From solid electrolyte to zinc cathode: vanadium substitution in ZnPS$_3$

To cite this article: Andrew J Martinolich et al 2021 J. Phys. Mater. 4 024005

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Abstract

Development of next generation batteries is predicated on the design and discovery of new, functional materials. Divalent cations are promising options that go beyond the canonical Li-based systems, but the development of new materials for divalent ion batteries is hindered due to difficulties in promoting divalent ion conduction. We have developed a family of cathode materials based on the divalent cation conductor ZnPS$_3$. Substitution of V for Zn in the lattice concomitant with vacancy introduction yields isostructural but redox-active materials that can reversibly store Zn$^{2+}$ in the vacancies. A range of voltammetry and galvanostatic cycling experiments along with x-ray photoelectron spectroscopy support that redox is indeed centered on V and that capacity is dependent on the V content. The voltage of the materials is limited by the irreversible decomposition of the [P$_2$S$_6$]$_4$$^-$ polyanion above 1.4 V vs. Zn/Zn$^{2+}$. The reversible capacity before anion decomposition is limited to half the vacancies and is due to the relative ratios of oxidized and reduced V centers. Such observations provide useful design rules for cathode materials for divalent cation based battery technologies, and highlight the necessity for a holistic interpretation of physical and electronic structural changes upon cycling.

1. Introduction

Energy storage technologies are a ubiquitous part of modern life. Devices based on Li$^+$ intercalation at the anode and cathode dominate the market of rechargeable devices, largely centered around Li intercalated graphite anodes and LiCoO$_2$ cathodes [1]. Li-ion batteries exhibit highly reversible electrochemistry due to the intercalation based behavior but are nearing theoretical limits [2]. Beyond performance, concerns regarding the sustainability of Li-ion batteries and their dependence on threatened resources, namely Li and Co, drive research into new chemistries [3]. Divalent working ions present attractive opportunities to help relieve the environmental and economic strain imposed by current technologies [4]. Despite being conceptualized as early as 1840 [5], development of batteries using divalent working ions such as Mg and Zn has been limited compared to the Li counterparts.

The development of divalent batteries necessitates the design and discovery of new cathode materials that can accommodate the reversible intercalation and deintercalation of the divalent cation via the redox of the framework. However, the design principles surrounding divalent ion mobility in solid state materials are limited. A few materials have been reported to function as cathodes for batteries based on divalent metal intercalation. The canonical example for Mg$^{2+}$ cations is the Chevrel phase Mo$_6$S$_8$ [6], which has also exhibited reversible Zn intercalation [7]. Computational results indicate that Mg$^{2+}$ intercalation into the Chevrel phase is aided by electronic screening of the high charge density of the divalent cation by the surrounding host lattice, enabled by the metallic nature of the Chevrel material. The importance of a metallic cathode was supported by the observation of a much higher Mg$^{2+}$ mobility in Ti$_2$S$_4$ than Zr$_2$S$_4$, which was attributed to the higher electronic conductivity in the former [8].

A range of intercalation cathodes for Zn batteries have been studied [9, 10], including vanadium oxides [11–13], manganese oxides [14, 15], Prussian blue analogues [16, 17], and beyond. Direct comparisons to
the traditional Li intercalation material LiCoO$_2$ have also been made. The material ZnCo$_2-x$Al$_x$O$_4$ exhibits reversible cycling in nonaqueous electrolytes [18]. Al was substituted into the spinel lattice to stabilize the material at high states of charge (low Zn content). However, at $x > 0.67$ no electrochemical activity is observed, which is attributed to poor electronic conductivity of the material with greater Al substitution, despite the possible low energy conduction pathways between tetrahedral sites in a spinel lattice [19].

In aqueous electrolytes, reversible Zn$^{2+}$ intercalation is facilitated by the coinsertion of water molecules into the lattice [12, 20]. The presence of water in the V$_2$O$_3$ cathode material, for example, is suggested to impart structural stability and promote Zn$^{2+}$ mobility. However, such attributes are limited to aqueous electrolytes and the kinetics of divalent ion conductivity and charge transfer are negatively impacted when measured in nonaqueous systems [21]. Proton intercalation can also occur in aqueous based electrolytes, which convolutes the charge storage mechanisms in prospective batteries aiming to use Zn$^{2+}$ working ions [22, 23]. Thus, broadening the design rules for divalent cation cathode materials is necessary to promote the development of next generation battery technologies.

