Mechanistic Insight and Local Structure Evolution of NiPS₃ upon Electrochemical Lithiation

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conversion reactions in a sequential manner. This study of $NiPS_3$ material exemplifies the Li-ion storage mechanism in transition metal phosphorus sulfide materials and provides insights into the challenges associated with achieving reliable, high-energy phosphorus trisulfide systems.

KEYWORDS: 2D materials, metal phosphorus trichalcogenides, Li-ion insertion mechanism, intercalation reactions, conversion reactions

INTRODUCTION

In recent years, transition metal chalcogenides (MX_z, where M = V,^{1,2} Mn, Fe,^{3,4} Co,^{5,6} Ni, Cd, Mg, Zn, Mo^{7,8} and X = S, Se), carbides,⁹ and nitrides^{10,11} (M'_{n+1}A_nT_x, where A = C or N and T = H, OH) have been extensively investigated as active materials for various electrochemical energy storage applications such as lithium-ion (Li-ion), sodium-ion (Na-ion), and lithium–sulfur (Li–S_x) based storage and metal–air batteries. One approach to design a new layered electrode material system for improved electrochemical performance is the modification of the electronic structure of 3d-metal centers by tuning its covalency and electronegativity.¹² Generally, by introducing polyanions in the material structure (i.e., oxy-sulfides), as opposed to a single anion (i.e., oxides and sulfides), an inductive effect is observed as a result of the change in distribution of electrons in a M–X bond, leading to an increase of the reduction–oxidation (redox) potentials.^{13,14}

Transition metal phosphorus trichalcogenides (MPX₃) are a potential polyanionic active material with the material having the CdCl₂-type layered structure (compact stacking of sulfur layers of ABC type), in which one-third of the transition metals are substituted by P–P pairs within the layers. Each $[P_2X_6]^{4-}$ unit occupies the center of six divalent transition metal ions M^{2+} forming a hexagonal lattice, leading to the general formula of $M_2P_2X_6$. In contrast to the transition metal dichalcogenides, MPX₃ compounds generally have a larger van der Waals gap (>6 Å) such that Li-ion intercalation would have a minimal effect on the lattice parameters. By analogy with the layered TiS₂ system, it was hypothesized that the intercalated Li-ions would sit in octahedral sites in the van der Waals gaps, leading to a theoretical maximum of 1.5 Li-ions in between each MPX₃ layer.¹⁵ Among various MPS₃ host systems with attainable transition metal centers (M = V, Mn, Fe, Co, Ni, Zn, Cd), NiPS₃, FePS₃, and CoPS₃ have shown to chemically intercalate Li-ions without kinetic limitations.¹⁶ This observation has been attributed to the ionic character, therefore the band energy level, of the M–S bond.¹⁷ For transition metals with higher bond ionicity, such as Ni, Fe, and Co, cationic electron transfers occur more readily from the lower Hubbard bands.¹⁸ Thus, the site potential in the host lattice is minimal in NiPS₃ due to the highest bond ionicity, leading to rapid Li-ion diffusion in the material and best electrochemical intercalation behavior.

In the 1970–1980s, significant effort was invested to explore Li-ion storage properties and chemical changes associated with it in NiPS₃ compounds.^{18–21} These early studies established reversible chemical and electrochemical insertion of a few Li-ions, but subsequent studies also revealed that the electrochemical redox reaction is not limited to the available redox

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Figure 1. Material characterization of as-prepared NiPS₃. (a) Morphology and microstructural characteristics observed by using SEM. (b) XRD confirms phase purity with preferred orientation in the (002) direction. (c) Surface chemical composition and bonding configuration probed by XPS. Ni 2p, S 2p, and P 2p binding energies are fitted to chemical states of spin–orbit components.

states on the transition metal and can continue with reasonable reversibility up to more than eight Li-ions with the proposed overall reaction: NiPS₃ + 9Li⁺ + 9e⁻ \leftrightarrow 3Li₂S + Li₃P + Ni.^{22,23} However, the charge storage mechanism and redox reaction characteristics around redox-active centers are still unclear, highlighting the need for an in-depth mechanistic study focused on electrochemical Li uptake in NiPS₃ compounds. A brief overview of Li-ion storage characteristics of various nickel sulfides and phosphides is presented in Table S1.^{24–26}

Here, we report mechanistic and structural evolution of NiPS₃ upon electrochemical Li-ion insertion by employing a library of operando and ex situ spectroscopic techniques. The electrochemical redox potential range investigated in our study was less than the theoretical capacity for full reduction of the cationic center and surrounding anions (nine Li-ions) but much greater than that for solid-solution intercalation reaction. Probing dual intercalation and conversion reaction pathways in the polyanionic active material involving redox reactions of three elements is far more complex to systemically study than similar electrochemical activities in the binary material. Although this could be a significant challenge, insight into and clarification of the fundamental insertion reaction mechanisms in the polyanionic materials are important steps toward enabling rational material design for advanced energy storage applications. Therefore, we use operando pair distribution function (PDF) and electrochemical methods to elucidate the initial lithium intercalation reaction and a combination of various ex situ characterization techniques to identify the subsequent conversion reaction pathways.

