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Electrochemically induced amorphization and unique lithium and sodium storage pathways in FeSbO₄ nanocrystals

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KEYWORDS

conversion anode, alloying anode, operando XRD, batteries, FeSbO₄, lithium, sodium

ABSTRACT

The increasing energy demands have prompted the research on conversion and alloying materials offering high lithium and sodium storage capacities. However, most of these materials suffer from huge volume expansion and degradation over the thousands of charging and discharging cycles required for commercial applications. In this study, we demonstrate a facile route to synthesize FeSbO_4 nanocrystals that possess theoretical lithium and sodium storage capacity of 1220 mAh g^{-1} . *Operando* X-ray diffraction studies reveal the electrochemically induced amorphization of the nanocrystals upon alkali-ion storage. We achieved specific storage capacities of $\sim 600 \text{ mAh g}^{-1}$ for lithium and $\sim 300 \text{ mAh g}^{-1}$ for sodium respectively. The disparity in the lithium and sodium electrochemistry arises from the unique lithiation/sodiation pathways adopted by the nanocrystals. This study offers new insights into the chemistry and mechanism of conversion- and alloying-based energy storage materials that would greatly assist the development of next generation active materials for energy storage.

INTRODUCTION

The indispensability of lithium-ion batteries (LIBs) in our day-to-day lives is evident from their growing use for powering automobiles, their widespread application in portable electronic devices, such as mobile phones and laptop computers, and their potential use in vehicles and for grid storage. However, according to recent reports, lithium reserves are becoming depleted, which has propelled intensive research into low-cost, “beyond-lithium-ion” electrochemical energy storage systems, such as sodium-ion batteries (SIBs).^{1, 2} Although graphite has remained the commercial LIB anode of choice for decades, it has been deemed unsuitable for SIBs.^{3, 4} Moreover, to achieve widespread implementation of renewable energy resources, such as solar, wind and tidal power, the development of low-cost and high-energy-density lithium-ion and sodium-ion batteries is crucial. Nevertheless, progress towards high-capacity lithium and sodium storage materials (commonly referred to as conversion and alloying materials) and their commercial implementation have not rapidly advanced. For LIBs, silicon has been the ideal choice for a lithium-alloying anode, whereas phosphorous, tin, antimony and germanium are considered prospective candidates for SIBs.⁵⁻⁸ Transition metal oxides and sulfides offering high lithium and sodium storage capacities have been extensively studied for both LIBs and SIBs.⁹⁻¹⁵ However, in addition to the prohibitive cost and toxicity of transition metals, the common challenges that can lead to poor cycling performance for both lithium and sodium alloying and conversion materials include a) high volume-expansion, b) active material pulverization, and c) detachment of active elements from the current collector.¹⁶ Accordingly, the development of both lithium- and sodium-based systems requires extensive research in the field of alloying and conversion materials to further improve performance metrics and thereby meet the demands for

large-scale applications. With a view to meeting these rapidly growing energy needs, such materials should be inexpensive and earth-abundant.

In this context, the selection of such raw materials and the extraction of lithium or sodium storage materials are challenging from both technological and commercial perspectives. While inexpensive carbon-based materials have been explored for both LIBs and SIBs, the low tap density of these materials significantly lowers the volumetric energy densities and thereby forfeit their use in large-scale applications. The rutile-type metal oxide FeSbO_4 (also known as Tripuhyite) was first discovered in the mines of Tripuhy, Minas Gerais, Brazil, and has since been found in several other locations around the world. Remarkably, upon full conversion and alloying reactions to store lithium/sodium, FeSbO_4 can deliver a theoretical capacity of 1220 mAh g^{-1} by forming $\text{Li}_3\text{Sb}/\text{Na}_3\text{Sb}$ phases. However, the lithium storage performance of FeSbO_4 microparticles has only recently been investigated.¹⁷ Despite the large theoretical capacity of FeSbO_4 , the reversible lithium storage capacity so far achieved is only 107 mAh g^{-1} . This was attributed to particle pulverization leading to incomplete lithiation, which is common for micron-sized particles.

