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Metal-Organic Open-Framework Molecular Magnet Based on Vanadium Hexacyanoferrate Prussian Blue Analogs as Cathode Material for Advanced Potassium Ion Aqueous Battery

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The development of high-performance electrode materials is vital for advancing nextgeneration energy storage systems. In this study, we successfully synthesized an open-framework vanadium hexacyanoferrate (VHCF) compound and explored its application as a cathode for aqueous potassium-ion batteries (AKIBs). Infrared and Raman studies confirmed VHCF formation through characteristic -C=N- stretching (\approx 1900–2200 cm⁻¹), while structural analysis revealed a stable face-centered cubic (Fm3m) framework with open tunnels enabling efficient K⁺ diffusion. Magnetic measurements and neutron depolarization confirmed the compound's paramagnetic nature. X-ray photoelectron, Mössbauer, and synchrotron X-ray absorption studies revealed Fe²⁺ (low spin) and V⁴⁺ oxidation states, with evidence of ligand-tometal and metal-to-ligand charge transfer. Electrochemical analysis showed high specific capacity (\approx 121 mAh g⁻¹ at 0.5 A g⁻¹) with \approx 99% coulombic efficiency, and \approx 96% efficiency at 2 A g⁻¹ with 45% capacity retention after 620 cycles. The opentunnel-like network of V(O)-Fe(CN)₆ is responsible for the compound's higher cyclic stability and reversibility. However, ex-situ X-ray diffraction showed slight amorphization and lattice contraction from 10.22 Å to 10.13 Å after 350 cycles. The K^+ diffusion coefficient (D_k^+) obtained from the galvanostatic intermittent titration technique displayed a V-shaped charging trend (9.46 \times 10⁻¹¹ cm²·s⁻¹), increasing to $1.96 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ during discharge. Density functional theory calculations indicated a low K⁺ migration barrier energy (\approx 0.45 eV). With cost-effective synthesis, a robust metal-organic framework, and excellent structural, magnetic, and electrochemical properties, VHCF is a promising cathode material for future AKIBs.

1. Introduction

The increasing demand for clean, renewable energy has gained significant attention due to fossil fuel depletion and rising carbon emission.^[1-4] While renewable energy sources like wind and solar provide viable alternatives, their intermittent nature limits their contribution to less than 10% of total energy demand. Thus, the development of alternative energy sources or devices based on energy conversion and storage are pivotal and highly desirable. At present, lithiumion batteries (LIBs) are widely used due to their portability, high energy density, and efficiency.^[5,6] However, limited lithium availability, high costs, and safety concerns, particularly from flammable organic electrolytes, restricted their use to grid-scale energy storage. To overcome these challenges, alternative batteries utilizing more abundant and cost-effective metal ions (Na⁺, K⁺, and Zn²⁺) are being explored.^[7–12] However, the larger ionic sizes of these charge carriers limit the ionic diffusion, thus rate capabilities, while also posing safety concerns comparable to those of LIBs. Recently, aqueous electrolytebased rechargeable batteries are finding its way to be an alternative of LIBs due to their

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PBAs as electrode material for potassium-ion batteries (KIBs). $^{[17,51,54,55,72,73]}$ This is largely due to K⁺ 's larger ionic radius

(1.38 Å) compared to Li⁺ (0.76 Å) and Na⁺ (1.02 Å), which hinders

ion insertion/extraction and affects long-term stability. Therefore,

search for an alternative stable cathode material for KIB is highly desirable, and various transition-metal ion combinations in PBAs

have been studied.^[2,3,7,12,13,39,49,51,52,58,63,64,67,72,74-77] Redox reac-

tions in PBAs primarily occur at transition-metal ions coordinated

to the −C≡N− group. Optimizing metal ions and oxidation states

has led to excellent electrochemical performance, capacity, and

cyclability. For instance, K1.82Mn[Fe(CN)6]0.96 0.47H2O synthesized

via surface engineering with Fe substitution for Mn, demonstrates

stable discharge capacities of 160 and 120 mAh g^{-1} at 300 and 2,500 mA g^{-1} , respectively, sustaining up to 130,000 cycles.^[36]

Similarly, composition-optimized K2Ni0.36Co0.64Fe(CN)6 exhibits

an initial capacity of 86 mAh g^{-1} with 98% retention after 50 cycles, outperforming $K_2NiFe(CN)_6$ and $K_2CoFe(CN)_6$.^[72] The

K1.67Mn0.65Fe0.35[Fe(CN)6]0.92 0.45H2O cathode delivers capacity

of 104 mAh g^{-1} at 100 mA g^{-1} with electrochemical mechanisms

explored using ex--situ and operando characterization.^[51] A novel

Mn-based PBA cathode designed with dual-coordinated states

achieves 90 mAh g⁻¹ over 600 cycles in ester electrolyte.^[35] A

low-strain potassium-rich K_{1.84}Ni[Fe(CN)₆]_{0.88}·0.49 H₂O synthe-

sized via co-precipitation using the facile synthesis exhibits superior cycling stability, delivering 62.8 mAh $\rm g^{-1}$ at 100 mA $\rm g^{-1}$ with a dis-

charge voltage of 3.82 V and retaining 88.6% of 45.8 mAh g⁻¹ at

 5000 mA g^{-1} after 100 cycles.^[55] Additionally, X-ray diffraction

(XRD), X-ray absorption spectroscopy, and Mössbauer spectroscopy

studies on $K_xMn_2/_3Fe_1/_3[Fe(CN)_6]_y \cdot zH_2O$ provide insights into volume expansion in the Fe—C=N—M (M=Mn, Fe) framework during

Introducing vanadium into PBAs has also been explored to

enhance capacity and cycling stability due to its high redox poten-

tial and electrochemical activity.^[39] For instance, vanadium fer-

rocyanides have demonstrated high stability in LIBs, retaining 92.7% of their initial discharge capacity even after 100 cycles.^[39]

However, to the best of our knowledge, no study has yet been

reported on KIBs utilizing VHCF as a cathode material.

VHCF offers several advantages over conventional Fe-based PBAs, primarily due to the unique electrochemical properties

of vanadium. Unlike Fe-based PBAs, which rely solely on

Fe²⁺/Fe³⁺ redox transitions, vanadium ions exhibit multiple

redox states ($V^{+2}-V^{+5}$), enabling a multi-electron energy storage

process that significantly enhances the specific capacity.

Vanadium's multiple oxidation states enable smoother charge

transfer without excessive volume changes, unlike Fe-based

PBAs, where structural distortions can occur. Additionally, vana-

dium has a lower atomic weight compared to other transition

metals, improving the gravimetric energy and power density

of the material. A key advantage of VHCF is its enhanced struc-

tural stability during repeated K⁺ insertion/extraction cycles. The

strong V-N and V-C bonding interactions within the open

framework reduce capacity fading by maintaining structural

integrity. Furthermore, the incorporation of vanadium slightly

expands the lattice, creating larger interstitial sites that facilitate

faster K⁺ diffusion and reduce diffusion resistance. In contrast,

Fe-based PBAs are more susceptible to structural distortion due

to Fe oxidation, which can degrade cycling performance.

Additionally, vanadium's partially filled d-orbitals enhance

K⁺ extraction.^[54]

numerous advantages, such as low-cost synthesis, safe, non-flammable, and environmentally friendly electrolytes. $^{\left[13-15\right] }$

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In this regards, amongst the most available electrode materials, Prussian blue (PB) and Prussian blue analogs (PBAs) have attracted significant interest as cathode materials due to their open-framework structures, cost-effectiveness, and excellent electrochemical properties.^[16-18] PBAs show interesting physical and magnetic properties,^[19,20] such as photo-induced magnetization,^[21–28] pressure induced magnetization,^[29–31] humidity induced magnetization,^[32] and possible wide technological applications in the field of catalysis,^[33,34] batteries,^[35–39] supercapacitors,^[40–42] hydrogen storage,^[43–46] electrochemical sensing,^[47,48] etc. The PBAs are represented by the chemical formula $A_1X_m[Y(CN)_6]_n zH_2O$ in which X and Y are 3-D transition-metal ions arranged periodically in the open-framework structure. The metal ion *X* is in a high-spin state and *Y* exists in a low-spin state surrounded octahedrally by $-N \equiv C-$ and $-C \equiv N-$ units, respectively, with alkali metal ions (A) and water molecules occupying the interstitial space. PBAs with tunable pore sizes can be synthesized by varying the combinations of transition-metal ions, controlling structural vacancies during synthesis, or incorporating surfactants, which provide excellent capacity and cycling performance, making them promising cathode material.^[7,9,36,39,49–59] Their rapid and reversible redox reactions facilitate the intercalation/deintercalation of alkali metal ions during charge/discharge cycles.^[16,51,58,60-62] Due to their cost-effectiveness and rational synthesis, PBAs have been explored with charge carriers such as Li⁺, Na⁺, K⁺, Zn^{2+} , Mg^{2+} , and Al^{3+} for electrochemical batteries based on PBAs.^[16,35,39,50–52,63–67]

PBAs have also been extensively investigated as electrode materials for $LIBs^{[39,63,68-70]}$ and sodium-ion batteries (SIBs).^[16,49,64,65,71] Though, potassium offers a lower working potential and is cost-effective, a few studies have focused on application of

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electron delocalization, improving electronic conductivity and lowering charge transfer resistance at the electrode–electrolyte interface. These unique properties make VHCF a superior cathode material, offering higher capacity, better cycling stability, and improved ion transport properties compared to conventional Febased PBAs.