RESULTS AND DISCUSSION

Material Synthesis and Structure. Solid-state chemical synthesis was performed using elemental precursors in stoichiometric ratios to produce NiPS₃ starting material. Sealed quartz ampules of precursor components were reacted in Ar atmosphere to prevent oxidized products similar to previously reported methodologies.¹⁶ Figure 1 and Figure S1 show the physical and structural characteristics of the assynthesized NiPS₃ material. The phase was first examined by powder X-ray diffraction (XRD). Pawley refinements based on the standard C2/m space group were performed to confirm the purity and determine the lattice parameters.

Pawley refinement was performed due to the large amount of preferred orientation in the (002) direction as evidenced by the high-intensity (002) and (004) reflections and lowintensity (001) reflection. Refinement indicated plate-like orientation by the resulting March-Dollase preferred orientation ratio of 0.40(6), which SEM confirmed as represented in Figure 1a. Because of this, the parameterweighted goodness-of-fit value, $R_{wv} = 18.88\%$, is relatively large (Figure 1b). The refined lattice parameters are as follows: a =5.88(3) Å, b = 10.164(2) Å, c = 6.66(3) Å, and $b = 107.91(8)^{\circ}$. These agree well with previously reported lattice parameters.²⁴ The small uncertainty values in the lattice parameters illustrate a good fit to the C2/m space group. From the lack of impurity peaks, the small uncertainty values in the lattice parameters, and the agreement between the refined lattice parameters and previously reported crystal structures phase purity of the assynthesized NiPS₃ can be concluded.

X-ray photoelectron spectroscopy (XPS) was performed to study the surface chemical composition and bonding configuration. The oxidation states of Ni, P, S, and C were probed. The XPS spectrum in the Ni 2p region (Figure 1c) shows two sets of three peaks at higher (872.1, 876.6, and 882.3 eV) and lower binding energies (854.6, 859.8, and 865.1 eV), corresponding to the $2p_{3/2}$ (854.8 eV) and $2p_{1/2}$ (872.0 eV) core levels of Ni^{2+,27,28} Each of the spin–orbit involves two satellite peaks, which is indicative of the ligand–metal hybridization between the polyanion cluster and transition metal.^{28,29} The characteristic peaks for both the P 2p and S 2p scans show a spin–orbit split doublet into $2p_{3/2}$ and $2p_{1/2}$ orbitals (P 2p $2p_{3/2} = 132.1$, $2p_{1/2} = 132.9$ eV and S 2p $2p_{3/2} =$ 162.5, $2p_{1/2} = 163.7$ eV, respectively), which is consistent with previous XPS measurements on NiPS₃.³⁰

Electrochemical Performance Testing. Galvanostatic profiles and cyclic voltammetry (CV) of the NiPS₃ (mass loading $\approx 1-2$ mg cm⁻²) are shown in Figures 2a and 2b, respectively. The lower cycling potential limit was set to 0.8 V vs Li/Li⁺ to avoid most side reactions involving the reduction decomposition of the electrolyte, which could complicate the chemical analysis of our system.³¹ Also, the formation of the fully reduced transition metal phase (biased potential toward 0 V) is known to be detrimental for the electrochemical reversibility and Coulombic efficiency.³² For the galvanostatic cycling between 3.0 V (open-circuit potential, OCV) and 0.8



Figure 2. Electrochemical characterization of NiPS₃ in 1 M LiPF₆ EC:DMC 1:1 mixture using a half-cell configuration. (a) Initial five galvanostatic charge–discharge curves at a constant current density of 100 mA g⁻¹. (b) Cyclic voltammogram of NiPS₃ cycled between 0.8 and 3.0 V at a sweep rate of 0.1 mV s⁻¹. Cycles 1, 2, and 5 are shown. (c) Capacity and Coulombic efficiency per cycle obtained from the galvanostatic cycling. (d) Impedance spectra of NiPS₃ electrodes at various cycles. Each data set was fit by using an equivalent circuit shown in the inset.

