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**Improved elevated temperature performance of Al-intercalated
V₂O₅ electrospun nanofibers for lithium-ion batteries**

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Abstract

Al-inserted vanadium pentoxide (V_2O_5) nanofibers (Al-VNF) are synthesized by simple electrospinning technique. Powder X-ray diffraction (XRD) patterns confirm the formation of phase-pure structure. Elemental mapping and XPS studies are used to confirm chemical insertion of Al in VNF. Surface morphological features of as-spun and sintered fibers with Al-insertion are investigated by field emission scanning electron microscopy (FE-SEM). Electrochemical Li-insertion behavior of Al-VNFs are explored as cathode in half-cell configuration (vs. Li) using cyclic voltammetry and galvanostatic charge-discharge studies. Al-VNF ($Al_{0.5}V_2O_5$) shows an initial discharge capacity of $\sim 250 \text{ mAh g}^{-1}$ and improved capacity retention of $>60\%$ after 50 cycles at 0.1 C rate, whereas native VNF showed only $\sim 40\%$ capacity retention at room temperature. Enhanced high current rate and elevated temperature performance of Al-VNF ($Al_{1.0}V_2O_5$) is observed with improved capacity retention ($\sim 70\%$) characteristics. Improved performance of Al-inserted VNF is mainly attributed to the retention of fibrous morphology, apart from structural stabilization during electrochemical cycling.

Keywords: Li-ion batteries; Cathode; Electrospinning; Vanadium pentoxide (V_2O_5) nanofibers; Rate capability; elevated temperature performance

1.0 Introduction

Lithium-ion batteries (LIB) are one of the promising energy storage technologies in this era for portable applications like camcorders, laptops and electronic gadgets¹⁻³. Several research works are devoted to employ such LIB power packs for zero-emission transportation applications like electric vehicle (EV) and hybrid electric vehicles (HEV)⁴. Since the commercialization of LIB power packs, graphite anode has dominated the battery industry. Nevertheless, graphitic anode serves essentially as a buffer medium for Li-storage which must be tuned to the inadequate capacity of the selected cathode material⁵. On the other hand, the commercially-available cathodes like LiCoO₂, LiMn₂O₄, LiFePO₄ and its derivatives are capable of exhibiting practical capacity of <200 mAh g⁻¹⁶⁻⁸. Obviously, the route to any appreciable advance in Li-ion battery performance must clearly lie in the direction of improving the cathodes with higher specific capacities. Layered V₂O₅ undergoes multiple Li-insertion/extraction reactions, thus resulting in high theoretical capacity of ~400 mAh g⁻¹. This can be attributed to its multiple oxidation states (V⁵⁺, V⁴⁺ and V³⁺) and hence is a promising candidate for high capacity cathodes.

V₂O₅ offers several advantages such as low cost and abundance on earth crust⁹. At the same time, problems such as severe capacity fading and poor rate capability inhibit its practical LIB application. Poor Li-diffusion kinetics, structural instability with Li-intercalation/de-intercalation and inherent electronic conductivity ($\sim 10^{-2} - \sim 10^{-3}$ S cm⁻¹) of V₂O₅ are main causes of the aforementioned issues^{10,11}. Studies have shown that nanostructured V₂O₅ exhibits higher initial capacity as compared to bulk V₂O₅ owing to their small particle size, micro/nano structure morphology which provides shortened Li-diffusion pathways¹²⁻¹⁴. In addition, to overcome the said issues the morphology is fine-tuned to improve the Li⁺ ion diffusion by creating more open structures and incorporation of conductive coatings¹⁵⁻¹⁷ to increase the conductivity by

synthesizing the V_2O_5 in one-dimensional (1D) nanostructures^{1,12-15,18-22}. Inclusion of transition metal cations like Al^{3+} and Ag^+ into V_2O_5 layers leads to the formation of $[MO_6]$ octahedral units that enhance the structural stability during Li-intercalation/de-intercalation²³.

In the present work, an attempt has been made to synthesize one-dimensional (1D) V_2O_5 nanofibers (VNF) with inclusion of various amounts of Al in the V_2O_5 interlayer ($Al_{0.5}$ VNF and $Al_{1.0}$ VNF) by electrospinning technique. Electrospinning is a simple, cost-effective method which enables the nanofibers with high aspect ratio and a large surface area-to-volume ratio^{1,12,13,15,21,24,25}. Tunable surface morphology and diameter of the fibers is easily controlled by varying parameters such as the applied potential, viscosity and flow rate of the precursor. For LIBs applications, porous and highly interconnected nanoparticle network of nanofibers electrode provides higher electrode/electrolyte contact surface with facile diffusion pathways. Extensive characterizations were carried out for the electrospun VNF, $Al_{0.5}$ VNF and $Al_{1.0}$ VNF fibers and electrochemical properties were evaluated by means of half-cell configuration with different testing conditions. The obtained results are described in detail.

