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Investigating FeVO₄ as a cathode material for aqueous aluminum-ion battery

Sonal Kumar^a

Rohit Satish^a

Vivek Verma^a

Ren Hao^a

Pinit Kidkhunthod^b

William Manalastas Jr. ^a

Madhavi Srinivasan^{a,*}

madhavi@ntu.edu.sg

^aSchool of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Ave, 639798, Singapore

^bSynchrotron Light Research Institute (SLRI), Nakhon Ratchasima, 30000, Thailand

*Corresponding author.

Abstract

Developing an aluminum-ion aqueous battery is extremely attractive for prospects of creating a super cheap, environmentally friendly and safe energy storage system. However, a lack of reversible cathode materials hampers the use of metallic Al as a high-capacity anode in an aqueous electrolyte. As opposed to insertion-type cathodes, the performance of conversion-type cathodes for Al-ion electrochemistry in an aqueous electrolytic environment remains poorly explored. As a first attempt to understand the performance of such conversion type materials for Al-ion intake, we herein report FeVO₄ as a potential cathode material with a significantly high capacity of 350 mA h g⁻¹. We use a combination of inhouse and synchrotron-based characterization techniques to confirm Al-ion electrochemical reaction with FeVO₄, and also determine how electrolyte pH has a mechanistic influence on the reversibility of aluminum-ion aqueous batteries.

Keywords: Aqueous Al-ion battery; High capacity cathode; Conversion-type electrode; Electrode dissolution; pH control; Electrolyte

1 Introduction

The rapid growth of energy demands and the movement towards environmental sustainability is prompting a shift towards alternative forms of energy which are non-exhaustive and sustainable. Though at present, the conventional power sources remain the main source of energy, the demand for cleaner forms of energies like solar, tidal and wind is also rising. It is predicted that solar photovoltaics is likely to push its installed capacity beyond that of hydropower around 2030 and past coal before 2040 [1]. This shifting trend is also evident from the rapid deployment and falling costs of clean energy technology [2]. For instance: 1) India expanded its solar-generation capacity 8 times from 2650 MW in 2014 to 20 GW in 2018 [3]. 2) China became the first country to pass 100 GW of installed photovoltaics capacity in 2017 [4]. Unfortunately, the unpredictable and intermittent nature of such energy sources makes their direct usage inefficient, leading to overgeneration/undergeneration of electricity for extended periods of time [5]. One logical solution to this problem is the incorporation of battery energy storage systems (BESS) in the electricity grid system, but the scales required mean such systems must be sustainable, environmentally benign, safe and cheap [6]. In this regard, aqueous battery systems are gaining significant attention because water as an electrolyte solvent is non-toxic, non-flammable and cheap. Though Li-aqueous batteries have been explored quite extensively [7-14], exclusively committing to Li-ion technology carries a high risk of material supply cutoff due to geopolitical reasons [15]. Therefore, hedging the long-term viability of BESS unto the exploration of non-lithium ion chemistries such as Na, Zn, Mg, Al is very much desired. Among these, aluminum-ion aqueous batteries (AIAB) are particularly promising as Al is very cheap, available abundantly and has high volumetric capacity (Fig. 1) [16,17]. This can help cutoff the cost of anode significantly and thus can bring down the overall cost of battery.

Fig. 1 Comparison of volumetric charge capacities, costs and natural abundance for different metal anodes [17,38,39].

alt-text: Fig. 1

Recently, Zhao et al. successfully demonstrated the reversible electroplating/electrostripping of metallic Al within an aqueous environment, and its potential direct use as an anode material [18]. However, prospective cathode materials including TiO₂ [19–26], CuHCF [27–29], V₂O₅ [30], MoO₃ [31], graphite [32], Na₃V₂(PO₄)₃ [33] and MnO₂ [18] have been reported to show only limited reversible cycling with Al-ions in an aqueous environment [16]. Making AIABs practically feasible is therefore highly dependent on the development of better electrode materials that can accommodate a higher charge capacity from aluminum ions in an aqueous electrolyte.

In the existing AIAB research there remains a gap wherein typical conversion materials are yet to be explored for AIABs [16,34]. Therefore, as a first attempt to understand the electrochemical behavior of conversion-type materials, we, in this report, explore FeVO₄ for Al-ion reaction in an aqueous electrolyte. We chose FeVO₄ for this purpose because 1) it has shown exceptional capacity in non-aqueous Li-ion batteries, allowing for the insertion of as much as 8 Li-ions [35,36], 2) its reaction potential allows for discharge/charge cycles within the potential stability window of water and 3) it had been reported to exhibit a conversion-type reaction mechanism for various cations [35,37]. In this work, we report the synthesis of FeVO₄ nanorods and further demonstrate its application as a cathode material in AIAB. We show that, in a pH- and concentration-modulated electrolyte, our material can deliver a capacity of ~350 mAh g⁻¹ at 60 mA g⁻¹, which is significantly higher than previously reported cathode materials for AIAB [16]. Further, using various inhouse and synchrotron-based analytical techniques, we explore the mechanism of Al-ion reaction with FeVO₄ and provide definitive proof of concomitant Al-ion intake during electrochemical cycling.

