Electrochemical Properties of Na$_{0.66}$V$_4$O$_{10}$ Nanostructures as Cathode Material in Rechargeable Batteries for Energy Storage Applications

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ABSTRACT: We report the electrochemical performance of nanostructures of Na$_{0.66}$V$_4$O$_{10}$ as cathode material for rechargeable batteries. The Rietveld refinement of room-temperature X-ray diffraction pattern shows the monoclinic phase with C2/m space group. The cyclic voltammetry curves of prepared half-cells exhibit redox peaks at 3.1 and 2.6 V, which are due to two-phase transition reaction between V$_{5+/4+}$ and can be assigned to the single-step deintercalation/intercalation of Na ion. We observe a good cycling stability with specific discharge capacity (measured vs Na$^+/Na$) between 80 (±2) and 30 (±2) mAh g$^{-1}$ at current densities of 3 and 50 mA g$^{-1}$, respectively. The electrochemical performance of Na$_{0.66}$V$_4$O$_{10}$ electrode was also tested with Li anode, which showed higher capacity but decayed faster than Na. Using density functional theory, we calculate the Na vacancy formation energies: 3.37 eV in the bulk of the material and 2.52 eV on the (100) surface, which underlines the importance of nanostructures.

INTRODUCTION

After commercialization in the early 1990s, rechargeable Li-ion batteries (LIBs) are being widely investigated and used as energy storage to power portable electronic devices and hybrid electric vehicles.1,2 This is mainly because LIBs show the lowest redox potential of the Li ($E_{Li/Li^+}$ = –3.04 V vs standard hydrogen electrode (SHE)), which allows possessing high voltage and energy density. Also, small ionic radius of Li$^+$ (≈0.76 Å in six coordination state) allows its smooth diffusion during charging/discharging, which makes long cycle life.3,4 However, due to huge demand, high cost, safety concerns, and limited and nonuniform Li resources,5 Na-ion batteries have generated considerable interest as a most promising alternative (due to the uniform distribution and abundance of Na resources in the earth crust) to the LIBs for large-scale energy storage systems.6–12 The elements Na and Li are from the same group in the periodic table and have similar properties such as reactivity, physical strength, etc. The global abundance, low cost, and appropriate redox potential ($E_{Na/Na^+}$ = –2.71 V vs SHE) prove its suitability as a good substitute for Li. However, large ionic radius of Na-ion (≈1.02 Å in the six coordination environment) compared to the Li leads to slow ionic diffusion and lower energy density.13,14 Owing to these facts, materials with open framework or materials that can exchange more than one Na per formula unit or Na-rich materials are crucial for the possibility of having high power and energy density.15,16

In this context, layered transition-metal oxides having formula NaTO$_2$ (T = transition metal) and polyaniionic compounds have been extensively explored and used as a cathode material for Na-ion battery.17–24 For example, vanadium oxychloride,25 Na$_{0.44}$Mn$_{1-x}$Zn$_x$O$_2$,26,27 Na-Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$,28 Na$_3$V$_2$(PO$_4$)$_3$,29 olivine-type phosphate- and sulfate-based cathodes like NaFePO$_4$,30 NaFeSO$_4$F,31 and even Prussian blue derivatives containing a suitable transition metal such as KFe(CN)$_6$ act as an open-host framework with a large interstitial space to absorb bigger Na$. However, due to their complex reaction mechanism and to improve thermal stability, energy density, and cycling performance, it is vital to search new cathode materials and investigate their physical/electrochemical properties for Na-ion batteries.32–34

Interestingly, in recent years, vanadium-based oxide materials have attracted worldwide attention as a possible alternate cathode material for both Li-ion and Na-ion batteries.35–41 Because of the variable oxidation state of vanadium (+5 in V$_2$O$_5$ to +2 in VO), it acts as electron donor and acceptor during the process of Na extraction and insertion.42 The crystal structure of β-Na$_2$V$_2$O$_5$ bronze consists of three different vanadium sites labeled as V(1), V(2), and V(3).43 The edge-sharing vanadium octahedra [V(1)O$_6$] and...
the corner-sharing vanadium octahedral \([V(2)O6]\) combine to form zigzag and double chains along the \(b\) axis, respectively. The edge-sharing \([V(3)OS]\) pyramid forms connection to the \([V6O11]\) layers, which are formed from the oxygen linkage to the \(V(1)\) and \(V(2)\) octahedra, thus yielding a tunneled structure.\(^{46}\) Among the vanadium-based oxides, \(V_2O_5\) has been studied extensively\(^{44-48}\) and the formed bronze tunneled structure is not only more stable compared to the layered structures, but also provide fast ion reaction kinetics. It has been reported that depending upon the \(Li^+/Na^+\) intercalation amount, \(V_2O_5\) can yield high discharge capacity, i.e., 442 mAh g\(^{-1}\) for 3 \(Li^+\) per formula.\(^{49,50}\) Furthermore, \(LiV_2O_5\) (Li-bronze) has been explored\(^{51-54}\) for Li-ion batteries, but it suffers significant capacity loss during repetitive charging/discharging for an intercalated amount of \(x > 1.50\) Analogous to \(LiV_2O_5\) in Li ion, \(NaV_2O_5\) (Na bronze) was also proposed for Na-ion battery, where the Na cations can be reversibly cycled along the \(b\) axis in a similar manner to the Li counterpart. Within pentoxide-based cathode, \(Na_{0.33}V_2O_5\) has gained significant attention as a cathode material for Li-ion/Na-ion batteries because of high experimental discharge capacity.\(^{55-57}\) Bach et. al. first investigated the \(Na\) intercalation and deintercalation behavior in \(Na_{0.33}V_2O_5\) bronze,\(^{55}\) and then similarly, \(NaV_2O_5\) \([(Na_{0.33}V_2O_5)]\) has been studied as a cathode material in various morphologies such as nanoplates, nanorods, nanoflowers, and nanoflakes for Li/Na-ion batteries by various research groups.\(^{39,49,58,59}\) Jiang et al. synthesized \(NaV_2O_15\) nanoplates and reported a discharge capacity of 116 mAh g\(^{-1}\) measured vs \(Na^+/Na\) with a cycle retention of 55% at a current density of 50 mA g\(^{-1}\).\(^{58}\) However, note that the electrochemical performance of \(Na_{0.33}V_2O_5\) critically depends on the synthesis conditions, size in nanometer, and morphology.\(^{39,49,58,59}\) Therefore, nanostructures of \(Na_{0.66}V_4O_{10}\) \([(Na_{0.33}V_2O_5)]_2\) in different morphologies still need to be explored in detail as cathode material for Na-ion batteries. Also, it has been reported that partial substitution of Li with Na in Li\(_{1-x}\)Na\(_{x}\)MnO\(_4\) improves the electrochemical performance and significantly enhances the cycling stability of Li-ion battery.\(^{60}\) This further motivates to test our \(Na_{0.66}V_4O_{10}\) cathode with Li as counter electrode.