2.0 Experimental

2.1 V_2O_5 Synthesis and Characterization

For the preparation of Al-VNFs, the precursors vanadyl acetylacetonate ($VO(acac)_2$, 98%, Sigma-Aldrich, 2.65 g), poly (vinylpyrrolidone) (PVP, M_w 360,000, Fluka), acetic acid (Tedia Company Inc.) and absolute ethanol (Fluka) were used as received. The synthesis procedure of VNF was slightly modified for chemical insertion of Al^{3+} ions from our previous work^{14,22,26}. Acetic acid and absolute ethanol was used in 1 : 9 volume ratio and 0.012 g ml^{-1} and 0.03 g ml^{-1} of aluminium nitrate ($Al(NO_3)_3$, Riedel de Haën, >98%) was added to obtain $Al_{0.5}$ VNF and

Al_{1.0}VNF phases respectively. The well-mixed precursor was electrospun using applied DC voltage of 10 kV between the needle tip and aluminium foil collector. The distance between needle and Al collector was kept a distance of 10 cm with flow rate of 1.5 ml h⁻¹. As-spun fibers were then heat-treated at 400 °C for 15 min in air with a heating and cooling rate of 2 °C min⁻¹ to yield the resultant phase.

Morphological features of Al-inserted and native VNFs were studied using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) with an accelerating voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100F) in high resolution mode operating at 200 kV attached with elemental mapping. Structural properties of Al-inserted and native VNF were examined using Bruker X-ray diffractometer using Cu-K α radiation between 10 to 80 °. The obtained X-ray diffraction (XRD) patterns were analyzed by Rietveld refinement^{27,28} using Topas V3 (Bruker-AXS) software by fundamental parameters approach²⁹. X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra (Kratos) spectrometer with monochromatic Al-K α excitation and analysed using CasaXPS software (Version 2.3.15).

2.2 Electrode Fabrication Process

Composite cathodes were formulated by mixing active material (V₂O₅), binder (Kynar 2801), and conductive additive (Super P Li carbon, Timcal) in the weight ratio 60:20:20, respectively, using 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich) as solvent for binder to form slurry. The resulting viscous slurry was subsequently coated over aluminium foil using a doctor blade. Al foils were dried in a vacuum oven for several hours to remove the solvent molecules and pressed in between the twin rollers to provide necessary adherence towards Al current collector. The dried composite VNF electrodes were punched out with 16 mm diameter blanks and same area

of counter electrode lithium foil (~ 0.59 mm thick, Hohsen Corporation, Japan) was used for the fabrication of test cells. The lithium insertion properties were evaluated in half-cell configuration using two-electrode CR 2016 coin cell assembly. The coin-cells were fabricated under Ar filled glove box (MBraun) and the electrodes were separated by Celgard 2400 separator. The 1 M LiPF_6 in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 wt.%, Danvec) binary mixture was used as electrolyte solution.

Galvanostatic discharge-charge profiles of Al-inserted and native VNF based test cells were conducted between 1.75-4 V vs. Li at ambient and elevated temperature (55°C) conditions, using battery testing systems (Neware) at constant current mode. Cyclic voltammetric (CV) traces were recorded using Solartron 1470E potentiostat in two-electrode configuration at scan rate of 0.1 mV s^{-1} , in which metallic lithium serves as both counter and reference electrode.

3.0 Results and Discussions

3.1 Morphological and Compositional Studies

Figure 1 represents the surface morphological features of as-spun and sintered VNFs with and without Al insertion. From Figure 1a, c, and e, it is apparent to notice the formation of smooth morphology with long aspect ratios and mainly with fiber diameters ranging from 500-800 nm for VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, respectively. Incorporation of $\text{Al}(\text{NO}_3)_3$ in to the VNF precursor leads to a slight decrease in viscosity of the solution, which results in a lower flow rate (1.5 ml h^{-1}) during the electrospinning process compared to native VNF fibers (2 ml h^{-1}). As a result, it gives rise to larger size distribution of fibers in the Al-VNFs with reduced thickness ($\sim 100\text{-}200 \text{ nm}$) as can be seen from the Figures 1c and e. Sintering at 400°C for 15 min in air results in the formation of porous fibers for pure V_2O_5 and the obtained morphology is