V, the first discharge curve exhibits a distinct, flat plateau at 1.9 V, characteristic of a two-phase reaction. After the initial plateau, a voltage drop is observed followed by another nearly plateau-like curve at 1.4 V until about four Li-ions are inserted per formula unit. Then the voltage sharply drops to 0.8 V with further insertion of Li-ions. The specific capacity observed from the first cycle down to 0.8 V is 871 mAh g^{-1} , which corresponds to insertion of six Li-ions. As for the deinsertion of Li-ions, a plateau-like curve at around 2.0 V was observed, and the voltage profile is reversible for a limited number of cycles (80% initial capacity at cycle 5). After the first cycle, the discharge voltage plateau at 1.9 V disappears. It is typical for the first discharge plateau of conversion materials to differ from the first cycle in subsequent discharges.³² This irreversible behavior, in general, has been attributed to the formation of many nanoscale domains and of new interfaces during the first discharge.³³ The disappearance of the 1.9 V plateau in the NiPS₃ discharge curve appears to depend on the current density at which the cell is cycled, and this has been addressed in the previous literature.³⁴

A cyclic voltammogram with a sweep rate of 0.1 mV s⁻¹ reveals two cathodic peaks at 1.75 and 1.1 V and broad anodic peaks around 2 V from the first cycle. The cathodic peak at 1.75 V disappears for subsequent cycles, and all remaining cathodic peaks become less pronounced. Based on the current response from CV measurement, about six Li-ions are inserted in the potential range between 0.8 and 3.0 V, which is in good agreement with galvanostatic experiments. Charging and discharging of NiPS₃ in this potential range confirms to be a multielectron process involving the redox of the Ni²⁺ cation and (PS₃)^{2–} anion based on the large voltammetric current responses.

Similar to typical lithium-sulfur and other conversion-based electrode cells, unsatisfactory capacity retention and poor longterm cyclability are observed (Figure 2c). Over the period of 50 cycles, a steady decrease in discharge capacity occurs. The gravimetric capacity upon the fiftieth discharge is 236.25 mAh g^{-1} , which corresponds to about 30% capacity retention. Figure S2 compares the Li-ion charge storage of NiPS₃ at C-rates ranging from C/5 to 2C. As expected, NiPS₃ materials demonstrate fair rate capability over the 0.8-3.0 V (vs Li/ Li⁺) range, reaching gravimetric capacities of 528.9 and 287.8 mAh g^{-1} at 1*C* and 2*C*, respectively. The initial electrochemical results, such as poor long-term performance and sluggish insertion kinetics, show archetypal characteristics of the conversion-based Li-ion storage mechanism that accompanies a large volume expansion of electrode materials during the discharge/charge process. Analysis of electrochemical impedance spectroscopy measurements suggests consistent series resistance at 3 V for 50 cycles, which is indicative of stable SEI in the operating voltage window. This observation also suggests that the poor long-term cyclability is not due to the degradation of the electrolytes or growth of the solidelectrolyte interphase layers but is likely due to the decomposition of the NiPS₃ active material.

Local Structural Changes during the Intercalation Process. For the layered materials with a viable transition metal redox center, electrochemically inserted Li-ions are preferably stored in the van der Waals gap.³⁵ Traditionally, monitoring the lithium intercalation in the layered structure has been done via X-ray diffraction by looking at the peak shifts/evolution accompanying structural changes or expansion in the interlayer spacing.³⁶ However, in the case of MPX_3 materials, the absence of structural changes upon lithium insertion in the intercalation region makes the characterization trickier compared with other layered hosts. To this end, operando total scattering with PDF analysis is used to reveal the local environments and short-range ordering of NiPS₃ upon Liion insertion. PDF analysis has previously been demonstrated to be an invaluable method for discerning local structure evolution of as-prepared active materials and cycled products.^{2,5,8,37,38} Operando PDFs have revealed chemical moieties that have illuminated Li-ion insertion mechanisms that contained dual modes of intercalation and conversion.³

To probe the local structural evolution, operando PDF of a cycling NiPS₃ cell was collected at a rate of 40 mA g^{-1} over the first nine cycles. The electrochemical voltage range was selected such that NiPS3 was subjected to reversible insertion/deinsertion of less than 1 mol of Li⁺ to avoid any conversion reactions beyond the intercalation regime. Despite an initial claim over the theoretical intercalation limit of x = 1.5(Li_xNiPS₃), previous ex situ XRD and NMR studies suggested the appearance of a second crystalline phase and change in its magnetic property around or before x = 1, which is indicative of the beginning of new phase evolutions.^{39,40} It should be pointed out that the electrochemical cycling results obtained during the operando measurement exhibit a highly polarized gravimetric voltage signature. This electrochemical response has been attributed to the low electrical conductivity of NiPS₃ compound $(\sim 10^{-9} \text{ S cm}^{-1})^{41,42}$ and high mass loading electrode (16.9 mg cm^{-2}) required to obtain an adequate signal for the total X-ray scattering experiments.^{8,43} The limited lithiation of NiPS3 over the similar voltage window has also been observed in an all-solid-state system and was



Figure 3. (a) Overlay of extracted PDFs across nine cycles from charge at 3.0 V and discharge at 1.0 V vs Li/Li⁺ demonstrates minimal changes in local structure, up to 4.5 Å, for NiPS₃. (b) Structure of the multilayer NiPS₃: side view (left) and top view (right). (c-f) Stability of the layered structure. Phase transformation occurs as the amount of Li increases. (c) $Li_{0.625}NiPS_3$, (d) $Li_{0.75}NiPS_3$, (e) $Li_{0.875}NiPS_3$, and (f) $LiNiPS_3$. Colors: green = Li, yellow = S, blue = P, and gray = Ni.