In this study, we synthesize nanorods of \(Na_{0.66}V_4O_{10}\) and investigate the electrochemical performance for a promising cathode material in Na-ion batteries. The Rietveld refinement of X-ray diffraction (XRD) pattern reveals the monoclinic phase with \(C2/m\) space group. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) studies reveal the rod-shaped morphology with agglomeration. The size and length of the rods were found to be 50–100 nm and a few micrometers, respectively. The cyclic voltammetry (CV) curves of the prepared half-cells exhibit redox peaks at \(\approx 3.1\) and 2.6 V, which indicate phase transition reaction in \(V^{5+/4}\) and can be assigned to the single-step deintercalation/intercalation of Na ion. Interestingly, we observed good cycling stability with specific discharge capacities of 80 (±2) and 30 (±2) mAh g\(^{-1}\) at current densities of 3 and 50 mA g\(^{-1}\), respectively, measured vs \(Na^+/Na\) anode. We have also tested the electrochemical performance with Li anode. The energetics of Na vacancy formation on discharging and Na vacancy filling on charging could form a potential descriptor for electrochemical performance. Since Na vacancy formation was relatively easier on the electrode surface, a surface diffusion pathway for Na transport could be hypothesized. For nanostructures, the available surface area for this pathway is likely to increase, which further alludes to the measured electrochemical performance.

### RESULTS AND DISCUSSION

#### Structural Analysis

To decide the annealing temperature for stable phase formation, we performed the thermal analysis of the resulting gel precursor under air atmosphere using thermogravimetric analysis (TGA) profile. Figure 1 shows the variation in mass (%) of the gel precursor with increase in temperature. The mass loss of around 10% below 180 °C (region 1) is due to the removal of physically adsorbed as well as some intercalated water molecules.\(^{61}\) The steep mass loss (\(\Delta m = 46.3\%\)) observed between 180 and 400 °C in region 2 is attributed to the removal of acetate precursors and volatile impurities in the form of \(NH_3\) and \(CO_2\) gases. Vigorous oxidation and decomposition reactions take place in this region, leading to the phase formation of NVO material. Further, negligible mass loss was observed in regions 3 and 4, i.e., above 400 °C in TGA profile. It can be observed from the TGA profile that annealing at about 400 °C would be sufficient for the phase formation of \(Na_{0.66}V_4O_{10}\) (NVO) material. We have also tried annealing at higher temperatures and found good thermal stability of the prepared material.

The X-ray diffraction (XRD) pattern along with the corresponding Rietveld refinement of the prepared \(Na_{0.66}V_4O_{10}\) (NVO) sample is shown in Figure 2a. The XRD pattern was matched with the standard phase using X’Pert HighScore Plus software with PDF2 reference data file. The obtained XRD pattern of the synthesized NVO powder could be well indexed with the pure phase of the pristine sodium vanadium bronze, i.e., \(β-Na_{0.33}V_2O_5\) having monoclinic structure with \(C2/m\) space group (JCPDS code: 48-0382), as also reported in ref 62. The sharp and intense peaks reveal the crystalline nature of the sample. The Rietveld refinement was performed to obtain the quantitative crystal structure information such as lattice parameters. The peaks were modeled using the pseudo-Voigt function, and the full width at half-maximum was refined using Lorentzian broadening of the XRD peaks. The structural refinement results (\(γ = 2.3\), \(R_p = 4.6\%, R_w = 6.3\%\)) indicate that the fitting is reliable and good. The obtained lattice parameters from refinement are: \(a = 15.425\ \AA\), \(b = 3.610\ \AA\), \(c = 10.073\ \AA\), and \(β = 109.54°\), which are in good agreement with previous reports of \(Na_{0.33}V_2O_5\).\(^{63}\)
Further, we have provided the fractional coordinates and site occupancies in Table 1.