similar to our previous work (Figure 1b)¹⁴. Nevertheless, polycrystalline fibers are obtained in the case of Al-VNF (Figures 1d, f and 2a, b) with surface area of $\sim 9\text{-}10\text{ m}^2\text{ g}^{-1}$ irrespective of the Al doping and heat treatment. Transmission electron microscopy (TEM) also revealed the presence of porous fibers, irrespective of Al insertion (Figure 2). The presence of such porous structure is expected to enable the facile insertion/extraction of Li-ions and thereby providing better electrochemical properties, especially at high current rates. Elemental analysis was carried out to estimate the amount of Al^{3+} present in the V_2O_5 layers of two samples synthesized resulted in Al:V molar ratios of 1:4 and 1:2, respectively. Hereafter, the former and latter compositions are denoted as $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$, respectively. Mapping is one of the efficient techniques to study the distribution of elements in the specified area. Figure 2 shows the elemental mapping of Al-VNF with two different compositions and it was recorded during TEM analysis. It is evident that, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ showed the even distribution of Al^{3+} throughout the area mapped according to the concentration of the inserted element.

The XRD patterns of Al-inserted and native VNFs were collected and presented in Figure 3. Rietveld refinements were carried out for all the three samples (VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$) using TOPAS software. The observed reflections for VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ clearly indicate the formation of phase pure structure without any impurity traces or preferred orientation. The crystalline peaks were indexed according to the layered Shcherbinaite structure with $Pmn2_1$ space group. The lattice parameter values of VNF are calculated by Rietveld refinement (Supporting information Figure S1) and found to be $a=11.5181(1)\text{ \AA}$, $b=4.3805(4)\text{ \AA}$ and $c=3.5671(2)\text{ \AA}$. Variations in the lattice parameter values are noted for inclusion of Al; $\text{Al}_{0.5}\text{VNF}$ is $a=11.5197(2)\text{ \AA}$, $b=4.3756(9)\text{ \AA}$ and $c=3.5675(6)\text{ \AA}$; and $\text{Al}_{1.0}\text{VNF}$ $a=11.5202(3)\text{ \AA}$, $b=4.3783(1)\text{ \AA}$ and $c=3.5704(1)\text{ \AA}$. The observed values are consistent with the literature

values (JCPDS 89-2482 $a=11.5202(3)$ Å, $b=4.3783(1)$ Å and $c=3.5704(1)$ Å) Inclusion of Al in the V_2O_5 structure results in the decrease of crystallite size values and found to be 98(2), 47(1) and 33(1) nm for VNF, $Al_{0.5}VNF$ and $Al_{1.0}VNF$, respectively. This clearly indicates influence of Al^{3+} ion towards the structural properties of V_2O_5 . Reduction in the crystallite size values are apparently reflected from the decrease in the intensity and broadening of the peaks evidenced from XRD patterns. From the increase in the a and c lattice parameters from the native VNF to the Al-inserted VNF, it can be deduced that the chemically-inserted Al^{3+} ions are likely to reside between the VO_5 slabs and forming the $[AlO_6]$ octahedra with oxygen atoms in the V_2O_5 structure^{23,30}. Schematic representations of the layered V_2O_5 crystal structure, formed by the VO_5 polyhedra, and the possible positions of Al^{3+} ions residing within the V_2O_5 layers, are given in Figure 3b and c, respectively. The occupancy of Al^{3+} will stabilize the VO_5 layers and thereby improving the facile insertion and extraction of Li-ions under high current operations.

X-ray photo electron spectrum (XPS) of VNF, $Al_{0.5}VNF$ and $Al_{1.0}VNF$ samples with energy level of V $2p_{3/2}$ are recorded and given in Figure 4. In the native VNF, the peak is observed at 517.6 eV corresponds to the V^{5+} oxidation state of V_2O_5 ^{30, 31}. Introduction of Al^{3+} into the V_2O_5 lattice leads to the shifting of binding energy in to lower energy levels and evident from the energy level spectra of V $2p_{3/2}$. The binding energy 516.0 - 516.1 eV indicates the presence of V^{4+} ions and the observed values are similar to VO_2 phase, in which vanadium is in 4+ state^{30, 31}. In the case of $Al_{1.0}VNF$, a small shoulder at 514.0 eV is noted which indicates the presence of mixed valence state of vanadium (V^{3+} and V^{4+})³¹. $Al_{0.5}VNF$ possibly contains the mixed valence states of V^{5+} and V^{4+} , which is necessary to balance the net charge in the crystal structure of V_2O_5 matrix due to the accommodation of Al^{3+} ions. At the same time, the crystal structure of V_2O_5 is still intact and evident from the XRD reflections obtained above. The molar