Despite the suggestions that divalent ionic conductivity requires either high electronic conductivity or co-intercalated solvent, we recently reported the mobility of Zn$^{2+}$ in the electronically insulating material ZnPS$_3$ with a low activation barrier of ionic conduction of 350 meV [24]. ZnPS$_3$ crystallizes in 2D honeycomb layers of edge sharing Zn octahedra surrounding the P$_2$S$_4^{6-}$ polyanion, with the layers separated by a van der Waals gap of approx. 3.3 Å. Theoretical data suggest that the flexibility of the polyanion and the low electron density in the van der Waals gap facilitate Zn$^{2+}$ conduction with a low activation energy. The material is amenable to a range of cation substitutions [25], including aliovalent substitution.

Here, we report the preparation and electrochemical behavior of vanadium substituted ZnPS$_3$. Substitution of V$^{3+}$ for Zn$^{2+}$ is charge compensated by vacancies on the metal site (figure 1) [26, 27] and provides us with the ability to tune the electronic properties of a lattice without altering the favorable ionic properties provided by the structure or anionic chemistry. Introduction of V into the lattice directly impacts the electronic structure of the material and enables reversible redox as evidenced by cyclic voltammetry (CV) and galvanostatic cycling data; greater capacity is observed at higher levels of vanadium substitution. At higher potentials (>1.4 V vs. Zn/Zn$^{2+}$), irreversible oxidation occurs at the polyanion, as indicated by x-ray photoelectron spectroscopy (XPS). Our results provide a promising new avenue toward the discovery of functional divalent cathodes, wherein the installation of redox active cations on lattices that allow divalent cation mobility enables the desired functionality.

2. Experimental methods

2.1. Material preparation

All manipulations were performed in an Ar-filled glovebox with H$_2$O and O$_2$ concentrations below 1 ppm. Zn$_{1-x}$V$_x$PS$_3$ was prepared from Zn (Alfa Aesar, 99.9%), V (Alfa Aesar, 99.5%), P$_2$S$_5$ (Acros Organics, 98+%), and S (Acros Organics, 99.5+%). The reactants were combined in stoichiometric quantities corresponding to x values of 0.067, 0.20, 0.33, 0.40, and 0.50, ground to homogeneity in a mortar and pestle, compressed into 0.25” cylindrical pellets, and sealed in an evacuated vitreous silica ampoule. The reaction
mixture was then heated at 2 °C min⁻¹ to 400 °C and annealed for 24 h. The product was then collected in the glove box, reground, repelleted, sealed in an evacuated silica ampoule, heated to 600 °C at 2 °C min⁻¹ and annealed for 24 h. The x = 0 end member does not require the second annealing step [24]. The resultant powders were collected in the glove box and stored under inert conditions.

2.2. Powder x-ray diffraction

Powder x-ray diffraction measurements were collected on a Panalytical X’Pert Pro Diffractometer equipped with a CuKα x-ray source. The diffraction patterns were fit by the Rietveld method using GSAS-II [28]. Crystal structures were visualized using Vesta [29].

2.3. Electrochemical measurements

CV and galvanostatic charge/discharge measurements were collected on composite electrodes of 60 wt% Zn₁₋₁.₅ₓVₓP₃S₅, 20 wt% PTFE binder (Sigma Aldrich), and 20 wt% Super P conductive carbon (Alfa Aesar, ≥99%). The composite mixture was ground to homogeneity using a mortar and pestle and pressed into 0.25m diameter discs. The mass of active material in each electrode was between 5 and 15 mg. The electrodes were assembled into 2032 coin cells with a spring, stainless steel spacer, 18 mm diameter Whatman GF-D glass fiber separator, and Zn foil counter/reference electrode (Sigma Aldrich, 99.9%). The Zn foil was cleaned with a razor blade prior to assembly to remove any oxidized surface species. All measurements used 500 mM Zn(TFSI)₂ (Sigma Aldrich, 95%) in propylene carbonate (Sigma Aldrich, >99%) electrolyte (8 drops, approx. 100 mg). Measurements were collected on a Biologic BCS 805 battery cycler or VMP3 potentiostat.

