Ni$_3$Sb$_4$O$_6$F$_6$ and Its Electrochemical Behavior toward Lithium—A Combination of Conversion and Alloying Reactions

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ABSTRACT: A group of oxohalides, where Ni$_3$Sb$_4$O$_6$F$_6$ is one example, has been investigated with respect to its electrochemical reactions toward Li$^{+}$/Li. In situ and ex situ XRD measurements reveal that the original structure collapses and the material becomes amorphous upon insertion of Li at low potentials versus Li$^{+}$/Li. With continued cycling, a nanocrystalline phase of NiSb, which reacts reversibly with Li, appears and steadily grows more stable. Electrochemical experiments (i.e., chronopotentiometry and cyclic voltammetry) show that multiple reactions of both conversion- and alloying-type are active in the system. High storage capacities are achieved initially but with rapid fading as a consequence of a limited reversibility of the Ni$^{2+}$/Ni redox process, as shown by X-ray absorption spectroscopy of the first discharge/charge cycle. Stable cycling can be achieved by optimizing the cutoff potentials (i.e., excluding poorly reversible reactions at high and low voltages, respectively), yielding long-term cycling with a practical gravimetric capacity of ~200 mAh g$^{-1}$.

1. INTRODUCTION

A little more than 20 years after their introduction to the market, Li-ion batteries have become completely dominant in fields of portable electronics and are of prime interest for electric vehicles (EVs). This is mainly due to their unrivaled energy densities, high efficiency, and high output voltages compared to other rechargeable power sources. However, because of their relatively high mass and frequent need for recharging as well as limited long-term cycling, they are in many cases still a limiting factor in both design and usage. To fulfill future demands for large-scale applications, further improvements with respect to these areas are required.

Since Poizot et al. presented the possible use of transition metal oxides (TMO), for example, FeO, NiO, and Cu$_2$O as negative electrode materials for Li-ion batteries, considerable research effort has been devoted to exploring this class of compounds, which can offer large storage capacities compared to conventional graphite anodes. Storage of Li in this family of materials is based on the conversion of the TMO into metallic nanoclusters and lithium oxide, according to reaction 1.

$$M_xO_y + 2yLi^+ + 2ye^- \rightarrow xM + yLi_2O$$ (1)

The material converts into metallic nanosized particles dispersed in a matrix of Li$_2$O. If the reduced metal itself is not electrochemically active (e.g., Fe, Cu, etc.), it may serve to enhance conductivity by ensuring electrical contact between particles or by alloying with other elements in the electrode material. If it is electrochemically active (e.g., Sb, Si, or Sn), it alloys with lithium leading to higher theoretical capacities than for graphite. A general way of formulating an alloying reaction is shown in reaction 2, where A is a metal or semimetal that can form alloys with Li.

$$A + xLi^+ + xe^- \rightarrow Li_xA$$ (2)

The electronically insulating Li$_2$O acts instead as a buffer to relieve the stress and strain induced by volume changes upon repeated lithiation and delithiation, thus contributing toward improved cycling stability. However, this reaction is somewhat sluggish, making it important to reduce the particle size of the starting material in order to achieve good electrochemical performance. Moreover, the relatively large voltage hysteresis generally observed in this type of process is an issue which needs to be addressed.

In general, alloying reactions with Li occur at lower voltages than conversion reactions and are therefore desirable for delivering high working potentials in full cells. Additionally, the relatively fast reaction kinetics of alloying processes gives rise to lower voltage hysteresis, which is also of importance in achieving high energy efficiency. However, the drastic volume...
changes induced by repeated insertion and removal of Li\(^+\) compromise the structural integrity of the materials, leading to capacity fading over time due to excessive electrolyte decomposition when new interfaces are continually formed when particles break and the fresh surfaces subsequently becomes directly exposed to the electrolyte solution.

