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Route of Irreversible Transformation in Layered Tin Thiophosphite and Enhanced Lithium Storage Performance

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ABSTRACT

Novel materials with high lithium-storage capacities are indispensable to substantially increase the gravimetric and volumetric energy densities of lithium-ion batteries. In this context, metal thiophosphites (MTPs) possessing a layered structure are considered as ideal candidates to serve as alkali-ion hosts. Herein, the lithium storage properties of layered tin thiophosphite (SnPS_3) crystals have been investigated in coin-cell configuration. The results reveal that SnPS_3 undergoes a conversion and alloying reaction to deliver high lithiation capacities. The SnPS_3 anode delivered a significant lithiation capacity of $\sim 800 \text{ mAh g}^{-1}$ at a specific current of 100 mA g^{-1} . Moreover, the layered structure was able to accommodate the volume changes upon (de)lithiation as evident from its excellent cycling stability. Additionally, the SnPS_3 anode demonstrated excellent rate capability as well and delivered $\sim 315 \text{ mAh g}^{-1}$ at a high specific current of 2 A g^{-1} . Furthermore, the lithium-storage mechanism was investigated through cyclic voltammetry and *ex-situ* X-ray diffraction and X-ray photoelectron spectroscopy studies. Studies of SnPS_3 anode in a full cell configuration by coupling with commercial $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cathode is also presented. The outstanding electrochemical performance demonstrated by the SnPS_3 anode calls for further research into this novel class of metal thiophosphites for energy storage applications.

TOC

Introduction

Ever since their inception in the 1990's, lithium-ion batteries have been deployed in a myriad of applications ranging from portable devices like mobile phones and laptops to high energy and power expending electric vehicles. In the past decade, the pursuit of novel materials that can deliver higher energy densities than the conventional graphite anode spawned the research on “beyond intercalation” based materials.¹ The primary objective was to develop high energy and high power batteries by making use of alloying and conversion-based materials that offer high gravimetric as well as volumetric energy densities. In this regard, lithium-alloying materials such as Sn, Si, P, among others, are of great interest as they offer manifold lithium storage capacities when compared to the conventional graphite anode.²⁻⁴ Additionally, metal chalcogenides such as MoS₂, TiS₂ and SnS₂ have been intensely investigated as alkali-ion hosts and were found to deliver high storage capacities by means of reversible conversion reactions.⁵⁻⁷ However, the alloying and conversion anodes present the challenges of rapid capacity fading due to the extreme volume changes and the accompanied pulverization and loss of electrical contact.

Metal thiophosphites (MTPs) are an intriguing class of layered materials with diverse tunable electrical, chemical and magnetic properties.⁸ The MTPs have layers of metal and phosphorous atoms sandwiched between the sulfur layers and this layered structure facilitates the intercalation of alkali metal ions. On account of their layered structure, MTPs have demonstrated anisotropic electrical and mechanical properties and additionally, the localization of magnetic

moments in the metal ions has revealed magnetic behavior.⁹ Recently, Du and others, synthesized and characterized monolayers of 2D MTPs and investigated the semiconducting properties. The cleavage energies of the MTPs were calculated and found to be less than that of graphite.¹⁰ Of late, Carmen and group investigated a library of MTPs with several transition metal or p-metal ions for their magnetic and electrochemical properties.¹¹ The oxygen evolution reaction and excellent lithium storage performance of nickel thiophosphite was recently investigated by Raksha and group.¹² Among the various MTPs, SnPS₃ exhibits a monoclinic structure and was previously investigated for its optoelectronic and magnetic properties.¹³⁻¹⁴ Assuming full conversion reaction, SnPS₃ exerts the potential to deliver high lithium storage capability with the formation of Li_xSn and Li_yP phases. Interestingly, Huang and group recently investigated the pseudocapacitive sodium storage of SnPS₃.¹⁵ However, the performance of SnPS₃ as a lithium-ion battery anode was yet to be explored.

Herein, we have grown phase pure SnPS₃ crystals via chemical vapour transport technique with elemental tin, phosphorous and sulphur as the starting materials. The as-grown crystals were used as the active material in conventional battery fabrication technique and evaluated as lithium-ion battery anode. The layered structure was found to facilitate excellent lithium storage with superior cycling stability and enhanced rate capabilities. The lithium storage mechanism was evaluated through electrochemical cyclic voltammetry and *ex-situ* X-ray diffraction and X-ray photoelectron spectroscopy studies. Additionally, preliminary studies of the SnPS₃ crystals were carried out in a full-cell assembly. The study would open the doors for the investigation of similar unexplored materials in the class of metal thiophosphites that would deliver high energy density and long calendar life for a wide range of applications.