We further characterize the prepared NVO cathode material to check the morphological properties. The SEM image reveals the formation of uniformly distributed highly agglomerated rod-shaped morphology, as shown in Figure 2b. However, the length of the rods varies dramatically, which gives rise to some regions corresponding to the NVO nanorods, which display uniform dimensions with width 50–100 nm and length several micrometers. The cathode materials in the nanosized particles/rod shape are expected to enhance the electrochemical performance of Na-ion batteries. Note that the characteristic diffusion length (L) of nanostructures and the diffusion coefficient (D) of Na ion are related as: \( r = L^2/D \), where \( r \) is the time for Na ion to diffuse through the electrode material. In this context, one can achieve better electrochemical performance by decreasing \( L \), which effectively reduces \( r \). The selected area electron diffraction (SAED) pattern for the synthesized NVO sample is shown in Figure 2c, which reveals the existence of sharp diffraction spots along with diffused circles that represents the polycrystalline nature of the synthesized sample. The interplanar spacing/distance (d = 0.47 nm) calculated using the SAED pattern matches to the (200) peak of the XRD pattern.

### Electrochemical Performance

Now, we present, in Figure 3a–d, the electrochemical performance of the prepared NVO cathode in terms of cyclic voltammetry, galvanostatic charge/discharge curves, rate performance, and Coulombic efficiency. Figure 3a shows the cyclic voltammograms (CV) of prepared NVO electrode in the potential range of 1.5–4.0 V at a scan rate of 0.05 mV s\(^{-1}\), measured vs Na/Na\(^+\) at room temperature. Interestingly, it exhibits redox peaks at around 3.1 and 2.6 V, which are due to two-phase transition reactions between V\(^{5+}/4+\) and can be assigned to the single-step deintercalation/intercalation of Na ion in the Na\(_{0.66}\)V\(_4\)O\(_{10}\) electrode. It is interesting to note that no such characteristics have been observed in vanadium-based oxide cathodes. Liu et al. reported the charge/discharge profile of Na\(_{2}\)V\(_5\)O\(_{15}\) [((Na\(_{0.33}\)V\(_2\)O\(_5\))\(_3\)] that has multiple steps/plateaus. The obtained CV results are consistent with the charge/discharge profiles, as shown in Figure 3c. The insertion and extraction behavior of Na ion can be tentatively given as

\[
\text{Na}_{0.66}\text{V}_4\text{O}_{10} \leftrightarrow \text{Na}_{0.66-x}\text{V}_4\text{O}_{10} + x\text{Na}^+ + xe^- \quad (1)
\]

Figure 3c shows the galvanostatic first charge/discharge curves of prepared CR2016 half-cells using NVO as cathode and recorded at various current densities from 3 to 50 mA g\(^{-1}\) in the potential range of 1.5–4.0 V vs Na\(^+\)/Na. The specific discharge capacities of the NVO sample are observed to be 80 (±2), 64 (±2), 56 (±2), 52 (±2), and 30 (±2) mAh g\(^{-1}\) at current densities of 3, 5, 11, 20, and 50 mA g\(^{-1}\), respectively. Assuming no electrolyte decomposition during the first charge, Na\(_{0.66}\)V\(_4\)O\(_{10}\) charged to Na\(_{0.09}\)V\(_4\)O\(_{10}\) (corresponding to the charge capacity of 80 mAh g\(^{-1}\)) and then back to Na\(_{0.66}\)V\(_4\)O\(_{10}\). Note that the discharge capacity of about 80 mAh g\(^{-1}\) (1C equated to 141 mAh g\(^{-1}\)) corresponds to +4.86 oxidation state of vanadium, consistent with the CV results. It can also be seen from Figure 3c that as the current density increases from 3 to 50 mA g\(^{-1}\), the specific discharge capacity decreases from 80 (±2) to 30 (±2) mAh g\(^{-1}\) with an apparent drop in potential plateau, which is due to the increase in polarization and resistance or iR drop of the electrode at high current densities. Note that the OCV for NVO cathode was observed to be around 2.8 V. The GCD results in Figure 3c show the charge/discharge voltage plateau around 2.9/2.8 V, respectively, at 3 mA g\(^{-1}\) vs Na/Na\(^+\).

### Table 1: Atomic Coordinates, Site Occupancies, and Isotropic Displacement Parameters for the As-Prepared Na\(_{0.66}\)V\(_4\)O\(_{10}\) Obtained from the Rietveld Refinement of Room-Temperature X-ray Diffraction Pattern