A variety of strategies to address issues related to the volume changes in alloying reactions have been employed. The most common being reducing the particle size\(^6\textsuperscript{–}\textsuperscript{8}\) (i.e., reducing the path length of Li diffusion), carbon coating,\(^9\) and using SEI-forming electrolyte additives, such as FEC (fluorinated ethylene carbonate).\(^\textsuperscript{10}\) Another approach in the case of Sb (as well as Sn) has been the use of intermetallic compounds,\(^\textsuperscript{11–13}\) for example, Cu\(_2\)Sb,\(^\textsuperscript{14}\) NiSb,\(^\textsuperscript{15}\) CoSb\(_3\),\(^\textsuperscript{16}\) and Cu\(_6\)Sn\(_5\).\(^\textsuperscript{17}\) Analogous to the conversion of TMOs, the intermetallic alloy may also undergo conversion reactions in which an extrusion of the metal, M, takes place according to reaction 3.

\[
\text{M}_x\text{Sb} \rightarrow x\text{M} + \text{Sb}
\] (3)

Here, the metal provides enhanced electronical conductivity and structural rigidity of the composite electrode. Following, or simultaneously to, this process, the alloying reaction 2 may take place. The use of intermetallics has been shown to significantly improve the cycle life compared to pure alloy electrodes.\(^\textsuperscript{14–16}\)

Conventional systems based only on the alloying-reaction of Sb have been studied quite extensively. Ternary Sb-oxides, on the other hand, have been explored to a much lesser extent. It is however known that the properties of the starting material (i.e., particle morphology, choice of transition metal, crystal structure, and oxygen coordination around Sb) play a subtle but crucial role in the electrochemical behavior, as in the case, for example, of MSb\(_2\)O\(_x\) (M = Cu, Ni, Co)\(^\textsuperscript{18}\) or MSb\(_2\)O\(_4\) (M = Ni, Co).\(^\textsuperscript{19}\) Others have created nanocomposites by adding inert buffer materials and mixing the components by ball-milling as a means to effectively achieve stable cycling performance.\(^\textsuperscript{20,21}\)

Due to the stereochemically active lone-pair electrons located at Sb\(^{3+}\), a combination with TMs and halides can form oxohalides adopting a wide range of different structures.\(^\textsuperscript{22}\) The lone pairs do not directly participate in forming bonds, instead second-order Jahn–Teller (SOJT) distortions induced by asymmetric coordination due to the nonbonding electron-pair enable the formation of frameworks, tunnels, layered builds, or other low-dimensional arrangements. These compounds thus comprise a large family of interesting structures in which the dimensionality can be controlled by the choice of TM/halide-pair and their relative amount. In the presence of both oxygen and a halide (e.g., X = F\(^-\), Cl\(^-\), Br\(^-\)), Sb\(^{3+}\) has a strong tendency to bond to O rather than X. By carefully adjusting the ratio of oxygen and halides in relation to both Sb and the TM, it is therefore possible to synthesize a wide range of structures with varying dimensionality. These mechanisms can be understood by considering Pearson’s Hard–Soft Acid–Base (HSAB) concept.\(^\textsuperscript{23}\) According to this theory, Sb\(^{3+}\) and O\(^{2-}\) are classified as a hard acid and hard base, respectively. Halide ions are considered to be soft bases and will not preferably bond to a hard acid. Transition metals, particularly M\(^{3+}\), can be considered to be borderline cases and will bond to both. With regard to Li-storage capabilities, it is therefore unlikely that Li\(^+\), also classified as a hard acid, will enter the structure and bond directly to the lone-pair of another hard acid (i.e., Sb\(^{3+}\)), especially if there are no chemically reducible species. In general, a relatively open structure may help to facilitate the lithiation preceding a conversion reaction of the type described earlier (eq 1), leading to a higher efficiency of the electrochemical milling process that is less dependent on the size of the original crystallites. Additionally, the potential at which initial Li-insertion takes places is highly influenced by the choice of TM and its oxidation state. If and when the oxidation state of said TM changes, so does its behavior on the hard–soft acid scale. Altogether, this makes predicting the manner in which lithiation and corresponding redox reactions proceeds somewhat difficult, especially in a highly dynamic system such as an electrochemical cell. Therefore, it is interesting to look at more complex materials to study the way various reaction mechanisms may compete and how they influence each other. Conventional conversion materials (TMOs and Sb-oxides) have been investigated thoroughly in the literature, as previously stated. However, to our knowledge, oxohalides comprising p-elements have remained largely unexplored as possible electrode materials. To this end, Ni\(_2\)Sb\(_2\)O\(_4\)F\(_6\)\(^\textsuperscript{24}\) has been studied as a candidate material for Li-storage in which the possibility for Li-insertion via multiple conversion reactions involving NiO\(_2\) and Sb\(_2\)O\(_4\) species as well as Li-NiSb and Li–Sb alloying may take place sequentially—all possibly aided by the initial framework structure which might facilitate lithiation. The compound crystallizes in the noncentrosymmetric space group \(\text{I}4\text{mmm}\). In this structure, which is displayed in Figure 1a,
magnetic properties.  