Results and discussions

The SnPS₃ crystals were grown via chemical transport route starting from elemental Sn, P and S precursors. (The synthesis process is detailed in Section 1.1 of the Supporting Information.) The as-synthesized SnPS₃ crystals were characterized by powder X-ray diffraction (XRD) to evaluate the phase purity and crystallinity. As shown in **Figure 1**, the Bragg reflections agree well with the monoclinic crystal system in the *P1c1* space group (ICSD-25357) and the sharp diffraction peaks attest the crystallinity of the as-grown sample.¹⁶ The crystal structure of the layered, monoclinic SnPS₃ phase is illustrated in **Figure 1b**. As seen, the Sn and P atoms are sandwiched between the layers of S atoms. Furthermore, the chemical states of the elements were investigated by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum shown in **Figure S1** indicates the presence of the elements Sn, P and S. The high resolution XPS spectra shown in **Figure 1c** has Sn (3d_{5/2}) and Sn (3d_{3/2}) peaks at 486.01 eV and 494.41 eV respectively, with spin orbital splitting of 8.4 eV corresponding to the Sn²⁺ state.¹⁷ The P (2p_{3/2}) and P (2p_{1/2}) peaks were observed at binding energies 130.86 eV and 132.28 eV respectively while the S (2p_{3/2}) and S (2p_{1/2}) peaks at 161.02 eV and 162.35 eV respectively. The XRD and XPS results confirm the formation of phase-pure SnPS₃ crystals.

Figure 1. Phase characterization of SnPS₃ crystals (a) X-ray diffraction pattern of the as-synthesized SnPS₃ crystals (b) Crystal structure of layered, monoclinic SnPS₃¹⁸ (c) High resolution XPS spectra of the Sn, P, and S elements in the crystal.

Furthermore, the morphology of the as-synthesized crystals was observed using scanning electron microscopy and is presented in **Figure S2**. The size of individual segments of SnPS₃ flakes was of the order of micrometers and had uniform elemental distribution of Sn, P and S as evident from the energy dispersive X-ray (EDX) spectrum. The high-resolution transmission electron microscopy (HR-TEM) images (**Figure 2a**) reveals a composition of highly ordered crystalline two-dimensional sheets of SnPS₃. The lattice fringes could be indexed to the (21-3) plane and the corresponding FFT (Fast Fourier Transform) is presented in the **Figure 2b** inset. The bright spots observed in the selected area electron diffraction (SAED) pattern further attest

the crystallinity and matches well with the d -spacing's of the SnPS₃ phase as indexed in **Figure 2c**.

Figure 2. HR-TEM analysis of SnPS₃ crystals. (a), (b) HR-TEM images of a segment comprising of layered SnPS₃ structure. The FFT of the lattice fringes is presented in the inset (b). (c) Corresponding selected area electron diffraction pattern.

The suitability of SnPS₃ to host Li ions was investigated in half-cell configurations in a coin-cell assembly. (The details of the coin cell fabrication and assembly are provided in section 1.3 of supporting information.) The electrochemical performance of SnPS₃ anode is presented in **Figure 3**. The cyclic voltammogram (**Figure 3a**) reveals the initial lithiation and conversion reaction of SnPS₃ occurring at a voltage of ~ 1.65 and 1.2 V vs. Li in the first cathodic cycle.¹⁹ This is followed by small shoulder peaks at ~ 0.7 and 0.5 V vs. Li which could be attributed to the electrolyte decomposition and solid electrolyte formation.²⁰ The cathodic peaks close to 0.26 and 0.15 V vs. Li corresponds to the lithiation of the extruded Sn and P to form Li_{4.4}Sn and Li₃P, consistent with the previous reports on tin and phosphide anodes.²¹ The broad anodic peak at ~ 0.5 V and the small peaks observed in the first cycle at ~ 0.8 , 1.3 , 1.8 and 2.4 V vs. Li corresponds to the de-lithiation reactions. The cyclic voltammograms since the second cycle overlap, which indicate the reversibility and the stability of the layered SnPS₃ anode as lithium-

ion host. Similarly, the potential profiles presented in **Figure S3** indicate a step at ~ 1.7 V followed by a plateau at ~ 1.4 V *vs.* Li, indicative of the conversion reaction of SnPS_3 . Below 1 V *vs.* Li, a sloping voltage profile was observed. Similarly, a sloping potential profile without any characteristic plateau was observed from the second cycle onwards.

Figure 3. Electrochemical performance of SnPS₃ anode for lithium-ion battery. (a) Cyclic voltammogram at scan rate of 0.1 mV s⁻¹, (b) Galvanostatic charge-discharge performance at specific current of 0.1 A g⁻¹ and (c) Rate test at different specific currents.

