



Multiscalar Investigation of FeVO₄ Conversion Cathode for a Low Concentration Zn(CF₃SO₃)₂ Rechargeable Zn-Ion Aqueous Battery

Sonal Kumar⁺,^[a] Vivek Verma⁺,^[a] Rodney Chua,^[a] Hao Ren,^[a] Pinit Kidkhunthod,^[b] Catleya Rojviriya,^[b] Suchinda Sattayaporn,^[b] Frank M. F. de Groot,^[c] William Manalastas, Jr.,^[a] and Madhavi Srinivasan^{*[a, d]}

Battery cathode materials operating on multivalent-ion intercalation are prone to short operational lifetimes, traditionally explained to be due to poor solid-state diffusion. Here, we overcome this problem by using a conversion-type cathode material and demonstrate the benefits in a FeVO₄ host structure. The rechargeable Zn-ion battery exhibits stability for an unprecedented operational lifetime of 57 days with a high capacity of 272 mAh g⁻¹ (60 mA g⁻¹) over 140 cycles. We use a combination of synchrotron-based XAS, SRXTM, Raman, XRD and HRTEM techniques to elucidate the cathode material evolution at multilength-scale for understanding the Zn-ion storage mechanism. We further highlight the benefits of using a low-salt concentration electrolyte and pH-consideration analysis in aqueous battery development, the optimization of which leads to a 4-fold increase in battery performance as compared to conventional high-salt concentration electrolyte formulations.

1. Introduction

Rapidly rising energy demands and resultant environmental concerns have directed battery research towards exploring 1) non-lithium chemistries owing to their high abundance, low cost, and high volumetric capacity^[1-8] and 2) water as an electrolyte solvent owing to superior ionic conductivity and lower desolvation penalty for the charge-transfer process occurring at the electrode-electrolyte interface.^[9] The use of an aqueous solvent opens new opportunities for high rate capabilities, non-toxicity and non-flammability, and therefore imply safer batteries at low cost.^[10–15] In this scheme of things, zinc-ion aqueous batteries (ZIAB) are particularly interesting because of the high stability of Zn metal (as anode) in water

[a]	S. Kumar, ⁺ V. Verma, ⁺ R. Chua, Dr. H. Ren, Dr. W. Manalastas, Jr., Prof. M. Srinivasan School of Materials Science and Engineering Nanyang Technological University 50 Nanyana Aye 639798. Sinaapore
[b]	Dr. P. Kidkhunthod, Dr. C. Rojviriya, Dr. S. Sattayaporn
	Synchrotron Light Research Institute (SLRI)
	Nakhon Ratchasima 30000, Thailand
[c]	Prof. F. M. F. de Groot
	Inorganic Chemistry & Catalysis,
	Debye Institute for Nanomaterials Science
	Utrecht University-99,
	3584 CG Utrecht, Netherlands
[d]	Prof. M. Srinivasan
	Energy Research Institute at Nanyang Technological University
	Research Techno Plaza, 50 Nanyang Drive,
	Singapore 637553, Singapore
	E-mail: madhavi@ntu.edu.sg
[+]	These authors contributed equally to this work.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/batt.202000018

and its low redox potential which makes the anodic stripping/ plating of Zn feasible without significant electrolytic decomposition.^[16]

However, the primary challenge lies in developing cathode materials that can reversibly store Zn ions. Most of the cathode materials reported so far show reversible Zn²⁺ storage via intercalation mechanisms and are restricted to mostly a few families of materials such as MnO₂ polymorphs, vanadiumbased oxides and Prussian Blue Analogues.^[2,17] The high charge-to-size ratio of Zn²⁺ diminishes its cation diffusivity in the host structure and can also induce a heavy structural distortion leading to the collapse of the host structure.^[18-19] Reversibly storing cations might be less problematic in a conversion-type host materials where cation storage proceeds through thermodynamically favorable reactions, thus avoiding the sluggish insertion kinetics.^[20] Until now, very few conversion-type cathode materials have been explored including VS₄/rGO, $^{[21]}$ Mn₃O₄, $^{[22]}$ VN $_{0.9}$ O_{0.15}, $^{[23]}$ and α -MnO₂; among which α -MnO₂ reaction mechanism is still unclear.^[24-28] Hence, it is worth exploring traditional conversion-type materials for Zn²⁺ storage and understand the concomitant storage mechanism.

In this study, we investigate FeVO₄ as a potential cathode material for ZIAB and elucidate the charge-storage mechanism. Although FeVO₄ has been previously demonstrated as a cathode material in multivalent systems such as Mg^{2+} & $AI^{3+,[29-31]}$ either the cation storage mechanism was not fully elucidated, or parasitic side reactions obscured the true cation storage mechanism. Investigating FeVO₄ is particularly interesting because: 1) it has two redox centers, namely, Fe and V, both of which can be electrochemically reduced to accommodate a large amount of reacting cation, 2) FeVO₄ is electrochemically active in a wide potential range (0.02-3.5 V vs. Li⁺/



Li), making it appropriate for the electrochemical studies within the stability window of water,^[32–33] and 3) FeVO₄ has been demonstrated to react with monovalent,^[34] bivalent,^[29] and trivalent ions,^[31] which makes it versatile and apt for applications where more than one aliovalent cation needs to react simultaneously.

We demonstrate that FeVO₄ can deliver a capacity of nearly 180 mAh g^{-1} for 300 cycles at a high current rate of 3 A g^{-1} and with an average discharge voltage of 0.6 V (vs. Zn^{2+}/Zn). To obtain the best performance of the FeVO₄ cathode material at slower current rates however, we show that electrolyte pH has an important role to play. Using a simple technique to make the electrolyte less acidic just by reducing the salt concentration in the electrolyte, we demonstrate an improved capacity retention from 18% to 78.8% in the first 50 cycles. Using this optimized electrolyte, the FeVO₄-Zn battery was fabricated, and a combination of in-house and synchrotron-based techniques were used to elucidate the Zn-ion reaction mechanism with FeVO₄. The storage mechanism was found to be conversiontype, and various phases forming during the electrochemical reactions were identified. As some reaction products were amorphous, techniques sensitive to short-range order such as Raman and X-ray absorption spectroscopy (XAS) were also used. Finally, the bulk evolution of the electrode was also elucidated at submillimetre scale using synchrotron-radiation X-ray tomographic microscopy (SRXTM), which shows a reversible material reorganization at the micron scale observed in the form of reversibly formed ridges/valley features and increasing/decreasing porosity in the material upon cycling.

2. Results and Discussion

2.1. Characterization of FeVO₄ Nanorods

Figure 1a shows the XRD pattern of the synthesized powder which was fitted by refining the $P\bar{1}$ space group Ziminaite phase and matches well with the triclinic FeVO₄ structure reported by Robertson et al. (PDF no- 01-071-1592) (Full refinement details in Table S1).^[35] The resultant lattice parameters were calculated to be a = 6.714(1) Å, b = 8.066(1) Å, c = 9.352(1)Å, $\alpha = 96.68(1)^{\circ}$, $\beta = 106.67(1)^{\circ}$, $\gamma = 101.53(1)^{\circ}$, similar to a previous report.^[31] The absence of any impurity peaks in the XRD pattern confirms that the synthesized material has a single crystalline phase. The FeVO₄ crystal structure consists of Fe atoms in three different coordination environments of oxygen. Both Fe1 and Fe3 centers (Figure 1b) form distorted FeO₆ octahedra with six unequal Fe-O bonds. On the other hand, Fe2 forms a distorted trigonal bipyramid with the oxygen atoms. Finally, the three V centers form distorted tetrahedra with the oxygen atoms and only share corners with the adjacent Fe polyhedra.