| atom | site | x     | y     | z     | Biso (Å\(^2\)) | occ. |
|------|------|-------|-------|-------|----------------|------|
| Na   | 4i   | 0.0040(13) | 0.0000 | 0.4115(18) | 0.50           | 0.50 |
| V1   | 4i   | 0.3379(3)   | 0.0000 | 0.0989(4)   | 0.50           | 1.00 |
| V2   | 4i   | 0.1190(3)   | 0.0000 | 0.1182(4)   | 0.50           | 1.00 |
| V3   | 4i   | 0.2886(3)   | 0.0000 | 0.4060(5)   | 0.50           | 1.00 |
| O1   | 2a   | 0.00000    | 0.0000 | 0.00000    | 0.50           | 0.69 |
| O2   | 4i   | 0.1867(9)   | 0.0000 | −0.0496(15) | 0.50           | 0.98 |
| O3   | 4i   | 0.3657(8)   | 0.0000 | −0.0822(13) | 0.50           | 1.00 |
| O4   | 4i   | 0.4318(9)   | 0.0000 | 0.2180(14)  | 0.50           | 1.00 |
| O5   | 4i   | 0.2682(9)   | 0.0000 | 0.2223(17)  | 0.50           | 0.99 |
| O6   | 4i   | 0.1053(9)   | 0.0000 | 0.2506(14)  | 0.50           | 1.00 |
| O7   | 4i   | 0.2388(10)  | 0.0000 | 0.5683(15)  | 0.50           | 0.92 |
| O8   | 4i   | 0.4025(10)  | 0.0000 | 0.4651(16)  | 0.50           | 0.97 |
overpotential indicates that the activation energy of the redox event is very high because of which the potential necessary to transfer an electron from NVO cathode is relatively high even at low current density. The comparison of the 1st, 2nd, and 10th cycle discharge capacity curves are shown in Figure 3d. The discharge capacity remains fairly constant for 10 cycles, which elaborates the structural stability of the electrode material. The cycling stability and rate performance for an electrode are very important parameters to determine the stability in long-term applications. Figure 3e,f shows the stepwise electrochemical rate and cycling performance, respectively. As observed from Figure 3e, the capacity decreases with increase in current density and goes to minimum for 50 mA g⁻¹. Figure 3f shows the cycling performance of the synthesized NVO sample at 5 mA g⁻¹ current density at room temperature. It shows an initial discharge capacity of 64 (±2) mAh g⁻¹ and retains nearly 100% capacity even after 50 charge/discharge cycles. The Coulombic efficiency of the NVO electrode for 50 charge/discharge cycles is also shown in Figure 3f. The Coulombic efficiency for all of the charge/discharge cycles is observed to be more than 95% (Figure 3f).

Furthermore, the electrochemical impedance spectroscopy (EIS) of fresh cells was performed to measure the electrode/electrolyte resistance. Figure 3b shows the impedance spectra of NVO sample measured with an AC voltage pulse having an amplitude of 5 mV. The EIS curve, measured in the frequency range of 10 mHz to 100 kHz, shows a depressed semicircle and a straight line in the high- and low-frequency regions, respectively. In general, the ohmic resistance ($R_s$) of the cell, i.e., the resistance due to electrolyte and electrode material, can be estimated by an intercept at the Z′-axis in the high-frequency region. The information about the electrochemical reactions taking place at the electrode/electrolyte interface, which indicates the charge transfer resistance ($R_{ct}$), can be obtained from the semicircle in the mid-frequency range. Also, the Warburg impedance ($Z_w$), which is associated with Na-ion diffusion in the electrode active material, can be represented by the inclined line in the low-frequency region. The cell parameters were obtained to be $R_s = 594 \Omega$ and $R_{ct} = 778 \Omega$.

The chemical diffusion coefficient of the Na ions inside an electrode material is calculated using the following equation

$$D = \frac{T^2R^2}{2n^2A^2F^4C^2\sigma_w}$$

where $D$, $T$, $R$, $n$, $A$, $C$, and $F$ are diffusion coefficient (cm² s⁻¹), absolute temperature (K), gas constant (8.314 J mol⁻¹ K⁻¹), number of electrons involved in the redox process, electrode area (2.2 cm²), Na-ion concentration (3.139 × 10⁻³ mol cm⁻³), and the Faraday constant (96 486 C mol⁻¹), respectively, and $\sigma_w$ is the Warburg impedance coefficient, which is related to $Z'$ by the following equation

$$Z' = R_s + R_{ct} + \sigma_w\omega^{-0.5}$$

In the inset of Figure 3b, we show the obtained value of $\sigma_w$ from the slope of $Z'$ and $\omega^{-0.5}$, which was found to be 7739 Ω s⁻⁰. The value of $n$ (≈59 mV/ΔV) can be calculated by taking the difference between oxidation and reduction peaks (ΔV = 0.53 V) in CV (see Figure 3a), which was found to be 0.1 (number of electrons participating in charging and discharging
processes). Finally, by using these values in eq 2, the obtained value of the diffusion coefficient is $1.239 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$, which is in good agreement with the one reported in ref 64.