attributed to the low active material electrical conductivity and high interfacial resistance.⁴⁴

An interesting observation here is that for the intercalation regime of NiPS₃ the PDF does not change over the period of six lithiation/delithiation cycles. Previously, ³¹P NMR of NiPS₃ demonstrated the unchanging peak center and shape for intercalation of x < 0.5 in Li_xNiPS₃, indicating a lack of local structure shift and minimal oxidation state change.^{39,45} Further analysis of this PDF series signals about 0.8 mol of Li has been intercalated with minimal structural changes up to 4.5 Å, indicating the avoidance of conversion reactions or phase transition, occupying possible Li-ion intercalation sites (2d, 4h, 8j, 4h, 2c, 4i) (Figure 3a and Figure S3). The local structure can be retained as previously proposed by Chianelli and Dines in which transition-metal trichalcogenides are exfoliated and only lose long-range ordering upon Li-ion intercalation.⁴⁶ From optical spectroscopy (Figure S4), it was observed that smaller crystals formed from striated larger crystals. Given the larger layer spacing of the NiPS₃ structure, the Li-ion is the appropriate size to occupy the octahedral interstices, and the intercalation of Li-ion into these sites would not cause any stress to the crystal structure.²⁰

The intercalation process of Li-ions into $NiPS_3$ structure was further investigated via the plane-wave-based density functional theory (DFT) package VASP. As shown in Figure 3b, our simulation cell has 8 Ni atoms, 8 P atoms, and 24 S atoms forming two layers of NiPS₃ with an interplanar distance of

3.389 Å. A vacuum of 20 Å is included to avoid the interaction between periodic images. After relaxation, Li-atoms are incrementally added to the Wyckoff sites, from 5 Li to 24 Li, corresponding to stoichiometries from Li_{0.625}NiPS₃ to Li₃NiPS₃ Despite the certain site preference for Li (Figure S5), the Li-atoms are not assigned to those favorable sites due to possible interactions between them, especially at higher concentrations. Instead, a Monte Carlo method is used to determine the favorable configuration for each composition.^{47,48} First, the simulation cells are constructed for a given concentration with Li-atoms randomly occupying the Wyckoff sites. Next, the atomic positions of a Li-atom and a vacant Wyckoff site are swapped, both of which are randomly chosen. Then the energy change associated with this Monte Carlo move ΔE is calculated, and this move is accepted with a probability $p = \min\{1, \exp(-\Delta E/k_{\rm B}T)\}$. Finally, this process is repeated until convergence has been reached. During the Monte Carlo steps, the atomic positions are not allowed to relax. After finding the favorable Li sites, these atoms are relaxed in search for the ground state. As can be seen in Figure 3c-f, both Li_{0.625}NiPS₃ and Li_{0.75}NiPS₃ maintain the layered structures without any phase transformation. Starting from Li_{0.875}NiPS₃, significant distortion is observed. As the concentration of Li reaches x = 1 (LiNiPS₃), the layered structure breaks down and excessive Li-atoms are ejected out of the central plane, suggesting a phase transition should take place at higher concentrations of Li. This is consistent with the



Figure 4. (a) Charge–discharge curve for the first cycle. Cells for the *ex situ* measurements were cycled to the potentials indicated. (b) *Ex situ* XRD patterns showing the evolution of crystalline phases upon lithium intercalation/deintercalation. (c) *Ex situ* Raman spectroscopy of NiPS₃ electrodes at various states of charge/discharge. *Ex situ* XPS spectra of (d) C 1s, (e) P 2p, (f) Ni 2p, and (g) S 2p. The general trend is observed that upon lithium insertion the Ni 2p and S 2p peaks shift toward lower binding energies while P 2p lines shift toward higher binding energies.

experimental results that phase transition happens for about 0.8 mol of lithium intercalation.

Two possible explanations for the limited intercalation behavior are the low oxidation state of the Ni d-band center and the thermodynamic instability of sulfide-based materials. The available valence state of Ni upon Li insertion is +1 or 0, given that the host NiPS₃ starts with Ni(II). Although Ni(I) is attainable, thermodynamically stable Ni(I) compounds have been exclusively seen in a highly coordinated bonding environment with organic moieties.⁴⁹ In addition, a recent computational study has shown that, generally, the thermodynamic driving forces for conversion reactions are higher than those for intercalation reactions in sulfides.⁵⁰ Both of these factors are unfavorable in accommodating a large amounts of cations and facilitating potential structural lattice reconstruction to reduce intercalation-induced stress.