SEM and TEM micrographs for synthesized powder (Figure 1c & 1d) show a predominantly high aspect ratio rod-like morphology with an average length and diameter of 4.7 μ m and 290 nm, respectively. The SEM micrograph also features few seed-like particles expected to be FeVO₄ nucleation points which had not grown fully during the synthesis because of insufficient reaction time. The HRTEM image (Figure 1e) shows a fringe spacing of 0.42 nm and 0.32 nm and could be ascribed to the *d*-spacing of the (102) and (022) planes of the FeVO₄ crystal structure, respectively. TEM-EDX elemental mapping



Figure 1. Structural characterization of the synthesized FeVO₄ powder: a) Experimental XRD pattern fitted with Rietveld refined Ziminaite phase, b) FeVO₄ unit cell showing the coordination environments of Fe and V. Morphology characterization of the FeVO₄ powder: c) SEM micrograph, d) TEM micrograph, e) HRTEM image, and f) TEM-EDX elemental mappings for Fe, V and O of the FeVO₄ nanorod.

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 2 These are not the final page numbers!



(Figure 1f) shows a homogenous distribution of Fe, V and O in the synthesized $FeVO_4$ powder and no other elemental impurity was detected in the TEM-EDX energy spectra (Figure S1).

ChemPubSoc

Europe

2.2. Electrochemical Activity

Cyclic voltammetry (CV) was used to evaluate the electrochemical activity of $FeVO_4$ -Zn system in 0.1 m Zn(CF₃SO₃)₂ (ZnTFS) aqueous electrolyte. The 1st negative sweep in the CV profile (Figure 2a) shows the presence of one sharp and one broad cathodic peak occurring at 0.62 V and 0.30 V, respec-



Figure 2. Electrochemical activity of the FeVO4: a) Cycling voltammograms in the 0.1 m ZnTFS between 0.05 V and 1.8 V vs. Zn^{2+}/Zn , at scan rate of 1 mVs⁻¹, b) Galvanostatic charge/discharge profiles in 0.1 m ZnTFS electrolyte between 0.05 V to 1.8 V vs. Zn^{2+}/Zn , c) Cycling stability of FeVO₄-Zn system in three different electrolytes with varying ZnTFS salt concentration, and d) The Pourbaix diagram of Zn/water system (developed using data guidelines from)^[50-51,90] depicting the thermodynamically stable states of zinc species in two different aqueous solutions with $[Zn^{2+}] = 0.1$ m and 2 m. Brown and grey rectangles highlight the operating voltage and pH region for FeVO₄-Zn cells cycled in 0.1 m and 2 m ZnTFS electrolytes, respectively. Extended cycling performance and corresponding coulombic efficiency at e) 60 mAg⁻¹ and f) 3 Ag⁻¹.

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 3 These are not the final page numbers! © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



tively. However, only one anodic peak was observed at 0.55 V in the 1st positive sweep, indicating only one cathodic reaction to be reversible. Similar irreversibility in the first cycle has also been observed for the Li⁺ and K⁺-FeVO₄ systems previously.^[34,36]

The galvanostatic charge-discharge (GCD) study (Figure 2b) concurs with the observations made in the CV study. Corresponding to the sharp cathodic peak at 0.62 V and broad cathodic peak at 0.3 V in the CV, the 1st discharge profile shows a flat plateau at ~0.65 V followed by a gradual sloping profile. This plateau feature has also been observed in the conversion-type transition metal oxides for Li-ion systems,^[37-40] and was ascribed to a two-phase reaction (see section 2.5 for details).^[39,41] Notably, subsequent charge or discharge cycles do not show the presence of any plateau feature, indicating that the irreversible reactions

occur only in the first discharge step. This irreversibility is also reflected in terms of the drastic drop in discharge capacity from ~348 mAh g⁻¹ in 1st cycle to ~272 mAh g⁻¹ in the 2nd cycle (Figure 2b). Based on CV and GCD studies, we find that the electrochemical behavior of the FeVO₄-Zn system resembles a conversion-type storage mechanism where an irreversible reaction occurring in first cycle leads to a high first discharge capacity, and reversible reactions follow in the subsequent cycles.^[20]

2.3. Electrolyte Optimization

Numerous works have demonstrated high cycling stability and high capacity retention at fast cycling rates for ZIAB systems.^[2,17] However, few investigations have reported that the capacity fading is much higher at slower cycling rates or longer cycling runtimes.^[42-43] This has been ascribed to the acidic nature of the electrolytes used in the ZIAB system.^[2,44] Specifically, the active material or the reaction products formed during charge/ discharge are susceptible to dissolve in the electrolyte when the electrodes are cycled in acidic pH conditions.^[2,45] One possible solution to curb this problem can be to increase the electrolyte pH and make the electrolyte less acidic.^[2,31,46] We demonstrate that electrolytes can be made less acidic by reducing the salt concentration. The measured pH values for three ZnTFS/water electrolytes with salt concentrations of 0.1 m, 1 m and 2 m were 5.6, 5.2 and 4.6, respectively. The difference in the pH values can be explained by the difference in the free H^+ concentration of the solution. The Zn^{2+} -ions in the aqueous solution exist as [Zn(H₂O)₆]²⁺ octahedral complexes.^[47] Since the Zn²⁺ ion center can act as Lewis acid, it can strongly polarize the coordinated water molecules to give H⁺.^[48] At high salt concentrations, a higher number of Zn²⁺ (or $[Zn(H_2O)_6]^{2+}$ species in the aqueous medium will result in an increased concentration of H⁺, thus making the solution more acidic. A similar trend of decreasing pH value with increasing salt concentration was also observed in the ZnSO₄/water system.^[46]

To test the effect of the electrolytes pH on the cycling performance of $FeVO_4$ -Zn system, we ran galvanostatic charge-

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 4 These are not the final page numbers!

discharge tests for the three cases (Figure 2c). While the 2^{nd} discharge capacity is nearly the same for all three systems, the capacity fading over subsequent cycles follow the trend: 2 m > 1 m > 0.1 m. The system with 0.1 m ZnTFS/water outperforms the other two systems with a high capacity retention of 78.8%, against 43.1% and 18.8% for 1 m and 2 m concentration, respectively, in the first 50 cycles.

This observed disparity in the cycling stabilities can be explained by using a potential vs. pH diagram, Pourbaix diagram, which depicts the thermodynamically stable state of a metal-ion in an aqueous medium.^[49] Figure 2d shows Pourbaix diagram for Zn, showing the different thermodynamically stable state of Zn such as ZnO, Zn²⁺, metallic Zn or ZnO²⁻ in two different systems with [Zn²⁺] of 0.1 m and 2 m in an aqueous medium.^[50–51] Note that the Zn²⁺/ZnO_(s) boundary and the ZnO_(s)/ZnO²⁻ boundary vary slightly for two different [Zn²⁺].