So far, no studies on electrochemical properties have been conducted. Given the fact that Sb alloys very well with Li, and TMOs also show promising Li-storage capabilities, we speculate that suitable materials for Li-ion battery applications may exist within the family of oxohalides, whether they are conversion-alloy types or intercalation compounds. This work is part of a series of studies which aims at increasing the understanding of how the elemental composition (i.e., the choice of transition metals and halides and their amount relative to Sb) relate to structure and electrochemical performance. It can be viewed as an additional step toward increasing the complexity of the electrode system, going from a single alloy to an intermetallic counterpart and subsequently to oxides and composites before arriving at more carefully designed materials.

2. EXPERIMENTAL SECTION

Phase-pure powders of Ni3Sb4O6F6 were prepared by a hydrothermal synthesis. The full details are reported elsewhere.  

In brief, NiF2 and SbO3 were mixed with a small amount deionized water in a Teflon-lined steel autoclave and heated to 230 °C for 4 days. Green crystals of phase-pure Ni3Sb4O6F6 were obtained after thorough washing with water and ethanol followed by drying at room temperature.

To make electrodes, the powder was first ground thoroughly by ball milling. Negative electrodes were prepared by blending a mixture of 75% active material, 15% carbon black (Super P, Timcal), and 10% of binder (water, PVDF, 1:1) to form a slurry, which was cast onto a nickel foil. Circular electrodes (diameter: 2 cm) were punched from this slurry and subsequently dried. Positive electrodes, to be used with the graphite anode, were made from a mixture of 80% active material, 15% carbon black, and 5% PVDF binder. The dried electrodes were disassembled in an Ar-filled glovebox (<3 ppm of O2 and H2O) before cell assembly. Cells comprising the dried electrodes were sealed in an aluminum/polymer laminate pouch in a so-called "peel-off" configuration.

Analogous to this, a corresponding reaction with a NiF2 species may also take place according to this reaction:

\[ 2y\text{Li}^+ + 2ye^- + y\text{NiO}_x \rightarrow y\text{Li}_2\text{O} + x\text{Ni} \]

(4)

The same general reasoning can be applied to the case of SbO3, which is also reduced to produce small clusters of elemental Sb and lithium oxide (or lithium fluoride) according to the reaction:

\[ 2y\text{Li}^+ + 2ye^- + y\text{Sb}_2\text{O}_3 \rightarrow y\text{Li}_2\text{O} + y\text{Sb} \]

(5)

At this point, a fine dispersion of Ni and Sb may join in the formation of new phases, such as NiSb. Additionally, SEI formation due to the decomposition of the FEC-additive can be expected to contribute significantly to the current response during the first cycle. These conversion processes are irreversible as any reduction peaks in this voltage range are clearly absent in the subsequent cycles.

Beginning slightly above 1 V, another cathodic current begins to emerge during the first discharge (II). This feature is also likely associated with SEI formation and marks the onset decomposition of other electrolyte components. Simultaneously, the newly formed NiSb (and NiSb2) phases undergo alloying reactions in which Li is inserted into the structures, forming solid solutions according to reaction schemes 7 and 8.

\[ x\text{Li}^+ + x\text{NiSb} + xe^- \rightarrow \text{Li}_x\text{NiSb} \]

(7)

\[ x\text{Li}^+ + x\text{NiSb}_2 + xe^- \rightarrow \text{Li}_x\text{NiSb}_2 \]

(8)