Aqueous KIBs offer some advantages over non-aqueous KIBs like enhanced safety due to non-flammable water-based electrolytes, lower production costs, higher ionic conductivity, and rapid K⁺ diffusion. However, they suffer from low energy density due to a narrow electrochemical stability window, and limited cycle life due to electrode degradation from side reactions, and dissolution of active materials. In contrast, non-aqueous KIBs provide higher energy density, faster ion transport, and flexible material compatibility, enabling performance optimization. Nonetheless, they present safety risks from flammable electrolytes and thermal instability, experience mechanical degradation from K⁺induced volume expansion, and face challenges with solid electrolyte interface instability. In this study, we demonstrate the synthesis and characterization of VHCF as a cathode material for aqueous KIBs. Detailed structural, magnetic, electronic, and electrochemical investigations aim to optimize its performance for practical applications. Additionally, density functional theory (DFT) calculations provide insights into K⁺ ion migration within VHCF, further enhancing our understanding of its potential as a high-performance KIB cathode.

2. Experimental Section

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2.1. Synthesis of Vanadium Hexacyanoferrate (VHCF)

The single phase nanocrystalline compound of VHCF is synthesized using co-precipitation method. The precursor chemicalsvanadium (III) chloride (VCl₃), potassium ferrocyanide (K₄[Fe(CN)₆]), and potassium chloride (KCl)-were obtained from Sigma-Aldrich as reagent-grade materials and used without further purification. For the synthesis, 10 mL of 0.1 M VCl₃, 10 mL of 0.1 M K₄[Fe(CN)₆], and 10 mL of 1 M KCl aqueous solutions (pH = 2) were prepared separately. These solutions were then combined dropwise under continuous stirring and maintained under ambient conditions for 5 h. The gradual addition ensured uniform mixing and controlled precipitation. Upon completion of the reaction, a precipitate of VHCF was formed. The resulting product was carefully filtered and repeatedly washed with doubly distilled water to remove any unreacted species or impurities. Finally, the purified precipitate was air-dried after filtration to obtain the desired nanocrystalline VHCF compound (Figure 1).

2.2. Characterization of VHCF

2.2.1. Chemical Analysis

Trace elemental analysis and combustion gas chromatography methods are used for the chemical analysis of the compound. The elemental composition (wt%) of the compound obtained from the chemical analysis is found to be for K: 3.4 (4.2), V: 12.4 (13.1), Fe: 11.2 (13.4), C: 17.3 (18.6), and N: 19.8 (21.6). The theoretically

Co-precipitation method



Figure 1. Schematic diagram of the synthesis of the VHCF compound via the co-precipitation method.

expected values, based on sample stoichiometry is mentioned in the bracket. The chemical composition of the synthesized compound, determined by the elemental composition, is found to be $K_{0.4}VO_{0.2}[Fe(CN)_6]$ ·5H₂O.

2.2.2. Physical Characterization

The chemical compositions have also been confirmed by the energy dispersive X-ray analysis (EDAX) measurements. The EDAX analysis has been done using an oxford instrument. The XRD measurement is performed using a 12 kW Rotating anode Rigaku make diffractometer over an angular (2 θ) range of 10°–65° in equal 2 θ steps of 0.02° with Cu-K_{α} ($\lambda = 1.54$ Å) radiation at room temperature in a Bragg-Brentano geometry. The Rietveld refinement method with the Fullprof program is used for detailed structural analysis.^[78,79] Thermogravimetric analysis (TGA) measurement is carried out using a Linseis STA PT1600 instrument. The sample and reference (empty alumina crucible) is heated in an inert atmosphere up to 800 °C at a rate of 10 K min⁻¹. The field emission scanning electron microscope (FESEM) {Carl Zeiss Germany, Model: GEMINISEM300} is used for studying the surface morphology of the compound. The X-ray absorption spectroscopy (XAS) measurements are carried out at room temperature using the BL14 beamline at the Hiroshima synchrotron radiation centre (HiSOR), Hiroshima university, Japan. The soft XAS measurement is used to investigate valence state of the metal ions in the VHCF compound. The base pressure in the experimental chamber is maintained below 3×10^{-10} Torr prior to measurement. The powder sample is sprinkled on the carbon tape for the measurement. XAS spectra is acquired through the total electron yield method by measuring the sample drain current, with a probing depth of 50-100 Å. The total resolution for the XAS is $\approx 100 \text{ meV}$. All spectrum is



normalized to the incident photon flux. The infrared spectroscopic data were recorded in the spectral range 400–4500 cm⁻¹ using the Bruker VERTEX 80v Fourier transform infrared (FTIR) spectrometer equipped with KBr beam splitter and liquid nitrogen cooled HgCdTe detector. A total of 100 scans were coadded at a resolution of 4 cm⁻¹. The sample was dispersed in KBr matrix and the measurements were carried out in transmission mode, under vacuum. The Raman measurements are carried out in the spectral range of 1000–2500 cm⁻¹. The Raman signal from the sample was excited using a 532 nm laser source. The spectrum was recorded using an Andor spectrometer coupled to a chargecoupled device (CCD) detector. Mössbauer spectroscopy in transmission geometry with constant acceleration mode is carried out at room temperature for determination of oxidation state and local surroundings of Fe ions for the compound. A Co-57 source in Rh matrix of strength 50 mCi is used for the measurements. A temperature dependent dc magnetization measurement in fieldcooled conditions down to 2 K has been carried out using a cryogenic Ltd. make vibrating sample magnetometer. The neutron depolarization measurement is carried out at Dhruva reactor BARC, India using a wavelength of 1.205 Å. The sample is cooled from room temperature to the lowest measurement temperature under a field of 10 Oe, subsequently, measurement is then carried out during the warming cycle. The detail on the experimental facilities is described in an earlier paper.^[80] High-resolution transmission electron microscopy (HRTEM) images were captured using a field emission gun-transmission electron microscope. XPS measurement is carried out using an Mg-Ka (1253.6 eV) X-ray source and a DESA-150 electron analyzer. The adventitious C 1s peak, overseed at 284.8 eV is used as the binding energy calibration reference.

2.2.3. Electrochemical Characterization

All electrochemical experiments are carried out using a CHI608 electrochemical workstation in a three-electrode system: the active material, VHCF, as working electrode, an Ag/AgCl reference electrode, and a graphite counter electrode. The electrolyte was $0.1 \text{ M K}_2\text{SO}_4 + 0.1 \text{ M H}_2\text{SO}_4$ aqueous solution. To fabricate the working electrode, the prepared active material (80 wt%) is mixed with carbon black (10 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone to form a uniform slurry. The slurry is then applied onto a carbon paper substrate and dried overnight at 70-80 °C. The electrode used for the electrochemical experiment contains a mass of \approx 5 mg, in dimensions of 2×2 cm⁻². To evaluate the performance of VHCF as cathode material for potassium ion aqueous battery, the GCD measurements were carried out by applying constant current densities of 0.5, 0.8, 1, 1.5, 2 and 5 A g⁻¹. GITT measurements are performed using Neware battery testing system.