2.4. X-ray photoelectron spectroscopy

Samples were oxidized or reduced to the specified voltages using linear sweep voltammetry in preparation for XPS measurements. The composite electrodes were dried under dynamic vacuum for >24 h prior to data collection. The samples were ground in a mortar and pestle and mounted on carbon tape in the glove box before transferring to the instrument, with brief air exposure. XPS data were collected using a Surface Science Instruments MProbe ESCA controlled by Hawk Data Collection software. Element-specific scans were collected with a resolution of 0.065 eV and a spot size of 500 × 1200 μm. The sample chamber was maintained at <2 × 10⁻⁸ Torr. The XPS data were analyzed using CasaXPS analysis software. All spectra were recorded with a neutralizer on to minimize charging effects and referenced to adventitious carbon at 285 eV.

3. Results and discussion

V substitution into ZnPS₃ is achieved via stoichiometric substitution during initial preparation of the material. A composition of Zn₁₋₁.₅ₓVₓP₃S₅ was targeted to introduce both redox-active V³⁺ centers and vacancies on the metal sites (figure 1). The stoichiometric mixture of Zn, V, P, S, and S was combined in an Ar-filled glove box and annealed at 400 °C and 600 °C to yield a black powder. The powder x-ray diffraction pattern and quantitative Rietveld refinement are shown in figure 2(a). The fit corresponds to a single phase that is isostructural to ZnPS₃, indicating that partial substitution of V for Zn does not induce a structural change to the parent material. Mixed valency and partial vacancy substitution in the MPS₃ family of materials is precedent, specifically in the case of V₀.₇₆PS₃ [26]. The color change from white to black upon partial substitution of V for Zn is a clear indicator of the effect of metal substitution on the electronic properties of the material.

The refined lattice parameters of Zn₁₋₁.₅ₓVₓP₃S₅ (0 ≤ x ≤ 0.50) are plotted as a function of V content in figure 2(b). The lattice contracts in all directions upon V substitution, which is expected due to the smaller ionic radius of V³⁺ than Zn²⁺, 0.64 Å and 0.74 Å respectively [30, 31], along with the introduction of vacancies into the lattice. The lattice contracts by 1.1% and 0.9% along a and b, respectively, but only 0.6% along c. The lesser contraction along c is expected due to layered nature of the material, in that the van der Waals gap will be more affected by the electron density around the sulfur anions than partial substitution in the metal layer. The contraction of the metal layer may increase the activation barrier due to restricted conduction pathways for the Zn²⁺. While the structural contraction may increase the activation barrier, we previously hypothesized that the ionic conduction in ZnPS₃ is mediated by entropic vacancy defects on the metal site. Thus, increasing the vacancy concentration through aliovalent substitution likely increases the bulk conductivity of the material. Additionally, the presence of electronic carriers in the material may also promote divalent ionic conductivity through the lattice, as previously hypothesized for Mg²⁺ in Mo₇S₈ and Ti₅S₄ [8, 32, 33].

CV was used to understand the redox properties of Zn₁₋₁.₅ₓVₓP₃S₅. CVs with varied positive switching potentials are shown in figure 3 for the x = 0.33 material. The first scan was initially swept positive to 1 V
Figure 2. (a) Powder x-ray diffraction of Zn$_{0.50}$V$_{0.33}$PS$_3$ and single phase quantitative Rietveld refinement. No crystalline impurities are observed. (b) Lattice parameters of the solid solution Zn$_{1-1.5x}$V$_x$PS$_3$. The linear decrease in the lattice parameter supports the quantitative substitution of V for Zn.