ratio of Al:V are in good agreement with elemental analysis described above and formula for $\text{Al}_{0.5}\text{VNF}$ can be written as $\text{Al}_{0.5}(\text{V}^{5+}_{0.5} \text{V}^{4+}_{1.5})\text{O}_5$. Similarly for $\text{Al}_{1.0}\text{VNF}$, the larger amount of Al^{3+} inserted leads to the formation of V^{4+} and V^{3+} ions in place of V^{5+} . In combination with the elemental analysis, the molecular formula is derived to be $\text{Al}_{1.0}(\text{V}^{4+}_{1.0} \text{V}^{3+}_{1.0})\text{O}_5$.

3.2 Electrochemical Studies

Electrochemical properties of the Al-inserted and native VNF were evaluated by means of both galvanostatic and potentiostatic modes in half-cell (Li/VNF) configurations. Generally, insertion of Li-ions into V_2O_5 layers results the transformation of V_2O_5 in to $\text{Li}_x\text{V}_2\text{O}_5$ phase. Thus results the distortion in layered structure due to the occupancy of Li^+ ions into the spaces between the layers of VO_5 octahedral unit. Slow scan (scan rate 0.1 mV s^{-1}) cyclic voltammograms (CV) of Li/VNF, Li/ $\text{Al}_{0.5}\text{VNF}$ and Li/ $\text{Al}_{1.0}\text{VNF}$ cells are collected in the range between 1.75-4.0 V vs. Li to understand the phase transformation during Li-intercalation/de-intercalation and presented in Figure 5. The following equation describes the overall Li-intercalation mechanism in V_2O_5 matrix,

The test cells are first discharged to intercalate the Li-ions in to V_2O_5 lattice. In the 1st cycle (Fig. 5a, c, e), several oxidation/reduction peaks are observed for the Al-inserted and native VNF corresponding to the intercalation/de-intercalation processes of Li-ions in V_2O_5 . For VNF and $\text{Al}_{0.5}\text{VNF}$, the reduction (cathodic) peaks are observed at ~ 3.37 , ~ 3.16 , ~ 2.22 , and ~ 1.90 V vs. Li. In addition $\text{Al}_{0.5}\text{VNF}$ has a smaller reduction peak at ~ 3.16 V vs. Li when compared to native VNF, and in addition smaller peaks are also observed at ~ 2.71 and ~ 2.54 V vs. Li. On the other hand, vanishing of reduction peaks at ~ 3.37 and ~ 3.16 V are noted for $\text{Al}_{1.0}\text{VNF}$ phase

when compared to native VNF and $\text{Al}_{0.5}\text{VNF}$ phases. Appearance of remaining reduction peaks are noted at ~ 2.66 , ~ 2.22 and ~ 1.9 V vs. Li in both cases. For VNF and $\text{Al}_{0.5}\text{VNF}$, showed a broad oxidation (anodic) peak at ~ 2.70 V vs. Li and showing variation in area under the curve, whereas two sharp oxidation peaks are observed for $\text{Al}_{1.0}\text{VNF}$ at ~ 2.28 and ~ 2.83 V vs. Li. Current densities of the Al-inserted Al-VNFs also appear to be less than that of native VNF, which could be attributed to the presence of Al^{3+} ions occupied between the layers. Wei *et al.*^{32,33} also noted the similar kind of reduction in current densities while introducing metal-ion on V_2O_5 lattice. The appearances of cathodic peaks are indicative of the multistep reduction of V^{5+} in V_2O_5 within the voltage range 1.75 to 4.0 V vs. Li¹⁴. The cathodic peaks at ~ 3.37 and ~ 3.16 V vs. Li indicates the reduction of V^{5+} to V^{4+} , leads to the formation of $\epsilon\text{-Li}_x\text{V}_2\text{O}_5$ phase, which is observed only for VNF and $\text{Al}_{0.5}\text{VNF}$ phases. The absence of V^{5+} in $\text{Al}_{1.0}\text{VNF}$ is well reflected in CV measurements and it is in good agreement with XPS data. The other cathodic peaks ~ 2.22 and ~ 1.90 V vs. Li belongs to partial reduction of V^{4+} to V^{3+} and this reduction reveal the formation of δ - and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ mixed phases. Presence of additional reduction peak at ~ 2.71 V vs. Li for $\text{Al}_{0.5}\text{VNF}$ and ~ 2.66 V vs. Li for $\text{Al}_{1.0}\text{VNF}$ could be attributed to the increased instances of reduction of V^{4+} . Cycling below 2.0 V vs. Li leads to the formation of irreversible $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase which is confirmed by the appearance of reduction peak at ~ 1.90 V vs. Li and it is noted for all three VNFs tested³⁴.