2.3. Computational Methods: Density Functional Theory Calculation

The first-principal calculation is conducted using DFT as implemented in the Vienna Ab initio Software Package (VASP 5.4.4).^[81–83] The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW)

method is applied. The kinetic cut off energy for the plane-wave basis is kept to 450 eV. Gaussian smearing of the population of partial occupancies with a width of 0.05 eV is used in diagonalization of the Kohn-Sham Hamiltonian. The threshold energy convergence for the iteration is 10^{-5} eV. The criteria for the geometry convergence are assumed if forces on each atom is less than $0.05 \text{ eV} \text{ Å}^{-1}$. The atomic positions and lattice constants are optimized during the calculation. The Brillouin zone of the surface unit cell is done using Monkhorst-Pack (MP) grids, which are also used for the optimization of VHCF. For bulk structure, a $3 \times 3 \times 3$ MP grid is employed. The calculated lattice constant for the compound a = b = c = 10.17 Å, is in good agreement with experimental value {a = b = c = 10.22(5) Å}. The climbing image nudged elastic band method is used to confirm the transition states, each possessing only one imaginary frequency along the reaction coordinates. The activation barrier (E_a) and reaction energy (E_r) are calculated as $E_a = E_{TS} - E_{IS}$, where E_{TS} represents the energy of the transition state, E_{IS} represents the energy of the initial state, and $E_{\rm FS}$ represents the energy of the final state. The calculations are done with intercalated cations with no hydration shell, with cations with six water molecules around them to understand the effect of solvent on the selectivity.^[84]

3. Result and Discussion

3.1. (A) SEM and XRD Study: Structural Properties

Figure 2 shows FESEM, EDAX, XRD, and TGA studies of the VHCF compound. Figure 2a shows FESEM image exhibiting surface morphology and corresponding crystallite size distribution of the compound. The FESEM image shows cluster of circular particles distributed uniformly in the compound. The particle size distribution is shown in the inset of Figure 2a. The average crystallite size is found to be \approx 300–400 nm. The uniform distribution of crystallites indicates homogenous nature of the compound. The EDAX analysis, shown in the inset of Figure 2b, confirms the presence of K⁺ in the compound. The stoichiometry, based on the EDAX analysis, is found to be K_{0.4}VO_{0.2}[Fe(CN)₆]·5H₂O. The number of water molecules are estimated from the fitted room temperature XRD data (shown in Figure 2c), further confirmed by using TGA measurement. The refinement of XRD data shows that the compound is in a pure nanocrystalline single phase with a cubic structure of space group *Fm3m*. The lattice constant is found to be \approx 10.22(5) Å for the compound. The crystal structure of the compound is shown in the inset of Figure 2d in which V and Fe occupy the 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2) crystallographic sites, respectively.

In general, two types of water molecules are present in the PBAs, that is, coordinated and un-coordinated water molecules, responsible for the structural disorder in PBAs.^[85] The water molecules present at the interstitial sites (8c and 32f) and connected to N atoms (situated at 24e sites) are known as uncoordinated and coordinated water, respectively. The alkali metal ion, K⁺ occupies some of the intestinal sites of un-coordinated water molecules as shown in the inset of Figure 2d, depending upon the vacancies present in the compound. The important structural parameters, derived from the Rietveld analysis of XRD, are shown in **Table 1**. The crystallite size (t) of the compound was estimated using the Scherrer formula as given below.

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Figure 2. a) SEM image, b) EDAX spectrum, c) XRD pattern, and d) TGA analysis of the VHCF compound. The inset in (a) shows particle size distribution with mean diameter of 300–400 nm. The inset in (b) shows chemical composition of the compound obtained using EDAX measurement. The room temperature XRD data are fitted using Rietveld refinement. The experimentally observed and fitted patterns are represented by open circles and solid lines, respectively, whereas the difference between the experimental and fitted patterns is shown by the solid line at the bottom. The positions of allowed Bragg peaks are also indicated by vertical lines, with the (hkl) values of the Bragg peaks of the compound. The schematic crystal structure {inset in (d)} of the compound showing the position of metal and alkali ions. Water molecules and alkali metal ions are depicted as occupying the same positions depending on the presence of vacancies, represented in red.

Table 1.	Rietveld refined	structural	parameters for the '	VHCF	compound.	The fractional	coordinates	are denoted as x	′ y′ and	z'.
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	Atom	Wyckoff	x′	γ'	z′	Occupancy
Space Group	V	4 <i>a</i>	0	0	0	1
Fm3m	Fe	4 <i>b</i>	0.5	0.5	0.5	0.67
Lattice Constants	С	24 <i>e</i>	0.32(7)	0	0	0.67
a = b = c = 10.22(5)	Ν	24 <i>e</i>	0.20(2)	0	0	0.67
-	O ₁	24 <i>e</i>	0.16(3)	0	0	0.34
-	O ₂	32f	0.41(5)	0.41(5)	0.41(5)	0.64
-	К	8 <i>c</i>	0.25	0.25	0.25	0.24

In this equation, λ represents the X-ray wavelength, β is the line broadening at half maximum intensity (FWHM) measured in radians, and θ is the Bragg angle. The most intense Bragg peak (200) has been used for line broadening. The crystallite size was found to be approximately \approx 150 nm. These results are in agreement with the size estimated from SEM images. It is important to note, that crystallite sizes measured by XRD and SEM can vary

due to the differences in their measurement principles. While XRD estimates crystallite size based on sample crystallinity using the Scherrer's equation, SEM provides a surface-level topographical view that measures the physical size, which may include particle aggregation or surface irregularities.

3.2. (B) Raman and IR Study

The information obtained from Raman and IR spectroscopy is extensively used to confirm the formation of PBAs, and are





Figure 3. a) Room temperature Raman spectrum, recorded in back-scattering geometry, and b) FTIR spectrum, recorded in transmission mode, of the VHCF compound. The insets show enlarged view of the marked regions in the respective figures.

complementary to each other. Figure 3a shows Raman spectrum of the compound, provides information on the vibrational modes associated with PBAs formation. In the low-frequency region, no prominent peaks are observed up to 1500 cm^{-1} . However, peaks in the higher wavenumber region of $1900-2200 \text{ cm}^{-1}$ are the characteristics of the PBAs. The C≡N bond, characteristic of PBA, shows Raman stretching vibrations between 1900 and 2200 cm^{-1} .^[86–88] In PBAs, the C=N ligand is coordinated to the transition-metal ions. When these transition metals exhibit different valence states, the $\nu(C \equiv N)$ stretching mode shows changes in the wavenumber within this range. It has been reported that for the Prussian blue and related analog's, the metal ions experience an ideally local octahedral (Oh) point group symmetry with an inversion centre.^[84] Three primary stretching modes, namely, A_{1g} , E_g , and T_{1u} vibrations are observed in the Raman spectra.^[44,89] Among these, the T_{1u} band provides information of structural distortions which arise from deviations from their ideal O_h symmetry. Two bands are observed in the Raman spectrum, shown in the inset of Figure 3a for clarity. These two sharp bands observed at \approx 2153, and \approx 2113 cm⁻¹ correspond to the ν (C \equiv N) modes with symmetry E_{σ} and $T_{1\mu}$, respectively. The observed bands are similar to those reported for other hexacyanoferrates based compounds.[89-91]

The FTIR measurement reconfirms the formation of PBAs, by identifying the characteristic $v(C\equiv N)$ frequencies. Figure 3b shows the FTIR spectrum of the compound. The IR spectrum of VHCF compound shows sharp peaks marked at 520, 980, 1410, 1603, 1670, 1900–2200, and 3500 cm⁻¹ corresponding to various IR-active modes of the compound. Of particular interest is the presence of strong and sharp peaks in the range of 1900–2200 cm⁻¹ that is, the characteristic frequencies of the $-C\equiv N-$ bonds, thus confirm the formation of PBAs. The peaks in the inset of Figure 3b, observed at 2078, and 2106, are attributed to Fe(II)–C \equiv N– and Fe(II)–C \equiv N–Fe(III) bonds, respectively.^[92,93] Additionally, a low intensity peak, observed as a shoulder mode near 2160 cm⁻¹, is associated with the stretching frequency of Fe(III)–C \equiv N– bond.^[94] The peak at 2096 cm⁻¹ corresponds to –C \equiv N–Fe(III) bond.^[95] The peaks at 520 and