2 Material and methods

2.1 Synthesis of FeVO₄

FeVO₄ nanorods were synthesized using a stepwise combination of both hydrothermal and dry annealing, as described elsewhere with minor modifications [36]. In this method, 1 mmol Fe(NO₃)₃·9H₂O (Sigma-Aldrich, purity >99.9%) was dissolved in 15 mL of deionized (DI) water at room temperature. A stoichiometric amount of NH₄VO₃ (Sigma-Aldrich, purity >99%) was also dissolved in 15 mL of DI water at 80 °C. Then, the two solutions were mixed as follows: the NH₄VO₃ solution was slowly added to the Fe(NO₃)₃ solution under magnetic stirring. Afterwards, the resulting mixture was left stirring for about 4 h s, providing sufficient time for reaction, such that the solution turned into a homogenous orange liquid. This mixture was then transferred into a 50-mL Teflon-lined autoclave which was tightly sealed, and heated to 160 °C for a 5hr-dwell in a heating oven. After cooling to room-temperature, the residue was filtered, then washed with both water (3 washings) and acetone (2 washings). This residue was dried overnight in a vacuum oven, subsequently calcined in air at 500 °C for 2 h s, recovered and analyzed for purity.

Synthesis reaction:

Upon calcination:

2.2 Characterization

The purity of the so prepared powder and the evolution of charged/discharge electrodes were investigated using a combination of characterization techniques as follow.

2.2.1 XRD

Crystal structures were determined using a Bruker D8 Advance diffractometer operating in a Bragg-Brentano geometry and using a Lynxeye-type detector with CuK α radiation (40 kV, 40 mA, 0.6 mm slit size). A scan time of 4 s/step was applied with a step size of 0.0248°. Commercially-available monocrystalline Si-based sample holders (Panalytical) were used in all runs to achieve zero-background diffraction peaks. For the synthesized FeVO $_4$ powder, the obtained XRD pattern was subsequently refined using the TOPAS 4.1 software. For the charged/discharged electrode samples, the electrodes were extracted from the electrochemical cells and scanned without removing the Ti current collector mesh. To facilitate pattern-to-pattern comparisons, the collected XRD patterns were calibrated against the strong, sharp Ti peak position instead of using offsets from routine refinement techniques which poorly converged due to the nanocrystallinity of the active material and the extraneous binder/carbon phases present. The pattern intensities were subsequently normalized against the most intense peak.

2.2.2 Microscopy

Morphological analysis was conducted using a field emission scanning electron microscope (JEOL, JSM-7600F) in SEI mode with an accelerating voltage of 5 kV and at 8 mm working distance. EDX elemental analyses of powder and electrode samples were conducted using silicon-drift detectors as implemented in the microscope-attached EDS systems (Oxford Aztec Energy). Each sample was probed at 20 kV accelerating voltage for about 600 s while maintaining an optimum deadtime between 20% and 30%. Due to nanometric dimensions of the FeVO $_4$ nanorods, a JEOL JEM-2100F TEM set at an accelerating voltage of 200 kV was also used to probe the finer details of the powder morphologies.

2.2.3 Raman spectroscopy

Raman shifts were measured on a WITec, Alpha300 SR Confocal Raman spectrometer. Powder and electrode samples were exposed to a 488 nm wavelength Argon type laser. Further, each spectrum was normalized with respect to the most intense peak and analyzed based on available literature.

2.2.4 XPS

The oxidation state of the surface particles was studied using a Kratos AXIS Supra XPS, which uses monochromated radiation (Al K α , 1486.69 eV) operating at 225 W. The pass energy was set to 20 eV. Obtained spectra were deconvoluted using the Casa XPS software. At first, each spectrum was calibrated such that adventitious C1s peaks were positioned at 284.8 eV binding energy value. The background was removed using a non-linear (Shirley) baseline. Each fitting peak was defined as a combination of Lorentzian (30%) and Gaussian distribution (70%). It is to be noted that in some cases narrow scans obtained for Fe were indistinguishable with the Fe satellite peaks. Hence, only Fe 2p $_{3/2}$ peaks were analyzed.

2.2.5 XAS

Fe K-edge spectra were obtained at beamline 5.2 at Synchrotron Light Research Institute (SLRI), Thailand. The beam can operate from 1.2 keV to 12.1 keV with a resolution of 2×10^{-4} . The spectra were recorded in fluorescence mode using a 4-element silicon-drift detector. The background was subtracted and intensities normalized for XANES analyses using the ATHENA software from the Demeter Suite [40]. The processed spectrum was subsequently used for EXAFS analysis and fitting using the ARTEMIS software [40].

2.2.6 UV-Vis

UV-Vis-NIR spectrophotometer (PerkinElmer, Lambda950) was used to measure the absorbance of electrolytes in the 190 nm–800 nm wavelength range of light. Liquid samples were diluted down by a factor of 10 and then measured in clean quartz cuvettes (PerkinElmer, B0631009) for absorbance. For the cycled electrolytes the equivalent non-cycled electrolyte was used as a reference for background subtraction.