It is important to compare the observed capacity in this manuscript with the other related cathode materials reported in the literature. For example, Liu et al. observed a discharge capacity of about 100 mAh g$^{-1}$ at 0.1C current rate in Na$_3$V$_2$(PO$_4$)$_3$/C nanofibers cathode materials. Zhang et al. found a reversible capacity of about 120 mAh g$^{-1}$ for NaVO$_3$ cathode after the activation at high voltage. More recently, Shinde et al. have used the ultrasonic sonochemical synthesis method to prepare Na$_{0.44}$MnO$_2$ cathode, which shows a reversible capacity of about 110 mAh g$^{-1}$ at a current rate of C/10 with good cycling stability. By changing the preparation method to self-combustion, the Na$_3$V$_2$O$_7$ nanorods show a capacity of about 157 mAh g$^{-1}$ at 20 mA g$^{-1}$ current density. Lee et al. compared discharge capacity and rate characteristics of $\alpha$-V$_2$O$_5$ and $\beta$-Na$_{0.33}$V$_2$O$_5$ single-crystalline nanowires in Na-ion batteries and found better performance in the latter case. The enhanced electrochemical performance was reported by Ali et al. by Na intercalation into the nanosized V$_2$O$_5$/C composite. Wang et al. synthesized nanoarrays of orthorhombic V$_2$O$_5$, which provides many advantages like shorter paths for Na$^+$ diffusion, more direct path for electron transport, and enhances surface area of electrode. V$_2$O$_5$ polymorphs were reported as better material for Na insertion with large capacity (120–200 mAh g$^{-1}$ at C/10 rate) and good cycle rate. Moretti et al. used V$_2$O$_5$ aerogel as anode material for Na-ion batteries and studied its low-voltage behavior, which shows about 200 mAh g$^{-1}$ capacity and good efficiency. Very recently, carbon-coated Na$_{0.4}$O$_{15}$ nanotubes have been reported as cathode with better Na-storage capacity. Here,
it should be noted that the discharge capacity of NVO cathode crucially depends on the preparation method, amount of Na content in the material, and morphology of the nanoparticles as well as type of intercalation Li+/Na+.

To test the feasibility of prepared Na$_{0.66}$V$_4$O$_{10}$ (NVO) as a cathode material for Li-ion batteries, we assembled the half-cells vs Li/Li$^+$ as an anode and performed the electrochemical measurements with two electrolytes, i.e., 1 M Na$_2$CO$_3$ and LiPF$_6$ (ethylene carbonate/dimethyl carbonate (EC/DMC) 1:1 V/V) to find which one is better suited for this purpose. These cells are abbreviated as NVON (for Na$_2$CO$_3$) and NVO (for LiPF$_6$), respectively. The cyclic voltammograms of the prepared NVO vs Li/Li$^+$ cells are shown in Figure 4a for both the electrolytes. The data were recorded at a scan rate of 0.1 mV s$^{-1}$. Both the half-cells show well-defined oxidation/reduction peaks (Figure 4a). However, the intensity of redox peaks in the NVO half-cell is higher than that of NVON redox peaks, which could be attributed to the better Na$_2$CO$_3$ diffusion. The redox pairs observed at 3.5/2.7, 3.8/3.1 V (for NVO) and 3.5/2.7, 3.9/2.8 V (for NVON) can be due to intercalation of Li ions in the host NVO structure (Figure 4a). The CV results of both the half-cells are presented in Figure 4b, where it can be observed that NVOL half-cell possesses lower charge transfer resistance compared to the NVON half-cell, which is well consistent with the CV results. The charge resistance was found to be around 800 and 1300 Ω for the NVOL and NVON half-cells, respectively (Figure 4b). The CV and EIS results indicate that NVOL half-cell would display better electrochemical properties compared to the NVON half-cell.

Figure 4c,d shows the initial charge/discharge curves for both the half-cells (NVOL and NVON) and the results are in well agreement with CV and EIS results. One slopping voltage plateau around 3.5 V and other flat plateau around 2.7 V can be clearly seen. However, as the current density increases from 3 to 11 mA g$^{-1}$, the voltage plateaus shift to the lower side due to an increase in the polarization and cell resistance. The specific discharge capacities were found to be around 101, 87, and 69 mA h g$^{-1}$ at current densities of 3, 5, and 11 mA g$^{-1}$, respectively, for NVOL half-cell. On the other hand, for NVON half-cell, the obtained values are around 97, 83, and 55 mA h g$^{-1}$ at current densities of 3, 5, and 11 mA g$^{-1}$, respectively. The intercalation and deintercalation of the Na ions in the host structure can be understood in the following reaction: during the first discharge process, Li ion moves in to the host NVO electrode

$$\text{Na}_0.66\text{V}_4\text{O}_{10} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Na}_{0.66}\text{V}_4\text{O}_{10}$$  \hspace{1cm} (4)

During the charging cycle, Na$^+$ ions together with Li$^+$ ions will be removed from the host structure

$$\text{Li}_x\text{Na}_{0.66}\text{V}_4\text{O}_{10} - x\text{Li}^+ - y\text{Na}^+ = (x + y)e^-$$

$$\rightarrow \text{Na}_{(0.66 - y)}\text{V}_4\text{O}_{10}$$ \hspace{1cm} (5)

Thus, the obtained Na$_{(0.66 - y)}$V$_4$O$_{10}$ will again combine with Li ions during discharge

$$\text{Na}_{(0.66 - y)}\text{V}_4\text{O}_{10} + z\text{Li}^+ + ze^- \rightarrow \text{Li}_z\text{Na}_{(0.66 - y)}\text{V}_4\text{O}_{10}$$ \hspace{1cm} (6)

Therefore, during repeated charging/discharging, both the Na and Li ions will contribute to the electrochemical performance of the battery.