Subsequent electrochemical cycling in potentiostatic modes are given in Figure 5b, d & f. The observed traces in the successive cycles are entirely different from the first cycle for the case of native VNF and $\text{Al}_{0.5}\text{VNF}$ phases. In VNF, the reduction peak is shifted from ~ 2.28 to ~ 2.31 V vs. Li for consecutive cycles, whereas oxidation peak remains at ~ 2.68 V vs. Li. On the other hand, in $\text{Al}_{0.5}\text{VNF}$ the oxidation and reduction peaks remains at same potentials. Contrary to

above, $\text{Al}_{1.0}\text{VNF}$ displayed the reduction and two oxidation peaks at ~ 2.65 and ~ 2.27 & ~ 2.84 V vs. Li, respectively. The observed redox potentials are same as that of in the first cycle with intense peaks, which is due to the influence of Al^{3+} insertion. It is evident that, presence of Al^{3+} ions between the layers effectively improves the structural properties during electrochemical Li-insertion/extraction and retains the crystal structure of V_2O_5 . However, in all three samples there is no deviation of shape noted from 2nd cycle onwards, which indicates the excellent reversibility of the V_2O_5 fibers during lithium intercalation and de-intercalation. Further, it is obvious to notice that for VNF and $\text{Al}_{0.5}\text{VNF}$, the net area under the curve tends to decrease, which is indicative of capacity fade during cycling. Nevertheless, very small amount of reduction in the net charge under the curve is noted for $\text{Al}_{1.0}\text{VNF}$. Hence, an improved cycleability is expected for the $\text{Al}_{1.0}\text{VNF}$ irrespective of the capacity.

Galvanostatic cycling profiles of Li/VNF, $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$ coin cells cycled between 1.75– 4.0 V vs. Li at 0.1 C rate (1 C is assumed to be 350 mAh g⁻¹) in room temperature is shown in Figure 6. As expected, all the three samples showed multiple plateaus during first discharge, which is consistent with the CV analysis and representative phase transitions occurring during Li-intercalation/de-intercalation^{1,13,17,35}. The first discharge plateau at ~ 3.18 V vs. Li which is attributed to the reduction of V^{5+} to V^{4+} to enable the intercalation of Li-ions in to layered V_2O_5 ^{12,16,36}. It is interesting to notice the vanishing of obvious plateau at ~ 3.18 V vs. Li upon introduction of Al^{3+} ions in to the V_2O_5 matrix. For $\text{Al}_{0.5}\text{VNF}$, it is observed that the plateau at ~ 3.18 V vs. Li is shortened when compared to native VNF which is attributed to the reduction of remaining V^{5+} in to V^{4+} . There is no such obvious plateau is observed for the $\text{Al}_{1.0}\text{VNF}$ due to the unavailability of V^{5+} ions. Upon further reduction, two prominent plateaus at ~ 2.28 and ~ 2.08 V vs. Li are observed for all the three cases with small shift in the range. The