The galvanostatic charge-discharge (GCD) tests were carried out at different cut-off voltages to enhance the cycling stability of the SnPS₃ anode (**Figure S4**). Additionally, the effect of carboxymethyl cellulose (CMC) binder and the conventional polyvinylidene fluoride (PVDF) binder on cycling performance was also evaluated (**Figure S5**). The GCD performance at the optimized voltage range of 0.2-1.5 V vs. Li is presented in **Figure 3b**. The initial coulombic efficiency was ~38%. However, 95% coulombic efficiency was attained in the second cycle and over 99% since the seventh cycle. The SnPS₃ anode retained a lithiation capacity of 532 mAh g⁻¹ after 100 cycles at a specific current of 100 mA g⁻¹. This performance is comparable and even superior to some of the recent reports on ternary chalcogenides for lithium storage (**Table S1**). The layered SnPS₃ also exhibited excellent high-rate performance as seen in **Figure 3c and S6**. The anode delivered a noteworthy lithiation capacity of ~315 mAh g⁻¹ at a high specific current of 2 A g⁻¹. This demonstrates the ability of the layered SnPS₃ structure to efficiently facilitate the lithium-ion and electron transport even at high current fluxes.

The (de)lithiation mechanism was investigated through *ex-situ* X-ray diffraction and X-ray photoelectron spectroscopy studies of the lithiated and de-lithiated SnPS₃ anode at various cut-off potentials. The details of the electrode preparations for the *ex-situ* studies are elaborated in our previous reports as well as in the Supporting Information section 1.4.²² The *ex-situ* XRD patterns at different cut-off voltages and the corresponding potential profile are depicted in the **Figure 4**. The initial discharge to 1.2 V vs. Li significantly reduced the crystallinity of the SnPS₃ phase upon the lithiation process. Upon discharge to 0.2 V vs. Li, the broad peaks of poorly crystallized Li_{4.4}Sn and Li₃P were visible.²³⁻²⁴ During the de-lithiation process, the SnPS₃ structure was not recovered but weakly crystallized Sn and P Bragg peaks appeared upon

charging to 1.5 V vs. Li.²⁵⁻²⁶ This amorphous Sn and P are electrochemically active in the subsequent (de)lithiation cycles.

Figure 4. Investigating the lithium-storage mechanism (a) *Ex-situ* X-ray diffraction patterns of SnPS_3 anode at different cut-off voltages (b) Voltage profile of SnPS_3 anode (c) *Ex-situ* XPS of SnPS_3 anode at lithiated and delithiated states.

The *ex-situ* XPS spectrum of lithiated and delithiated SnPS_3 anode is presented in **Figure 4c**. Upon lithiation, the Sn (3d) peaks shifted to lower binding energies, indicating a lowering of the oxidation states which is expected due to the formation of Li_xSn phases.²⁷ The P (2p) peaks of lithiated phase nearly vanished, however, in the delithiated electrode, the peak close to ~130.25 eV suggests the presence of elemental phosphorus in the electrode.²⁷⁻²⁸ No major shift in the S (2p) peaks was observed, probably indicating the formation of Li_2S .²⁹

From the cyclic voltammetry and *ex-situ* XRD and XPS investigations, the reaction mechanism of SnPS₃ towards lithium can be described as follows:

Initially, Li intercalation into the SnPS₃ structure occurs as:

In addition to the formation of Li₂S, the first lithiation involves the extrusion of Sn and P culminating in the alloying reaction to form Li_xSn and Li_yP phases.

The subsequent reversible reaction is the alloying and dealloying of Sn and P as:

The excellent electrochemical performance of SnPS₃ anode motivated us to further investigate the performance in full cell configurations. Commercial cathode, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (LNMC) was coupled with the SnPS₃ anode. The cyclic voltammogram revealed the (de)lithiation peaks in the voltage range 2.5-4.8 V. The preliminary results seem promising as the full cell delivered over 92% coulombic efficiency for over 160 cycles (**Figure 5**). However, the capacity retention was poor (**Figure S7**) and needs further optimization of the anode to cathode mass ratios.

Figure 5. Full cell configuration with LNMC cathode and SnPS_3 anode (a) Schematic diagram (b) Cyclic voltammogram at 0.1 mV s^{-1} between 2.5-4.8 V (c) Coulombic Efficiency of the full cell

Conclusion

In conclusion, we have successfully synthesized high-purity, layered SnPS₃ crystals by chemical vapor transport technique and investigated its electrochemical performance as alkali-ion host. The layered SnPS₃ demonstrated excellent lithium storage performance and was found to accommodate the volume changes upon (de)lithiation as evident from the superior cycling stability. The SnPS₃ anode delivered ~800 mAh g⁻¹ lithiation capacity at a specific current of 0.1 A g⁻¹ and a noteworthy ~300 mAh g⁻¹ at a high specific current of 2 A g⁻¹. Furthermore, the mechanism of lithium storage was elucidated through cyclic voltammetry and *ex-situ* X-ray diffraction studies. The SnPS₃ anode was found to undergo a conversion and alloying reaction mechanism towards lithium storage. Preliminary full cell studies showed promising electrochemical performance with high coulombic efficiency. The study demonstrates the suitability of metal thiophosphites as alkali-ion hosts and calls for more research into this novel class of materials for electrochemical applications.

ASSOCIATED CONTENT

Supporting Information. A Supporting Information is available for this manuscript. Details of electrode preparation, electrochemical characterization and morphological analysis of active materials are incorporated.

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