Investigation of the Lithiation and Delithiation Conversion Mechanisms of Bismuth Fluoride Nanocomposites


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Conversion reactions are lithiation reactions in which the active material is fully reduced by lithium to the metal according to the following equation

\[ \text{M}^+\text{X} + y\text{Li} \rightarrow \text{M}^y + y\text{Li}_x\text{X} \]

where M stands for a cation and X an anion. As all the oxidation states of the material are utilized, capacities much higher than in the intercalation reactions currently used in rechargeable Li-ion batteries can in theory be obtained, thereby leading to much higher energy densities.

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Combined in situ X-ray diffraction, in situ X-ray absorption spectroscopy, and selected area electron diffraction analyses have confirmed the occurrence of a reversible conversion reaction in the BiF$_3$/C nanocomposite upon cycling, which leads to the formation of Bi$_2$ and LiF during lithiation and the reformation of BiF$_3$ during delithiation. It has been shown that only the high-pressure tysonite phase of BiF$_3$ reforms during the oxidation sweep and that no bismuth fluoride compound with an oxidation state of the bismuth lower than 3 is formed as intermediate during the lithiation or delithiation reactions. Finally, it has been demonstrated that the different plateaus or pseudo plateaus observed on the lithiation and delithiation voltage profiles stem from polarization changes brought about by the dramatic structural changes occurring in the nanocomposite upon cycling. A model, based on the variation of the electronic and ionic transport mechanisms as a function of the state of completion of the conversion and reconversion reactions, is proposed to explain those polarization changes.

Experimental

The tysonite BiF$_3$/C nanocomposite, denoted r-BiF$_3$ thereafter, has been prepared by high-energy milling for 1 h in a Spex 8000
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mill 85 wt % of BiF₃ (Alfa Aesar) with 15 wt % carbon black (Super P, MMM). The high-energy milling cell was sealed and reopened after milling inside an He-filled glove box at −80°C dew point, thus preventing the powder from moisture or oxygen contamination. The orthorhombic BiF₃/C nanocomposite, denoted o-BiF₃ thereafter, has been prepared by treating the t-BiF₃ nanocomposite with 48% concentrated hydrofluoric acid in a Teflon container. The powder obtained was placed overnight in an oven at 95°C to let the HF evaporate and dried a second time overnight at 120°C under vacuum before entering the glove box. Results previously presented by our group indicated that the tysonite to orthorhombic phase transformation occurs via a dissolution/reprecipitation mechanism.14

X-ray diffraction (XRD) analyses were performed on a Scintag X2 using Cu Kα radiation. Samples to be analyzed ex situ were placed on glass slides and covered with a Kapton film sealed with silicon-based vacuum grease inside the glove box to minimize air exposure. For the in situ XRD the electrode was placed in an in situ cell prepared by our group. A Beryllium window and an isolation film of Kapton were placed on top of the working electrode to isolate it and the electrolyte from the atmosphere while allowing the X-ray to penetrate. A detailed description of this in situ XRD cell will be provided in an upcoming paper.

The transmission electron microscope (TEM) was a Topcon 002B. The powders were first dispersed in anhydrous dimethyl carbonate (DMC), a few drops of which were then disposed on a lacey carbon grid and allowed to dry overnight inside the glove box. The grids were then placed in bags sealed inside the glove box that were reopened at the last moment, thereby minimizing the exposure time to the atmosphere to a few seconds. In order to avoid the decomposition of the material, which occurs relatively quickly under the electron-beam, the samples were scanned in diffraction mode at low brightness until sharp rings appeared and the exposure time to collect the images was kept under 15 s. The selected area electron diffraction (SAED) patterns were interpreted using Process Diffraction software.15

For the in situ X-ray absorption spectroscopy (XAS) experiments, the electron storage ring operated at energy of 2.8 GeV and a current in the range of 150–300 mA. Spectra of the Bi L₂-edge (13,419 eV) were collected in the transmission mode at room temperature with energy intervals per step of 5 eV for the pre-edge region (13,119–13,489 eV) and 0.5 eV for the edge region (13,469–13,489 eV). A k-space interval of 0.05 Å⁻¹ was used for the extended X-ray absorption fine structure (EXAFS) region (13,469–14,168 eV). Integration intervals per point were set to 1 s for all regions. A delay time of 0.3 s was used between successive data points in order for the monochromator to equilibrate at each point. The X-ray absorption fine structure (XAFS) analysis area was set to 10⁻² × 10⁻³ m². The zero of energy for the photoelectron was taken at the inflection point of the absorption edge. The spectra were normalized to a per atom basis using the average of the absorption cross section over the energy range of 100–400 eV above the edge energy. The EXAFS spectrum, χ(k), was extracted by fitting a cubic spline procedure to the EXAFS region, which minimized the amplitude of nonphysical peaks in the 0–1 Å region of the Fourier transforms. Fourier transforms were generated from k³-weighted EXAFS spectra (k-range 2.45–10.0 Å⁻¹ and a Hanning window of 20%). The data analysis was carried out using the WinXAS software package (ver. 2.3).16,17 A detailed description of the in situ cell has been provided elsewhere.18