For FeVO₄-Zn systems with two different electrolytes: 0.1 m and 2 m ZnTFS/water, we mark the operating voltage-pH region on the Pourbaix diagram and identify the respective stable Zn species. The operating battery voltage for both the systems is in the range 0.05 to 1.8 V vs. Zn²⁺/Zn (the applied voltage), and the operating pH for these two systems was determined by in-operando pH measurements for the first few cycles (Figure S2). The pH values stabilized to ~6.1–6.3 (\pm 0.1) and ~4.5-4.9 (\pm 0.1) for 0.1 m and 2 m electrolytes, respectively. These two different operating ranges of pH are critical in governing the stability of the ZnO phase which, as we show later in section 2.5, is also the primary phase responsible for storing Zn-ions. While the ZnO phase is stable for the 0.1 m ZnTFS system (brown rectangle), it is unstable in the 2 m ZnTFS electrolyte system (grey rectangle) and can spontaneously dissolve into the electrolyte as Zn²⁺-ions. The lower stability of ZnO phase in the 2 m ZnTFS electrolyte system results in the poor cycling stability (Figure 2c). A similar idea of phase stability/instability, determined using Pourbaix diagram, has been used previously to explain the cycling stabilities in the oxides of Mn, Mo and V.^[45]

2.4. Electrochemical Performance

Long cycling stability was further investigated at slow (60 mAg⁻¹) and fast (3 Ag⁻¹) current rates for two different coin cells (Figure 2e and Figure 2f). At a low current rate of 60 mAg^{-1} and after 140 cycles (roughly 57 days of runtime), the battery could still retain a capacity of 156 mAh q^{-1} (57.3%) of its 2nd discharge capacity). To the best of our knowledge, the combination of the observed discharge capacity and capacity retention is one of the best values reported in the aqueous ZIAB systems at such a slow current rate. For the first 100 cycles, we demonstrate a capacity retention of 64.3%, which is on par with one of the best capacity retention of 51.1% demonstrated by Zhang et al. (see Table S2 for comparison with existing reports on ZIAB).^[42] At a high current rate of 3 A g⁻¹, galvanostatic charge-discharge test shows that FeVO₄ can maintain a high capacity of ~180 mAh q^{-1} for nearly 300 cycles (Figure 2f). Notably, the initial cycling performance at



BATTERIES SUPERCAPS

two cycling rates do contrast strongly. At a slower cycling rate of 60 mAg⁻¹, the capacity decreases rapidly in the first few cycles. This can be explained by the probable irreversible reactions taking place in the cathode material which is discussed in detail within the main text (sections 2.5-2.6) in terms of the formation of irreversible phases consisting of V and Fe species. On the other hand, at a higher rate of 3 Ag^{-1} , a gradual rise in the capacity is observed. This rise can be ascribed to the gradual activation of ZIAB electrodes^[43,52-53] wherein, due to the high rate of charge/discharge, the reaction of the cathode with ${\sf Zn}^{2+}$ is initially kinetically limited. EIS spectra of the Zn-FeVO₄ system (Figure S3a& b) show this activation phenomenon in terms of higher charge-transferresistance at electrode-electrolyte interface for the first few cycles, which later decreases through the 20th cycle, indicating that by the 20th cycle the cathode is fully active towards Zn²⁺ reaction.

2.5. Phase Eolution of FeVO₄ on Zn-Ion Reaction

Ex situ XRD studies were performed on the cycled electrodes to gain insights into the $FeVO_4$ phase-evolution upon electrochemical reaction with Zn-ions. For the first discharge cycle, three electrodes discharged to different depths of discharge (0.7 V, 0.6 V and 0.05 V; as shown in the inset of Figure 3), were investigated to study the phase evolution in the first discharge step. Further, XRD patterns of electrodes charged/discharged in the 4^{th} cycle (4 C and 4D) and 10^{th} cycle (10 C and 10D) were also taken. In the 1st discharge cycle, we find that the main FeVO₄ peaks are still present when discharged to 0.7 V and then disappears after the GCD plateau region (in electrode discharged to 0.6 V). This indicates a possibility of FeVO₄ amorphization, which is later confirmed using Raman Spectroscopy (see Section 2.7). This amorphization process occurs through a two-phase reaction and is consistent with the observations made for conversion reactions of transition metaloxides with Li.^[40-41] In the subsequent cycles (4C, 4D, 10C, 10D), the characteristic FeVO₄ peaks do not appear back, indicating that the amorphization of FeVO₄ in the first discharge was irreversible, as also observed in Li-FeVO₄ system.^[54] Additionally, three new phases: ZnO (PDF- 01-083-6338),^[55] metallic Fe (PDF-04-017-1577),^[56] and Zn₃V₂O₇(OH)₂·2H₂O (PDF- 00-057-0572),^[57] were detected in the cycled electrodes as discussed below.

The formation of ZnO phase starts during the appearance of the plateau region in GCD (indicated by the appearance of its main peaks in the electrode discharged until 0.6 V), and continues to form until fully discharged, as indicated by an increase in the ZnO peak intensities (1D). In the subsequent cycles, ZnO disappears in the charged electrodes (4 C and 10 C) and then reappears in the discharged electrodes (4D and 10D); indicating its high reversibility. The formation of ZnO phase



Figure 3. Ex situ X-ray diffractograms of the FeVO₄ cathode collected at the different stages of charge/discharge. 1D (0.7 V), 1D (0.6 V) and 1D (full discharge until 0.05 V) are the diffractograms collected at the different voltages during the first discharge, as shown in the inset figure. 4C and 4D are diffractograms taken at the end of the 4^{th} cycle in the charged and discharged state, respectively. 10C and 10 D are diffractograms taken at the end of 10^{th} cycle in the charged and discharged state, respectively. 10C and 10 D are diffractograms taken at the end of 10^{th} cycle in the charged state, respectively. The two figures at the right represent the zoomed-in region of the two metallic Fe peaks, showing the shifts in peak position upon cycling.

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 5 These are not the final page numbers!



was further confirmed by other techniques such as HRTEM, TEM-EDX and XPS analysis, as discussed along with Figure S4 in supplementary.

Metallic Fe phase appears after the appearance of the plateau region, indicating that the metallic Fe is formed in the plateau region during the FeVO₄ amorphization and ZnO formation. The formation of metallic-Fe during the FeVO₄ amorphization has also been previously observed in the Li-FeVO₄ system.^[54,58] After the 1st discharge step (1D), metallic Fe phase is present in all the subsequent cycles of the FeVO₄-Zn system, indicating that the formation of the metallic Fe is not reversible. When comparing the XRD peak positions of the metallic-Fe phase in charged and discharged electrodes we find that the Fe peaks shift to lower 2θ angles in the discharged state. Indeed, a Pawley fitting for the discharged (10D) and the charged (10 C) electrode reveals lattice parameter values of a =2.922(1) Å and 2.9090 (7), respectively. Although the exact reason for the peak shifts is not very clear, only picometer length scale change in the lattice parameter suggests that the possibility of electrochemical alloying of Zn with metallic-Fe is unlikely.^[59–60]

