insertion of Li^+ ($\sim 3.2 \text{ Li}^+$); however, deconvoluted of V2p3/2 best fit with ~ 515 eV and ~ 516.7 eV. It is noteworthy to mention here that spectrum due to V^{3+} is $\sim 315.35 \pm 1.58$ eV overlap with V^{4+} peak [41]; thus, it is quite difficult to resolve V^{3+} and V^{4+} peak from the observed spectrum. Further, at 100 % SOC, the XPS spectrum shifted towards high binding energy (BE) where peak due to V2p1/2 shifted by 1.5 eV compared to the pristine material. Moreover, the deconvoluted peak for V^{4+} and V^{5+} were ~ 516.2 eV and 517.2 eV, respectively (which is within

the limit of standard deviation) [41]. Thus, it can be summarized that mixed phase of V^{5+} and V^{4+} co-exist in $H_2V_3O_8$ material. Also, lithium environment of electrode material is investigated using XPS experiment and Fig. S8b shows the $Li1s$ spectrum during lithiated state. The peak at 55.1 eV was assigned to $Li1s$, whereas the signal between 56 eV to ~ 60 eV could be assigned to partially decomposed electrolyte component [42].

Further, to understand interface behavior during the insertion process in $H_2V_3O_8$, EIS experiment is performed at various potentials during charge/discharge process (10 mA g^{-1} current rate, and shown in Fig. S9a-b). Fig. S9a shows EIS during discharge process, it is evident from EIS (at OCV) that three different phenomena occur, (i) "at high-frequency region"- due to formation of lithium surface film (LSF), (ii) "at intermediated frequency region"- due to charge transfer resistance and (iii) "lower frequency region"- the process is due to solid state diffusion to the active material. LSF region during insertion process increases and stabilized after 2.5 V plateau region; however, at 2.2 V and onset of the two-phase zone (1.9 V) the phenomenon is quite complex, and all the three-time scales are merged. At 1.5 V region, the curve is well resolved for ($Li_{3.5}H_2V_3O_8$) between high to intermediated frequency and low-frequency region. During charge process (Fig. S9b) at various potentials is unique compared to discharge process (OCV- 2.5 V), the curve is a single depressed semicircle similar to 1.5 V region EIS. The fitted data for EIS (Fig. S9c) shows increasing trend for R_{ct} during insertion process ~ 3.2 V region; however, it decreases and gets stabilized between 2.2 V region and the onset of 1.9 V (two-phase region). Similarly, during charge process (Fig. S9d) R_{ct} stabilized at various potentials; however, at the end of charge process, R_{ct} increased. Moreover, from the fitted data it can be concluded that R_{sf} decreases during charge/discharge process, with stabilized LSF, signifies better electrochemical

performances (capacity retention). The EIS is fitted with parallel RC circuit for porous electrode system (Fig. S9e).

4. CONCLUSION

As observed from the above discussion that $\text{H}_2\text{V}_3\text{O}_8$ synthesized at 190° and 3 h synthesis time shown better electrochemical performance, which is associated with the optimum growth of $\text{H}_2\text{V}_3\text{O}_8$ nanobelts that facilitates the lithium ion diffusion. As a result, $\text{H}_2\text{V}_3\text{O}_8$ cathode material delivered a high discharge capacity of 308 mAh g^{-1} at 50 mA g^{-1} current rate for the sample prepared at 190°C for 3 h. The sample withstood the high current test performance and delivered high capacity of 180 mAh g^{-1} , 168 mAh g^{-1} , and 144 mAh g^{-1} at 1000 mA g^{-1} , 2000 mA g^{-1} , and 3000 mA g^{-1} current rates, respectively. Further, the first time we have used DFT studies to established the hydrogen position and lithium intercalation stages in $\text{H}_2\text{V}_3\text{O}_8$ material. At the current stage of understanding, we showed that the hydrogen stays as part of the intercalation framework as hydroxyl unit, which plays a vital role in structural stability and facilitates the high ion movement in the crystal structure. Prolonged cycle life and stability at high rates indicate its application as next generation cathode material for high-performance Libs. Furthermore, the excellent capacity retention observed in $\text{H}_2\text{V}_3\text{O}_8$ cathode material shows the significance of morphology in insertion type electrochemistry. Thus, we summarize the present report that includes (i) the unique morphology of $\text{H}_2\text{V}_3\text{O}_8$ cathode materials described using atomic scale simulations, (ii) electrochemical stability of $\text{H}_2\text{V}_3\text{O}_8$ cathode depends on synthesis parameters and optimum growth, (iii) structural retention of $\text{H}_2\text{V}_3\text{O}_8$ at high current rates, and (iv) demonstrated a high rate performance of $\text{H}_2\text{V}_3\text{O}_8$ cathode with long cycle life. Currently, we accomplished the improve cycling performance without any ceramic coating that used to protect the electrode material from HF side reaction and resulted in capacity fading. Here, we are not

claiming that our particular morphology stabilizes the side reaction rather we are saying that using this morphology and coating technology we can further enhance the cathode performance.

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Notes

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