plateau at ~ 2.24 V is an indication of the formation of $\delta\text{-Li}_x\text{V}_2\text{O}_5$ phase and V^{4+} is partially reduced to V^{3+} forming $\delta\text{-}$ and $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ mixed phases. The plateau ~ 2.08 V vs. Li is believed to be the transformation of $\delta\text{-Li}_x\text{V}_2\text{O}_5$ to $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase. Further discharge into 1.75 V vs. Li causes the irreversible formation of $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase, and this is in good agreement with CV traces obtained above. Further, the plateau ~ 2.3 V is also shortened and this leads to the lower initial discharge capacity of ~ 250 mAh g^{-1} (~ 1.7 moles of lithium). However, in $\text{Al}_{1.0}\text{VNF}$ phase distinct plateau at ~ 3.12 V vs. Li is not observed. Instead, observation of a broad plateau at ~ 2.67 V and a shortened plateau at ~ 2.3 V vs. Li indicates the reduction of V^{4+} to V^{3+} , consistent with the CV data obtained above. The plateau observed at ~ 2.0 V vs. Li in $\text{Al}_{1.0}\text{VNF}$ is also not as sharp as observed in the case of VNF and $\text{Al}_{0.5}\text{VNF}$. In the second charge-discharge cycle, there are no plateaus observed for VNF and $\text{Al}_{0.5}\text{VNF}$, whereas shortened plateaus are observed ~ 2.7 V and ~ 2.76 V vs. Li in the discharge and charge curves respectively for $\text{Al}_{1.0}\text{VNF}$, corresponding to the improved structural stability of $\text{Al}_{1.0}\text{VNF}$ phase rendered by Al^{3+} insertion. This is an indication that an irreversible phase transformation of V_2O_5 to $\text{Li}_x\text{V}_2\text{O}_5$ occurred during the first discharge for VNF and $\text{Al}_{0.5}\text{VNF}$, but there is some reversibility of the phase transformation occurring in the more heavily-inserted $\text{Al}_{1.0}\text{VNF}$ phase which is in good agreement with the observations in CV trace. In all three samples, first charge capacity is slightly higher than discharge capacity and the observed excess capacity is obtained from the interfacial storage across the electrolyte/electrode interface. Except for the initial cycle, all the three materials exhibited columbic efficiency over 99% in subsequent cycles, which indicates excellent reversibility during galvanostatic cycling.

As mentioned earlier, all VNF cells were cycled galvanostatically between 1.75 to 4.0 V vs. Li at 0.1 C rate (35 mA g^{-1}) at room temperature and presented in Figure 7a. VNF delivered

an initial discharge capacity of 316 mAh g^{-1} (~ 2.2 moles of lithium) and retained only 43% of initial capacity upon cycling to 50 cycles. $\text{Al}_{0.5}\text{VNF}$ starts off with initial capacity of $\sim 250 \text{ mAh g}^{-1}$, which is equivalent to ~ 1.7 moles of lithium and retains 63% of initial capacity after 50 cycles. The lower initial capacity could be due to the reduced transformation of V^{5+} to V^{4+} . As for $\text{Al}_{1.0}\text{VNF}$, it also displayed higher initial discharge capacity of $\sim 350 \text{ mAh g}^{-1}$ and maintained $\sim 85\%$ of cyclic retention within 20 cycles. The higher initial capacity is possibly due to the increased space between the VO_5 layers (Figure 3c), enabling initial intercalation of larger amount of Li^+ ions and conductivity as well (Supporting information Figure S2).

To study the influence of Al^{3+} insertion towards the electrochemical properties of VNF at elevated temperature conditions (55°C) with same current rate (0.1 C), galvanostatic charge-discharge studies were conducted and corresponding cycling profiles are illustrated in Figure 7b. The native VNF fibers delivered the discharge capacity of ~ 285 (~ 2 moles lithium) and $\sim 120 \text{ mAh g}^{-1}$ (~ 0.8 moles lithium) for first and 50th cycle, respectively with $\sim 40\%$ capacity retention. Incorporation of Al^{3+} , $\text{Al}_{0.5}\text{VNF}$ showed the initial discharge capacity of $\sim 360 \text{ mAh g}^{-1}$ (~ 2.4 moles lithium) with improved capacity retention of over 50% after 50 cycles. For $\text{Al}_{1.0}\text{VNF}$, the insertion of Al^{3+} is beneficial for achieving highest discharge capacity of $\sim 350 \text{ mAh g}^{-1}$ (~ 2.4 moles lithium) with capacity retention of $\sim 66\%$ after 50 cycles. It is interesting to note that the $\text{Al}_{1.0}\text{VNF}$ has the highest initial capacity at 0.1 C rate for both room temperature as well as elevated temperature (55°C) cycling. Also, the obtained result clearly shows the influence of Al^{3+} ions towards thermal stability of V_2O_5 at elevated temperature conditions. Unfortunately, there are no reports available on the high temperature performance of V_2O_5 to compare the obtained results.