Nanostructured materials are known to promote efficient lithium and sodium storage because of their large surface area as well as their increased resistance to pulverization.¹⁸ We rationalized that nano-structuring of FeSbO_4 would promote faster and easier lithium and sodium diffusion and enable the effective buffering of the resulting stresses induced in the material, leading to enhanced cycling stability. Here, we reveal a facile and scalable synthesis technique to yield ultrafine powders of nanosized FeSbO_4 particles. The FeSbO_4 nanocrystals exhibited exceptional lithium and sodium storage capacities of $\sim 600 \text{ mAh g}^{-1}$ and $\sim 300 \text{ mAh g}^{-1}$ respectively with enhanced cycling stability. We observed an electrochemically induced amorphization of FeSbO_4

nanocrystals upon lithium and sodium storage. This amorphization could possibly explain the enhanced cycling stability by effectively buffering the volume changes associated with the alkali-ion insertion and removal. Furthermore, we elucidate the lithiation and sodiation pathways adopted by FeSbO₄ nanocrystals. Our study provides insight into the mechanisms involved in conversion at the anodes; consideration of such mechanisms may be valuable when selecting conversion- and alloying-based materials for alkali-ion batteries.

RESULTS AND DISCUSSIONS

Synthesis and structural characterization of the FeSbO₄ nanocrystals

We synthesized highly phase-pure FeSbO₄ nanocrystals by a facile slurry-mixing technique followed by calcination, as shown in **Scheme 1**. We studied the effect of calcination temperature on the phase purity of FeSbO₄ and confirmed the highest purity yield at 1000 °C (**Figure S1**). Polyvinylpyrrolidone (PVP) acts as a stabilizer, size control agent and prevents the agglomeration of the particles.¹⁹ Hence, nanosized FeSbO₄ particles were synthesized by maintaining a concentration of 0.1 g mL⁻¹ PVP during the calcination process (**Figure S2**). The resulting FeSbO₄ nanocrystals have a rutile-type structure comprising both Fe³⁺ and Sb⁵⁺ cations distributed in the octahedral sites of an oxygen lattice.^{20, 21}

Scheme 1. Synthesis route of FeSbO₄ nanocrystals.

The X-ray diffraction (XRD) spectrum of the synthesized FeSbO₄ powder (**Figure 1a**) is consistent with a *P42/mnm* rutile-FeSbO₄ structure (**Table S1**).²² Sharp and intense Bragg reflections indicate the crystalline nature of the powder, and direct visualization of the crystal structure of the FeSbO₄ nanocrystals was achieved by atomic-scale imaging. The scanning transmission electron microscopy high-angle annular dark-field (STEM HAADF) image intensity provides elemental discrimination with an approximate Z^2 dependence, where Z is the atomic number.²³ A low magnification STEM HAADF image of FeSbO₄ nanocrystals is presented in **Figure 1b**. In **Figure 1c**, the representative large-area STEM HAADF image provides direct evidence of the excellent crystallinity of the FeSbO₄ nanocrystals. Since Fe and Sb randomly occupy the cation sites, such sites are expected to have equal intensities.²⁴ The observed gradual change in contrast is due to thickness variations near the edge of the particle, from which the image has been obtained. Since O has a much lower Z than Sb and Fe, the

contrast of O atomic sites is very low, as seen in the higher magnification image shown in **Figure 1d**. Almost perfect agreement between the experimental STEM HAADF image and the structure model can be seen from the overlay of atoms shown in **Figure 1d**. The simulated STEM HAADF image shown in **Figure 1e** as well as comparison with the model crystal structure in the viewing direction $[3\bar{1}\bar{1}]$, as shown in **Figure 1f, g**, further confirm the observed high-intensity sites as due to Fe/Sb columns.

Furthermore, the morphological features of the FeSbO₄ particles were also studied using high-resolution transmission electron microscopy (HR-TEM). The HR-TEM micrographs reveal the formation of multi-faceted polyhedral-shaped particles ~40–80 nm in size (**Figure S3a**). The FeSbO₄ nanocrystals show lattice fringes with d-spacing values of 0.328 nm (**Figure S3b**) corresponding to the (110) plane of the FeSbO₄ phase, and the selected-area electron diffraction (SAED) pattern (**Figure S3c**) could be indexed to the rutile-FeSbO₄ phase.

Figure 1. Phase and structure of FeSbO₄ nanocrystals. **a**, X-ray diffractogram showing the phase-purity of the synthesized FeSbO₄. **b**, Low magnification STEM HAADF image showing FeSbO₄ nanocrystals. **c**, Large-area raw STEM HAADF image. **d**, Atomic scale STEM HAADF image with the model crystal structure overlaid. **e**, Simulated STEM HAADF image. **f**, Unit cells with the c-axis pointing up in the plane of the paper (top panel) and in the experimental orientation (bottom panel). **g**, View of the model crystal structure in the experimental orientation.