Upon further discharging the cell, these solid solutions may in turn go through a (partial) conversion-type reaction where
additional Li will enter the material and displace Ni, which is then separated as a new phase, see reactions 9 and 10.\textsuperscript{29,31}

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\begin{align*}
\text{Li}_x\text{NiSb}_2 & \rightarrow 2\text{Li}_x\text{Sb} + \text{Ni} \\
\text{Li}_x\text{NiSb} & \rightarrow \text{Li}_x\text{Sb} + \text{Ni}
\end{align*}
\]

This takes place in the region marked (III) during the first cycle. Apart from the initial destruction of the pristine material, these reactions 7–10 are clearly the major contributors to the overall capacity of the system. In the subsequent cycles, the voltage polarization for the alloying–dealloying reaction decreases, and the potential shifts to a higher value of 0.6–0.7 V.

Finally a small cathodic current appears at about 0.2 V. It becomes less prominent in the 2nd cycle, and by the 10th cycle, it has diminished significantly, indicating that it is associated with an irreversible process (IV).

In the following anodic sweep (i.e., Li\textsuperscript{+} removal), a broad peak appears during the first and second cycles, but disappears by the 10th cycle (V). This feature is likely coupled to the aforementioned cathodic peak at 0.2 V. Possibly, this is coupled to an irreversible surface process involving Sb-species, or simply the insertion/deinsertion of lithium in the carbon black component of the electrode.

With continued cycling, a prominent peak appears in the region around 1.1–1.2 V, corresponding to the conversion of the Ni/LiSb composite matrix back to a mixture of NiSb and NiSb\textsubscript{2} (VI). During the first cycle, this occurs at a higher potential than the subsequent cycles. Between the 2nd and 10th cycle, the features of these reactions on both charge and discharge only change very little, indicating good reversibility of the process.

Centered at about 1.4 V, a weaker anodic current appears (VII). This feature is attributed primarily to the oxidation of Sb. Following this, there is an irreversible process centered at around 1.8 V (VIII). This can only be observed during the first cycles, when electrochemical milling is expected to expose new surfaces to SEI formation. The effect of this has diminished significantly by the 10th sweep, reflecting the self-limiting nature of the SEI dynamics.

In the range of 2.2 to 3 V, a broadly smeared out peak emerges (IX), corresponding to the amorphization of the electrode material (see the description of operando XRD in Experimental Section). Following the plateau, the voltage drops rapidly to 1.1 V after which the discharge profile adopts a sloping behavior where the alloying between Li and NiSb/NiSb\textsubscript{2}/Sb contributes to flattening the appearance of the voltage curve. Below 0.4 V versus Li\textsuperscript{+}/Li, electrolyte decomposition and various parasitic surface reactions are speculated to be the main contributors to the overall capacity.

3.1.2. Galvanostatic Experiments. The potential profile of the first discharge–charge cycles during galvanostatic (chronopotentiometric) conditions between voltages 0.05 and 3 V are shown in Figure 2b. The first discharge exhibits a behavior typical of many TMOs undergoing a conversion reaction with Li\textsuperscript{+}. The plateau seen at 1.55 V upon insertion of Li\textsuperscript{+} corresponds to the amorphization of the electrode material (see the description of operando XRD in Experimental Section). Following the plateau, the voltage drops rapidly to 1.1 V after which the discharge profile adopts a sloping behavior where the alloying between Li and NiSb/NiSb\textsubscript{2}/Sb contributes to flattening the appearance of the voltage curve. Below 0.4 V versus Li\textsuperscript{+}/Li, electrolyte decomposition and various parasitic surface reactions are speculated to be the main contributors to the overall capacity.

![Figure 2.](image)

The gravimetric charge and discharge capacities for Ni\textsubscript{2}Sb\textsubscript{2}O\textsubscript{6}F\textsubscript{6} electrodes calculated from galvanostatic cycling at different voltage cutoffs are displayed in Figure 2c. In the range of 3–0.05 V (black markers), the discharge capacity is

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initially high, ~970 mAh g$^{-1}$, but the Coulombic efficiency is low, leading to a rapid capacity drop in the subsequent cycles due to the poor reversibility of the Ni$^{2+}$/Ni redox couple at higher potentials as well as parasitic surface reactions at low potentials. Based on an idealized assumed reaction in which the amorphization leading to the formation of Ni, Sb, Li$_2$O, and LiF followed by the two-step formation of Li$_x$Sb, the expected theoretical uptake is 30 mol of Li per 1 mol of Ni$_3$Sb$_4$O$_6$F$_6$ or 929 mAg$^{-1}$. This corresponds rather well to the experimental capacity of 970 mAg$^{-1}$ observed for the first discharge.