In Figure 4e,f, we show the charging/discharging comparison of the 1st, 2nd, and 10th cycles for both the half-cells recorded at the current density of 11 mA g$^{-1}$. The NVO half-cell displays a large capacity fading over consecutive cycles compared to the NVON cell. The specific discharge capacity of NVOL half-cell decreases from 69 to 20 mA h g$^{-1}$ (72% decrease), while in NVON half-cell, the decrease is 31% (from 53 to 38 mA h g$^{-1}$) in the 10th cycle. Figure 4g shows the rate and cycling performance of the two half-cells vs Li/Li$^+$, which show comparable capacities up to 5 mA g$^{-1}$, and for 11 mA g$^{-1}$, the capacity in NVOL cells decays faster compared to NVON cells (see Figure 4g). The specific discharge capacity decays 76% for NVOL, while for NVON half-cell, the capacity decays 64% when the current density changes from 3 to 11 mA g$^{-1}$. Now we show in Figure 4h the cycling performance measured at the current density of 5 mA g$^{-1}$ up to 50 charge/discharge cycles. Both the cells show a gradual decrease in the discharge capacity as capacity decreases from 106 to 69 mA h g$^{-1}$ for the NVOL and from 83 to 57 mA h g$^{-1}$ for the NVON half-cell. The Columbic efficiency for both the half-cells is measured at 5 mA g$^{-1}$ current density (Figure 4i). For both the half-cells, we observed 100% Coulombic efficiency for all of the cycles except the first one for NVOL, which is unexpectedly higher 176%. The possible explanation for such a high value in the first cycle is that during the discharge, there is an extra charge (or electrons) because of the presence of Li in the host structure in the alloy form (Li$_x$Na$_{0.66}$V$_4$O$_{10}$). This extra charge contributes to the capacity during the discharge, while during charging, only Na$_{0.66}$V$_4$O$_{10}$ remains (see eqs 4 and 5) and therefore, the charge capacity is lower, which reflects in the calculation of the Coulombic efficiency.

**Density Functional Theory.** Density functional theory (DFT) is used to calculate the charging and discharging energies of NVO structures with different Na contents. The optimized NVO crystal structures with different Na contents are shown in Figure 5 (top). Here, the structures of Na$_{1.0}$V$_4$O$_{10}$, Na$_{0.66}$V$_4$O$_{10}$, Na$_{0.33}$V$_4$O$_{10}$, and V$_4$O$_{10}$ were obtained by sequential removal of Na atoms, whereas the structure of Na$_{0.66}$V$_4$O$_{10}$ was obtained by adding one Na atom to Na$_{0.33}$V$_4$O$_{10}$. The sequential removal of Na atom from Na$_{1.0}$V$_4$O$_{10}$ to Na$_{0.66}$V$_4$O$_{10}$ and Na$_{0.33}$V$_4$O$_{10}$ was done keeping in mind the highest separation of Na vacancy. The other structures obtained by sequential removal of Na atoms are unique as the Na atoms are equivalent. Charging represents the energy gain by the addition of Na, whereas discharging represents the energy required to remove a Na ion. Thus, charging and discharging processes can be defined as

$$\text{Na}_x\text{V}_4\text{O}_{10} + \text{Na} \rightarrow \text{Na}_{x+1}\text{V}_4\text{O}_{10}$$ \hspace{1cm} (7)

$$\text{Na}_x\text{V}_4\text{O}_{10} \rightarrow \text{Na}_{x-1}\text{V}_4\text{O}_{10} + \text{Na}$$ \hspace{1cm} (8)

As the number of Na atoms in Na$_x$V$_4$O$_{10}$ decreases from 1.33 to 0.33, a gradual increase in both the energy gain during charging and the energy required for discharging is observed. Na$_{1.33}$V$_4$O$_{10}$ has the lowest Na vacancy formation energy ($E_{	ext{Na}} = 2.84$ eV), but the energy gain during the charging is low ($E_{	ext{Na}} = -1.48$ eV). Hence, Na$_{1.33}$V$_4$O$_{10}$ cannot be a good candidate for the battery operation, whereas Na$_{0.33}$V$_4$O$_{10}$ shows a very high energy storage capability due to its high energy gain during the Na addition ($E_{	ext{Na}} = -3.37$ eV), but it also has a very high Na vacancy formation energy ($E_{	ext{Na}} = 3.71$ eV) and hence, also not a good candidate for battery application. The Na$_{0.66}$V$_4$O$_{10}$ samples have the moderate values for both the
The nanostructured morphologies of the cathode materials are in general known to show better electrochemical activities, as also shown in our experimental results. It is understood that the nanostructuring opens up the surface diffusion channels, where the formation of the Na vacancy and the diffusion of Na are known to be easy compared to the bulk. To understand the nanostructuring phenomenon for our target NVO material Na0.66V4O10, we studied the surface Na vacancy formation energy and Na filling energies at three different surfaces of NVO, (100), (010), and (110), as shown in Figure 6. The DFT calculated energies for Na vacancy formation and Na filling are listed in Table 2, for all of the three surfaces. The surface energy calculation shows that the (100) surface is more stable than the (010) and (110) surface, and hence will cover most of the exposed surface of the nanoscale material. The Na vacancy formation energy is calculated to be the lowest for the (100) surface (EF\text{Na} = 2.52 eV), which is lower by 0.85 eV compared to the bulk (EF\text{Na} = 3.37 eV). The (010) surface has a similar Na vacancy formation energy to the bulk, whereas on the (110) surface, it is a little lower (EF\text{Na} = 3.01 eV). The lower values of Na vacancy formation energy at the (100) surface will enhance the concentration of Na vacancy at the surface, which will result in a higher diffusion and hence better electrochemical performance.