The third phase detected was, $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$ (PDF- 00-057-0572),^[57] which is layer-type structure wherein, the layers consisting of Zn oxide/hydroxide octahedra and are supported by the V_2O_7 pillars and the water molecules (Figure S4d).^[61] This phase does not appear until discharge to 0.7 V (electrode 1D (0.7 V)) and only appears after the emergence of a plateau region in the 1st discharge in electrode 1D (0.6 V). Further, this phase is present in all the subsequent cycles irrespective of the charge/discharge process, indicating its permanent irreversibility. Formation of this phase is expected at pH values higher



than 5,^[57] and is consistent with the pH of our electrolyte (~ 6.1–6.3). Here we would like to note that the capacity is continuously declining with every cycle even in the later stages of cycling (Figure 2e & 2f). We did ex situ XRD of electrodes charged/discharged for 20 cycles (Figure S3 c) to gain insight into this decline. It is observed that the amount of inactive phase (Zn₃V₂O₇(OH)₂·2H₂O) side product increases upon repeated cycling which may have occurred because the transformation of the active phases (ZnO to Zn) has not occurred 100% reversibly during cycling, i.e. small amounts of the active phase become orphaned as Zn₃V₂O₇(OH)₂·2H₂O (more details in Figure S3c and its associated caption).

2.6. Redox Reactions of Transition Metal Centers

XPS was used to study the oxidation state changes occurring on the Fe and V metal centers during the electrochemical cycling. Figure 4a shows the Fe $2p_{3/2}$ region of the XPS spectra exhibited during the 4th cycle (showing three panels for pristine, discharged (4D) and charged electrodes (4 C)). The pristine Fe $2p_{3/2}$ spectrum was fitted with two model peaks (blue and green), which most likely represent two different coordinating environments of Fe³⁺ (trigonal bipyramidal and octahedral; as also discussed in section 2.1),,^[32] Upon discharge, a broad low binding energy peak (705.37 eV) was detected corresponding to the metallic phase of Fe;^[62–64] consistent with the XRD results. However, no metallic Fe was detected in the XPS spectrum of the charged electrodes, even though XRD results showed that metallic Fe is present (Figure 3). This ambiguity can be because, unlike XRD, XPS is a surface



Figure 4. a) Fe $2p_{3/2}$ and b)V $2p_{3/2}$ region of XPS spectra for pristine, discharged (4D) and charged (4C) electrodes. Open circles: experimental data; grey line: background; blue and green lines: deconvoluted model peaks; orange line: overall fitted spectrum. c) Ex situ Raman spectra for the pristine electrode and the evolution of the spectrum during the 4th and 10th cycle (electrodes – 4D, 4C, 10D and 10C).

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 6 These are not the final page numbers!



BATTERIES & SUPERCAPS

technique capable of detecting only a few nm below the surface. It is also observed that the low energy modeled peak (green peak) in the pristine electrode shifts to a lower binding energy value upon discharge (electrode 4D), and that this shift to lower energy is more clearly observed in the 10th cycle (Figure S5a, electrode 10D), indicating a partial reduction of the Fe³⁺ species to Fe^{2+,[65]} Upon subsequent charging (electrode 4 C), this green model peak recovers back to the original energy value of the pristine sample, indicating that the reduced Fe species oxidizes back to Fe³⁺. Therefore, based from the above observations, we infer that the Fe species in FeVO₄ undergo two kinds of reduction: 1) irreversible Fe³⁺ to metallic Fe transformation, which primarily occurs in initial stages of reaction with Zn-ion and 2) reversible Fe³⁺ to Fe²⁺ reduction/ oxidation taking place during the discharge/charge process.

Figure 4b shows the V 2p_{3/2} region of XPS spectra for the 4th cycle (showing three panels for pristine, discharged (4D) and charged (4C) electrodes). The pristine V 2p_{3/2} spectrum was fitted with one model peak (at 517.38 eV) and represents +5oxidation state.^[66] Upon discharge, this original peak at 517.38 eV splits into two peaks: 1) higher energy peak (blue model peak), which may correspond to only a slight modification of the local coordination environment of $V^{5+[67]}$ and 2) lower energy peak (green model peak), which indicates reduction of $V^{\text{\tiny 5+}}$ to a lower oxidation state. Upon subsequent charging (electrode 4C), the spectra were deconvoluted into two peaks: 1) the peak at ~517.38 eV indicates that the original coordination environment of V is recovered upon charging and 2) the peak at ~515.96 eV (green peak) indicates that a small amount of reduced V⁵⁺ remains irreversibly reduced. Interestingly, the area ratio between the above two peaks (green model peak to blue model peak) remained constant (~25:75) in the 4th and 10th cycle charged electrode samples- 4C (Figure 4b) and 10C (Figure S5b). This reveals that the amount of irreversibly reduced V is constant and hence this reduction may have taken place along with the formation of irreversible phases like metallic Fe and Zn₃V₂O₇(OH)₂·2H₂O in the first discharge step. Based on the above observations we infer that, like Fe, V species in FeVO₄ undergoes two kind of reduction: 1) irreversible reduction speculated to occur in the initial stages of reaction with Zn-ion and 2) reversible reduction/oxidation of V^{5+} species during discharge/charge process.

2.7. Local Structural Evolution

The Raman spectra for the pristine FeVO₄ powder shows four broad peaks corresponding to different vibration modes (Figure 4c). Raman shifts between: 1) 300 and 550 cm⁻¹ correspond to V-O-V deformation and Fe-O stretching; 2) 550 to 700 cm⁻¹ represents a mixed bridging V-O…Fe & V…O…Fe stretching; 3) 700 and 880 cm⁻¹ are bridging V-O…Fe stretching and 4) 880 to 950 cm⁻¹ range arise from terminal V-O stretching modes.^[31,68–70] Upon discharging (4D and 10D): 1) the peak between 300 to 350 cm⁻¹ shifts to a lower wavenumber and recovers to the original position upon subsequent charging (4C and 10C). This might indicate a reversible expansion in local crystal lattice upon Zn-ion reaction, as also observed for LiNi₁. _yCo_yO₂ and Li_xV₂O₅.^[71] and 2) the high wavenumber peaks in 700 to 1000 cm⁻¹ range broaden to give rise to a single and broad band centered at ~850 cm⁻¹(4D and 10D), which reversibly disbands into original FeVO₄ peaks upon charging (4C and 10C). The Raman spectrum with broad peaks has also been observed for FeVO₄ powder synthesized at various calcination temperatures, wherein the peak broadening phenomenon was more prominent in FeVO₄ calcined at lower temperatures and was ascribed to loss in crystallinity.^[69] A similar broadening of Raman peaks has also been observed during the Li-ion insertion in V₂O₅.^[72]

Further, even though the overall spectrum differs between the discharged (4D and 10D) and the charged electrodes (4C and 10C), the spectrum for the charged electrodes appears very similar to the pristine electrode. This indicates that the original short-range ordering in the crystalline $FeVO_4$ is modified upon discharging and recovers back upon subsequent charging, even though the XRD results suggesting a permanent loss in the long-range order. The Raman study provides sufficient proof that the amorphous-FeVO₄ participates in the Zn-ion storage mechanism, and we use XAS technique to study the coordination environments of Fe and V centers.