2.3 Electrochemical performance measurement

The active material, binder (Teflonized Acetylene Black) and conductive carbon (acetylene black) were mixed in a ratio of 6:2:2 (3 mg:1 mg:1 mg) and was pressed repeatedly to form a pellet and finally pressed onto a Ti mesh

under a force of 7 tons. The formed electrode was then dried for ~1 h in a vacuum oven prior to testing. All the electrochemical testing was done in a 3-electrode flooded beaker cell using a Solartron Analytical 1470 E for cyclic voltammetry (CV) and BTS Neware for galvanostatic charge-discharge (GCD) studies. No metal was submerged in the electrolyte during applied-bias testing, except for the Ti current collector. In this system, the pressed tablet composite formed the working electrode, whereas carbon paper (AV carb GDS22100) functioned as the counter electrode and Ag/AgCl (in 3.5 M KCl) electrodes served as reference systems for voltage measurements. All testing was done either in so prepared aqueous AlCl_3 solution or pH-modified aqueous AlCl_3 solution (basified dropwise using ammonium hydroxide solution).

It is worth mentioning here that the AlCl_3 electrolyte is highly acidic and can significantly corrode auxiliary battery parts, including battery casing and current collectors [24,41]. Therefore, only glass-based casing was used and Ti was used as the current collector. The use of titanium as a current collector is critical from two perspectives: 1) It is corrosion-resistant [42] and 2) It facilitates a large overpotential for hydrogen evolution thus enabling wider voltage operation in an aqueous electrolyte [43,44]. For a more detailed discussion on the choice of the current collector, the reader is referred to our review article on aqueous batteries [16].

3 Results and discussion

3.1 Materials characterization

XRD patterns were Rietveld refined based on $P-1$ space group with full occupancy of Fe, V and O at 2i sites (Fig. 2a). The resultant lattice parameters were determined to be as $a=6.72 \text{ \AA}$, $b=8.07 \text{ \AA}$, $c=9.35 \text{ \AA}$, $\alpha=96.65^\circ$, $\beta=106.57^\circ$, $\gamma=101.6^\circ$ with a crystallite size of 62.9 nm (Full details of refinement in Table S1). The FeVO_4 structure closely resembles the Zimnaitite phase (PDF no- 38-1373) and has three independent Fe atoms. Two of these non-equivalent Fe (Fe1 & Fe3) are in a distorted octahedral environment of oxygen atoms whereas the third Fe (Fe2) is in a trigonal bipyramidal environment of oxygen atoms (Fig. 2b and c). Finally, the three independent V atoms are in distorted tetrahedral environments (red polyhedra).

Fig. 2 Structural characterization of the synthesized FeVO_4 : (a) Rietveld-refined XRD pattern, (b) FeVO_4 unit cell (Fe1, Fe2, and Fe3 are three different environments of Fe) and (c) FeVO_4 crystal structure as viewed from the b -axis. FeVO_4 powder morphology study: (d) & (e) SEM micrographs, (f) & (g) TEM micrographs and (h) Energy-dispersive X-ray spectroscopy (EDX) elemental mappings of Fe, V, and O distributions in the FeVO_4 nanorods.

alt-text: Fig. 2

Fig. 2d-g shows the morphological features of the synthesized FeVO_4 . SEM images revealed that the obtained material crystallized in a predominantly nanorod morphology with seed-like particles. The SEM-EDX elemental maps (Fig. 2h) confirmed a uniform distribution of Fe, V, and O in the nanostructure, with no other elements detectable in the EDS energy spectra. As no crystalline impurities were detected in the XRD spectra, the nanorod formations were expected to be FeVO_4 crystals. The seed-like particles can be FeVO_4 that nucleated but could not grow within the allowed reaction time. A statistical analysis of the SEM micrograph in Fig. 2d reveals a high aspect ratio of nanorods, about 10, and average diameter & average length of 190.5 nm and 1.70 μm , respectively (Fig. S1 a & S1 b). The powder geometry implies a propensity that nanorods might get preferentially oriented during the electrode fabrication process which may have caused compression. Thus a comparative analysis of the XRD patterns for the pristine FeVO_4 powder and pressed electrodes were done (Fig S1 c). As can be seen in Fig S1 c, the XRD patterns of the pristine powder and pressed electrode samples overlap very well. This essentially indicates that there was no significant texturing taking place during electrode fabrication even though there were compression forces applied. It is speculated

that the high ratio of binder and conductive carbon (active material: binder: conductive carbon = 6:2:2) acted as mechanical buffers and suppressed preferential orientations. TEM micrographs (Fig. 2f and g) indicate a rather porous nature of particles which can be beneficial for better electrode-electrolyte contact and enhance the material performance.

3.2 Electrochemical performance

Fig. 3a shows the CV plot of FeVO₄ as cycled within a voltage range of -0.8 V to 1 V (vs Ag/AgCl). The working electrode was first discharged (negative voltage sweep) such that Al-ions and electrons travel towards it through the electrolyte and through the external circuit, respectively, and vice versa on the subsequent charging step (positive voltage sweep). In the first cycle, two cathodic peaks can be identified at 0.2 and -0.2 V (vs Ag/AgCl) with two anodic peaks at 0.1 and 0.5 V (vs Ag/AgCl); these peaks become more defined in subsequent cycles. The existence of these peak pairs can be due to reduction/oxidation processes taking place on the transition metal centers of FeVO₄ and indicates a reversible electrochemical phenomenon taking place. The broadened profiles of the CV plots hint towards a complex insertion/reaction mechanism and poor insertion kinetics, similar to what has been observed for Mg-ion in FeVO₄ [45] and Al-ion in CuHCF [27–29]. We also carried out blank CV tests in absence of Al-ion in the electrolyte (Fig. 3b) and observed no redox peaks in NH₄OH or NH₄Cl electrolyte. This essentially indicates that the electrochemical activity observed in our study is only due to Al-ion insertion/reaction while other spectator ions (NH₄⁺, Cl[−], OH[−]) did not react.