The Na filling energy also follows the same trends as the Na vacancy formation energy. The energy gain due to the addition of Na at the (100) surface is calculated to be the lowest (E_f\text{Na} = −2.19 eV), whereas the energies are also lower for (010) and (110) surfaces (E_f\text{Na} = −2.74 and −2.47 eV, respectively) compared to the bulk (E_f\text{Na} = −3.01 eV), as given in Table 2. Furthermore, for the calculations of Na vacancy formation energy and Na filling energy, we have tested different possible configurations, and the most stable configuration was used to calculate the Na vacancy formation energy and Na filling energy. The two Na atoms present at the (100) surface are equivalent; hence, unique geometry was obtained for Na vacancy formation energy and Na filling energy. For the (010) surface, there is only one Na atom present at the surface; hence, the geometry obtained for Na vacancy formation energy was similar to the (100) surface. On the other hand, the two Na atoms present at the (110) surface are equivalent; hence, only one unique geometry was obtained for Na vacancy formation energy. Also, two different configurations were obtained for the Na atom filling energy at the (110) surface (see Figure 6e,f).

### Table 2. Calculated Energy Gain Due to the Addition of Na at the Different Surfaces

| NVO(Na0.66V4O10) | surface energy (eV/Å²) | Na vacancy formation energy (eV) | Na filling energy (eV) |
|------------------|-------------------------|-------------------------------|---------------------|
| bulk             |                         | 3.37                          | −3.01               |
| (100)            | 0.031                   | 2.52                          | −2.19               |
| (010)            | 0.039                   | 3.36                          | −2.74               |
| (110)            | 0.046                   | 3.01                          | −2.47               |

In summary, the rod-shaped Na0.66V4O10 (NVO) nanostructured cathode material was prepared using the sol–gel method. The XRD patterns confirm the formation of pure monoclinic phase with the C2/m space group, and no impurity or secondary phases were observed. The SEM and TEM studies reveal the rod-shaped agglomerated morphology of the prepared cathode material with width 50–100 nm and the length a few micrometers. The observed selected area electron diffraction pattern is in good agreement with the XRD pattern. The cyclic voltammetry (CV) results showed the two-phase transition reaction between V5+/4+, which is in good agreement with the galvanostatic charge/discharge curves. The electro-
chemical performance indicates that the NVO cathode exhibits specific discharge capacities of \(80 (\pm 2), 64 (\pm 2), 56 (\pm 2), 52 (\pm 2),\) and \(30 (\pm 2) \text{ mAh g}^{-1}\), measured vs Na\(^+\)/Na at the current densities of 3, 5, 11, 20, and 50 mA g\(^{-1}\), respectively.

The electrochemical performance of Na\(_{0.66}\)V\(_4\)O\(_{10}\) electrode with Li anode is found promising, but decays faster compared to the Na anode. The energetics of Na vacancy formation and filling on discharging and charging, respectively, could form a potential descriptor of the electrochemical performance. The available surface area for Na transport is likely to increase for nanostructures, which further supports the experimental results.

### MATERIALS AND METHODS

**Experimental Details.** The nanostructured Na\(_{0.66}\)V\(_4\)O\(_{10}\) (NVO) samples were synthesized by sol–gel route using sodium acetate (C\(_2\)H\(_3\)NaO\(_2\)) and ammonium metavanadate (H\(_4\)N\(_2\)O\(_7\)V) in 1–6.06 molar ratio, from Sigma-Aldrich, \(\geq 99.0\%\). The starting precursors were homogeneously mixed in deionized water with continuous stirring. Citric acid (anhdyrous, C\(_6\)H\(_8\)O\(_7\), from Fisher Scientific, 99.5\%) was used as a chelating agent in a molar ratio of 1:1 with metal ions. The resulting mixture of citric acid and precursors was heated at 80 °C with continuous stirring at 400 rpm until a homogenous gel was obtained. Then, the gel was dried overnight at 120 °C to obtain the powder, followed by heat-treating in a muffle furnace in air at 400 °C (with 5 °C/min rate) for 5 h. The final powder was stored in a vacuum desiccator for physical and electrochemical characterizations. The thermal decomposition of the resulting gel precursors was examined by thermogravimetric analysis (NETZSCH, TG 209 F3 Tarsus) at a ramp rate of 10 °C/min in air from room temperature to 900 °C.

The crystallographic structure and phase purity of the prepared samples were determined by room-temperature powder X-ray diffraction (from Panalytical) with Cu K\(\alpha\) radiation (\(\lambda = 1.540 \text{ Å}\)) operating at 40 kV voltage and 40 mA current. The XRD pattern was recorded in 2\(\theta\) angular range between 10 and 70° with a step size of 0.02°. The XRD data have been analyzed by Rietveld refinement using FullProf package, and the background was fitted using linear interpolation between the data points. We study the morphology of the prepared cathode using a Zeiss EVO 50 scanning electron microscope working at 20 kV in scattered electron mode. A JEOL JEM-1400 Plus microscope coupled with energy-dispersive X-ray spectroscopy (EDX) facility has been used for the transmission electron microscopy (TEM) measurements at 120 kV.