980 cm⁻¹ are characteristic frequencies of the $-\text{Fe}\equiv\text{C}-$ and V=O bonds respectively.^[95-97] In addition, the broad peaks observed at \approx 3500 and \approx 1600 cm⁻¹ reflect the existence of the zeolitic and ligand water molecules typically incorporated in the structure of PBAs.^[81,97]

3.3. (C) Mössbauer, dc Magnetization, and Neutron Depolarization Study

A room temperature Fe^{57} Mössbauer spectroscopy is carried out for studying oxidation and spin states of Fe ions and their local atomic environment. **Figure 4** shows a fitted Mössbauer spectrum of the VHCF and K₄Fe(CN)₆ compounds recorded at a



Figure 4. a) Room temperature Mössbauer spectra of K_4 [FeCN₆], b) VHCF compounds. The recorded experimental data (open circles) are fitted with a singlet, shown by the thick blue line.



velocity of $\pm 4 \text{ mm s}^{-1}$. Figure 4a presents the Mössbauer spectrum of the K₄Fe(CN)₆ compound, which is fitted with a singlet. The isomer shift (δ) and line width (Γ) are found to be -0.053 mm s^{-1} and 0.327 mm s⁻¹, confirming that Fe exists in a low-spin Fe²⁺ state. The addition of vanadium and KCl to K₄Fe(CN)₆ leads to the formation of VHCF, whose Mössbauer spectrum is shown in Figure 4b. This spectrum is fitted using one singlet and two doublets. The isomer shift of the singlet is $-0.137 \,\mathrm{mm \, s^{-1}}$, while the isomer shifts of the two doublets are ≈ 0.397 and -0.121 mm s⁻¹. These values confirm the presence of Fe²⁺ in a low-spin state, along with Fe³⁺ in both high-spin and low-spin states. The presence of a single component (singlet) in the Mössbauer spectrum, confirms that Fe-ions are present only at 4b crystallographic site only in the cubic symmetry. The value of δ of the singlet confirms that Fe ions are in low-spin $Fe^{II}(t_{2g}^{6} e_{g}^{0}, Fe^{LS}, S = 0)$ state in a cubic octahedral molecular symmetry, and shows no quadrupole splitting.^[98,99] The absence of a Zeeman splitting six-line hyperfine pattern confirms that the compound is in the paramagnetic ground state. Additionally, the quadrupole splitting values of the two doublets, 0.506 and 0.774 mm s⁻¹, indicate two distinct Fe environments in the VHCF compound. The fitted Mössbauer parameters, including isomer shift (δ), quadrupole splitting (ΔE_{Ω}), and line width (Γ) , for VHCF are listed in Table 2.

The dc magnetic measurements of VHCF compound as a function of temperature and magnetic field are presented in **Figure 5**. Field-cooled (FC) and zero field-cooled (ZFC) magnetization (M) versus temperature (T) curves of the compound under an external applied magnetic field of 100 and 500 Oe are shown in Figure 5a. The compound does not show any magnetic transition down to 5 K, and found to be paramagnetic in nature. Further, no branching in FC and ZFC has been observed.

The Figure 5b shows χT versus *T* curve at 100 Oe for the compound. The χT versus *T* curve is found to decrease with decreasing temperature down to 20 K and thereafter increases with further decrease in temperature. This characteristic behavior is a signature of ferro/ferrimagnetic nature of the compound. The constant value of χT versus *T* is characteristic of a paramagnetic material. The inverse of the susceptibility (χ^{-1})

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as a function of temperature is shown in Figure 5c. The susceptibility is fitted using the Curie-Weiss law down to 100 K, using

$$\chi = \frac{C}{T - \theta_{\rm p}}$$

where, θ_{p} is the paramagnetic Curie temperature, and *C* is the Curie constant. The value of θ_p is found to be -22.7 K, suggests antiferromagnetic interactions between spins of V ions. The spin only effective paramagnetic moment, μ_{eff} is estimated using $(3Ck_B/N_A)^{1/2} \mu_B \approx (8C)^{1/2} \mu_B$, where N_A is the Avogadro's number, and $k_{\rm B}$ is the Boltzman constant, and found to be $\approx 1.84 \,\mu_{\rm B} \, {\rm f.u^{-1}}$. The theoretically expected (spin only) value of μ_{eff} is calculated by using the formula $(\mu_{\rm eff})^2 = \Sigma[g^2\{n.S(S+1)\}] \mu_{\rm B}^{-2}$, where g is gyromagnetic ratio (\approx 2), *n* is the number of magnetic ions with spin *S* in the formula unit, and summation Σ runs over all magnetic ions in the formula unit. The theoretically calculated value of spin only $\mu_{\rm eff}$ is found to be 2.4 $\mu_{\rm B}$ f.u⁻¹. for the compound. Figure 5d shows the magnetization (*M*) as a function of the applied magnetic field (*H*) measured \pm 7 Tesla. The shape of *M*–*H* loops indicates a paramagnetic nature of the compound at 5 K, however, the *M*-*H* loop at 2 K shows some ferro/ferrimagnetic interaction due to a short-range magnetic ordering. The saturation magnetization is found to be $0.42 \,\mu_{\rm B} \, {\rm f.u^{-1}}$ at 2 K. The theoretically expected (spin only) value of the ordered magnetic moment, μ_s per formula unit is calculated by using the formula $\mu_{\rm s} = \Sigma({\rm g}nS) \,\mu_{\rm B}$, where g is gyromagnetic ratio (≈ 2), *n* is the number of magnetic ions and *S* is the spin of magnetic ions. The μ_s per formula unit (spin only) is found to be $1\,\mu_{\rm B}\,{\rm f.u}^{-1}$ for the compound considering Fe (II) and V (IV) are in their low-spin states.

To confirm the magnetic nature of the compound, a neutron depolarization measurement is carried out. It is a very useful technique to get information about size and magnetization of domains of ferro/ferrimagnetic compounds by using polarized neutrons which get depolarized owing to the Larmor precession of neutron spins in the magnetic fields of randomly oriented magnetic domains,^[20,100–103] The schematic representation of the experimental technique is presented in **Figure 6**. The incoming neutron beam (P_0) gets polarized (P_r) after leaving

Table 2. Hyperfine parameters for K₄[FeCN₆] and VHCF compounds revealed from fitted Mössbauer spectra.

Samples	Fe-sites and ionic states	Isomer Shift (δ) [mm s ⁻¹] ± 0.008	Quadrupole splitting (ΔE_Q) [mm s ⁻¹] ± 0.005	Relative area [%]	Line width (Γ) [mm s ⁻¹] ± 0.005	Goodness of fit (x ²)
K ₄ [FeCN ₆]	Singlet (Fe ⁺² -LS)	-0.053	-	100	0.327	1.17
VHCF	Singlet (Fe ⁺² -LS)	-0.137	-	84.6	0.285	-
	Doublet (Fe ⁺³ HS)	0.397	0.506	12.5	0.4	1.05
	Doublet (Fe $^{+3}$ LS)	-0.121	0.774	2.9	0.3	-
VHCF After 100 cycles	Singlet (Fe ⁺² -LS)	-0.134	_	93.9	0.365	-
	Doublet (Fe ⁺³ HS)	0.251	0.493	4.3	0.251	0.81
	Doublet (Fe $^{+3}$ LS)	0.010	2.025	1.8	0.267	-
VHCF After 350 cycles	Singlet (Fe ⁺² -LS)	-0.140	_	86.2	0.362	-
	Doublet (Fe ⁺³ HS)	0.182	0.446	11.4	0.374	0.93
	Doublet (Fe ⁺³ LS)	0.017	1.61	2.4	0.23	_



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Figure 5. dc magnetization data of VHCF compound. Magnetization (*M*) versus temperature (*T*) a), χT versus temperature (*T*) b) curves for the compound. The inverse susceptibility (χ^{-1}) versus temperature curves, fitted by using the Curie-Weiss law c). Magnetization as a function of field at 5 and 2 K for the VHCF compound d).



Figure 6. Temperature dependent neutron depolarization data of the VHCF compound recorded under a magnetic field of 10 Oe. The experimental setup is schematically depicted in the figure, where *H* represent the guide field used to maintain the beam polarization.

the sample. The information on the phase fraction of ferromagnetic domains in paramagnetic matrix could also be revealed by monitoring the rotation angle of neutron beam. In addition, magnetic correlation length is also extracted. Figure 6 shows the neutron depolarization data for the VHCF compound. The compound does not show depolarization of the polarized neutron beam down to \approx 3 K indicating absence of ferro/ferrimagnetic ordering. The neutron depolarization data are consistent with dc magnetization study, and confirms a paramagnetic behavior of the compound.