Figure 5 shows the X-ray absorption near-edge structure spectra (XANES) of Fe and V K-edges which provide information on their local coordination environments and electronic structures.^[73] A comparative study was done on pristine, discharged and charged electrodes. The pristine Fe K-edge shows the presence of three absorption peaks noted as- A, B, and C (Figure 5a and 5b), as also observed in other Fe K-edge XAS studies.^[31,74–75] Peak A corresponds to a local electronic transition from Fe 1s to Fe 3d states. $^{\scriptscriptstyle [76]}$ Peak B, located ~4.5 eV higher than peak A, corresponds to a similar but non-local 1 s to 3d transition also referred to as an intersite hybrid.^[77-78] Such a transition occurs due to electronic excitation of a 1 s electron from the absorbing metal center (Fe) to 3d states of the nextnearest-neighboring Fe (here denoted as Fe'). Since this transition occurs through Fe(4p)-O(2p)-Fe'(3d) hybridization, peak B is sensitive to the Fe-O-Fe' bond geometry, including angle & length and the coordination number of the absorbing site-Fe.^[75,78] Finally, peak C (the rising edge) represents the excitation from the 1 s core state to the 4p conduction band of Fe.^[76]

The following observations are made from the Fe K-edge XANES spectra (Figure 5b): 1) Upon discharging, peak C shifts to lower energy values and recovers back upon charging. This shift of ~0.8 eV to lower energy indicates the reduction of Fe³⁺. Notably, this reduction may have occurred partially in the bulk as a downward energy shift of 4 eV is expected for the complete reduction of Fe³⁺ to Fe²⁺.^[79] 2) The peak A intensity increases upon discharge and reverts back to its original intensity upon charging. This increase in intensity indicates a distortion in the inversion symmetry of the Fe coordination environment (originally present as distorted octahedra), which would have resulted from local 3d-4p mixing, imparting a dipolar nature to this electronic transition.^[76] 3) The peak B intensity irreversibly diminishes upon discharge, indicating the



BATTERIES & SUPERCAPS



Figure 5. Local structural study of the pristine, discharged (4D) and charged (4C) electrodes: a) Background subtracted and normalized XANES spectra for the Fe K-edge (inset: the first derivative curve of XANES spectra for better identification of pre-edge peaks). b) Zoomed in XANES spectra for the Fe K-edge showing the change in the pre-edge intensities and the shift in rising edge upon cycling, c) background subtracted and normalized XANES spectra for the V K-edge showing the change in the pre-edge intensity and the shift in rising edge upon cycling, and d) summary of local structural changes upon Zn intake/ removal.

absence of the unoccupied next-nearest-neighbor 3d state to the Fe atom. This effectively indicates the formation of a new phase wherein the Fe-O-Fe' bond is absent/weak or the modified coordination of Fe where Fe(4p)-O(2p)-Fe'(3d) hybridization is no more possible, unlike FeVO₄. Similar observations were made by Jessica et al. in terms of diminished non-local/ intersite excitations when the concentration of Ga was increased in Fe_{1-x}Ga_xSbO₄.^[78]

Regarding V K-edge, XANES spectra of the pristine sample shows one pre-edge feature, indicative of the presence of a tetrahedral environment,^[80–81] along with the main rising edge (Figure 5c) as also observed by Hellier et al. for FeVO₄.^[82] It is observed that: 1) The intensity of the pre-edge peak decreases upon discharge and recovers partially on charging. The reduction in the intensity during discharge indicates an increase in the local symmetry of the vanadium environment.^[81,83] Such an increase in the symmetry primarily occurs during the conversion of some tetrahedral symmetry to octahedral.^[84] 2) The rising edge shifts reversibly to lower energy indicating a reduction in the V oxidation state during the discharge.^[80]

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 8 These are not the final page numbers!

In summary (Figure 5d), upon Zn-ion intake, the local structure of Fe destabilizes by losing its inversion symmetry; the local structure of V stabilizes by becoming more symmetrical; and Fe-O-Fe band breaks/weakens irreversibly. This observation concurs with the idea of Fe and V metal centers of amorphous-FeVO₄ participating in the discharge reaction, as also indicated in XPS and Raman studies.

2.8. 3D Morphological Evolution of FeVO₄

SRXTM study supports a conversion-type mechanism occurring in the FeVO₄ material and gives a visual idea of the development of new phases upon Zn-ion cycling in FeVO₄ at submillimeter length-scales. A comparative study is done on pristine, discharged and charged electrodes (Figure 6). All electrodes exhibit two regions of x-ray attenuating phases: high absorption for the deep material (colored in red) and low absorption for the surface material (colored in blue). SRXTM relies on differences in elemental composition, densities and pathlength considerations to achieve absorption contrast. Notably, the air absorbs x-rays as well, but the majority of its







Figure 6. Representative tomography images of pristine, 4D, 4C, 10C and 10D electrode showing morphological evolution in electrode upon discharge-charge. Blue and red colors represent low and high X-ray attenuating phases, respectively. The smaller figures adjacent to the electrodes represent the sectioned blue and red-colored phases in respective cases.

contribution has been nullified for these images by careful selection of transference function cut-offs.

The maximum X-ray absorption for point-volumes within the pristine cathode laminate must originate from the highatomic-number (or high-density) FeVO₄ particles. Hence, FeVO₄ can be mapped in 3D to be constrained within the red-phase region. Quantitatively, however, this red-phase region averages out the contiguous absorption contributions of the composite binder and the conductive carbons due to two technical considerations: (a) the synthesized FeVO₄ is nanosized and (b) the voxel resolution is limited to 2.88 µm. By globally considering these point-volume averages, we see clearly through SRXTM that for the pristine, discharged and charged electrodes, the heavy materials (or high-density) are localized deep within the electrode material, at least on the maximum 2.88-µm resolution scale. We also observe that the low-atomicnumber or low-density regions, if any, which are represented by the blue-colored phase tend to be localized nearer the electrode surface.

As expected, the pristine electrode displays a flat uniform morphology at this juxtaposition scale, as a direct consequence of the electrode fabrication process. Upon discharging (4D), the electrode surface exhibits significant roughening from the formation of ridge/valley-like features throughout the electrode surface, consistent with material electrodeposition. Further, upon charging (4 C), the electrode surface exhibits significant smoothening and regions of non-uniform X-ray attenuation. This roughening/smoothening behavior continues through to the 10th charge/discharge cycle (electrode 10D/10C). Porosity analyses further give insight into the bulk material volume expansion. Increased porosity is observed further down the cycle number. (9.9% porosity for the pristine material, 13.9% for 4D, 12.3% for 4C, 15.4% for 10D and 13.2% for 10C). A clear trend of increased porosity is observed upon discharge, which decreases reversibly upon charging.

All the above observations indicate that the formation of new phases upon discharge is resulting in material reorganization at the micron scale, and not simply on the atomic scale. A clear visual indication of the reversible phases forming at the micron scale presents strong evidence for the conversion-type storage mechanism for Zn-ions.

2.9. Reaction Mechanism

Overall, the Zn storage mechanism in the FeVO₄ host can be summarized as follows: XRD study indicates that after the first discharge, ZnO and metallic Fe phases form together with irreversible amorphization of FeVO₄. During the subsequent cycling steps, the ZnO phase appears/disappears upon discharge/charge, whereas metallic-Fe remains irreversibly reduced in metallic form. Parallelly, an irreversible phase $Zn_3V_2O_7$ (OH)₂·2H₂O and a small amount of permanently reduced V also forms in the first cycle discharge. Further, XPS, Raman and XAS studies unanimously show a reversible change in the local coordination and electronic environment of Fe and V metal centers of amorphized-FeVO₄ upon cycling, indicating their participation in Zn-ion storage.