Figure 3. Cyclic voltammetry of Zn$_{0.50}$V$_{0.33}$PS$_3$ using 500 mM Zn(TFSI)$_2$ in propylene carbonate electrolyte and a Zn metal reference/counter electrode. The voltammetry was collected at 0.1 mV s$^{-1}$ and initially swept to positive potentials. After two cycles, the upper voltage cutoff was successively increased by 200 mV. The cathodic wave observed at approx. 500 mV shifts to lower potentials once the second anodic wave is observed. Then negative to 0.1 V. A cathodic wave is observed at approx. 500 mV on the negative sweep, with no correlated anodic wave observed on the reverse sweep. After reaching the upper voltage cutoff for the first cycle (1 V), a small wave is observed on the second negative sweep at a similar voltage to the cathodic wave in
scan 1, but with smaller peak current. The smaller peak current indicates that most of the redox-active material was reduced on the first sweep and very little remains in the material by the second sweep.

After two scans with a switching potential of 1 V, the switching potential was increased to 1.2 V. Sweeping to more positive potentials above 1 V yields an incomplete anodic wave, which appears to be coupled to the cathodic wave observed in the initial CVs. On the negative sweep, the cathodic wave shifts to slightly higher potentials than originally observed to approx. 700 mV. The next CV scan overlays the preceding scan, indicating that the oxidation and reduction processes are reversible. The peak splitting is wide (530 mV), however, suggesting that the processes are not Nernstian, which is likely due to overpotentials associated with ionic conduction or charge transfer resistance. Increasing the anodic voltage cutoff to 1.4 V maintains the reversibility and yields a more symmetrical wave, with no changes observed between the first and second cycle.

Sweeping to higher potentials affects the reversibility and redox properties of Zn$_{0.50}$V$_{0.33}$PS$_3$. The reversibility of the redox processes is determined by both the peak splitting and evaluating the charge passed on oxidation vs. the charge passed on reduction with the capacitive background subtracted. A less sensitive method is to evaluate the peak current of the anodic and cathodic waves and this can give a general idea of reversibility. If a process were reversible, the peak current would be the same for both waves. Deviations from such behavior indicate some degree of irreversibility. After twice sweeping to a switching potential of 1.4 V, two CVs each were swept to 1.6, 1.8, 2.0, and 2.2 V (figure 3). The CVs to 1.6 V begin to show an increase in the current at the highest voltages on both cycles. On the reverse sweep, the cathodic wave changes shape and begins to broaden, indicating alteration to the kinetics of the redox properties of the material, which could be due to either a structural transformation or distortion yielding poorer Zn$^{2+}$ mobility through the lattice.

Upon sweeping to a positive switching potential of 1.8 V, a second oxidative wave is clearly observed. The second oxidation precedes a broad reduction wave that is shifted to lower potentials than originally observed, centered at approx. 450 mV. The second oxidation also affects the oxidation processes in later cycles. The original anodic wave observed below 1.4 V broadens and shifts to higher potentials, mirroring the behavior of the cathodic wave. The redox behavior for the $x = 0.33$ material is also observed for the $x = 0.20$ and $x = 0.40$ materials (see the SI available online at stacks.iop.org/JPMATER/4/024005/mmedia). Slightly higher current densities are observed for the first oxidative wave for the $x = 0.40$ material, suggesting that the first wave is related to vanadium redox. For $x = 0.067$ and $x = 0.50$, much smaller oxidative waves are observed before the large, irreversible wave above 1.4 V, suggesting that a threshold amount of vanadium is required to enable redox activity, while too much changes the properties of the material and disallows reversible redox.

Voltammetry for all materials are shown in the SI.

XPS spectra in the Zn, V, P, and S regions were collected on the $x = 0.33$ material at various oxidation states after voltammetry to determine the redox mechanism of Zn$_{1-1.5x}$V$_x$PS$_3$ (figure 4). The material was either reduced to 0.1 V or reduced to 0.1 V then subsequently oxidized to 1.4 or 2.0 V at 0.1 mV s$^{-1}$. The Zn binding energy remains unchanged in all cases (figure 4(a)). The V binding energies shift as a function of oxidation and reduction, indicating the direct involvement of the metal in the redox (figure 4(b)). The V binding energy of the pristine material is centered at 514 eV, which then shifts to 513 eV upon reduction to 0.1 V. Subsequent oxidation to 1.4 V shifts the V binding energy back to 514 eV and is nearly identical to the pristine sample, indicating reversible V redox below 1.4 V. Subsequent oxidation to 2 V results in the observation of a second peak at higher binding energy (517.5 eV), indicating further oxidation of the V at 2 V [34]. The low signal-to-noise ratio from V in the XPS spectra is likely a combination of low V content in the sample and the comparatively small relative sensitivity factor.