Lithium and sodium storage performance of FeSbO₄ nanocrystals

To determine the lithium/sodium storage performances of FeSbO₄, we carried out cyclic voltammetry and galvanostatic charge-discharge tests in conventional coin cell assemblies with lithium/sodium metal as the counter electrodes. The FeSbO₄/Li cyclic voltammograms show sharper and more distinct peaks than those of the sodium counterpart (**Figure 2a, b**). This result may be attributed to faster lithiation/delithiation kinetics due to the smaller Li ion radius. The first lithiation of FeSbO₄ shows a sharp reduction peak at ~1.25 V vs. Li, which is absent in subsequent cycles (**Figure 2a**). This change can be ascribed to the conversion reaction of FeSbO₄ nanocrystals promoting the structural transformation of FeSbO₄ to a new phase, which appeared to stabilize in subsequent cycles.²⁵ A second reduction peak at a lower potential of ~0.69 V vs. Li is also visible during the first cycle but progressively shifts to ~0.8 V vs. Li from the second cycle onwards. This phenomenon is common for conversion-type anodes because of structural modifications occurring in the first few cycles and the consequent thermodynamic relaxations.²⁶ During the delithiation process, three oxidation peaks are visible at ~1.08, 1.48 and 2.25 V vs. Li. Compared to the previous report on microparticulate FeSbO₄,¹⁷ our FeSbO₄ nanocrystals exhibited sharper current peaks- possibly because of the rapid electrochemical kinetics achieved, which are due to shorter diffusion distances on the nanoscale. Thus, the FeSbO₄/Li cyclic voltammograms reveal the high electrochemical activity of the synthesized FeSbO₄ nanocrystals as well as indicate phase transformations occurring during the initial lithiation cycles.

Figure 2. Electrochemical performance of FeSbO₄. **a-b**, Cyclic voltammogram at 0.1 mV s⁻¹ in **(a)** Li and **(b)** Na half-cells; dotted line depicts first cycle and solid line depicts second cycle. **c-d**, Galvanostatic cycling at **(c)** 0.5 A g⁻¹ versus Li and at **(d)** 0.2 A g⁻¹ versus Na. **e-f**, Galvanostatic cycling at different current rates in **(e)** Li and **(f)** Na.

In the case of FeSbO₄ vs. Na, the first sodiation of FeSbO₄ exhibits a cathodic peak close to 0.3 V vs. Na (**Figure 2b**), which can be attributed to electrolyte decomposition and, analogously to the lithium results, a structural transformation and formation of a solid electrolyte interphase.²⁷ This peak is absent in subsequent cycles; instead, a broad peak at ~0.5 V vs. Na appears, corresponding to the alloying reaction to form Na₃Sb. The anodic peaks at ~0.84 and ~1.34 V vs. Na correspond to the de-alloying reaction and the oxidation reactions, respectively.^{28, 29}

Hence, the cyclic voltammograms suggest high electrochemical activity of FeSbO₄ nanocrystals for both lithium and sodium and indicates notable differences in the reaction routes adopted by FeSbO₄ towards lithium and sodium storage.

We carried out galvanostatic charge-discharge tests to further evaluate the electrochemical performance of FeSbO₄ anode and to assess the cycling stability in lithium-ion and sodium-ion batteries. During the galvanostatic cycling test at a specific current of 0.5 A g⁻¹, the FeSbO₄/Li system (**Figure 2c**) delivered a highly stable capacity close to 600 mAh g⁻¹ for over 1000 cycles, whereas the FeSbO₄/Na counterpart (**Figure 2d**) showed a stable capacity of nearly 200 mAh g⁻¹ for 200 cycles at a specific current of 0.2 A g⁻¹. This difference might arise from the different reaction routes adopted during lithium and sodium storage, which is apparent from the cyclic voltammograms. The potential profiles presented in **Figure S4a, b** are consistent with the cyclic voltammograms and further attest the different lithium and sodium reaction routes for FeSbO₄ nanocrystals. The cycling performances at lower and higher current rates are presented in **Figure 2e, f** and **Figure S4c, d**. The observed capacities indicate that the FeSbO₄ phase could promote storage of up to six moles of lithium and three moles of sodium, respectively. The intriguing difference in the lithium and sodium storage capacities motivated us to further investigate this disparity. We decided to probe the phase transformations occurring in FeSbO₄ nanocrystals upon

lithium or sodium insertion as well as the structural and morphological evolution of the nanocrystals with the anticipation of elucidating the lithium and sodium storage pathways.