The red markers in Figure 2c show the capacity retention between 2.2 and 0.05 V. Here, the drop in capacity corresponds well to the exclusion of the Ni$^{2+}$/Ni redox process, but otherwise, the general evolution of the capacity plot as a function of cycle number follows the same trend as when the upper cutoff is 3 V; however, it has been shifted toward lower values. Even though the conversion reversibility of Ni$^{2+}$/Ni is poor, the limited cycling behavior must thus mainly be due to processes occurring at low potentials. More likely, reactions at potentials below 0.4 V play a more important role in explaining the poor cyclability. This proposition is strengthened by observing the behavior in the potential window of 0.4 to 3 V, shown as green markers in Figure 2c. Here, the capacity is very similar to the previous case during the first 10 cycles, after which the capacity retention becomes more stable. However, the Coulombic efficiency is still low, leading to a slow capacity fade with increased cycling.

By limiting the cycling window to 0.4−2.2 V, effectively excluding poorly reversible and/or parasitic reactions suspected to be responsible for the poor cycling behavior in all the previous cases, a stable performance can be achieved, as seen by the blue markers in Figure 2c. Here, the primary reactions taking place are the conversion reaction of Sb$_2$O$_3$ and the Li-NiSb/NiSb$_2$/Sb alloying reactions. Obviously, the overall gravimetric capacity becomes lower when only a relatively small mass percentage of the composite electrode undergoes electrochemical cycling with Li$^+$. However, additional species such as Ni metal, though not electrochemically active, may still contribute to stabilizing the performance by enhancing electrical conductivity and providing mechanical support. After 100 cycles, the discharge capacity is ~200 mAh g$^{-1}$ (corresponding to the reversible reaction of ~6.2 Li) with a Coulombic efficiency of 99.7%. Altogether, these properties and the limitations needed to achieve stable cycling impede the practical applicability of this compound.

3.2. Morphological Study. High-resolution scanning electron microscopy (HRSEM) was used to check the particle size of the active material and the general morphology of the composite electrodes. Figure 3 compares two micrographs of a pristine and a cycled sample. Figure 3a presents an SEM image that shows that the particles of the active material Ni$_3$Sb$_4$O$_6$F$_6$ consists of dark micron-sized crystals with a block-like morphology embedded in a matrix of brighter and smaller carbon black particles. It should be noted that apart from ball-milling the powder, no additional measures have been taken in an effort to optimize cycling performance with respect to particle size. Ideally, the particle size should be smaller in order to compensate for the poor reversibility of the conversion of the insulating Li$_2$O matrix formed when cycling Ni$_2$O$_3$ and Sb$_2$O$_3$ species.

The electrode morphology after one cycle in galvanostatic mode is shown in Figure 3b. There is no apparent change in particle size due to, for example, electrochemical milling, apart from a roughening of the surface and possible SEI deposits.

3.3. X-ray Diffraction Study. XRD patterns were obtained in operando at 2-h intervals during the first discharge and charge cycle of the Ni$_3$Sb$_4$O$_6$F$_6$/Li half-cell. The voltage profile and the corresponding diffraction patterns at each interval are shown in Figure 4a. Peaks originating from the cell hardware, such as the separator, current collector, and the pouch cell laminate, are marked in the figure. The most intense peaks of the pristine material are clearly visible at roughly 27° and 35° 2θ. The open-circuit voltage of the newly assembled cell was 2.95 V. When discharging the cell in galvanostatic mode, the voltage immediately drops to a plateau at 1.55 V vs Li$^+$/Li. This voltage plateau, seen only during the first cycle discharge, apparently corresponds to a process of structural degradation (i.e., amorphization) of the material, as witnessed by the gradual decrease in peak intensity in the XRD patterns. No peak shifts or intensity drops for a specific (hkl) indicate the structure collapses in a rather isotropic manner. After approximately 12 h of slowly discharging the cell (i.e., inserting Li$^+$), all original peaks seem to have completely vanished without any indication of new phases appearing during continued cycling. A small peak can be seen at 36° 2θ; this feature is attributed to the relatively grainy textured Li-foil used as a counter/reference electrode.