To prepare the electrodes an acetone-based slurry containing the active material, a poly(vinylidene fluoride-co-hexafluoropropylene) (Kynar 2801, Elf Atocheim) binder, carbon black (Super P, 3 M), and dibutyl phthalate (Alrich) plasticizer in the ratio 39:21:8:32 was first prepared. The slurry was then tape casted. Once dried, the tape was placed in 99.8% anhydrous ether (Alrich) to extract the DBP. After DBP extraction the active material loading of the tape was 57 ± 1%. Disks of about 1 cm² punched from these tapes were tested in coin cell against lithium metal (Johnson Matthey). The coin cells were cycled under controlled temperatures. The batteries were cycled either on an Arbin, a Maccor, or a MacPile (Biologic). Three different electrolytes were used: LiPF₆ salt in a mixture of ethylene carbonate (EC)/propylene carbonate (PC)/diethyl carbonate (DEC)/DMC solvents at 1 M, LiPF₆ in EC/DMC at 1 M, or LiClO₄ in EC/DMC at 0.4 M.

Results and Discussion

Physical characterization.— The XRD patterns of the pristine macro BiF₃ powder and of the macro BiF₃ powder high-energy milled in He for 1, 2, 3, and 4 h in the presence of carbon Super P, showing the phase transformation from orthorhombic (SG Pnma) to tysonite [SG P(3)c1].

![Figure 1. XRD patterns of the pristine macro-BiF₃ and of the macro-BiF₃ high-energy milled in He for 1, 2, 3, and 4 h in the presence of carbon Super P, showing the phase transformation from orthorhombic (SG Pnma) to tysonite [SG P(3)c1].](image-url)
the orthorhombic BiF$_3$ upon annealing to 350°C in an inert atmosphere as opposed to the oxyfluoride that should retain its tysonite structure. Our nanocomposite retransformed into orthorhombic BiF$_3$ after such a treatment, suggesting that it is the pure BiF$_3$ tysonite and not BiO$_x$/H$_2$O/F$_2$-$x$/$H_2$O.

After 1 h of high-energy milling, the ratio of tysonite/orthorhombic phases has been evaluated as 70:30 from the relative intensity of their respective I$_{100}$ Bragg reflections. This ratio increases with milling time, and the transformation is complete after a milling time between 3 and 4 h. SAED has been performed on the BiF$_3$/C nanocomposite high-energy milled for 1 h, and the electron diffraction patterns are presented in Fig. 2. Many patterns collected could be indexed either as the pure tysonite phase (pattern a) or the pure orthorhombic phase (pattern b). As the area under scrutiny when the SAED is performed is of about 0.25 m$^2$, this result suggests that the phase transformation is pressure-induced upon contact with the milling balls, as opposed to a gradual transformation induced by the already disproved oxygen substitution route. The residual orthorhombic BiF$_3$ particles may be a result of the initial o-BiF$_3$ material that may have been buffered from direct impact during high-energy milling.

Another feature clearly apparent on the XRD patterns of Fig. 1 is the broadening of the diffraction peaks between the macro-BiF$_3$ and the BiF$_3$/C nanocomposite high-energy milled for 1 h. The majority of the broadening is due to the dramatic diminution of the primary crystallite size, but also has a small contribution from the strain induced in the material by the high-energy milling process. Combined Williamson-Hall$^{21}$ and TEM analyses conducted on the BiF$_3$/C nanocomposite high-energy milled for 1 h have shown that the BiF$_3$ crystallite size in this material is widely distributed, with an upper distribution limit in the order of 30 nm. The BiF$_3$ Bragg reflections did not broaden significantly when the high-energy milling time was further increased, indicating that the size of the primary crystallite did not decrease much further.