Fig. 3 (a) CV plot in 1 M AlCl₃, pH ~1.9 at 10 mV s⁻¹. (b) CV plots in different electrolytes at 10 mV s⁻¹. (c) GCD plot in 1 M AlCl₃, pH = 3.5 at 60 mA g⁻¹ (d) Cycling performances in 1 M AlCl₃ under various pH (e) Cycling performances at pH = 3.5 for various concentrations of AlCl₃.

alt-text: Fig. 3

To measure the charge capacity of FeVO₄, GCD study was performed on the electrodes in 1 M AlCl₃ at 60 mA g⁻¹. Though we observed an initial capacity of $\sim 250\text{ mA h g}^{-1}$, it decayed to 25 mA h g^{-1} within merely the first 3 cycles (Fig. S2 a). We observed that an originally transparent electrolyte turned yellowish after the first few cycles, indicating probable vanadium dissolution into the electrolyte, as theoretically predicted by the Pourbaix diagram of V [46]. To solve this problem, the pH of 1 M AlCl₃ electrolyte was increased from an original value of ~ 1.9 to 3.5 by adding ammonium hydroxide solution, making sure that the electrolyte remained homogenous and no precipitate formed. This step significantly reduced the visually observed color change of the electrolyte upon cycling. The effect of pH was also reflected in the charge/discharge study, wherein the initial capacity increased to $\sim 350\text{ mA h g}^{-1}$ (Fig. 3c) and the cycling stability improved in high pH electrolyte (Fig. 3d).

3.2.1 Effect of electrolyte pH

This electrochemical improvement can be further explained based on the equilibrium between a discharged cathode material (here: Al-reacted FeVO₄) and ionic/molecular species present in the aqueous electrolyte (here: Al³⁺, H⁺, OH[−], O₂, H₂, and H₂O).

To maintain charge balance, the introduction of cations into a host material results in a reduced oxidation state for redox-active centres. But this reduction process can take place only for a certain amount of cation intake. At this limit, the host material can be described to exist at a minimum reduction potential ($V_{\min}$) below which the material becomes unstable. Forcing current beyond this potential limit may lead to irreversible decomposition of either the electrode, the electrolyte or both, the above reaction in our case. This means that an applied potential (V_{app}) lower than $V_{\min}$ would drive the above reaction in the forward direction, resulting in destabilization of the host material. Here, $V_{\min}$ can be expressed as a function of electrolyte pH and

Al³⁺ activity (derivation details in Refs. [16,47,48]):

$$V_{min} = 4.290 - 0.059\,pH - 0.0066\,\log\left[Al^{3+}\right]\,\left(vs\,Li^{+}/Li\right)$$

This equation implies that a higher pH electrolyte results in a lower V_{min} . Thus, in a higher pH electrolyte, we have a wider potential window for cycling the host material with reduced risk of electrode destabilization and electrolyte decomposition, and therefore we do expect an improvement in cycling stability. We also studied cycling stability as a function of AlCl₃ concentration (Fig. 3e), but no significant improvement of cycling stability with AlCl₃ concentration was observed. Presumably, the logarithmic term preceding [Al³⁺] may play a role, nonetheless, 1 M AlCl₃ (pH = 3.5) was observed to be the superior electrolyte for this series.

Fig. 3c shows the cycling behaviour of the FeVO₄ electrode in 1 M AlCl₃ (pH = 3.5) cycled between −0.7 and 0.9 V (vs. Ag/AgCl). At a current rate of 60 mA g^{−1}, a high capacity of 350 mA h g^{−1} was observed. This cycling range was suitable as there was no significant H₂ or O₂ evolution even for multiple iterations, usually characterized by an infinite flat plateau (Fig. S2 b) in GCD experiments (see Table 1).

Table 1 Abbreviations.

alt-text: Table 1			
SLRI	Synchrotron light research institute	SEM, TEM	Scanning/Transmission electron microscopy
BESS	Battery energy storage systems	CuHCF	Copper hexacyanoferrate
AIAB	Aluminum ion aqueous battery	EDX	Energy dispersive X-ray
XRD	X-ray Diffraction	FWHM	Full width at half maximum
XPS	X-ray photoelectron spectroscopy	XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy	EXAFS	Extended X-ray absorption fine structure
UV-Vis	Ultraviolet-visible	CN	Coordination number
CV	Cyclic voltammetry	TAB	Teflonized acetylene black
GCD	Galvanostatic charge-discharge	EEI	Electrode-electrolyte interface

3.3 Characterization of electrodes

To further investigate whether Al-ions were truly reacting with the electrode and to gain insight into the Al-ion charge/discharge mechanism, we performed ex-situ SEM-EDX, XRD, Raman spectroscopy, XPS, and XAS. For this purpose, 9 different electrode samples namely A0, A1, A2, A3, A4, B2, B4, C2 and C4 were discharged/charged at 60 mA g^{−1} in 1 M AlCl₃, pH 3.5 (Sample details in Table 2 and represented in Fig. 4c) and halted at varying depths of discharge/charge. The electrodes were then recovered, thoroughly washed with deionized (DI) water, dried and subjected to further characterization.