XRD patterns of cycled electrode material were also recorded ex situ in order to investigate the possible emergence of new phases without interference from the cell hardware. Figure 4b shows a selection of ex situ XRD patterns after a variable number of cycles. Here, a couple of rather indistinct features are revealed, centered at approximately 30° and 45° 2θ in the lithiated material. For stoichiometric reasons, these peaks are primarily attributed to nanosized clusters of NiSb, although it should be noted that the coexistence of a high-pressure
polymorph of NiSb observed by Villevieille et al. cannot be excluded. After the first charge, these peaks have disappeared. As the number of cycles increases, the peaks become more distinct. In the first 20 cycles, the two peaks at $\sim 45^\circ 2\theta$ are only visible as a broad hump, whereas after 50 cycles, the NiSb phase has grown sufficiently to hint at a separation between the peaks. Surprisingly, none of the diffraction patterns show the appearance of a lithiated Sb phase (e.g., Li$_3$Sb) or metallic Ni at low potentials.

3.4. XANES Study on Ni and Sb. X-ray absorption near edge spectroscopy (XANES) data for Ni in the Ni$_3$Sb$_4$O$_6$F$_6$ composite electrode at different stages of lithiation (i.e., different oxidation states of Ni) during the first cycle is shown in Figure 5a. The solid blue line represents Ni in the pristine state before any insertion of Li$^+$ has taken place. The position of the absorption edge and the shape of the postedge features are typical of Ni$^{2+}$ in an octahedral coordination site and are similar to that of NiO, which is to be expected considering the original crystal structure. The dashed blue line in Figure 5a shows that the reduction of Ni begins during the early stages of lithiation. Here, the spectrum collected at 1.5 V vs Li$^+/Li$ immediately after the voltage plateau in the first cycle, reveals that the absorption edge of Ni has shifted toward a lower energy by $\sim 5$ eV. The intensity of the postedge features at this stage has also diminished significantly compared to the pristine state, indicating that the local geometry surrounding the Ni-atom has changed drastically. This apparent change clearly corresponds to the irreversible transformation also observed from XRD-data. In the fully lithiated sample (solid black line), the Ni is assumed to be completely reduced to a metallic state as indicated by the position of the edge. In contrast to all other spectra collected in these experiments, the Ni in the fully discharged state shows the appearance of a shoulder roughly in the photon energy range of 8330–8340 eV—a strong indicator that metallic Ni is present. This is consistent with previous work from our group. Complementary to the findings from ex situ XRD, this provides more evidence for the presence of nanoclusters of metallic Ni within the material close to 0 V vs Li$^+/Li$. Because Ni does not alloy with Li, it will not contribute directly to the Li-storage capability; however, it might indirectly serve to enhance the electronic conductivity within the electrode by forming an alloy with Sb. Although not performed here, magnetization measurements could also be used as a complementary technique to detect the presence of metallic Ni. This could also provide additional information about possible superparamagnetism of the metallic nanoparticles.

Figure 4. (a) Operando X-ray diffraction patterns of the Ni$_3$Sb$_4$O$_6$F$_6$ electrode for the first full cycle illustrating the collapse of the pristine material. The corresponding galvanostatic discharge—charge curve is shown in the lower right to help guide the eye. Peaks originating from the cell hardware are marked with black asterisks. (b) Ex situ diffraction patterns of the electrode material after a different number of cycles showing the gradual growth of the NiSb-phase.