Chemical and Phase Evolution during the Conversion Reactions (x > 0.8). With continuous lithium insertion beyond x = 0.8, substantial structural and chemical evolutions were observed from *ex situ* XRD, XPS, Raman, electron energyloss spectroscopy (EELS), and high-resolution transmission electron microscopy (HRTEM). For *ex situ* characterization, samples were prepared just prior to measurements and without any exposure to air to minimize changes of the material between cycling and measurements. The discharge–charge curves for the first cycle are shown in Figure 4a and are marked at each point a cell was prepared for *ex situ* measurements.

The *ex situ* XRD patterns of the NiPS₃ electrode during the first lithiation and delithiation of an ~1–2 mg cm⁻² electrode are shown in Figure 4b. In general, the peaks corresponding to the NiPS₃ phase decrease upon lithiation, while two new peaks corresponding to the Li₂S phase appear around 1.6 V ($2\theta = 28^{\circ}$, 31°) and continue to grow until 0.8 V is reached. This

observation indicates that the NiPS₃ phase is electrochemically converted into decomposition products including Li2S and other noncrystalline phases when the cell is discharged below 1.6 V with the insertion of 1.5 Li-ions. The formation of the Li₂S phase as well as the large capacity obtained from electrochemical measurements confirms that lithiation of NiPS₂ in this voltage range is a multielectron process involving redox activities of both cations and anion. At 0.8 V, there is an absence of Bragg diffraction corresponding to the parent NiPS₃ C2/m phase with all peaks corresponding to Li₂S (Figure S6). This electrochemical conversion process appears to be partially reversible during delithiation, as evidenced by the recovery of NiPS₃ peaks in the XRD spectra. However, the small peaks corresponding to the Li₂S phase remained at the end of the first cycle, confirming the partial irreversibility. The amorphization process upon Li insertion beyond the intercalation limit makes it problematic to gain a crystallographic understanding of the structural evolution of NiPS₃. However, the presence of Li₂S and amorphous thiophosphate-based compounds suggests that the likely pathway for decomposition reactions revolves around the formation and transformation of Li thiophosphate glass ceramics. Detailed investigations into the structural evolution of the possible thiophosphate units and the local bonding environment could illuminate the conversion reaction mechanisms related to the multielectron redox process. To this effort, ex situ Raman spectroscopy was performed at various states of charge to probe crystal structures and intermediate species from molecular vibrations.

In pristine NiPS₃, the thiophosphate anion $P_2S_6^{4-}$ forms ethane-like polyhedra with a P–P bond. The Raman spectrum (Figure 4c) of as-prepared NiPS₃ is consistent with previously reported literature⁵¹ and shows strong E_g doubly degenerate modes with 514 nm excitation. The high-frequency peak at 133

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Figure 5. *Ex situ* EELS of (a) P L-edge, (b) S L-edge, and (c) Ni L-edge spectra. The EELS spectra provide insight concerning the electrochemical reversibility of the conversion process. HRTEM images and corresponding Fourier Transformations of (d) pristine NiPS₃ (e) after Li-ion insertion at 0.8 V and (f) after 1 cycle at 3 V.

cm⁻¹ has been attributed to translational motions of Ni²⁺ cation,⁵² but all other peaks in the frequency range correspond to PS₃²⁻ anions. Upon lithiation, all Raman bands assigned to motion of Ni^{2+} and PS_3^{2-} from NiPS₃ disappear, and a number of peaks around 300 and between 380 and 500 cm⁻¹ emerge. Discharging to 1.6 V, notable peaks centered at 375, 410, and 435 cm^{-1} appear. These peaks are signatures of the E2, A1, and E3 symmetry species of the P-S bond and confirm the formation of other thiophoshate compounds consisting of PS_4^{3-} and $P_2S_7^{4-}$ polyhedra as a result of lithium insertion. ⁵³⁻⁵⁵ In particular, a lack of T_2 P=S groups (685) cm^{-2}) and a sharp A P=S mode (715 cm^{-2}) at 1.6 V suggests that the phosphorus sulfur compounds are still sulfur-rich in nature with the sulfur to phosphorus ratio below 1. Further lithiation below 1.6 V induces the active formation of Li₂S with sulfur reduction (evidenced by both XRD and Raman results), and correspondingly, phosphorus-rich polysulfidophosphate groups are formed. The destabilization of the anion structure and the cleavage of bonds upon substantial Li-ion insertion have also been predicted by our Monte Carlo simulation. With the continuous insertion of up to x = 2 and 3 in Li_xNiPS₃, the $P_2S_6^{4-}$ hypo-thiophosphate anion structure is significantly distorted, and the P-S bond is subsequently broken (Figure S7).