Table 2 Details of electrode state of charge/discharge.

alt-text: Table 2	
Sample	Discharge (D)/Charge (C) (vs. Ag/AgCl)
A0	Pristine electrode
A1	1 st cycle: 0.2 V (D)
A2	1 st cycle: 0.7 V (D)
A3	1 st cycle: 0.7 V (D) and −0.3 V (C)
A4	1 st cycle: 0.7 V (D) and 0.9 V (C)
B2	2 nd cycle: 0.7 V (D)
B4	2 nd cycle: 0.7 V (D) and 0.9 V (C)

C2	<i>5th cycle: 0.7 V (D)</i>
C4	<i>5th cycle: 0.7 V (D) and 0.9 V (C)</i>

Fig. 4 EDX elemental quantification of electrodes A0-C4: (a) Al/V ratio and (b) Fe/V ratio. (c) GCD profile showing the state of charge/discharge for electrodes A0-C4. (d) Ex-situ XRD pattern of electrodes A0-C4.

alt-text: Fig. 4

3.3.1 EDX

SEM-EDX maps for the fully-discharged sample A2 (Fig. S3) shows a uniform distribution of Al in the scanned area and matches well with the elemental Fe, V, and O distributions, indicating a uniformly reacted electrode surface. SEM-EDX spectra were also acquired to study the variation in Al content for the other samples in the A0-C4 series, and these EDX spectra were further used to compute the Al/V (Fig. 4a) and Fe/V (Fig. 4b) ratios. The Fe/V ratio was quantified to be around 1 in all the samples, confirming a consistent ratio. Further, the Al/V ratios showed a very consistent pattern wherein all the discharged samples (A1, A2, B2, C2) showed a higher value of the Al/V ratio, whereas all the charged samples (A3, A4, B4, C4) showed a lower value of the Al/V ratio. This observation clearly indicates that Al-ions reacted reversibly during the discharging and charging processes.

3.3.2 XRD

Ex-situ XRD patterns of samples A0-C4 further support the reaction of Al-ions with the FeVO₄ lattice. Fig. 4d shows the most significant portions of the θ -2 θ scans in the XRD patterns. (The full 2 θ ranges are shown in Fig. S4).

17–20°: The pristine sample A0 did not show any peaks; a new peak starts to appear in the discharge steps (A1 and A2), exhibits stronger intensity at the onset of charging (A3) and disappears completely in the fully-charged sample (A4). On further cycling, this peak reappears during discharge (B2), weakens with charging (B4), and again reappears with discharge (C2) and again weakens with charging (C4). Evidently, the new peak appears in all discharged electrodes and disappears/weakens in charged electrodes, in a consistent trend for all samples except for sample A3. Sample A3 is part of the first charge/discharge cycle, and presumably suggests some form of an initial activation step for the material. For later cycles, the Al-ion reaction leads to the creation of a new phase which was originally not present in the so prepared electrode material. This new peak closely indexes to spinel Al_xV_yO₄ phases (AlVO₃, AlV₂O₄) [49,50], and appears to be quite reversible. AlV₂O₄ and AlVO₃ are trigonal and cubic crystal systems, respectively. This is a clear indication that Al-ions are interacting with the active materials to convert the initial triclinic FeVO₄ lattice into a more symmetrical system.

41–46°: There are two peaks of interest in this region, one at 44.3° (appearing in discharged samples) and another at 44.8° (appearing in charged samples). The peak at the 44.3° also closely corresponds to the Al_xV_yO₄ phase and appears simultaneously with the peak in 17°–20° 2 θ region. On the other hand, the peak at 44.8° was difficult to index & we name it phase “P” for the time being.

62–66°: In this range, there are two peaks. The peak at 63.5° is from the Ti substrate. The other peak at 64.5° does not appear in the pristine sample, but upon cycling, it starts to appear. This particular peak shows a pattern where it distinctly appears in charged samples, more clearly in A4, B4, and C4, and disappears in the discharged samples (B2 and C2). Again, this indicates that Al-ion extraction leads to the creation of a new phase which was originally not present in the electrode material. Interestingly, this peak appears/disappears along with the peak at 44.8°. Thus we consider the peaks at 44.8° and 64.5° to correspond to the same phase “P” which will be discussed in more detail later in the XAS section.

XRD shows that the FeVO₄ cathode material accommodates Al-ions not by a typical intercalation mechanism. We observe that straight away from the 1st discharge, there is a permanent loss of original long-range order (Fig. S4) but new phases start to appear reversibly. Here we find the reversible formation of a Al_xV_yO₄ phase upon Al-intake and formation of a phase P upon Al-removal. This permanent transformation to new phases completely unrelated to the original crystal structure agrees with a conversion-type mechanism. Our observation agrees well with what has been observed for the reaction of lithium with FeVO₄ for non-aqueous batteries [35,51]. Researchers in the past have reported that the original FeVO₄ reflections indeed disappear in the initial stages of lithiation and new peaks emerge which correspond to new phases such as LiFeO₂ [51].