Notably, in our system, only two sources of oxygen exist for Zn^{2+} -ions to form its oxide: 1) Oxygen from the amorphous-FeVO₄ matrix and 2) Oxygen from the water used as electrolyte solvent. Since three different studies, namely XPS, XAS and Raman, clearly indicate the participation of Fe and V metal centers in the Zn-ion storage mechanism, we expect the ZnO phase to be formed as a result of oxygen donation from the amorphous-FeVO₄ matrix. Such mechanisms have also been commonly observed in the transition metal oxides like







Figure 7. The proposed reaction mechanism for reversible Zn-ion storage in the FeVO₄: The 1st discharge step shows the formation of ZnO, metallic-Fe, oxygen-deficient amorphous-FeVO₄ (or FeVO_{4-x}) and Zn₃V₂O₇(OH)₂·2H₂O. Hereafter, during charging, the metallic-Fe unit cell volume contracts, the ZnO phase disappears, the amorphous-FeVO_{4-x} gains oxygen ions and Zn₃V₂O₇(OH)₂·2H₂O remains irreversibly present; and vice versa during discharging.

Li₂MoO3, Li₂RuO3 and metal-vanadates reacting with Li.^[41,85-88] Based on our study, we propose a two-step Zn-ion storage mechanism in FeVO₄ (Figure 7): 1) In the initial stages of reaction, crystalline FeVO₄ amorphized along with formation of irreversible phases including $Zn_3V_2O_7(OH)_2 \cdot 2H_2O$, metallic-Fe and some amount of irreversibly reduced V which accounts for initial loss of capacity and 2) Subsequently, Zn-ion storage takes place by the formation of ZnO phase where oxygen-ion is donated by the amorphous-FeVO₄ matrix leading to the formation of oxygen-deficient FeVO₄ (or FeVO_{4-x}).

3. Conclusions

From this study, we highlight two crucial ramifications for multivalent aqueous batteries. Firstly, from the cathode material's perspective, we show that as an alternative to intercalation-type cathode materials, reversibly storing multivalent cations is feasible in conversion-type transition metal oxides in an aqueous electrolyte, and we demonstrate this in a FeVO₄-Zn system. Not only can the cathode material demonstrate a high 2^{nd} discharge capacity of 272 mAh g^{-1} at 60 mA/g, but it can also demonstrate a high reversibility of 300 cycles at a high current rate of 3 Ag^{-1} and retaining a high capacity value of ~ 180 mAh g⁻¹. Further, a combination of complementary characterization techniques including structural investigation at different length scales also highlights a general strategy that can be adopted to study a complex conversion mechanism for other multivalent ions such as Mg²⁺, Ca²⁺ and Al³⁺.

Secondly, from the electrolyte's perspective, we show that the electrolyte pH is a key factor in deciding the cycling stability and the battery lifetime of the system in our case, especially at slower cycling rates or in a longer cycling duration.

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 10 These are not the final page numbers!

We demonstrate a battery with an unprecedented operational lifetime of ~57 days. The battery lifetime is particularly important for practical applications in the grid-scale energy storage as frequently replacing the batteries can increase the maintenance cost. Through our study, we have demonstrated that electrolyte pH can be easily increased by reducing the salt concentration of the electrolyte. Contrary to various other studies which use high concentration electrolytes (~3 m ZnTFS),^[28,89] we show that a 0.1 m ZnTFS/water electrolyte outperforms the more concentrated electrolyte system with a high capacity retention of 78.8%, against 18.8% for 2 m concentration electrolyte in the first 50 cycles. Reducing the salt concentration from 2 m to 0.1 m (by 20 times) can reduce the electrolyte cost by 20 times, which has bigger impact when upscaling this technology and is a step towards the commercialization of rechargeable ZIAB.

Experimental Section

Refer to supporting information for details on experimental section.

Acknowledgements

This work was financially supported by the National Research Foundation of Singapore (NRF) Investigatorship Award Number NRFI2017-08/NRF2016NRF-NRFI001-22. S.K. and V.V. would like to thank Dr. Samuel Morris (NTU, Singapore) for insightful discussions on X-ray diffraction data and Facility for Analysis Characterization Testing and Simulation-NTU, Singapore for the usage of characterization facility. We also thank Dr. Phakkhananan ChemPubSoc

Pakawanit and Chalermluck Phoovasawat for their assistance in operating synchrotron-beamline stations at SLRI, Thailand; and Dr. Arun Nagasubramanian (TUM-CREATE, Singapore) for fruitful discussions.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aqueous zinc-ion battery · conversion mechanism · tomography · x-ray absorption spectroscopy · electrolyte pH