Phase transformation and structural/morphological evolution of FeSbO₄ during lithium/sodium storage

Operando XRD studies

Changes in the crystal structure during lithium/sodium storage in FeSbO₄ were traced by operando XRD studies (**Figure 3** and **Figure S5**), which enabled the structural transformations occurring in FeSbO₄ to be visualized throughout lithium/sodium insertion and extraction. Clearly, the (110) peaks of pristine FeSbO₄, observed at $2\theta=27.19^\circ$, shifted by $\sim 0.08^\circ$ and by $\sim 0.054^\circ$ during Li and Na insertion, respectively. Furthermore, the Bragg peaks observed in the pristine FeSbO₄ sample, including the sharp (110) and (101) reflections, seem to completely disappear during lithium/sodium insertion into the FeSbO₄ host structure. Moreover, the FeSbO₄ Bragg reflections did not reappear after extraction of lithium/sodium ions during charging, indicating the formation of a highly disordered amorphous phase. This electrochemically driven solid-state amorphization is possibly a precursor to the conversion reactions and was previously observed in the Li-Si system by Limthongkul *et al.*³⁰, who attributed the amorphization to thermodynamic limitations for the crystallization of intermediate phases during the alloying reaction. However, as a result of the amorphization, we were unable to detect the phase transformations via XRD and opted to understand the thermodynamic processes during lithiation/sodiation by means of theoretical calculations.

Figure 3. Phase evolution of FeSbO₄ nanocrystals during Li/Na storage. Operando XRD patterns collected during (a) lithium and (b) sodium storage in FeSbO₄ anode and the corresponding voltage profiles at a specific current of 30 mA g⁻¹.

Density functional theory calculations

Density functional theory (DFT) investigations on the structural changes of the FeSbO₄ unit cell with varying lithium/sodium concentrations indicate that the ground-state energy of the unit cell decreases monotonically with increasing alkali ion content (**Figure S6a**). However, lithiation appears to be energetically more favorable than sodiation, which is evident from the greater decrease in energy of the unit cell for each additional lithium atom than for each additional sodium atom. The change in volume of the unit cell was also calculated with varying

lithium/sodium content (**Figure S6b**). The change in volume per atom is significantly greater (almost twice as great) for sodiation than for lithiation.

The optimized crystal structure of $\text{Li}_x\text{FeSbO}_4$ (**Figure S7**) indicates that lithium incorporation proceeds in two steps. Initially, at very low Li concentrations ($< 2 \text{ Li}^+$), the Li ions occupy the larger octahedral voids. Upon further incorporation of Li, the crystal structure distorts along the *a*-axis, pushing Sb atoms to the sides of the unit cell, those Sb atoms later being surrounded by Li atoms. After the incorporation of five Li atoms, the system likely undergoes atomic reorganization, which is somewhat difficult to visualize with manual DFT calculations. Nonetheless, at a high concentration of Li atoms, a two-dimensional layer of Li_2O starts to form. Upon further lithiation, Sb atoms are surrounded by Li atoms, resulting in the formation of the Li_3Sb phase, and Fe is coordinated by six oxygen atoms.

The structural changes that occur during Na storage are presented in **Figure S8**. The lower Na storage capacity could be explained by the larger size of the Na ions as well as the irreversibility of the initial conversion reaction forming Na_2O . Only the alloying reaction reversibly forms Na_3Sb , leading to storage of three sodium ions. This could be attributed to kinetic factors involved in the non-equilibrium experimental conditions, which cannot be fully accounted for in the DFT calculations. We were, therefore, compelled to investigate the structural and morphological evolution of the FeSbO_4 particles to further visualize the amorphization processes. We also decided to employ X-ray photoelectron spectroscopy technique to deduce the reaction routes adopted by the FeSbO_4 anode towards lithium/sodium storage.