3.4. (D) Soft X-ray Absorption Spectroscopy (XAS) Study

Soft XAS study has been carried out to investigate the electronic structure of the VHCF compound. The mixed valence states of V and Fe, and nature of charge transfer are studied for the present compound. Since, there is a possibility of charge transfer from metal to ligand or vice versa, the local coordination geometry and electronic structure of the compound have been analyzed using configuration-interaction cluster model calculations. For the light elements C, N, and O, the K-edge which originated from $1s \rightarrow 2p$ electronic transitions, whereas for the K, Fe and V the L-edge absorption spectra, which include $2p \rightarrow 3d$ electron transitions have been used. Two main peaks exist for the $L_{2,3}$ edges which are originated from the transitions from the $2p_{3/2}$ (L₃ edge) and $2p_{1/2}$ (L₂ edge) to d orbitals. These two peaks are separated by the spin-orbit splitting of the inner 2p shell, with the L_2 edge situated on the high energy side of the L_3 edge with peak intensity ratio variations.

Figure 7 shows the K (2*p*), V (2*p*), and Fe (2*p*) *L* edge and N–*K* edge XAS data for the VHCF compound at 300 K. Figure 7a shows *L* edge XAS spectrum of potassium, which shows a transition from $2p \rightarrow 3d$. The spectrum consist of two intense peaks situated at \approx 300.6 and 303.2 eV, respectively originated by 2*p*3/2, 2*p*1/2 \rightarrow 3*d* transitions. A low intensity broad peak at \approx 297 eV is also observed, which could arise due to beamline artifacts. Figure 7b shows the V *L* edge XAS spectrum of VHCF compound. The spectrum consists of two main peaks at 517.6 and 524.5 eV due to *L*₃ and *L*₂ edges originated from V 2*p*3/2 to

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Figure 7. a) The L edge soft XAS spectra of K-2p, b) V-2p, c)Fe-2p, and d)K edge soft XAS spectra of N-1s for the VHCF compound. The spectral peaks are fitted using Gaussian function.

V 3d and V 2p1/2 to V 3d transitions, respectively. In addition, low intensity peaks at \approx 529.7 and 532.2 eV are also observed. These peaks are originated from the electronic transitions of O 1s electrons to V 3d-O 2p $(t_{2\sigma})$ and V 3d-O 2p (e_{σ}) states, respectively, corresponding to π and σ interactions. The broad peak observed around 544 eV is associated to the mixture state of V 4sp and O 2p (28). Figure 7c shows the measured Fe 2p (L-edge) XAS spectrum of VHCF compound. It is evident that the Fe 2p XAS spectrum is very much similar to the PBAs synthesized using $K_4[Fe(CN)_6]$ compound.^[104,105] Therefore, the presence of Fe (II) oxidation state is confirmed in the VHCF compound. Our Mössbauer spectroscopy study also supports the presence of low-spin Fe^{II} in the compound. For the PBAs compounds, with Fe (III) valence state, a low intensity peak at \approx 707 eV due to 2*p* $\rightarrow t_{2g}^{5}$ appears which is absent in the XAS spectrum as shown in Figure 7C. The splitting in the Fe L₂₃ XAS spectrum also suggests a strong bonding of Fe with the C≡N ligand. The octahedral ligand field splits the Fe 3*d* orbitals into e_{g} and t_{2g} orbitals and found to be at 711.1 and 712.8 eV, respectively.

Figure 7d shows N K edge spectrum of the VHCF compound. The spectrum is dominated by a strong peak at low energy around 400 eV followed by many weak intensity peaks at higher energies. The low intensity peaks are originated from the main π^*2p and σ^*2p resonances of C=N. A prominent single peak at 400.8 eV is evident which is very close to the N K edge of the $K_4[Fe(CN)_6]$ compound where N is found to be at 399.8 eV. This peak arised due to the $1s^2 2p^n \rightarrow 1s^1 2p^{n+1}$ dipolar transition.^[106] In PBAs, d orbitals of metal ions mix with the empty ligand's π orbitals, that is, the antibonding π^* orbitals of $(C\equiv N)^{-1}$ which results back donation of metal electrons to ligands.^[29,105,107–110] The back donation introduces 3d character into the π^* molecular orbitals of $(C\equiv N)^{-1}$ due to back-bonding interactions. Hence, the two peaks arising at 710.1 eV (722.2 2p $\rightarrow e_{\rm g}^{0}$) and 711.5 (724.2 $2p \rightarrow e_{\rm g}^{0}$) eV are observed corresponding to transitions to e_{g^*} and t_{2g^*} molecular orbitals, respectively in the $K_4[Fe(CN)_6]$.

The microscopic understanding of electronic structure of Fe and V 2p XAS spectra of VHCF compound has been derived by employing the configuration-interaction (CI) cluster model calculations using the CTM4XAS software.^[111] The calculation is based on the consideration of charge transfer both from the ligand-to-metal charge transfer (LMCT), that is, the ligand-donor bonding, and the metal-to-ligand charge transfer (MLCT), that is, the ligand-acceptor bonding. The LMCT and MLCT take place because of the π/σ donation and the π back-donation, respectively. The schematic representation of the π/σ donation and the π back-donation is shown in **Figure 8**. The energy levels modifications due to interactions of metal (Fe) ion and ligand (C=N) in $[Fe(CN)_6]^{-4}$ are shown Figure 8a. Due to the crystal field strength of ligand, the octahedral environment of metal centres in PBAs splits the metals 3d-energy levels into two sets of orbitals $(t_{2g} \text{ and } e_g)$. In a molecular orbital's context, these are antibonding states with specific symmetry (π,π^* and σ, σ^*). In cyanide complexes, the existence of empty π^* orbitals on the ligands,



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Figure 8. a) Schematic energy level diagram showing the interaction among the Fe ion and C=N ligand. The possible σ -donation and the π back-donation occur between the Fe ion and the CN ligand in [Fe(CN)₆]⁻⁴. b) The orbital representation of charge transfer, showing σ donation, π donation and π back-donation between Fe and C=N.

close to the *d* orbitals, significantly affects the crystal field energy.^[112] These empty orbitals allow back donation of electrons from the metal to the ligand. The Fe L-edge spectra of PBAs have also been analyzed earlier by considering MLCT, also known as π back-donation, and LMCT, which includes π/σ back-donation (Figure 8b), in the CTM calculations.

In the calculations, the atomic multiplets, due to the six C≡N ligand-ion environment, have been simulated by considering 1) crystal-field energy, 10 Dq, 2) hybridization hopping parameters of V_{eg} and V_{t2g} , 3) repulsive 3*d*-3*d* Coulomb energy U_{dd} , and 4) the attractive 2p-3d core-hole potential $U_{\rm pd}$. The crystal-field energy 10 Dq is the energy difference between the 3d ($e_{g \downarrow}$) and 3d ($t_{2g \downarrow}$) levels. The hybridization hopping parameters of V_{eg} and V_{t2g} take account of the covalency between metal's 3d and ligand's p states^[109,113] and correspond to the hopping energy between Fe $e_g(t_{2g})$ and C=N σ/π orbitals. Figure 9a shows the Fe L-edge XAS spectrum in comparison to the simulated XAS spectra of various oxidation state of Fe. The simulated XAS results for Fe^{+2} and Fe⁺² states without charge transfer clearly show the difference in their peak positions, and confirm the presence of mainly Fe^{+2} state. Though, a weak contribution from the Fe⁺³ state may also exist in the XAS spectra of the VHCF compound as evident from the appearance of a very low intensity peak at \approx 706.5 eV. While considering LMCT alone, the simulated XAS result for Fe⁺² state does not resemble much to the experimental XAS data. However, by considering both LMC and MLCT, the simulated XAS spectra of Fe⁺² state match well with the experimental XAS spectra of the VHCF compound. This confirms that the VHCF compound exhibits strong MLCT. The best simulated LMCT-MLCT calculations are achieved with the parameters of 10 Dq = 3.7, charge-transfer (CT) energy, $\Delta = 1.0$, $U_{dd} = 2.0$, and $U_{pd} = 1.0 \text{ eV}$ for Fe²⁺ states.