3.3.3 Raman spectroscopy

We further performed Raman analyses for all the samples A0 - C4. As shown in Fig. 5, the pristine FeVO_4 sample A0, has four Raman peak features. These features are a combination of multiple undulations corresponding to various FeVO_4 bond stretching and vibrational modes: 1) The Raman shifts between 300 and 550 cm^{-1} correspond to V-O-V deformation and Fe-O stretching; 2) shifts from 550 to 700 cm^{-1} are mixed V-O $\cdots$ Fe & V $\cdots$ O $\cdots$ Fe stretching; 3) shifts in the 700 to 880 cm^{-1} range represent bridging V-O $\cdots$ Fe stretching and 4) shifts in the 880 to 950 cm^{-1} range arise from terminal V-O stretching modes [52-54].

Fig. 5 Ex-situ Raman shifts of electrodes A0-C4.

alt-text: Fig. 5

The Raman spectra display an obvious trend, with the characteristic FeVO_4 peaks diminishing in all the discharged samples (A1, A2, B2 and C2), but re-emerging in the charged samples (A4, B4 and C4). Notably, after discharge, the FeVO_4 characteristic peaks had not been completely eliminated, but were simply weaker in intensity, such that they almost disappeared upon normalization against the highest peak intensity per spectrum (carbon from binder in this particular case). These have two implications: 1) the diminishing trend of all the Raman peaks indicate that the V and Fe local environments undergo significant changes. The original FeVO_4 may have disappeared either due to interaction with Al-ions to form a new solid phase or underwent selective dissolution leaving behind only carbon residue from the binder and the conductive additive. Later we will discuss the possibility where FeVO_4 from the electrode surface dissolves into the electrolyte as V^{+5} and leaves metallic Fe_3Al phase on the surface; 2) even though the XRD reflections suggested a non-reversible structural transformation of FeVO_4 due to permanent loss of original long-range order upon electrochemical charge/discharge with Al^{3+} ions, the Raman data suggested otherwise. The reappearance of the characteristic peaks indicates that FeVO_4 is structurally reversible, at least locally.

3.3.4 XPS

Further, samples were probed for changes in oxidation states using XPS. As shown in Fig. S5, there was no Al 2p signal detected for the pristine sample A0 whereas the discharged electrode C2 showed a distinct Al 2p peak. Based on the available literature we predict this Al phase to be an oxide phase of Al [55-57]. This phase can very well be spinel $\text{Al}_x\text{V}_y\text{O}_4$ (as detected in XRD) where Al is in +3 oxidation state. Additionally, the evolution of V $2p_{3/2}$ (Fig. 6) and Fe $2p_{3/2}$ (Fig. 7) peaks at all different stages of charge/discharge (A0 - C4) was studied.

Fig. 6 Ex-situ XPS spectra for electrodes A0-C4 showing experimentally obtained and fitted V 2p_{3/2} peaks.

alt-text: Fig. 6

Fig. 7 Ex-situ XPS spectra for electrodes A0-C4 showing experimentally obtained and fitted Fe $2p_{3/2}$ peaks.

alt-text: Fig. 7

Firstly, it was observed that all the V $2p_{3/2}$ peaks for the discharged electrode samples were significantly broader than for the pristine and charged samples (FWHM in Table S2). This observation indicates that multiple vanadium oxidation states were present in the discharged samples [58]. We fitted all the broad peaks with 2 model peaks whereas all the narrow peaks were sufficiently well fitted with just one model peak. We observe: 1) In the first cycle: Upon partial discharge (A1), a relatively small amount of low-oxidation phase forms. On full discharge (A2), the original FeVO_4 peak splits into two peaks representative of a high and a low oxidation state of V. Further upon charging, the peak becomes narrow with maxima close to the pristine peak value of 517.31 eV. 2) In the 2nd and 5th cycles: A similar observation as the first cycle is made wherein the original peak splits into two peaks upon discharging (B2 & C2) and reversibly narrows down to a single peak value (similar to A0) upon charging (B4 & C4).

Based on the aforementioned observations we infer that upon discharge at least two different oxidation states of V are forming (lower oxidation state: simulated in green & higher oxidation state: simulated in blue). For the lower oxidation states, in addition to the XRD finding that spinel phases of the $\text{Al}_x\text{V}_y\text{O}_4$ family were likely forming, we determine with XPS that the average oxidation states of vanadium which include +3 and + 2.61 in such spinel phases are indeed present in our samples (modeled in green) [49,50,59]. For the higher oxidation state (simulated in blue), V in pristine FeVO_4 is already in the +5 state and hence cannot be further oxidized. Therefore this shift to higher binding energy might be explained with the change in coordination environment of V. Based on available literature, V $2p_{3/2}$ energy peak in 517.9–518.5 eV (same as ours) correspond to a $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ phase wherein vanadia are possibly monomolecularly dispersed on an Al_2O_3 substrate [58,60]. Thus we expect that upon Al-ion insertion there is a formation of V_2O_5 which co-exist with an oxide phase of Al. The formation of V_2O_5 is quite likely as it is one of the thermodynamically stable phases in which FeVO_4 can disintegrate into [61]. We also infer that the aforementioned phases reversibly transform back into FeVO_4 upon charging as the V $2p_{3/2}$ peaks in the charged sample narrows and recovers a peak maxima close to the original energy value of the pristine sample.