Considering reported Raman spectra in the literature of chemically lithiated Li_xNiPS_3 , the chemically and electrochemically lithiated NiPS_3 produced drastically different spectra (Figure 4c).⁵² The primary reason for this is that the driving force of chemical lithiation is considerably lower than that of electrochemical lithiation so that it does not induce formation of new phases.⁵⁶ The maximum amount of Li-ions intercalated via chemical lithiation was $\text{Li}_x \text{NiPS}_3$, x = 1.16 mol equiv. These chemically intercalated Li-ions occupy the vacant sites within the 2D layer. It was reported that the Raman normal mode positions were not shifted upon chemical lithiation, although a considerable decrease in intensity was observed.⁵² This finding further confirms that the electrochemical lithiation process leading to complete disappearance of the normal mode peaks must involve the decomposition of the starting material and the formation of new phases, such as phosphorus sulfides.

One interesting phenomenon that has been captured by the Raman spectroscopy is that upon delithiation the bands attributed to decomposition products still dominate the Raman spectra, and the normal modes for pristine NiPS₃ do not recover, suggesting that this process is not completely reversible. Polysulfidophosphate groups with P₄S_{10+n} compositions are in general decent Li-ion battery active materials with redox potentials above 2.0 V.^{54,57} Because our system lacks significant electrochemical redox activity above 2.0 V, the phosphorus- and sulfur-based decomposition products are likely partially reduced inorganic phosphides (i.e., Ni_xPS_y, $Li_x PS_y$). It is important to note that partially reduced phosphide intermediates could be good ionic conductors, but many of these compounds are electrochemically inactive and are used most often as a solid electrolyte in Li-ion batteries.^{58,59} This mechanism correlates well with the irreversibility in the Raman spectra and electrochemical capacity fade observed in our system.

X-ray photoelectron spectroscopy (XPS) has been performed on cycled electrodes to further identify and elucidate redox activities during the first cycle (Figure 4d-g). The evolution of the XPS spectra core peaks was recorded at various degrees of lithiation (1.6 and 0.8 V) and delithiation (2.0 and 3.0 V). Upon lithium insertion, both Ni $2p_{3/2}$ and 2p1/2 peaks shift toward lower binding energies, and the intensity of the $2p_{3/2}$ and $2p_{1/2}$ satellite peaks is decreased, suggesting a change in the Ni 3d electron configuration. This reveals that the Ni²⁺ in the NiPS₃ starting material undergoes a multistep reduction process. The Ni²⁺ shows signs of partial reduction at 1.6 V, and the partial reduction continues with deep discharge (0.8 V vs Li/Li⁺). The formation of heterogeneously reduced, near-amorphous transition metal has also been observed in other conversion material systems at the end of their first discharge.^{60,61} Upon delithiation of NiPS₃ at 2.0 V vs Li/Li⁺, the Ni 2p spectrum is comparable to the pristine material with a Ni²⁺ oxidation state and remains constant throughout the remainder of the delithiation process to 3.0 V vs Li/Li⁺. Because of the near-surface sensitivity of XPS, the complete dynamics of conversion reactions cannot be captured as the Ni oxidation proceeds into the bulk of the material.

Similarly, for the $(P_2S_6)^{4-}$ cluster, it has been observed that the P 2p core-level shifts toward higher binding energies, while the S 2p peak shifts toward lower binding energies with the insertion of Li-ions. In previous literature, this trend is attributed to a charge redistribution around these atoms, as occurs in conversion reactions, due to the Li insertion and subsequent Ni reduction.⁶² Specifically, one reason for the shift in S 2p peak position is that during the formation of Li₂S a higher net charge is distributed on the sulfur anions. Also, for these elements, upon the delithiation at 2.0 and 3.0 V, the spectra trends similarly to the pristine material. Overall, the reversibility of Ni, P, and S oxidation and reduction has been observed through XPS of elements during the first cycle.

To further probe multielectron redox processes in the key elements, their composition and local coordination effects with other elements were analyzed by using ex situ EELS for the P, S, and Ni $L_{2,3}$ -edges (Figure 5a-c). The trend in EELS $L_{2,3}$ edge observations is consistent with earlier XPS results in that the energy-loss near-edge structure (ELNES) evolution based on elemental composition, local bonding, and oxidation state changes upon charging/discharging is reasonably reversible for all three elements. The changes in the ELNES fine structure may come from (1) the electron count around elements that affects the white line intensity, mirroring the unfilled densityof-states above the Fermi energy and/or (2) the point group symmetry, for which any distortion or lowering of the point symmetry will result in a lifting of the degeneracies in the unoccupied molecular orbitals and in peak broadening with additional orbital options for the electrons to excite into.⁶³

One interesting observation here is that the change in the ELNES fine structure for P, S, and Ni is significant when the discharge voltage reaches 1.6 V, indicating these redox centers likely experience considerable valence changes and/or local structural distortion with the insertion of only 1.5 Li-ions. In particular, the P $L_{2,3}$ -edge fine structure for the pristine material starts with P in a symmetric environment with tetrahedral point symmetry based on the thiophosphate anion structure. With Li-ion insertion, lowering of the intensity of the peak at 138 eV and increase in the pre-edge tail were evident in the 1.6 and 0.8 V spectra. This behavior can be attributed to both the redox reactions around phosphorus and distortion in the local point symmetry as predicted by earlier simulation result (Figure S7).^{64,65} The re-emergence of the peak around

168 eV in the 2.0 and 3.0 V spectra during charge is consistent with a return to the more symmetric tetrahedral point symmetry and the initial valence state, suggesting that the process is partly reversible.