XPS of the P and S in Zn$_{0.50}$V$_{0.33}$PS$_3$ were collected to understand the changes in anion oxidation state when the material is oxidized or reduced (figures 4(c) and (d)). The new peak denoted with an asterisk in the S region of the XPS spectra after oxidation or reduction is attributed to adsorbed TFSI$^-$ anions, which remain after exposure to the electrolyte. Upon reduction to 0.1 V or oxidation to 1.4 V, no major changes are observed in either the P or the S regions of the XPS spectra, indicating that the polyanion is stable below 1.4 V. However, upon oxidation to 2 V, both spectra exhibit a shoulder at higher binding energies suggesting polyanion oxidation. Based on the XPS data, general assignments to the different redox properties observed in the CV (figure 3) can be made. V in reduced during the initial reduction process at 500–700 meV and is then reversibly oxidized at approx. 1.2 V. Sweeping to voltages $>1.4$ V yields a second anodic wave that we assign to polyanion oxidation.

To confirm the contribution of the redox from the [P$_2$S$_6$]$^{14-}$ polyanion, CV was executed on unsubstituted ZnPS$_3$. No cathodic wave is observed on the initial negative sweep. However, a single oxidative wave is observed at approx. 1.7 V (figure S3). The oxidative wave is in the same position as the irreversible wave observed in the V substituted material. The observation of an irreversible wave in both materials suggests that the [P$_2$S$_6$]$^{14-}$ polyanion is oxidized in both cases. Irreversible polyanion oxidation is likely to
Figure 4. (a) Zn, (b) V, (c) P, and (d) S regions of the XPS spectra of \( \text{Zn}_{0.50}V_{0.33}\text{PS}_3 \) at various states of oxidation. Reduction to 0.1 V only affects the XPS spectrum in the V region, while oxidation to 2 V yields changes in the V, P, and S regions. The peak at 168 eV in the S 2p region of the spectra is due to the TFSI\(^-\) counteranion present in the electrolyte, denoted with (\(\ast\)).

significantly alter the structure and shift the subsequent redox features, as observed in figure 3 and in electrochemical cycling experiments at high potentials. Various oxidation states of [P\(_x\)S\(_y\)]\(^{\alpha-}\) polyanions are accessible beyond [P\(_2\)S\(_6\)]\(^{4-}\), including the [P\(_2\)S\(_6\)]\(^{2-}\) in the mixed polyanion compound \( \text{Zn}_4(\text{P}_2\text{S}_6)_{3} \) and [PS\(_4\)]\(^{3-}\) in \( \text{Zn}_3(\text{PS}_4)_{2} \) [35, 36]. Zn is tetrahedrally coordinated in both materials, which would require significant structural rearrangement from the structure of ZnPS\(_3\), as suggested by the changes in the electrochemistry after oxidation beyond 1.4 V.

The reversibility of the V centered redox is supported by rate dependent voltammetry between 1.4 and 0.1 V (figure 5). Upon increasing the scan rate from 0.1 to 10 mV s\(^{-1}\), the peak current of the reversible anodic and cathodic waves increases as well. The current is linearly correlated to the square root of scan rate, indicating electrochemical reversibility of the low voltage redox couple. Above 1 mV s\(^{-1}\), the voltage of the waves begins to shift, indicating some irreversibility which may be related to slower kinetics of Zn diffusion through the \( \text{Zn}_{1-x}\)\(_{1.5x}\text{V}_x\text{PS}_3 \) lattice rather than in the nonaqueous electrolyte. However, changing the concentration of the electrolyte does lead to a slight decrease in the maximum observed current (figure 5(b)), suggesting that the kinetics of Zn mobility in the solid state lattice are not completely resolved from kinetic limitations in the liquid electrolyte.