High-rate performance is one of the pre-requisite for cathode materials and in order to establish the effect of Al^{3+} insertion, the test cells were cycled at 1 C (350 mA g^{-1}) in room temperature conditions and corresponding cycling profiles are given in Figure 7c. The cell comprising VNF showed the lower initial discharge capacity of $\sim 114 \text{ mAh g}^{-1}$ (~ 0.8 moles lithium) when compared to $\sim 320 \text{ mAh g}^{-1}$ at 0.1 C rate. However, the capacity retention is improved to 60% after 50 cycles. The $\text{Al}_{0.5}\text{VNF}$ cell exhibited the capacity of 240 mAh g^{-1} which is almost same capacity at low current rates ($\sim 250 \text{ mAh g}^{-1}$), however improvement in the capacity retention is noted after 50 cycles ($\sim 60\%$). As for $\text{Al}_{1.0}\text{VNF}$, the larger amount of Al-inclusion led to the slightly less initial capacity of $\sim 208 \text{ mAh g}^{-1}$ when compared to low rates ($\sim 250 \text{ mAh g}^{-1}$ at 0.1 C rate), but enhanced capacity retention of $\sim 70\%$ is noted after 50 cycles. Zhan *et al.*^{30,37} reported the synthesis of Al-inserted V_2O_5 nanopowder ($\text{Al}_{0.2}\text{V}_2\text{O}_5$) and delivered the initial discharge capacity of $\sim 190 \text{ mAh g}^{-1}$ at ~ 0.1 C rate with $\sim 76\%$ capacity retention after 50 cycles. When increasing the current rate to 0.2 C, the cell displayed a discharge capacity of $\sim 140 \text{ mAh g}^{-1}$ with cyclic retention of $\sim 57\%$ after 50 cycles. In the present work, increasing the concentration of Al^{3+} ions in the VNF matrix contributed to higher cycling stability and capacity retention at higher C-rates. Furthermore, the porous morphology of the fibers contributed the advantage of higher initial capacity and improved capacity retention when compared to Al-inserted nanopowders.

Post-mortem analysis was carried out after electrochemical cycling to ensure the retention of fibrous morphology after the cycling. Hence, the cycled test cells were opened in an Argon-filled glovebox and electrodes were carefully taken and washed with DEC and subsequently dried. For comparison, fresh test electrodes are also subjected for the FE-SEM investigations and obtained images are presented in Figure 8. From Figure 8a, it can be seen that,

as-prepared VNF electrode shows the presence of nanofibers (indicated by arrow) morphology before cycling and there is no fibrous morphology is retained after cycling (Figure 8b). Nanofibrous morphology is observed in as-prepared electrodes of Al-VNF (arrowed, Figures 8c & e). In contrast to native VNF, the fibers are still intact (arrowed, Figures 8d & f) after the electrochemical cycling. The improved tenacity of the Al-VNF could contribute to the improved electrochemical properties, especially capacity retention during high rate testing, when compared to native VNF.

In general, Al-insertion to VNF is observed to improve the high-rate and high temperature cycling properties to a certain extent. Firstly, the addition of Al^{3+} ions into the V_2O_5 structure leads to the reduction of V^{5+} to V^{4+} (for both $\text{Al}_{0.5}\text{VNF}$ and $\text{Al}_{1.0}\text{VNF}$) and also to V^{3+} (for $\text{Al}_{1.0}\text{VNF}$) during the *in-situ* synthesis of Al-VNFs. The presence of these pre-reduced vanadium ions (V^{4+} and V^{3+}) before the electrochemical Li-intercalation/de-intercalation reduces the extent of electrochemically induced phase changes, related to the conversion of V_2O_5 to $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ phase. Further, Al^{3+} insertion leads to increased *c*-spacing in the layered structure and it is believed to occupy between the VO_5 layers, thus provides the necessary structural stability for V_2O_5 phase. Once the crystal structure is stabilized and less susceptible distortion due to the intercalation/de-intercalation of Li-ions during electrochemical cycling^{23,30}. In comparison, $\text{Al}_{0.5}\text{VNF}$ has more similar phase transitions during Li-intercalation/de-intercalation with native VNF due to the smaller increase in the lattice parameters and presence of V^{5+} ions remains within the structure. On the other hand, $\text{Al}_{1.0}\text{VNF}$ has a much larger deviation in *a* and *c* lattice parameters, and also the complete reduction of V^{5+} ions to a mixed valence states of V^{4+} and V^{3+} ions which leads to the larger differences in phase transitions related to Li-intercalation/de-intercalation during electrochemical cycling. From the galvanostatic studies, it is evident that,