First lithiation.—The galvanostatic discharge curve and the XRD patterns obtained during in situ XRD conducted on the BiF$_3$/C nanocomposite high-energy milled for 1 h during the first lithiation down to 2 V vs Li/Li$^+$ are presented in Fig. 3 a and b, respectively. The progressive appearance of the Bi$^0$ Bragg reflections and disappearance of the BiF$_3$ Bragg reflections from the XRD patterns when $x$ in “Li$_x$BiF$_3$” increases clearly demonstrate that a conversion reaction is taking place in the BiF$_3$/C nanocomposite during the lithiation, according to

$$\text{BiF}_3 + 3\text{Li}^+ + 3e^- \rightarrow 3\text{LiF} + \text{Bi}^0$$

The Bi$^0$ Bragg reflections become visible at a very early stage of the lithiation, at an $x$ in “Li$_x$BiF$_3$” smaller than 0.1. The BiF$_3$ reflections do not exhibit any shift, indicating that the conversion reaction starts from the very beginning of the lithiation and that there is no concomitant intercalation reaction of the lithium in the metal fluoride, unlike what has been observed in FeF$_3$$^{10}$ and TiF$_3$$^{9,23}$ The LiF Bragg reflections cannot be observed on these patterns as they are overlapped by the Bi$^0$ reflections and because the X-ray scattering factors of Li and F are much smaller than the X-ray scattering factor of Bi. As the intensities in the in situ experiment are low, those

![Figure 2. SAED on the BiF$_3$/C nanocomposite high-energy milled for 1 h, characteristic of (a) the pure tysonite or (b) the pure orthorhombic phases.](Figure_2.png)

![Figure 3. In situ XRD of the t-BiF$_3$/C nanocomposite during the 1st lithiation in a LiPF$_6$ EC/PC/DEC/DMC electrolyte. The experiment was conducted at room temperature at a current density of 7.58 mA/g. (a) Galvanostatic curve with integrated intensities of the Bi$^0$ (012), BiF$_3$ tysonite (111), and BiF$_3$ orthorhombic (210) peaks and (b) XRD patterns.](Figure_3.png)
peaks cannot be resolved. However, LiF clearly forms during the lithiation and this has been confirmed by SAED as shown on the pattern of Fig. 4 collected on the BiF3/C nanocomposite lithiated to 2 V. The major LiF rings are, obviously, also overlapped by Bi0 rings on the SAED pattern of Fig. 4. The overlapping Bi0 rings are mentioned in the figure caption but have not been indexed on the figure itself for the sake of clarity. In spite of this overlapping issue, the LiF diffraction rings can be clearly observed on this SAED pattern that was collected on an area of the sample where the LiF/Bi0 ratio was greater than average and where the diffracting conditions for LiF were particularly well obeyed. A clear distinction between the LiF rings, which appear relatively intense and very diffuse, and the Bi0 rings, which are less intense and more “spotty,” can thus be made on the SAED pattern presented in Fig. 4. The fact that the (200) and (220) LiF rings on this SAED pattern are very diffuse confirms that the LiF crystallite size is extremely small.

The evolution of the integrated intensities with x of the Bi0 (012) Bragg reflection, (111) Bragg reflection from the t-BiF3 phase, and (210) Bragg reflection from the o-BiF3 phase are overlaid to the galvanostatic curve of Fig. 3a. As the XRD patterns have a poor signal over noise ratio and the peaks are broad, it was quite difficult to accurately fit the patterns for the integrated intensities calculations. The lines added to the figure were obtained by a linear fitting of the integrated intensities data point, but due to the low accuracy of these data points, the fit was not good and those lines should be considered as guides for the eyes only, emphasizing only the general trend. This is also true for all the other in situ XRD figures presented throughout this article.

The integrated intensity of the Bi0 (012) reflection increases continuously when x increases in Fig. 3a, indicating that the completion of the conversion reaction progresses linearly with x, as expected.

From the evolution of the integrated intensities of the two BiF3 Bragg reflections it can be inferred that the conversion reaction occurs preferentially in the orthorhombic phase rather than in the orthorhombic phase. The integrated intensity of the (111) t-BiF3 peak decreases indeed much faster with x than the integrated intensity of the (210) peak from the o-BiF3 phase. At an x in “Li4BiF6” of about 1.8, only the peaks from the orthorhombic phase can be seen, with integrated intensities similar to their integrated intensities at x = 0. We do not know at that point why the conversion reaction occurs preferentially in the t-BiF3 phase.