The presence of Zn\(^{2+}\) cations, vacancies, and redox active V centers in the pristine material suggests that the material can be either oxidized or reduced as synthesized. Thus, CVs were measured on \( \text{Zn}_{0.50}V_{0.33}\text{PS}_3 \) initially sweeping to either positive or negative potentials (figure 6). Indeed, we observe that the material can be either oxidized or reduced from its pristine state, indicating that Zn incorporation is possible without the necessity of charging first. When sweeping to more positive potentials first, Zn must be removed from the octahedral sites within the metal layer as V is oxidized. When sweeping to more negative potentials initially, it is possible that Zn could occupy either the vacancies in the metal layer, introduced due to aliovalent substitution, or vacancies in the van der Waals gap as the V is reduced. On the return sweep in both cases, the correlated wave increases in current density. The increase in current density on the return wave provides further support that the redox features at 0.6 and 1.1 V are related to the same electrochemical processes and are reversible. The correlation between the waves also provides indirect evidence that Zn is being introduced into the metal layer rather than into the van der Waals gap, as it may only originate from the transition metal when sweeping to more positive potentials initially, and no changes in potential are observed on subsequent cycles.
Figure 5. (a) Scan rate dependent cyclic voltammetry of Zn$_{0.50}$V$_{0.33}$PS$_3$. (b) The linear relationship between the square root of the scan rate and the maximum observed current indicates the reversibility of the reduction and first oxidation observed. Using a less concentrated electrolyte slightly decreases the observed maximum current, indicating that the observed kinetics cannot be isolated from the kinetics of the electrolyte.

Figure 6. CVs of Zn$_{0.50}$V$_{0.33}$PS$_3$ swept to either positive or negative potentials from open circuit potential, indicating the intermediate state of charge of the pristine material.

Based on the observation of the reversible, low voltage redox wave in the voltammetry, Zn$_{1-x}$V$_x$PS$_3$ was cycled galvanostatically with a current density of 1 mA g$^{-1}$ between 1.4 and 0.1 V, starting first with the charge cycle (figure 7). The first cycle exhibits a Coulombic efficiency much greater than 100% (defined here as $Q_{\text{out}}/Q_{\text{in}}$ or $Q_{\text{discharge}}/Q_{\text{charge}}$) because Zn is able to occupy the vacancies present in the pristine material upon discharge. A >100% Coulombic efficiency on cycle 1 is observed for $x = 0.20$, $x = 0.33$, and $x = 0.40$. The second cycle exhibits much higher capacity on the charge, and a comparable capacity on discharge, indicating that the extra Zn$^{2+}$ introduced during discharge can be removed. The materials exhibit reversible capacity that is dependent on the V content, with greater V content yielding higher capacity. The correlation between capacity and V content further supports that the reversible charge storage is enabled by V redox.
Figure 7. Galvanostatic cycling data of $\text{Zn}_{1-x}V_x\text{PS}_3$. (a) The discharge and charge curves of the first two cycles of the $x = 0.20$, 0.33, and 0.40 materials with a current density of 1 mA g$^{-1}$. The materials are first charged then discharged. (b) The capacity normalized to the number of vacancies in the materials plotted as a function of cycle number. All materials exhibit a maximum reversible capacity of half of the available vacancies.

The capacity over several cycles is normalized to the vacancy content and plotted in figure 7(b). The materials show gradual capacity fade followed by more stable cycling. When normalized to the number of vacancies in the material, we observe that all materials are reversibly accessing approximately half of the vacancies present in the vanadium substituted materials. Such an observation elucidates the nature of divalent cation intercalation and mobility in the lattice. Filling half the vacancies on discharge correlates to reduction of half of the $V^{3+}$ to $V^{2+}$. Once half of the $V^{3+}$ is reduced, Zn incorporation ceases, even if the vacancy concentration remains relatively high. For example, filling half the vacancies in the $x = 0.40$ material leaves 0.1 equivalents of unfilled vacancies per formula unit. The same number of vacancies are present in the pristine $x = 0.20$ material, however, the presence of 0.1 equivalents of vacancies alone does not provide the same electrochemical activity. Instead, it appears that the mixed valency on the substituted vanadium centers (dis)allows the reversible redox. Such behavior highlights the delicate balance between electronic and crystal structure that may influence divalent ion based energy storage materials. Capacity retention data for the $x = 0.20$, 0.33, and $x = 0.40$ materials with replicate cells are shown in the SI.