Figure 9b shows simulated XAS spectra of various oxidation state of V and experimental data of V 2p XAS of VHCF compound. Form the simulated XAS spectra of V, it is found that V exist in +4 state. In addition, it has been observed that the spectral ordering is the shift to higher energy side with increasing oxidation state of the V along the sequence $V(II) \rightarrow V(III) \rightarrow V(IV) \rightarrow V(V)$. The V L_{2.3} edge XAS spectra have been simulated to match the experimental XAS spectra in which charge transfer process has been also considered. Since, V is oxidized in VHCF compound, the charge transfer energy between the V $3d^n$ and the $3d^{n+1}L$ configurations considered, where L denotes hole state in the O 2p ligand band. The values of ligand field and the configuration mixing strength parameter are systematically varied and continued until simulated XAS spectra are found to match with the experimental data. The best fit XAS spectrum is achieved with the parameter values of the 10 Dq = 1.1, $U_{dd} = 2$, $U_{pd} = 1$ and $\Delta = 1$ eV. It is important to note that the parameters derived from the calculation are merely adjustable to obtain the best match with the experimental data. Consequently, we can estimate changes in the physical properties, but not the precise quantitative values. The CI cluster model calculations have been used in analyzing XAS data of similar PBAs compounds.[108,109,114-117]

3.5. (E) Electrochemical Study

The electrochemical properties of VHCF compound have been investigated by cyclic voltammetry. **Figure 10**a shows the CV of the VHCF compound recorded at 30 mV s⁻¹ for five cycles. The CV data shows the cyclic stability of the compound during the electrochemical measurements. Two pairs of redox peaks located at $\approx 0.4/0.3$ and 0.9/0.7 V may correspond to the Fe^{II}/Fe^{III} and V^{III}/V^V redox couples^[94,97,118,119] suggesting multistep insertion/extraction of K⁺ ions through the VHCF lattice. The following reversible redox process can be attributed to the redox peaks at $\approx 0.4/0.3$ V.

$$K^{+}(V^{III})[Fe^{II}(CN)_{6}] \rightarrow (V^{III})[Fe^{III}(CN)_{6}] + e^{-} + K^{+}$$

CV curves were obtained at different scan rates from 5 to 90 mV s^{-1} . The change in current intensity and peak positions



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Figure 9. Comparison of the experimental and simulated *L* edge XAS spectra of a) Fe-2*p* and b) V-2*p* of the VHCF compound. The simulated XAS spectra for various oxidation states of the metal ions are calculated by considering both with and without charge transfer effects between the metal and the ligand.

of redox peaks were observed with increasing scan rates. As shown in Figure 10b, two pairs of redox peaks were observed at 0.4/0.3 and 0.9/0.7 V at 5 mV s⁻¹. When the scan rate increases to 90 mV s⁻¹, two pairs of redox peaks were observed at 0.4/0.2 and 1.0/0.6 V. The current intensity of redox peaks increased with increasing scan rate. The V^{III}/V^V redox peak at 0.9/0.7 V can be attributed to the following reversible redox process.

$$(V^{III})[Fe^{III}(CN)_6] + 2K^+ + 2 H_2O$$

 $\rightarrow K^+_2(V^VO_2)[Fe^{III}(CN)_6] + 4H^+ + 2e$

To further analysis the K^+ storage mechanism, CV curves at different scan rates (5–90 mV s⁻¹) shown in Figure 10b are

further analyzed. The total charge storage mechanism involves both the capacitive (surface) and diffusion-controlled intercalation process. The relation between peak current (*i*) versus scan rate (ϑ) is plotted in the inset of Figure 10b, which follows the power law relation as follows.

$$i=a\vartheta^{\mathrm{b}}$$

 $\log(i) = \log(a) + b\log(\vartheta)$

where, *a* is a coefficient, and *b* determines whether the redox process is controlled by diffusion (b = 0.5) or capacitive (b = 1) processes. In this study, the value of *b* is found to be 0.7, indicating that both the capacitive and diffusion behaviors synergistically controlled the charge storage process, thus, enabling faster



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Figure 10. a) CV curves recorded at a scan rate of 30 mV s⁻¹ within the potential range of 0–1.2 V versus Ag/AgCl for the VHCF compound, showing cyclic stability. b) CV curves recorded at different scan rates for the VHCF compound. The inset in b) shows linear fitting (red line) of the peak current (Ip) versus scan rate (in mV s⁻¹). c) The contribution of diffusion and capacitive control to the charge storage kinetics. d) Crystal structure of the VHCF compound during the charging (presence of K⁺ ion) and discharging (presence of vacancies) states. The electrochemical performance is primarily controlled by the Fe (II)/Fe (III) and V (III)/V (V) redox active centres, as shown in (d). e) A schematic diagram of the aqueous K⁺ ion battery with VHCF as cathode material is presented.

K⁺ ion diffusion kinetics and high-rate capability. In addition, using the Dunn's equation $(i_p = K_1 \vartheta^{0.5} + K_2 \vartheta)$, the surfacecontrolled (capacitive) and diffusion-controlled (diffusive) contributions to charge storage are quantified. Figure 10c shows the diffusion and capacitive controlled contribution to the charge storage from 5 to 90 mV s^{-1} . With the increase in scan rate, the contribution of surface-controlled (capacitive) process increases gradually from 40 to 70%, demonstrating that the capacitive process dominates the electrochemical reaction and charge storage. Crystal structure of the compound during charging and discharging state is shown in Figure 10d. The presence and absence of the K⁺ ions in the interstitial sites during the charging and discharging state can be visualized in the compound in which two active redox centers (Fe and V) govern the electrochemical performance of the compound. A schematic diagram of the aqueous K⁺ ion battery based on VHCF as cathode and graphite as anode material is presented in Figure 10e. For the K⁺ ion insertion/extraction in VHCF, the GCD (Galvanostatic charging-discharging) measurements are carried out in 0.1 M K₂SO₄ + 0.1 M H₂SO₄ electrolyte. Since, vanadium ion exists in the form of vanadyl ion (VO) in the compound, their large hydrated diameter makes it difficult to move interstitial ions during the processes of charging-discharging. Therefore, it is important to optimize the electrolyte solution. The VO bond observed in the IR spectra suggests the presence of vanadyl ions

 (VO^{2+}) in VHCF. This is further corroborated by the XAS results, which confirm that vanadium exists in the (IV) oxidation state (V^{IV}) in VHCF. According to Rietveld-refined XRD analysis, vanadium ions occupy the 4a crystal lattice sites and are octahedrally coordinated by nitrogen atoms. The VO²⁺ ions can also be considered as integral to the lattice structure. However, in this case, vanadium is not ideally octahedrally coordinated, as it is bonded to a terminal oxygen atom along with five cyanide ligands.^[120] This arrangement introduces distortions into the crystal lattice, leading to different coordination environments for the iron ions as the structure adjusts to minimize the distortion. Iron ions may be coordinated to one or more bridging cyanide ligands or to water molecules. Mössbauer spectroscopy confirms the presence of Fe²⁺ ions in VHCF, consistent with the Fe³⁺/Fe²⁺ redox activity observed in the system. Here, the relatively low cutoff voltage of 1 V is primarily dictated by the stability of the aqueous electrolyte, as higher voltages may lead to electrolyte decomposition and structural degradation of the electrode material. However, to enhance the cutoff voltage, future work could explore the use of optimized electrolyte compositions, pH adjustments, or hybrid aqueous-organic electrolytes like use of amphiphilic supramolecule^[121] and 1,3,6-hexanetricarbonitrile^[122] which enhances the stability of water by weakening the hydrogen bond network to widen the electrochemical stability window". For example, amphiphilic supramolecule modified

aqueous K-ion electrolytes with synergistic functions of excludedvolume effect and hydrogen bond networks, which greatly reduce the activity of water molecules, inhibit the dissolution of active materials, and expand the operation voltage window (>3.4 V). In another example, 1,3,6-hexanetricarbonitrile enhances the stability of water by weakening the hydrogen bond network. Consequently, increases the cutoff to 3.5 V at a relatively low concentration. In addition, weak-polar solvents have more advantages in increasing in cut off voltage than strong-polar solvents.