Figure 5. XANES spectra for (a) K-edge of Ni at various stages of lithiation and (b) L-edge of Sb during the first discharge—charge cycle.
Lastly, the spectrum for the fully delithiated state at 3 V vs Li+/Li is displayed as the solid red line in Figure 5a. It is clearly demonstrated that the Ni ends up only being partially oxidized, as witnessed by the position of the absorption edge, indicating some irreversibility of the Ni$^{2+}$/Ni redox reaction within the chosen voltage window. Complementary to the electrochemical analysis, these results suggest that Ni stays in a metallic state during cycling in the narrow potential window, giving rise to the best cycling stability.

The Sb L1 edge XANES measurements for the pristine, the lithiated (0.05 V), and the delithiated (3 V) material are shown in Figure 5b together with reference samples. Rockenberger et al.35 reported that the Sb L1 edge is mainly a contribution of Sb$s^{+}$ in Figure 5b together with reference samples. Rockenberger et al.35 reported that the Sb L1 edge is mainly a contribution of Sb$s^{+}$ is not significantly reduced in the first cycle when the electrode material is fully lithiated, as shown by only a minute shift in the edge position. Also, upon charging, the oxidation state seems to be lowered. As the ex situ XRD measurements indicate, an alloy of nanosized NiSb is formed during the first discharge. This phase is dominant in a wide voltage range, as witnessed by its apparent growth with increased cycling. Additionally, the related NiSb2 could also be expected to contribute to the complex behavior of the system. Any attempts to interpret the XANES-spectra of Sb must take this into account because assigning oxidation states in alloys is not always a straightforward task. In addition to Li$_x$Sb and Sb, both these alloys are likely to exist simultaneously in the material. At higher potentials, conversion of Sb in a previously metallic state into some Sb$_2$O$_3$ species should occur, analogous to the case of Ni. However, in competition with various reactions, this mechanism might be slow or somehow unfavorable, causing Sb to remain at a low valence state even at relatively high potentials. Moreover, the reduction of Sb$^{5+}$ might be incomplete during the first cycle, due to the relatively large particle size of the starting material. As Villevielle et al.17 clearly demonstrated via $^{125}$Sb Mössbauer spectroscopy in the NiSb$_2$ system with μ-sized particles, significant amounts of Li$_x$Sb, Sb, NiSb$_2$, and Sb$_2$O$_3$ can all coexist in a wide voltage range. Probably, this is the case here as well, thus rendering Sb L$_1$ XANES an insufficient probe to unravel the full details of the reaction mechanism.

4. CONCLUSIONS

To summarize, a novel electrode material with the elemental composition Ni$_3$Sb$_4$O$_6$F$_6$ within the family of oxohalides has been shown to react reversibly with Li+. With the possibility of multiple reactions taking place in a complex system with a combination of conversion-alloying mechanisms, the material has been investigated further by means of an extensive electrochemical and structural analysis. It is demonstrated by operando XRD that the initial framework structure is not preserved during the first stages of lithiation. Instead, the material undergoes amorphization. XAS-data on the K-edge of Ni shows that Ni$^{2+}$ is reduced to a metallic state early during the first discharge and that the subsequent oxidation process of Ni to Ni$^{2+}$ is incomplete within the chosen voltage window. Ex situ XRD strongly suggests that a stable phase of NiSb-alloy is formed during the first cycle and remains the backbone of the electrode material during continued cycling, in which its alloying reaction with Li is the most important contributor to the overall Li-storage capacity. Additionally, the structurally related NiSb$_2$ may also contribute. XANES performed on the L-edge of Sb are somewhat inconclusive. The spectra imply the valence state of Sb changes very little during the first cycle, even at the two voltage extremes.

Stable cycling can be achieved by applying voltage cutoffs at low and high potentials versus Li+/Li. Likely, this is by excluding the poorly reversible Ni$^{2+}$/Ni conversion reaction above 2.2 V and by preventing undesirable surface reactions below 0.4 V.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b01914.

XPS spectra of O 1s, Sb 3d3/2, and Sb 3d5/2 peaks at various states of charge (PDF)

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Notes

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REFERENCES


(16) Xie, J.; Zhao, X.; Cao, G.; Zhong, Y.; Zhao, M. Ex-situ XRD studies of CuSb3 compound as the anode material for lithium-ion batteries. J. Electroanal. Chem. 2003, 542, 1–6.