Structural and morphological evolution during lithium/sodium storage

We carried out an *ex situ* HR-TEM analysis (**Figure 4**) of lithiated and sodiated FeSbO₄ to observe the structural and morphological evolution and further confirm the amorphization upon insertion of Li/Na into the structure. When compared to the pristine FeSbO₄ powder, which was highly crystalline, lithiated/sodiated FeSbO₄ appeared to be highly structurally disordered due to electrochemically driven amorphization upon Li/Na insertion. Furthermore, the diffuse rings observed in the SAED pattern (**Figure 4c, f**) also suggest amorphization.³¹ The evolution of such an amorphous intermediate phase during Li/Na insertion might explain the excellent cycling stability of the FeSbO₄ conversion anode in Li storage: amorphous phases are considered more effective at buffering the associated volume changes compared to their crystalline counterparts.^{32,}
³³ Interestingly, *ex situ* HR-TEM showed the formation of a thick solid electrolyte interphase (SEI) layer (~12 nm thickness) in the sodiated FeSbO₄ particle surface (**Figure 4e**) when compared to the lithiated counterpart. The thick SEI could possibly be the limiting factor for the observed lower sodiation capacities.³⁴ This is further evident from the higher impedance values of the FeSbO₄ anode against sodium when compared to lithium (**Figure S9**). Additionally, the FE-SEM images of the FeSbO₄ electrodes (**Figure S10**) cycled against sodium showed formation of tiny cracks which could explain the comparatively lower electrochemical performance.

Figure 4. Structural evolution of FeSbO_4 during Li/Na storage and the proposed reaction pathways. a and d, *Ex situ* HR-TEM images of lithiated/sodiated FeSbO_4 . b and e, Magnified views showing the highly disordered structure after lithiation/sodiation. c and f, SAED patterns indicating the amorphization of FeSbO_4 nanocrystals. g, Proposed reaction mechanism showing

different reaction routes during lithium/sodium storage leading to a disparity in the electrochemical performance.

Lithium/sodium storage pathways in FeSbO₄ nanocrystals

While the operando XRD and *ex situ* HR-TEM measurements clarified the electrochemically driven amorphization process, the experiments could not explain the different reaction routes adopted by FeSbO₄ towards lithium/sodium storage. Therefore, we extended the study to clarify the different reaction mechanisms of FeSbO₄ towards Li and Na storage by using *ex situ* high resolution X-ray photoelectron spectroscopy (XPS) measurements. The XPS survey spectrum of the as-synthesized FeSbO₄ powder is presented in **Figure S11a**, and the Sb 3d and Fe 2p peaks are shown in the inset. The Sb 3d peaks are comparatively stronger than the Fe 2p peaks, and hence, we used the Sb 3d peaks to gauge the chemical-state transitions to elucidate the reaction mechanism. Pristine FeSbO₄ contained Fe and Sb in the trivalent and pentavalent states, respectively. The lithiated FeSbO₄, however, exhibited a shift of nearly 2 eV in the binding energy of the Sb 3d_{5/2} doublet peak (**Figure S11b**), indicating the transition from Sb⁵⁺ to Sb⁰, which was also observed by Allen *et al.* during FeSbO₄ ammoxidation reactions.³⁵ This observation further confirms the high lithiation capacity observed for FeSbO₄ due to formation of the Li₃Sb phase. Conversely, during the delithiation of FeSbO₄, the Sb³⁺ peak was observed at approximately 529.8 eV, confirming the irreversible conversion of FeSbO₄ during the first cycle.³⁶

The reaction mechanism of FeSbO₄ towards Li storage can be described as follows:

Initial lithiation:

From the cyclic voltammogram as well as the XPS analysis, initial lithiation yields Sb and Fe₂O₃:

Subsequent lithiation/delithiation:

From the second cycle onwards, there is reversible lithiation and de-lithiation of the Sb and Fe₂O₃ phases as follows:

Moreover, the Sb 3d_{5/2} doublet peak for sodiated FeSbO₄ exhibits a shift of nearly 0.3 eV (**Figure S11c**), suggesting the transition from Sb⁵⁺ to Sb³⁺ and indicating the formation of Sb₂O₄. The presence of both Sb³⁺ and Sb⁵⁺ further confirms the presence of Sb₂O₄, which contains Sb in mixed valence states.^{37, 38} Additionally, the broad peak at ~536 eV indicates the formation of Na₃Sb.^{39, 40} However, only up to three sodium ions could be reversibly stored, as observed from the experimental capacity achieved, suggesting that only the alloying reaction proceeds reversibly.