irrespective of the inclusion of Al^{3+} at low and high current rates and testing temperature, the layered V_2O_5 showed capacity fading during cycling. There are several reasons believed for such fading, which includes vanadium dissolution³⁸, poor compatibility of vanadium towards linear carbonates (DEC)^{39,40} and also intrinsic nature of the native compound¹⁰. Further, the presence of Al^{3+} drastically improved the electrochemical performance of V_2O_5 by stabilizing the structure during high current rate and elevated temperature operations. Similar kind of improvement in the elevated temperature performance for Al^{3+} inclusion has also been noticed in other systems like LiMn_2O_4 ⁴¹ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ⁴². At the same time, one-dimensional fibrous morphology of V_2O_5 nanofibers cannot be ruled out, which enables facile insertion/extraction of Li-ions during high current testing. The presences of voids in the fibers enable more contact area towards electrolyte solution leads to the faster diffusion of Li-ions. In addition, the retention of fibrous morphology during electrochemical testing is also one of the factors for such performance as shown by post-mortem electrode analysis.

4.0 Conclusion

Al-inserted electrospun VNF were synthesized via *in-situ* addition of Al^{3+} ions and compared with native VNF. Formation of high aspect ratio nanofibers with diameters in the range of 500-800 nm were observed in FE-SEM. The XRD patterns reveal the formation of polycrystalline single phase V_2O_5 in Al-VNF and the inserted Al^{3+} ions occupies between the VO_5 layers of the V_2O_5 structure. The XPS studies confirm the formation of $\text{Al}_{0.5}\text{V}_2\text{O}_5$ and $\text{Al}_{1.0}\text{V}_2\text{O}_5$ phases through the valence state of vanadium. Electrochemical studies conducted in half-cell configurations reveal phase transformations in Al-VNFs, as compared to native VNF during both galvanostatic and potentiostatic measurements. The $\text{Al}_{1.0}\text{VNF}$ showed enhanced high rate and

elevated temperature performance due to the retention of fibrous morphology and inclusion of Al^{3+} in its crystal structure.

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Supplementary information

Rietveld refinement and electrochemical impedance spectroscopic studies were conducted for electrospun Al-intercalated V_2O_5 nanofibers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure captions

Fig. 1 Field emission secondary electron (FE-SEM) images of as-spun (a) VNF, (c) Al_{0.5}VNF, (e) Al_{1.0}VNF and sintered (b) VNF, (d) Al_{0.5}VNF and (f) Al_{1.0}VNF respectively

Fig. 2 Transmission electron (TEM) images and corresponding Al, V and O (as labeled) elemental maps of (a) Al_{0.5}VNF and (b) Al_{1.0}VNF respectively

Fig. 3 (a) X-ray diffraction (XRD) patterns of VNF, Al_{0.5}VNF and Al_{1.0}VNF and schematic representation of (b) V₂O₅ (Shcherbinaite) crystal structure and (c) V₂O₅ lattice (not to scale) with possible positions of Al atoms, as indicated by blue spheres, and possible movement of V₂O₅ layers upon intercalation of lithium ions, as indicated by arrows.

Fig. 4 V2p_{2/3} X-ray photoelectron spectra (XPS) of VNF, Al_{0.5}VNF and Al_{1.0}VNF.

Fig. 5 Cyclic voltammograms showing first cycles of (a) VNF, (c) Al_{0.5}VNF, (e) and subsequent cycles of (b) VNF, (d) Al_{0.5}VNF and (f) Al_{1.0}VNF respectively, in which metallic lithium serves as both counter and reference electrodes in two electrode coin cell configuration at scan rate of 0.1 mV s⁻¹ between 1.75-4.0 V vs. Li. Integer represents cycle number.

Fig. 6 Typical galvanostatic traces of first two charge-discharge curves of (a) VNF, (b) Al_{0.5}VNF and (c) Al_{1.0}VNF cells between 1.75-4.0 V vs. Li at 0.1 C rate in room temperature.

Fig. 7 Plots of specific discharge capacity vs. cycle number of VNF, Al_{0.5}VNF and Al_{1.0}VNF cycled at (a) 0.1 C rate at room temperature and (b) 0.1 C rate at 55 °C and (c) 1 C rate at room temperature

Fig. 8 Field emission secondary electron (FE-SEM) images of as-prepared electrodes of (a) VNF, (c) $\text{Al}_{0.5}\text{VNF}$, (e) $\text{Al}_{1.0}\text{VNF}$ and electrochemically cycled electrodes of (b) VNF, (d) $\text{Al}_{0.5}\text{VNF}$ and (f) $\text{Al}_{1.0}\text{VNF}$ respectively

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Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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Figure 7

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