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From charging–discharging curves, the calculated specific capacity is presented in **Figure 11**. The voltage versus time response of VHCF compound at various current density is presented in Figure 11a. The GCD profile shows two distinct humps confirming the presence of two redox centers. The hump voltages correspond to the position of redox peaks in CV curves (Figure 11 (b)). The GCD curve is found to be symmetrical in shape indicating their higher electrochemical reversibility and faster electron kinetic. Moreover, the symmetric charge/discharge profiles also indicate a high Coulombic efficiency for VHCF compound. The Figure 11b shows charge–discharge profile of 200 cycles of VHCF compound at 2 A g⁻¹ current density. The initial discharge capacity is found to be 80 mAh g⁻¹, which increases after few cycles and reached maximum up to 90 mAh g⁻¹ due to activation process.

The cyclic performance is shown in Figure 11c in terms of specific capacity as a function of the number of cycles at different current densities. The maximum specific capacity of \approx 121 mAh g⁻¹ is observed at a current density of 0.5 A g⁻¹. As the current density increases, the specific capacity gradually

decreases, reaching 65 mAh g^{-1} at a higher current density of 5 A g^{-1} . This reduction in specific capacity at higher current densities is attributed to the reduced contribution of one of the redox reactions, whereas, at lower current densities, both redox reactions contribute to the capacity. Moreover, the formation and breaking of the vanadyl ions (VO²⁺) with current density may also contribute to the specific capacity. At the highest current density of 5 Ag^{-1} , the coulombic efficiency remains high at 98%. When the current density is reduced from 5 to 1.5 and further to 0.8 Ag^{-1} , the specific capacity, rather than declining due to cyclic degradation, increases to 84 and 100 mAh g⁻¹, respectively. The coulombic efficiencies at these lower currents are \approx 93 and \approx 90%, demonstrating a recovery of capacity and excellent structural stability for the K⁺ ions. All specific capacities exhibit stable performance, nearly returning to the values recorded during the initial stages of the rate study. Figure 11d shows the long-term cycling performance and corresponding coulombic efficiency at a higher current density of 2 A/g for the VHCF electrode material. The measurement shows that a complete charge/ discharge cycle takes \approx 3 min, with 620 cycles completed in about 31 h. During the initial cycles, a slight decrease in capacity is observed, followed by an increase over the first 50 cycles. Subsequently, the capacity gradually declines. The coulombic efficiency remains steady at \approx 96% throughout the cycles, with a capacity retention of \approx 45% at the 620 cycle for a current density of 2 Ag^{-1} . This demonstrates the electrode material's performance and stability over extended cycling. The initial capacity drop, followed by an increase over 50 cycles can be understood from the structural and electrochemical changes that occurring



Figure 11. a) Electrochemical performance of the VHCF electrode in $0.1 \text{ M } K_2\text{SO}_4 + 0.1 \text{ M } H_2\text{SO}_4$ electrolyte. The voltage vs. time curve at different current densities recorded using GCD. b) The voltage versus specific capacity for various charging-discharging cycles at a current density of 2 A g^{-1} . c) The rate performance and corresponding coulombic efficiency. d) Long-term cyclic stability and coulombic efficiency at a current density of 2 A g^{-1} for the VHCF cathode.



due to the initial stage of charging-discharging cycling. In the first few cycles, capacity decreases due to the structural defects, interstitial water, and vacancies that are inherently introduced in VHCF during synthesis. These interstitial water molecules occupy ion insertion sites, temporarily hindering K⁺ insertion/extraction initially. Additionally, in aqueous ion batteries, interstitial water may diffuse into the electrolyte, leading to a dilution effect that impacts electrolyte concentration and accelerates structural dissolution. Thus, the initial drop in capacity is likely due to the gradual release of interstitial water and the stabilization of electrolyte concentration during early cycles. As cycling continues, the material undergoes electrochemical activation, improving electrolyte penetration into the VHCF structure. This activation enhances ion diffusion pathways and electrode utilization, leading to a gradual increase in specific capacity. Once the electrode is fully activated, the VHCF material achieves a peak specific capacity of 121 mAh g^{-1} . However, with prolonged cycling, capacity degradation sets in due to the dissolution of vanadium-based materials in aqueous electrolytes. The high polarity of water molecules accelerates vanadium dissolution, ultimately causing capacity decay over extended cycles. This behavior is often attributed to delayed electrolyte penetration, which initially limits electrode utilization but gradually enhances performance as cycling progresses.

Electrochemical impedance spectroscopy (EIS) is performed to study the reaction kinetics of the VHCF electrode, and data are presented in Figure 12a. The impedance data shown in the form Nyquist plots (Figure 12a) consist of a semicircle in the high-frequency region, and a linear segment in the lowfrequency region. The semicircle corresponds to the charge transfer resistance (R_2) at the interface between electrode and electrolyte, whereas, a linear part of the graph is related to the Warburg impedance (W_0) , which is associated with K⁺ ion diffusion. The intercept data on the real axis provide a solution resistance (R_1) . The impedence data are further analyzed as an equivalent circuit model to determine the kinetic parameters. The equivalent circuit is shown in the inset of Figure 12a. The charge transfer resistance (R_2) are found to be 80 and 3Ω , at 0.4 and 0.6 V, respectively. The specific capacity of VHCF compound at different current densities is compared (Figure 12b) with other PBAs compounds reported in the literature for K^+ and Na^+ ion batteries. The present study shows that the compound exhibits a superior electrochemical performance among all reported PBAs.

3.6. (F) Study of VHCF Electrode for Aqueous K⁺-ion Battery

In order to investigate the structural stability of the VHCF electrode and the changes in the oxidation states of metal ions after GCD cycling, ex situ analyses including HRTEM, XRD, XPS, and Mössbauer spectroscopy were performed on both pristine and cycled VHCF materials. The microstructure of VHCF was analyzed using a HRTEM before and after cycling. As shown in Figure 13a, VHCF exhibits well-dispersed nanostructures with a relatively uniform morphology and irregular clusters of small particles, ranging from 50 to 100 nm in diameter. Figure 13b presents a HRTEM image, revealing clear lattice fringes, which indicate a well-ordered crystalline structure with a visible (2,0,0) plane, suggesting a stable framework before cycling. Lattice fringes with a *d* spacing of ≈ 0.51 nm are observed for (200) plane, confirming the good crystallinity of the compound. After 350 cycles, Figure 13c shows that the nanostructures appear more aggregated and interconnected, likely due to cycling-induced stress or partial degradation. Figure 13d presents a HRTEM image where lattice fringes remain visible but are less distinct than in Figure 13b, indicating slight structural distortion or amorphization after 350 cycles. The inset further highlights preserved short ordered crystalline domains despite extended cycling, with visible lattice fringes of *d* spacing of 0.49 nm for (200) plane.

Structural changes in terms of phase stability and degradation are further examined using exsitu XRD. Figure 13e shows the Rietveld-refined XRD patterns after 100 and 350 cycles, demonstrating that the material remains stable even after 350 cycles. However, a slight change in the lattice constant is observed compared to the uncycled material, measuring 10.18(7) after 100 cycles and 10.13(4) Å after 350 cycles, in contrast to 10.22(5) Å for the uncycled material.

Figure 14 presents the V 2*p* and Fe 2*p* core-level spectra of the VHCF compound before and after 350 cycles. The V 2*p* spectrum (Figure 14a) is fitted with two peaks at 516.4 and 517.4 eV, confirming the presence of V⁴⁺ and V⁵⁺ oxidation states,



Figure 12. a) EIS data presented as Nyquist plots recorded at 0.4 and 0.6 V for the VHCF compound and corresponding equivalent circuit model. b) The specific capacity vs. current density of the VHCF compound compared with specific capacity values of other PBAs reported in the literature.



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Figure 13. HRTEM images of the VHCF electrode in the uncycled a,b) state and after 350 charging-discharging c,d) cycles. The Rietveld-refined room temperature XRD patterns of the VHCF compound after 100 and 350 cycles e).