To support these spectroscopic observations, the theoretical EELS spectra with varying amounts of Li-ions were calculated based on the atomic positions of Li_xNi₈P₈S₂₄ structures as predicted by the plane-wave-based DFT coupled with a Monte Carlo method.⁶⁶ The EELS P L-edge fine structure simulations, as shown in Figure S8, indicate the same trend in peak shift, displaying reduction in the intensity of the lowenergy peak and increase in the pre-edge tail with higher degree of lithiation. Overall, the calculation result matches with the experimental peak features, confirming that the evolution in experimental P L-edge EELS data was primarily due to the distorted structures and loss of local symmetry. In the case of the S $L_{2,3}$ -edge, the emergence of more dominant fine structure in the 1.6 and 0.8 V discharge spectra is attributed to the formation of Li_2S that exhibits higher point symmetry around the S compared to the pristine $NiPS_3$.⁶⁷ This result agrees well with what we observed in XRD and in electron diffraction that the partial conversion of Li2S has been observed upon the initial lithiation below 1.6 V.

With the Ni $L_{2,3}$ -edge, the dominant effect altering the fine structure is the presence of a core excitation, which continues to be reduced with Li-ion insertion based on the correlation between the higher L_3 and L_2 ratio.^{68,69} As with the S and P EELS spectra, the local environmental changes around Ni also appear to be partly reversible with the lithiation–delithiation process.

Overall, during the electrochemical cycling in the conversion region, a decent degree of reversibility has been evidenced based on structural evolution, key element valence state transitions, and changes in molecular symmetry from XRD, XPS, and EELS techniques. The Li-ion reaction mechanism of NiPS₃ during the first insertion–deinsertion process between 0.8 and 3.0 V (vs Li/Li⁺) can be described as follows:

$$x \text{Li}^+ + x \text{e}^- + \text{NiPS}_3 \rightarrow \text{Li}_x \text{NiPS}_3 \quad (x \le 2)$$
 (1)

$$x \text{Li}^{+} + x \text{e}^{-} + \text{Li}_{2} \text{NiPS}_{3} \rightarrow \text{Li}_{2} \text{Ni}_{1-\delta} (\text{PS}_{3})_{1-y} + \text{Li}_{2}$$

$$(\text{PS}_{1+n})_{y} + \frac{x-2}{2} \text{Li}_{2} \text{S} + \delta \text{Ni}^{0}$$

$$\left(2 < x < 6; \ 0 \le y \le 1; \ n = 3 - \frac{x-2}{2}\right)$$
(2)

$$x \text{Li}^{+} + x \text{e}^{-} + \text{Li}_2 \text{NiPS}_3 \rightarrow \text{Li}_3 \text{PS}_{4+n} + \frac{x-1}{2} \text{Li}_2 \text{S} + \text{Ni}^0$$

(2 < x < 4) (3)

The Fourier transform of HRTEM images (Figure 5d–f and Figure S9) intriguingly provide further evidence for the formation of the crystalline parent NiPS₃ phase after cycling. However, the irreversible nature of conversion reactions was also observed from the Raman vibrational modes and poor electrochemical cyclability. The discrepancy can be reconciled by the nanoscale chemical inhomogeneity produced from electrochemically driven conversion reactions. The HRTEM images highlight significant morphological changes after cycling with regions of crystalline NiPS₃ and other amorphous phases. Because of incremental chemical inhomogeneity that develops every cycle, the pristine material is amorphized and

decomposed to form electrochemically inactive species upon continuous charge/discharge process (Figures S10 and S11). Figure 6 summarizes the structure and phase evolution of NiPS₃ undergoing a series of complex redox reactions upon insertion/deinsertion of Li-ions.



Figure 6. Galvanostatic profile with chemical species representing the redox processes occurring during the first discharge/charge cycle of NiPS₃.

CONCLUSION

In this study, we illuminate the lithiation process in NiPS₃ polyanionic materials, which undergo two-step intercalation and conversion reactions, sequentially. PDF and DFT Monte Carlo molecular dynamic simulations revealed that the lithium intercalation without phase transition occurs up to about 0.8 mol of Li per NiPS₃ unit, occupying the thermodynamically favorable Wyckoff sites. With continuous Li-ion insertion, the P-S anion structural backbone is destabilized, and the crystalline NiPS₃ host phase subsequently undergoes conversion reactions to form binary and ternary chemical moieties based on Li, Ni, P, and S. Our findings have revealed chemical and structural reversibility in the macroscopic representation of the electrochemical intercalation and conversion process occurs in NiPS₃ but have also successfully captured nanoscale inhomogeneity and formation of electrochemically inactive species that lead to poor long-term behavior. These findings highlight an important aspect of mechanistic studies that a combination of multiple characterization techniques is essential in capturing the complex chemical dynamics during electrochemical reactions. Insights into the electrochemical reaction mechanism, which might be common among phosphorus sulfide materials, should be helpful in the design of novel phosphorus and sulfur anion-based electrode materials.