![Figure 6. DFT optimized geometry of (100), (010), and (110) surfaces of Na\(_{0.66}\)V\(_4\)O\(_{10}\), showing the position of Na vacancy (violet circle with V) and extra Na (green circle). (a–f) Position of extra Na atom during the Na filling (green circle) for different surfaces, with energies indicated at the bottom. The distances between the Na atoms in (a) and (b) are given in angstrom unit.](image-url)
For the electrochemical measurements, cathodes were prepared by mixing prepared active material poly(vinylidene difluoride) as a binder and super P (conductive carbon) in a weight ratio of 80:15:5 in N-methyl-2-pyrrolidinone (NM2P) as a solvent. Then, we stirred the resulting mixture for 5 h to achieve homogeneous mixing and then coated over Al foil (as a current collector) using the doctor blade technique. The coated Al sheet was then dried overnight in a vacuum oven at 80 °C to evaporate the solvent. The sheet was then roll-pressed and punched into a circular electrode with 12 mm diameter. The active mass loading on the electrodes was between 2 and 3 mg. Before bringing inside the glovebox workstation, we dried the electrodes in vacuum at 60 °C to remove any moisture. Na chips (16 mm diameter) were extracted from Na cubes (Sigma-Aldrich, 99.9%) by cutting, rolling, and pressing sodium cubes into thin sheets inside the glovebox and used as both counter and reference electrodes. For electrochemical measurements, the CR2016 coin half-cells were assembled in an argon-filled glovebox (Jacomex ≤ 0.5 ppm of O2 and H2O levels) with the cathode electrode, Na metal, and a glass fiber (Advantec, GB-100R) as the separator. The electrolyte used was 1 M NaClO4 dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) in a volume ratio of 1:1. Electrochemical impedance spectroscopy (EIS) using an AC voltage pulse of 5 mV in the frequency range of 100 kHz to 10 mHz was also performed to measure the electrode resistance. We have also assembled and tested the half-cells vs Li+/Li as an anode to study the feasibility of the prepared NVO cathode as a material for Li-ion batteries. The assembled cells were tested anode to study the feasibility of the prepared NVO cathode as a material for Li-ion batteries. The assembled cells were tested anode to study the feasibility of the prepared NVO cathode as a material for Li-ion batteries.

Computational Method. Periodic plane-wave-based density functional module implemented in Vienna Ab Initio simulation package74 is applied to calculate the energy of the cathode material with six different NaV4O10 compositions, where \( x = 1.66, 1.33, 1, 0.66, 0.33, \) and 0. The model structure of \( \text{Na}_{1.5}V_4O_{10} [\text{Na}_2V_6O_{15}] \) composition was obtained from \( \text{The Materials Project} \) database https://materialsproject.org/ (materials ID. mp-778594),70 having monoclinic crystal structure with \( C2/m \) space group. The lattice parameters \( a = 15.7845 \text{ Å}, b = 3.6662 \text{ Å}, c = 10.6182 \text{ Å}, \) and \( \alpha = 90\degree, \beta = 103.093\degree \) match well with the experimentally obtained cell parameters. The sodium bulk metal geometry is modeled as cubic body-centered cubic bulk with lattice parameters \( a = 4.2906 \text{ Å} \) and \( \alpha = 90\degree \). Geometry optimization is performed on the structures, with energy and force convergence criteria set to \( 1 \times 10^{-4} \text{ eV} \) and \( 0.05 \text{ eV/Å} \), respectively. RPBE75 GGA exchange correlation functional and ultrasoft pseudopotentials (USP)76 are used. Plane-wave basis sets are expanded to an energy cutoff value of 396 eV. Monkhorst-Pack77 k-points grid of \( 1 \times 3 \times 1 \) is utilized for all of the calculations on different NVO structures, whereas a \( 5 \times 5 \times 5 \) grid is used for Na bulk lattice geometry optimization. The Na vacancy formation energy \( (E_{f}^{Na}) \) of NVO structure \( \text{Na}_xV_4O_{10} \) is calculated using the following formula

\[
E_{f}^{Na} = E[\text{Na}_{(x-1)}V_4O_{10}] + E(Na) - E(\text{Na}_xV_4O_{10})
\]

where \( E(\text{Na}_xV_4O_{10}), E(\text{Na}_{(x-1)}V_4O_{10}), \) and \( E(Na) \) are the energies of NVO structure \( \text{Na}_xV_4O_{10}, \text{Na}_{(x-1)}V_4O_{10} \), and energy of bulk Na, respectively. Similarly, the energy gain from Na addition \( (E_{f}^{Na}) \) to NVO structure \( \text{Na}_xV_4O_{10} \) can be calculated as

\[
E_{f}^{Na} = E[\text{Na}_{(x+1)}V_4O_{10}] - E(\text{Na}_xV_4O_{10}) - E(Na)
\]

To study the nanostructuring effect on the Na vacancy formation and Na filling energies, three different low-index surfaces, (100), (010), and (110), are created for the NVO structure studied experimentally, \( \text{Na}_{0.66}V_4O_{10} \). A \( 2 \times 1 \) supercell was used for (100) surface, whereas for both the (010) and (110) surfaces, a \( 1 \times 1 \) unit cell is used for the surface calculation. For all of the three surfaces, a four-layer surface slab is used, where two bottom layers are kept fixed to their bulk positions and the top two layers are allowed to relax. A vacuum of 20 Å is used to model the surface slabs. Calculations of Na vacancy formation energy and Na filling energy are performed by removing and adding Na at the corresponding surface, respectively. For the addition of Na to the surface, two distinct adsorption sites were studied and the geometry and energy of the most stable adsorption site were reported. Equations 9 and 10 are used to calculate the surface Na vacancy formation energy and Na filling energy, respectively.

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Notes

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