Figure 14. Core level XPS spectra of a) V-2*p* and b) Fe-2*p* for the VHCF compound before cycling (uncycled) and after 350 charging–discharging cycles. Figure c) shows the fitted room temperature Mössbauer spectra of the VHCF compound after 100 and 350 cycles.

respectively, before cycling. The small presence of V⁵⁺ in this case may be attributed to vanadium oxide formation. After 350 cycles (Figure 14a), the V 2*p* spectrum still exhibits peaks at 516.4 and 517.4 eV, indicating the persistence of both V⁴⁺ and V⁵⁺ oxidation states, with an increased proportion of V⁵⁺. Similarly, the Fe 2*p* core-level spectra (Figure 14b) before and after cycling are deconvoluted into two peaks at 708 and 709.5 eV, indicating the coexistence of Fe²⁺ and Fe³⁺ oxidation states. After 350 cycles, the contribution from Fe³⁺ increases, suggesting enhanced redox activities. These XPS results confirm the presence of Fe²⁺ and V⁵⁺/V⁴⁺ redox activities in VHCF, which facilitate potassium-ion storage through a highly reversible intercalation process.

Mössbauer spectroscopy further supports these findings, confirming the presence of both Fe^{2+} (in a low-spin state) and Fe^{3+} (in both high-spin and low-spin states) after 100 and 350 cycles (Figure 14c). The exact percentages of high-spin and low-spin Fe^{2+}/Fe^{3+} states were determined through Mössbauer spectral fitting and are presented in Table 2.

Figure 15 shows the galvanostatic intermittent titration technique (GITT) measurement of aqueous K^+ -ion battery to investigate the K^+ -ion diffusion kinetics in a VHCF electrode. A constant current pulse of 25 mA g⁻¹ was applied for 5 min (τ) to charge the electrode, followed by a 25 min. relaxation period to allow the system to reach equilibrium at the open-circuit potential (OCP), characterized by a stabilized voltage (E_s). This



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Figure 15. GITT curve showing voltage versus time response for the VHCF electrode in the voltage range of 0.2–0.9 V during a) discharging and b) charging cycle. The calculated corresponding diffusion coefficient of K^+ ion during the c) discharging and d) charging cycle. e) EIS data as Nyquist plot, recorded at 0.6 V for K^+ ion aqueous battery based on VHCF cathode). f) The corresponding equivalent Randle's circuit, and g) schematic diagram showing internal resistance of the circuit.

charge–relaxation sequence was systematically repeated across a voltage range of 0.2–0.9 V during charging and discharging. The K^+ -ion diffusion coefficient was subsequently calculated using Fick's second law of diffusion as follows.

$$D = \frac{4}{\pi \tau} \times \left(\frac{m_{\rm B} V_{\rm m}}{M_{\rm B} S}\right)^2 \times \left(\frac{\Delta E_{\rm s}}{\Delta E_{\rm \tau}}\right)^2 \quad \text{valid for } \tau \ll \frac{L^2}{D_{\rm K^+}}$$

where, π represents the mathematical constant Pi; τ is the pulse duration; $m_{\rm B}$ denotes the mass of the active material (in grams); $V_{\rm m}$ is the molar volume; S is the geometrical surface area (1 cm^{-2}) ; ΔE_s is the voltage change during the relaxation (open-circuit) period; and ΔE_{τ} is the total transient voltage shift during the applied current pulse. The K⁺-ion diffusion coefficient (D_k^+) is shown in Figure 15c,d for both discharging and charging processes. The VHCF electrode exhibits relatively low values of ΔE_{τ} and ΔE_{s} , which are indicative of a low K⁺ion diffusion coefficient. The VHCF electrode exhibits both low ΔE_{τ} and ΔE_{s} values, which correspond to a low diffusion coefficient. Notably, during the charging process, $D_{\rm K}^{+}$ displays a distinctive V-shaped trend which starts at $\approx 1.77 \times 10^{-9}$ cm⁻² s⁻¹, then sharply declines to a minimum of $9.46 \times 10^{-11} \text{ cm}^{-2} \text{ s}^{-1}$ at the charge plateau. Following this, the diffusion coefficient rises again to about $8.99 \times 10^{-10} \, \text{cm}^{-2} \, \text{s}^{-1}$. Conversely, during the discharge process, the diffusion coefficient rises notably to 1.96×10^{-8} cm⁻² s⁻¹, signifying enhanced transport kinetics of potassium ions. This higher D_{K}^{+} value during discharge indicates more efficient ion movement, pointing to better transfer dynamics within the electrode material relative to the charging stage.

The reaction kinetics of the VHCF electrode are investigated using EIS. Figure 15e presents the impedance data for the VHCF cathode-based K^+ ion aqueous battery. The corresponding

equivalent Randle's circuit and a schematic diagram illustrating the internal resistance components are shown in Figure 15f,g, respectively. A low charge transfer resistance (R_2) of approximately $\approx 12 \Omega$ is observed for the VHCF electrode, indicating enhanced K⁺ ion kinetics.

3.7. (G) DFT Analysis of VHCF

To further understand the K⁺ ion transport in the VHCF compound, theoretical calculations are carried out using DFT. The calculation related to the energy barrier of migrating ions using DFT for other PBAs has also been recently reported in the literature.^[73,81,123,124] The electrochemical behavior of the VHCF compound is significantly influenced by the movements of the K⁺ ions in terms of ionic conductivity and diffusivity within the framework structure. Hence, the activation energy for ion migrations which corresponds to the energy barrier is calculated for the compound. The total density of states (DOS) and energy barrier for K⁺ ion migration in the VHCF compound are shown in Figure 16a,b respectively. The band gap is found to be $\approx 1.9 \text{ eV}$ for the compound. The of K⁺ ion migration has been investigated by considering various cases like the unit cell having 1) K^+ ions and vacancy, 2) K^+ and O ions, and 3) K^+ and K^+ at 8*c* crystallographic positions. The K⁺ ions movement between the two crystallographic sites is shown in bottom right side of Figure 16. The comparisons between the barrier energy for K⁺ ions for all three cases are shown in Figure 16b. It has been found that the energy barrier for K⁺ ion migration in VHCF is higher as compared to cases where K⁺ ions are present along with oxygen and vacancies. The lower value of $\approx 0.45 \text{ eV}$ energy is required for the easy migration of K⁺ ion in the compound. Further, the lower value energy barrier helps to make the crystal





Figure 16. a) Calculated DOS and b) barrier energy for K⁺ ion migration in VHCF. The dotted line in (a) shows the Fermi energy, which is set to zero. The crystal structures illustrate various configurations 1) K⁺ ion and vacancies (top left), 2) K⁺ ion and O atoms from a water molecule (top right), and 3) all K⁺ ion (bottom left) occupying interstitial sites in the compound. The energy barrier for K⁺ ion migration (bottom right) from the lattice is also shown.

structure stable, thereby enhances the cycling stability of the material.

4. Conclusion

The successfully synthesized VHCF compound shows as a promising electrode material for aqueous potassium-ion batteries, particularly as a cathode. The structural properties extensively investigated using XRD reveal a face-cantered cubic crystal structure of space group Fm3m. The paramagnetic behavior of the compound is confirmed by dc magnetization and neutron depolarization measurements. The low-spin Fe (II) state and their local environment are investigated using Mössbauer spectroscopy. The presence of specific oxidation states of iron (II) and vanadium (IV) is further supported by the XAS measurement. The XAS data analyzed using charge transfer multiplet calculations confirm both ligand-to-metal and metal-to-ligand charge transfer processes. The electrochemical performance investigated using CV and GCD measurements demonstrates a maximum specific capacity of \approx 121 mAh g⁻¹ at a current density of 0.5 A g⁻¹, with coulombic efficiency of over \approx 99%. At a higher current density of 2 A g⁻¹, the specific capacity is found to be 90 mAh g^{-1} with coulombic efficiency remains steady at \approx 96% throughout the cycles, with a capacity retention of \approx 65% after 240th cycle. The opentunnel-like framework of V(O)-Fe(CN)₆ contributes to its superior cyclic stability and reversibility. Impedance analysis shows kinetic behavior of the compound, and charge transfer resistance (R_2), calculated form Nyquist plots, is found to be $\approx 80 \Omega$. DFT calculations has been used to calculate the barrier energy for potassium-ion migration, and found to be $\approx 0.45 \text{ eV}$ for the case where both K⁺ ions are present at 8*c* crystallographic positions in the unit cell. The room temperature synthesis, cost-effectiveness, and unique structural properties of VHCF make it highly desirable candidate for future potassium ion energy storage applications.

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Conflict of Interest

The authors declare no conflict of interest.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

density functional theory calculation, K ion batteries, metal organic framework, molecular magnet, neutron depolarization, Prussian blue analogues, X-ray absorption

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