Similar to V $2p_{3/2}$, all the Fe $2p_{3/2}$ peaks were observed to have a wider FWHM for the discharged samples, such that the Fe $2p_{3/2}$, Fe satellite peak, and Fe $2p_{1/2}$ peaks became indistinct. We performed 3 peak fitting on all (except A0) XPS Fe $2p_{3/2}$ spectra. It was observed that: 1) upon discharging, the low energy peak (blue) shifts to lower binding energy and returns to its original position on charging; the high energy peak (green) remains at the same position 2) A low binding energy (706–708 eV; brown model peak) peak can be found in both charged and discharged samples. Based on these aforementioned observations, we infer that: 1) there is a formation of a reversible low-oxidation phase (represented by the blue line) in discharged samples, 2)

a small amount of a new phase formed at ca. 707 eV after the 1st discharge, attributable to metallic Fe₃Al [62]. The formation of such metallic phase was previously reported by Denis et al. for a non-aqueous Li-ion battery wherein iron was observed to attain a metallic phase upon Li uptake and reoxidized upon charging [37]. This Fe₃Al phase was observed in both charged and discharged samples. We believe that this metallic phase forms along with V₂O₅ upon discharging, but at the same time it is likely that a small amount of vanadium will dissolve in the electrolyte. Therefore a proportion of Fe₃Al remains irreversibly present in the sample. We also performed XANES to confirm the reduction of Fe and study changes in its immediate co-ordination environment.

3.3.5 XAS

XAS studies have been extensively used to investigate the immediate coordination environments of Fe complexes [63]. Any XAS spectrum can be divided primarily into two regions: 1) XANES- This is the rising edge region of the spectrum (7100–7140 eV in (Fig. 8a)). It provides information about the active site geometry and changes in oxidation state and 2) EXAFS- The spectral region from 7140 eV towards higher binding energy; this region provides accurate information on the first shell Fe-ligand distance.

Fig. 8 (a) Comparative XANES spectra for sample A0 and A2 (inset: first derivative of XANES spectra). (b) Zoomed in XANES spectra for sample A0 and A2 showing an increase in peak A intensity and decrease in peak B intensity upon discharge. (c) UV-vis spectra of 1M AlCl₃, pH –3.5 electrolyte after 100 cycles. (d) E vs pH diagram for V; Reproduced with permission from [46] Copyright 2018, RSC. (e) Mechanism of Al reaction with FeVO₄.

alt-text: Fig. 8

We did a comparative study of samples A0 and A2 for the full spectra as follows. For the pristine sample, three characteristic peaks are observed: peaks A and B are in the pre-edge region with an energy difference of about 3 eV, as also observed for Fe₂O₃ and FeVO₄ [64,65]. The main K-edge peak, peak C, lies at 7123 eV. Peak A corresponds to the local quadrupolar transitions wherein an electron is excited from a core *1s* orbital to an empty *3d* orbital of Fe [66]; peak B corresponds to a similar *1s3d* excitation which is non-local. Here a *1s* electron of the central atom - metal M (here: Fe) is excited to the unoccupied *3d* state of a next-nearest-neighbor metal M' (here: Fe') atom. Such a transition proceeds through an intersite hybridization M(*4p*)-O(*2p*)-M'(*3d*) (here: Fe(*4p*)-O(*2p*)-Fe'(*3d*)). The intensity of peak B is a direct representation of the strength of this oxygen-mediated *4p-3d* hybridization which is dependent on M-O-M' bonding [65,67]; peak C corresponds to the *1s4p* dipolar excitations, wherein excitation takes place from the core *1s* to the *4p* conduction band [66].

From the XANES spectra, we make the following observations: 1) The rising edge of the discharged sample A2 shifts to a lower energy value (clearly seen in first derivative of the spectra in the inset of Fig. 8a), indicating a reduction in Fe-oxidation state [68] (as was also observed in the XPS study). Notably, this shift was only about 1.5 eV (Fig. 8b), indicating that Fe may have only been partially reduced as a shift of 4 eV is expected when Fe⁺³ reduces to Fe⁺² [68]. No metallic Fe in the discharged electrode was observed in the XANES spectra, contrary to the XPS data. This can be because XPS and XAS are surface and bulk techniques, respectively, and hence have distinct interaction volumes; 2) interestingly, the discharged sample showed an increase in peak A intensity. This is indicative of partial breaking of inversion symmetry for the Fe shell, wherein the Fe octahedral coordination is changing to a lesser symmetrical system causing *3d-4p* wavefunction mixing that allows electronic excitation to the *4p* character of the *3d* band [66]. 3) the peak B intensity decreases significantly upon discharging. This correlates to the factors that can influence Fe(*4p*)-O(*2p*)-Fe'(*3d*) hybridization, namely, Fe-O-Fe bond angle and/or Fe-O-Fe bond length [66]. Similar observation is made later on EXAFS analysis, where Fe-O bond length is inferred to reduce upon Al-ion reaction. From the above observations, we infer that upon Al-intake, Fe reduces such that it forms a phase where Fe resides in a lesser symmetrical environment with weaker or no Fe-O-Fe bonds.

In order to gain insight into the local environment change around Fe atoms, EXAFS analysis was also carried out. The fitting was done only for the first coordination shell because of the non-optimal data quality. As discussed previously there are 3 different environments of Fe in FeVO₄. Each of these Fe was fitted to the experimental data individually for both pristine and discharged samples. Fe1 was fitted with only one path corresponding to 6 Fe-O bonds of similar lengths. Fe2 was fitted with two paths corresponding to 4 Fe-O bonds of similar length & 1 relatively longer Fe-O bond. Fe3 was also fitted with two paths corresponding to 4 Fe-O bonds & 2 Fe-O bonds of shorter & longer lengths, respectively. Fitting results are in Table S3.