- [1] Z. Xing, S. Wang, A. Yu, Z. Chen, Nano Energy 2018, 50, 229-244.
- [2] V. Verma, S. Kumar, W. Manalastas Jr, R. Satish, M. Srinivasan, Adv. Sustainable Syst. 2019, 3, 1800111.
- [3] H. Ren, J. Zhao, L. Yang, Q. Liang, S. Madhavi, Q. Yan, Nano Res. 2019, 12, 1347-1353.
- [4] D. Yuan, W. Manalastas Jr, L. Zhang, J. J. Chan, S. Meng, Y. Chen, M. Srinivasan, ChemSusChem 2019, 12, 4889-4900.
- [5] J. Zhao, H. Ren, Q. Liang, D. Yuan, S. Xi, C. Wu, W. Manalastas, J. Ma, W. Fang, Y. Zheng, C.-F. Du, M. Srinivasan, Q. Yan, Nano Energy 2019, 62, 94-102.
- [6] V. Verma, S. Kumar, W. Manalastas Jr., J. Zhao, R. Chua, S. Meng, P. Kidkhunthod, M. Srinivasan, ACS Appl. Energy Mater. 2019.
- [7] G. A. Elia, K. Marquardt, K. Hoeppner, S. Fantini, R. Lin, E. Knipping, W. Peters, J.-F. Drillet, S. Passerini, R. Hahn, Adv. Mater. 2016, 28, 7564-7579.
- [8] Y. Hu, D. Sun, B. Luo, L. Wang, Energy Technol. 2018, 0.
- D. Kundu, S. Hosseini Vajargah, L. Wan, B. Adams, D. Prendergast, L. F. [9] Nazar, Energy Environ. Sci. 2018, 11, 881-892.
- [10] W. Manalastas Jr, S. Kumar, V. Verma, L. Zhang, D. Yuan, M. Srinivasan, ChemSusChem 2019, 12, 379-396.
- T. Liu, X. Cheng, H. Yu, H. Zhu, N. Peng, R. Zheng, J. Zhang, M. Shui, Y. [11] Cui, J. Shu, Energy Storage Mater. 2018.
- [12] M. R. Lukatskaya, J. I. Feldblyum, D. G. Mackanic, F. Lissel, D. L. Michels, Y. Cui, Z. Bao, Energy Environ. Sci. 2018.
- [13] L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, M. Russell Selena, M. Armand, A. Angell, K. Xu, C. Wang, Angew. Chem. Int. Ed. 2016, 55, 7136–7141; Angew. Chem. 2016, 128, 7252-7257.
- [14] R. Chua, Y. Cai, Z. K. Kou, R. Satish, H. Ren, J. J. Chan, L. Zhang, S. A. Morris, J. Bai, M. Srinivasan, Chem. Eng. J. 2019, 370, 742-748.
- [15] D. Yuan, J. Zhao, W. Manalastas, S. Kumar, M. Srinivasan, Nanomaterials 2019.
- [16] X. G. Zhang, Google Patents, 1996.
- [17] D. Selvakumaran, A. Pan, S. Liang, G. Cao, J. Mater. Chem. A 2019, 7, 18209-18236.
- [18] Z. Rong, R. Malik, P. Canepa, G. Sai Gautam, M. Liu, A. Jain, K. Persson, G. Ceder, Chem. Mater. 2015, 27, 6016-6021.
- [19] M. J. Park, H. Yaghoobnejad-Asl, S. Therese, A. Manthiram, J. Mater. Chem. A 2019
- [20] Z. Zhao-Karger, M. Fichtner, Front. Chem. 2019, 6, 656.
- [21] H. Qin, Z. Yang, L. Chen, X. Chen, L. Wang, J. Mater. Chem. A 2018, 6, 23757-23765.
- [22] C. Zhu, G. Fang, J. Zhou, J. Guo, Z. Wang, C. Wang, J. Li, Y. Tang, S. Liang, J. Mater. Chem. A 2018, 6, 9677-9683.
- [23] J. Ding, Z. Du, B. Li, L. Wang, S. Wang, Y. Gong, S. Yang, Adv. Mater. 2019, 31, 1904369.
- [24] H. Pan, Y. Shao, P. Yan, Y. Cheng, K. S. Han, Z. Nie, C. Wang, J. Yang, X. Li, P. Bhattacharya, K. T. Mueller, J. Liu, Nat. Energy 2016, 1, 16039.
- [25] C. Xu, B. Li, H. Du, F. Kang, Angew. Chem. Int. Ed. Engl. 2012, 51, 933-935.
- [26] B. Lee, H. R. Lee, H. Kim, K. Y. Chung, B. W. Cho, S. H. Oh, Chem. Commun. 2015, 51, 9265-9268.
- [27] B. Lee, C. S. Yoon, H. R. Lee, K. Y. Chung, B. W. Cho, S. H. Oh, Sci. Rep. **2014**, *4*, 6066.
- [28] N. Zhang, F. Cheng, J. Liu, L. Wang, X. Long, X. Liu, F. Li, J. Chen, Nat. Commun. 2017, 8, 405.

[29] H. Zhang, K. Ye, K. Zhu, R. Cang, J. Yan, K. Cheng, G. Wang, D. Cao, Electrochim. Acta 2017, 256, 357-364.

Articles

BATTERIES

- [30] H. Zhang, K. Ye, K. Zhu, R. Cang, J. Yan, K. Cheng, G. Wang, D. Cao, Chem. Eur. J. 2017, 23, 17118-17126.
- [31] S. Kumar, R. Satish, V. Verma, H. Ren, P. Kidkhunthod, W. Manalastas, M. Srinivasan, J. Power Sources 2019, 426, 151-161.
- [32] S. Denis, R. Dedryvère, E. Baudrin, S. Laruelle, M. Touboul, J. Olivier-Fourcade, J. C. Jumas, J. M. Tarascon, Chem. Mater. 2000, 12, 3733-3739
- [33] S. Patoux, T. J. Richardson, Electrochem. Commun. 2007, 9, 485-491.
- [34] X. Liu, Y. Cao, H. Zheng, X. Chen, C. Feng, Appl. Surf. Sci. 2017, 394, 183-189.
- [35] B. Robertson, E. Kostiner, J. Solid State Chem. 1972, 4, 29-37.
- [36] X. Niu, Y. Zhang, L. Tan, Z. Yang, J. Yang, T. Liu, L. Zeng, Y. Zhu, L. Guo, Energy Storage Mater. 2019.
- [37] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Tarascon, Nature 2000, 407, 496-499.
- [38] P. Balaya, H. Li, L. Kienle, J. Maier, Adv. Funct. Mater. 2003, 13, 621-625.
- [39] M. Reddy, T. Yu, C.-H. Sow, Z. X. Shen, C. T. Lim, G. Subba Rao, B. Chowdari, Adv. Funct. Mater. 2007, 17, 2792-2799.
- [40] S.-H. Yu, X. Feng, N. Zhang, J. Seok, H. D. Abruña, Acc. Chem. Res. 2018, 51, 273-281.
- [41] J. Jang, Y. Kim, O. B. Chae, T. Yoon, S.-M. Kim, H.-s. Kim, H. Park, J. H. Ryu, S. M. Oh, Angew. Chem. Int. Ed. 2014, 53, 10654-10657; Angew. Chem. 2014, 126, 10830-10833.
- [42] L. Zhang, I. A. Rodríguez-Pérez, H. Jiang, C. Zhang, D. P. Leonard, Q. Guo, W. Wang, S. Han, L. Wang, X. Ji, Adv. Funct. Mater. 2019, 1902653.
- [43] M. H. Alfaruqi, V. Mathew, J. Song, S. Kim, S. Islam, D. T. Pham, J. Jo, S. Kim, J. P. Baboo, Z. Xiu, K.-S. Lee, Y.-K. Sun, J. Kim, Chem. Mater. 2017, 29, 1684-1694.
- [44] R. Demir-Cakan, M. R. Palacín, L. Croguennec, J. Mater. Chem. A 2019.
- [45] S. Boyd, V. Augustyn, Inorg. Chem. Front. 2018, 5, 999-1015.
- [46] A. S. Poyraz, J. Laughlin, Z. Zec, Electrochim. Acta 2019, 305, 423–432.
- [47] M. Hartmann, T. Clark, R. van Eldik, J. Am. Chem. Soc. 1997, 119, 7843-7850.
- [48] C. F. Baes, R. S. Mesmer, The Hydrolysis of Cations, 81, John Wiley & Sons Ltd, 1977, 245-246.
- [49] M. Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, Houston, Texas : National Association of Corrosion Engineers, 1974., 1966.
- [50] B. Beverskog, I. Puigdomenech, Corros. Sci. 1997, 39, 107-114.
- [51] K. A. Persson, B. Waldwick, P. Lazic, G. Ceder, Phys. Rev. B 2012, 85, 235438.
- [52] N. Zhang, Y. Dong, M. Jia, X. Bian, Y. Wang, M. Qiu, J. Xu, Y. Liu, L. Jiao, F. Cheng, ACS Energy Lett. 2018, 3, 1366–1372.
- [53] P. He, G. Zhang, X. Liao, M. Yan, X. Xu, Q. An, J. Liu, L. Mai, Adv. Energy Mater. 2018, 8, 1702463.
- [54] S. Denis, E. Baudrin, F. Orsini, G. Ouvrard, M. Touboul, J. M. Tarascon, J. Power Sources 1999, 81-82, 79-84.
- [55] L.-L. Zhao, J.-Y. Wang, X.-L. Wang, Z.-X. Cheng, J. Wang, N. Yin, Z.-G. Gai, A. Jalalian, S.-X. Dou, J. Alloys Compd. 2015, 628, 303-307.
- [56] G. P. ArneWestgren, J. Iron Steel Inst. London 1922, 105, 241-273.
- [57] D. Hoyos, L. A. Palacio, J.-L. Paillaud, A. Simon-Masseron, J.-L. Guth, Solid State Sci. 2004, 6, 1251-1258.
- [58] S. Denis, R. Dedryvere, E. Baudrin, S. Laruelle, M. Touboul, J. Olivier-
- Fourcade, J. Jumas, J. Tarascon, Chem. Mater. 2000, 12, 3733-3739.
- [59] G. R. Speich, L. Zwell, H. A. Wriedt , Trans. AIME 1964, 230, 939-940.
- [60] A. Grabias, M. Pękała, D. Oleszak, M. Kowalczyk, J. Magn. Magn. Mater. 2012, 324, 2501-2505.
- P. Y. Zavalij, F. Zhang, M. S. Whittingham, Acta Crystallogr. Sect. C 1997, [61] 53, 1738-1739.
- [62] A. Lebugle, U. Axelsson, R. Nyholm, N. Mårtensson, Phys. Scr. 1981, 23, 825-827.
- [63] P. Mills, J. L. Sullivan, J. Phys. D 1983, 16, 723-732.
- [64] I. N. Shabanova, V. A. Trapeznikov, J. Electron Spectrosc. Relat. Phenom. 1975, 6, 297-307.
- [65] T. Yamashita, P. Hayes, Appl. Surf. Sci. 2008, 254, 2441–2449.
- [66] Y. Zhao, K. Yao, Q. Cai, Z. Shi, M. Sheng, H. Lin, M. Shao, CrystEngComm 2014, 16, 270-276.
- [67] D. Kim, M. Kim, J. Yi, S.-H. Nam, J.-H. Boo, Y. S. Park, J. Lee, Sci. Adv. Mater. 2017, 9, 1415-1419.
- [68] L. Grazia, D. Bonincontro, A. Lolli, T. Tabanelli, C. Lucarelli, S. Albonetti, F. Cavani, Green Chem. 2017, 19, 4412-4422.
- [69] A. Š. Vuk, B. Orel, G. Dražič, F. Decker, P. Colomban, J. Sol-Gel Sci. Technol. 2002, 23, 165-181.