In the case of Na storage, the mechanism can be explained as follows:

Initial sodiation:

The XPS analysis as well as the cyclic voltammogram of the first cycle suggests the formation of Sb₂O₄ phase and Fe as follows:

The Sb peaks observed in XPS upon full sodiation could be explained by the reaction:

Subsequent sodiation/desodiation

Subsequently, only the alloying/dealloying reaction of Sb is reversible according to the following reaction:

To further elucidate the kinetics of Li/Na storage in FeSbO₄, we measured the electrochemical response to increasing voltage scan rates (**Figure S12a, b**). An increase in peak current and peak shifts were observed when the scan rate was increased from 0.1 to 2 mV s⁻¹. The peak current was plotted according to the power law:

$$\log i_p = b \log v + \log a \quad (6)$$

where i_p is the peak current, v is the scan rate, and a and b are constants.

For FeSbO₄ vs. Li, b value of 0.87 was deduced from the slope of the line, whereas for FeSbO₄ vs. Na, b was 0.61 (**Figure S12c**). A value of b close to 0.5 indicates a semi-infinite linear-diffusion-controlled regime, and a value of unity indicates a pseudocapacitive/surface-controlled regime.⁴¹ Hence a higher value of b for FeSbO₄/Li indicates the comparatively faster lithiation kinetics and the comparatively better electrochemical performance. This also implies the

dominance of the faster capacitive reaction processes in FeSbO₄/Li as opposed to the diffusion limitations in FeSbO₄/Na. Hence, the differences in the lithiation/sodiation kinetics further supports the observed differences in the electrochemical performances of FeSbO₄ vs. Li and Na.

Electrochemical performance of FeSbO₄ anode in full-cell configurations

Finally, we investigated the performance of the FeSbO₄ anode in full-cell configurations by coupling the anode with LiCoO₂ and NaVPO₄F cathodes (**Figure 5a**). The cathodes were chosen because of their high capacities and high redox voltages (**Figure S13**) with good cycling stability.⁴² Two commercial red LEDs could be powered by the assembled full cells (**Figure 5b**). Moreover, the LCO/FeSbO₄ full cell cycled at 0.1 A g⁻¹, delivered a capacity of ~200 mAh g⁻¹ anode at an average voltage of 3 V and hence a high energy density close to 600 Wh kg⁻¹ anode (**Figure 5c, d**), while the NVPF/FeSbO₄ full cell cycled at 0.05 A g⁻¹, delivered a capacity of ~283 mAh g⁻¹anode at an average voltage of 2.76 V and, hence, a high energy density of 781 Wh kg⁻¹ anode (**Figure 5e, f**). The full cells also exhibited high coulombic efficiencies over 99% in the galvanostatic cycling tests. We expect that the cycling stability and the energy density could be further improved by further optimizations. Nevertheless, the high coulombic efficiency and high average voltage are at par with the values reported in the literature (**Table S2** and **S3**).

Figure 5. Full-cell performance of FeSbO₄. **a**, Schematic diagram of the coupling of the FeSbO₄ anode with the LiCoO₂ or NaVPO₄F cathode. **b**, Digital photograph showing lit LED powered by the FeSbO₄–LiCoO₂ and FeSbO₄–NaVPO₄F full cells. Voltage profiles of FeSbO₄

anode in half-cell and full-cell configurations in **c**, lithium-ion configuration. **d**, sodium-ion configuration. Galvanostatic cycling performance (capacity, filled circles; coulombic efficiency, open circles) of the full cells **e**, LCO/FeSbO₄ at 100 mA g⁻¹ and **f**, NVPF/ FeSbO₄ at 50 mA g⁻¹, with capacities calculated per unit mass of the FeSbO₄ anode.

CONCLUSION

Through a facile and scalable calcination process, we synthesized novel FeSbO₄ nanocrystals and investigated the lithiation and sodiation mechanisms. The FeSbO₄ nanocrystals were found to undergo an electrochemically driven amorphization process upon alkali-ion insertion. The structural and morphological evolution of the nanocrystals upon lithium/sodium storage revealed unique lithiation and sodiation pathways leading to the disparity in the electrochemical performance. Preliminary investigations carried out on lithium and sodium-ion full-cells making use of the FeSbO₄ anode revealed good lithiation and moderate sodiation performances. The results provide new insights into the fundamental understanding of the mechanism of conversion and alloying anodes to advance the development of future materials for energy storage.

ASSOCIATED CONTENT

Supporting Information Available: Experimental methods and supporting figures and tables.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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