$\text{Zn}_{0.50}V_{0.33}\text{PS}_3$ was cycled at 60 $^\circ$C in an attempt to increase the experimental capacity of the material. While the hysteresis between the charge and discharge curves decreases, no significant increase in capacity is observed (figure S7). Additionally, the Coulombic efficiency begins to decrease drastically at later cycles, eventually giving way to parasitic current on the charge curve and cell failure. We hypothesize that the poor Coulombic efficiencies and cell failure are due to slow oxidation of the $[P_2S_6]^{4-}$ polyanion, which is accessed at lower potentials when higher temperatures are applied. The inability to access greater capacities at elevated temperatures suggests that the capacity is thermodynamically limited to filling half of the vacancies (approx. 26 mAh g$^{-1}$ for $x = 0.33$) and it is not an issue of kinetics.

While the materials with $x = 0.20$, 0.33, and $x = 0.40$ all exhibit reversible Zn storage upon galvanostatic cycling, no appreciable reversible oxidation is observed for the $x = 0.067$ or $x = 0.50$ materials at room temperature or at 60 $^\circ$C (figures S4–S6). For $\text{Zn}_{0.90}V_{0.067}\text{PS}_3$, it is likely that the low vanadium content and even lower vacancy concentration in the material leads to no appreciable charge storage ($Q_{\text{theoretical}} = 9.5$ mAh g$^{-1}$ if 100% of the vacancies are filled). However, the material with the most V also exhibits no reversible charge storage. Multiple hypotheses can be provided to account for this unexpected behavior. It is possible that when a majority of the metal centers in the material are V instead of Zn, the electronic structure of the material changes greatly and disallows vanadium oxidation and reduction. For example, $V_{0.0}P_{2}S_3$ is a Mott insulator, where both the highest occupied valence band and lowest unoccupied conduction band are composed of $V d$ states [37, 38]. At high V content it is possible the materials become poorer electronic conductors which leads to electrochemical inactivity. An alternative hypothesis is that there is a threshold amount of Zn necessary in the lattice to support divalent ion mobility. When the amount of V
is greater than the amount of Zn, it is likely that the percolative pathways for Zn\(^{2+}\) mobility and conduction are disrupted and thus the ions are immobilized [39]. However, all materials exhibit irreversible oxidation above 1.4 V, further supporting that the second anodic wave is due to the oxidation of the [P\(_2\)S\(_6\)]\(^{4-}\) anion but also confirming that Zn\(^{2+}\) can be removed from the material. Therefore, it is unlikely that the high V content material is inactive due to sluggish Zn\(^{2+}\) conduction.

4. Conclusion

Here, we have shown that V substitution into the Zn\(^{4+}\) cation conductor ZnPS\(_3\) yields reversible redox activity. The introduction of vacancies allows for either electrochemical oxidation or reduction from the pristine state. The storage capacity is directly correlated to the V content of the material, suggesting that the V centers are redox active, which is supported by voltammetry in concert with XPS measurements at various redox states. The charge storage capacity of the materials is limited to half of the synthetically-introduced vacancies, which is hypothesized to be due to the ratio of oxidized and reduced V centers and their influence on the electronic structure of the material. These insights provide a useful new design principle for prospective cathode materials for divalent working ions, and highlight the importance of both electronic structure as well as a suitable host lattice for divalent cation conduction and mobility in the pursuit of next generation energy storage materials.

Acknowledgments

This research was supported by the Arnold and Mabel Beckman Foundation through the Beckman Young Investigator Award. The authors thank Dr FAL Laskowski for many enlightening discussions. AJM was partially supported through a postdoctoral fellowship from the Resnick Sustainability Institute at Caltech. XPS data were collected at the Molecular Materials Research Center in the Beckman Institute at Caltech.

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