EXPERIMENTAL SECTION

Lab X-ray diffraction was performed by using a P'analytical Empyrean. Refinement was performed by using GSAS-II.⁷⁰ The Pawley refinement was performed over a Q range of 0.38–4.83 Å⁻¹ with a Pawley negative weighting factor of 0.001. Parameters that were refined included (1) lattice parameters, (2) sample displacement, (3) March–Dollase preferred orientation ratio, (4) peak shape, (5) peak position, (6) peak intensity, (7) background Chebyshev coefficients of degree eight, and (8) histogram scale factor separate from Pawley intensity refinement. Refinements utilized the following CIF file: ICSD-602341. SEM was performed by using an FEI Nova 230 Nano system. Half-cell galvanostatic cycling and cyclic voltammetry from 0.8 to 3.0 V at a current density of 100 mA g⁻² and sweep rate of 0.1 mV s⁻¹, respectively, were performed. Electrochemical impedance spectroscopy between 1 MHz and 100 mHz using a 10 mV amplitude

and bias at 0 V versus open circuit was performed periodically. Carbon Black Super P (+99%, Alfa Aeser), styrene-butadiene rubber (SBR, MTI Corp.), and carboxymethylcellulose (CMC, DOW Chemical) were used without further processing. Electrode slurries were made with 80 wt % active material, 10 wt % Super P, and 10 wt % CMC/SBR (4:6) dispersed in deionized water and doctor bladed onto a stainless-steel foil. Mass loading of the electrodes was typically 1.5–2 mg/cm² with a film thickness of approximately 30–40 μ m. Raman spectroscopy was performed by using a Renishaw inVia confocal Raman microscope. The analysis was performed with a 514 nm Ar laser and 1800/mm grating through a 20× objective lens. XPS using a Kratos Axis Ultra with a monochromatic aluminum X-ray source was performed on the pristine NiPS3 after dispersing from a methanol solution. The cycled electrodes were prepared by imposing the potentiostatic hold at a specified voltage for 30 min and transferred by using an inert-atmosphere chamber. Charge calibration was performed based on the adventitious carbon peak. Microstructural analysis was performed by using the scanning-TEM (STEM) mode on a JEOL 2100 field emission TEM, equipped with a high-resolution pole piece, and direct detection electron energy loss spectroscopy (EELS). X-ray absorption near edge structure (XANES) spectra were calculated by using FDMNES software. The atomic coordinates of lithiated NiPS3 compounds were obtained from the DFT calculations.

For the computational effort, the plane-wave-based density functional theory package VASP was used to investigate the intercalation limit of Li.⁷¹ The ion-electron interactions are described by using the projector augmented wave pseudopotentials,⁷² and the exchange correlation functionals are treated within the generalized gradient approximation by Perdew, Burke, and Ernzerhof with a cutoff energy of 364 eV.73,74 An on-site replacement of the exchange correlation functionals is necessary for the accurate description of the ground state because of the strongly correlated d electrons of nickel. Here the formalism by Dudarev is implemented with a Coulomb interaction parameter U of 7.15 eV and the interaction exchange parameter J of 0.95 eV.⁷⁵ The valence electron configurations are $3d^84s^2,\;3s^23p^3,\;3s^23p^4,$ and $2s^1$ for nickel, phosphorus, sulfur, and lithium, respectively. A Monkhorst–Packk-point mesh of $6 \times 4 \times 2$ is used for the integration in the Brillouin zone.⁷⁶ The relaxation convergence criteria are 10^{-6} and 10^{-4} eV for electronic steps and ionic steps, respectively. A correction term from the DFT-D2 method by Grimme is also included to account for the long-range van der Waals interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c19963.

Experimental data and analyses, including Figures S1–S11 and Table S1 (PDF)

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Author Contributions

C.C. conducted electrochemical measurements, X-ray diffraction, and Raman spectroscopy, and analyzed all *ex situ* data. D.A. performed XPS measurements and analysis. E.L. and V.D.N. synthesized NiPS₃ powders. D.B. performed X-ray diffraction. C.E.W. performed Rietveld refinement, assisted in synchrotron data collection, and processed PDF data. E.A. and J.H. collected EELS and electron diffraction data. M.T. supervised TEM experiments. Y.R. and M.G. performed the DFT calculations and analysis. B.S.D. supervised the electrochemical measurements. C.C. and V.D.N. wrote the manuscript. D.A. and D.B. edited the manuscript. V.D.N. conceived of the original idea, supervised the findings of this work, and collected synchrotron X-ray scattering data. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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