Batteries & Supercaps 2020, 3, 1–13 www.batteries-supercaps.org 11 These are not the final page numbers!

© 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



BATTERIES & SUPERCAPS

- [70] H. Tian, I.E. Wachs, L.E. Briand, J. Phys. Chem. B 2005, 109, 23491– 23499.
- [71] R. Baddour-Hadjean, J.-P. Pereira-Ramos, Chem. Rev. 2010, 110, 1278–1319.
- [72] R. Baddour-Hadjean, J. P. Pereira-Ramos, C. Navone, M. Smirnov, Chem. Mater. 2008, 20, 1916–1923.
- [73] T. E. Westre, P. Kennepohl, J. G. DeWitt, B. Hedman, K. O. Hodgson, E. I. Solomon, J. Am. Chem. Soc. 1997, 119, 6297–6314.
- [74] F. Liu, H. He, Z. Lian, W. Shan, L. Xie, K. Asakura, W. Yang, H. Deng, J. Catal. 2013, 307, 340–351.
- [75] F. M. F. de Groot, P. Glatzel, U. Bergmann, P. A. van Aken, R. A. Barrea, S. Klemme, M. Hävecker, A. Knop-Gericke, W. M. Heijboer, B. M. Weckhuysen, J. Phys. Chem. B 2005, 109, 20751–20762.
- [76] G. Frank de, V. György, G. Pieter, J. Phys. Condens. Matter 2009, 21, 104207.
- [77] P. Glatzel, A. Mirone, S. G. Eeckhout, M. Sikora, G. Giuli, *Phys. Rev. B* 2008, 77, 115133.
- [78] J. A. Sigrist, M. W. Gaultois, A. P. Grosvenor, J. Phys. Chem. A 2011, 115, 1908–1912.
- [79] W. M. Heijboer, P. Glatzel, K. R. Sawant, R. F. Lobo, U. Bergmann, R. A. Barrea, D. C. Koningsberger, B. M. Weckhuysen, F. M. F. de Groot, *J. Phys. Chem. B* 2004, *108*, 10002–10011.
- [80] J. Wong, F. W. Lytle, R. P. Messmer, D. H. Maylotte, Phys. Rev. B 1984, 30, 5596–5610.
- [81] M. Ruitenbeek, A. J. van Dillen, F. M. F. de Groot, I.E. Wachs, J. W. Geus, D. C. Koningsberger, *Top. Catal.* **2000**, *10*, 241–254.

- [82] P. Hellier, P. P. Wells, D. Gianolio, M. Bowker, Top. Catal. 2018, 61, 357-
- 364.[83] K. Palanisamy, J. H. Um, M. Jeong, W.-S. Yoon, *Sci. Rep.* 2016, *6*, 31275.
- [84] G. S. Henderson, F. M. F. de Groot, B. J. A. Moulton, *Rev. Mineral. Geochem.* 2014, 78, 75–138.
- [85] C. H. Kim, Y. S. Jung, K. T. Lee, J. H. Ku, S. M. Oh, *Electrochim. Acta* 2009, 54, 4371–4377.
- [86] Y. Shi, B. Guo, S. A. Corr, Q. Shi, Y.-S. Hu, K. R. Heier, L. Chen, R. Seshadri, G. D. Stucky, *Nano Lett.* **2009**, *9*, 4215–4220.
- [87] O. B. Chae, S. Park, J. H. Ryu, S. M. Oh, J. Electrochem. Soc. 2013, 160, A11-A14.
- [88] J. Wang, N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. Kisailus, H. Zhao, Z. Tang, D. Wang, Angew. Chem. Int. Ed. 2013, 52, 6417–6420; Angew. Chem. 2013, 125, 6545–6548.
- [89] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, J. Am. Chem. Soc. 2016, 138, 12894–12901.
- [90] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Materials* 2013, 1, 011002.

Manuscript received: January 24, 2020 Revised manuscript received: February 26, 2020 Version of record online:





ARTICLES

Conversion-type cathode materials may help circumvent the problem of poor solid-state diffusion commonly occurring in intercalation-type cathode materials for high chargedensity guest-ions. Here, $FeVO_4$ is demonstrated to show Zn-ion storage by a conversion-type mechanism, elucidated at multilength scale. The strong dependence of cycling stability on the electrolyte concentration is also demonstrated, which mechanistically relates to the electrolyte pH.



S. Kumar, V. Verma, R. Chua, Dr. H. Ren, Dr. P. Kidkhunthod, Dr. C. Rojviriya, Dr. S. Sattayaporn, Prof. F. M. F. de Groot, Dr. W. Manalastas, Jr., Prof. M. Srinivasan*

1 – 13

Multiscalar Investigation of FeVO₄ Conversion Cathode for a Low Concentration Zn(CF₃SO₃)₂ Rechargeable Zn-Ion Aqueous Battery