Fig. S6 shows a fitted Fourier transform of XAS spectra. EXAFS fitting for the discharged sample renders an average Fe-O bond length about 0.03 Å shorter than for pristine samples. Though it is counterintuitive to think that the Fe-O bond length in reduced Fe would be shorter, the phenomenon has been demonstrated for Fe in oxides [69]. For example, the ionic radii of Fe in oxidation state +3 and + 2 are 1.759 Å and 1.734 Å, respectively [70]. Such anomaly can be an effect of increased covalence character in Fe-O bond and has been observed for compounds like FeAlO₃ and FeGaO₃ in terms of shorter than usual Fe-O bond lengths [69].

Overall a considerable change in Fe geometry and oxidation state was observed upon discharge. Though we cannot assert the exact Fe phase forming upon Al-intake, it is expected that an amorphous (as no crystalline FeO phase was detected for A2 in the XRD study) oxide of Fe forms which has a relatively shorter covalent Fe-O bond wherein the average oxidation state of iron is in between +3 and + 2. This phase has considerably weak or no Fe-O-Fe bond, and we propose this to be a Fe-O-Al phase. Upon charging, this phase is most probably converting to a crystalline Fe-O phase which was detected by XRD as phase "P".

3.3.6 UV-Vis spectroscopy

Fig. 8c shows the UV-Vis spectrum of 1 M AlCl₃, pH-3.5 electrolyte which has been through 100 cycles of charge/discharge. This spectrum resembles the UV-Vis spectra of an aqueous solution of sodium metavanadate and sodium orthovanadate wherein V is in +5 oxidation state [71]. Thus we believe that FeVO₄ while reacting with Al is also under going some parasitic reaction with the electrolyte. Though by increasing electrolyte pH, we suppress the dissolution of V into the electrolyte, it is not stopped completely. As per the Pourbaix diagram of vanadium (Fig. 8d) [46], such dissolution for the vanadium-based compound is likely to happen in an electrolyte like ours (pH 3.5).

3.4 Mechanism of Al-intake

Based on the aforementioned characterization and analysis, we find two parallel sets of ongoing reactions: "FeVO₄ reacting with Al" and "FeVO₄ reacting with electrolyte". Though the ongoing parasitic reactions make it difficult to assert exact mechanism of Al reaction with FeVO₄, we propose that Al-ion intake into FeVO₄ produces an Al_xV_yO₄ spinel phase and an amorphous Fe-O-Al phase, both of which are reversible and electrochemically active (Fig. 8e). At the same time, FeVO₄ from the surface reacts with the electrolyte to form V₂O₅ and metallic Fe₃Al. Further, upon charging, FeVO₄ and Fe-O phase forms, V₂O₅ dissolves into the electrolyte as V⁺⁵ and metallic phase Fe₃Al can still be detected on the surface. We propose with every cycle, some V⁺⁵ is dissolving and remains trapped in the electrolyte which could have otherwise reversibly converted back to FeVO₄. This is the probable reason why capacity degrades with every cycle.

4 Conclusions

In summary, we examined FeVO₄ as a potential cathode material for AIAB, which happens to be the first conversion material ever investigated for Al-ion reaction in an aqueous system. We have been able to show unprecedented capacity ~350 mA h g⁻¹. Further, we demonstrated the positive effect of increasing pH for an AIAB system using AlCl₃. Using a combination of various characterization techniques, we have given sufficient proof of Al-ion

intake in FeVO₄ and explored the probable mechanism in play. We found that FeVO₄ while reacting Al is also showing some parasitic reactions with electrolyte, similar to previously-reported AIAB systems [28,33], resulting in a rapid fading in capacity. Though these parallel ongoing reactions make it difficult to assert exact mechanism for Al-ion intake, detection of Al-based phases and charge/discharge mechanism discussion on multiple cycles (cycle no. 1,2 & 5) are likely to add significantly to the study of aqueous battery systems, specifically AIABs.

As a future perspective to this work, we believe that the electrolyte may have a very important role to play [72]. Electrolytic parasitic reactions could have been avoided if an EEI (electrode-electrolyte interface) layer would have existed in the aqueous system. To our understanding, for a conversion material like FeVO₄, an EEI layer is necessary for long-term cycling stability. Therefore, as a continuation to this work, we will explore EEI enabling techniques like usage of concentrated electrolyte [11,73–75], artificial electrode coating [76] and EEI enabling electrolyte additives [77].

Declaration of interest

None.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jpowsour.2019.03.119>.

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Appendix A Supplementary data

The following is the supplementary data related to this article:

[Multimedia Component 1](#)

Multimedia component 1

alt-text: Multimedia component 1

Graphical abstract

alt-text: Image 1

Highlights

- A novel Al-ion battery using FeVO₄ as cathode material is reported.
 - A high capacity of 350 mA h g^{−1} is demonstrated.
 - A conversion mechanism is elucidated via XRD, XPS, XAS and Raman spectroscopy.
 - The discharged states involve the formation of Al_xV_yO₄ & Fe-O-Al.
 - Electrolyte pH is shown to have a deterministic effect on the electrode stability.
-

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