Although the conversion reaction takes place preferentially in the t-BiF3 phase, it is clear that it also occurs in the o-BiF3 phase. This is demonstrated in Fig. 5 with an in situ XRD experiment conducted on the pure o-BiF3/C nanocomposite. The experiment was conducted in a LiPF6 EC/DMC electrolyte and the current density was 7.58 mA/g. Figure 5 is divided into two parts: part (a) describes the variation with x of the voltage and of the integrated intensities of the Bi0 (012) and BiF3 orthorhombic (111) peaks and (b) XRD patterns.

The galvanostatic curve of the first lithiation of the BiF3/C nanocomposite high-energy milled for 1 h shown in Fig. 3a is divided into two pseudo plateaus at 2.95 and 2.75 V. The occurrence of the first plateau seems to be associated with the t-BiF3 because the...
galvanostatic curve of the pure $\alpha$-BiF$_3$/C nanocomposite in Fig. 5a only exhibits one single plateau at 2.7 V. However, the same type of division in two plateaus has also been observed in other Bi$_{\mathrm{O}_x}$F$_{3-2x}$/C nanocomposites such as Bi$_{\mathrm{O}_{0.5}}$F$_{2}$/C during the fluoride conversion. An identical separation of the two pseudo plateaus also occurs on the voltage profile of the BiF$_3$/C nanocomposite high-energy milled for 4 h, which has no residual $\alpha$-BiF$_3$ phase at all. The separation is more or less severe depending on the electrolyte. It is, for instance, very pronounced in a LiClO$_4$ EC/DMC electrolyte, as shown in Fig. 6. As it can be seen from the same figure, the voltage on this first plateau is much more rate-sensitive than on the second plateau, thus suggesting that the reaction associated with the plateau is not capacitive or pseudocapacitive in nature. As shown in Fig. 7, when the temperature is increased the voltage on the first plateau increases significantly and at 75°C the separation of the lithiation into two distinct plateaus has been virtually eliminated, with the higher voltage plateau region being the preferred reaction.

The results of Fig. 6 and 7 suggest that this separation of the lithiation in the two plateaus is a pure kinetics effect. This is confirmed on the galvanostatic intermittent titration technique (GITT) curves of the $\alpha$-BiF$_3$ and $\beta$-BiF$_3$ nanocomposites presented in Fig. 8 and 9, respectively. It is clear in these two figures that the lithiation output voltage after relaxation is perfectly flat, as expected from thermodynamics because conversion reactions are two-phase reactions.

If the occurrence of these two plateaus during the lithiation is due to kinetics effects, the kinetics that develop the pseudo plateaus are most likely associated with different electronic and ionic transport mechanisms of the different phases present at the different stages of the lithiation reaction. Considering the dramatic difference in nature of the lithiation reactant (BiF$_3$) and products (LiF + Bi$_3^+$), this seems a plausible hypothesis. Schematics of the two suggested
Figure 10. Schematics of the two different transport mechanisms suggested for the lithiation. Mechanism A (x in “Li_xBiF_3-y” < 1.5): the electrons are transferred to the BiF_3 surface via the carbon matrix and the Li^+ ions migrate to the BiF_3 surface directly from the electrolyte, inducing the reduction into Bi_0 and LiF. Mechanism B (x in “Li_xBiF_3-y” > 1.5): all the surface of the BiF_3 particles has been reduced. To reach the unreduced BiF_3 in the core of the particles the Li^+ ions diffuse through the defect boundaries of the LiF and Bi nanoparticles and the electrons are transferred to BiF_3 via the Bi_0 metal.

Figure 11. In situ XRD of the t-BiF_3/C nanocomposite during the 1st delithiation in a LiPF_6 EC/DMC electrolyte. The nanocomposite was first lithiated in the in situ cell at a current density of 45.45 mA/g without the X-ray. One XRD pattern was collected at the end of the lithiation at 2 V. The nanocomposite was then delithiated until x ~ 1.55 in the in situ cell at a current density of 45.45 mA/g without X-ray before the start of the actual in situ XRD. The experiment was conducted at room temperature at a current density of 7.58 mA/h. (a) Galvanostatic curve with integrated intensities of the Bi_0 (012) and BiF_3 tysonite (111) peaks and (b) XRD patterns.
possible doubt that the conversion reaction that takes place in the BiF3/C nanocomposite during the lithiation is reversible. The over-all chemical reaction is

\[ \text{BiF}_3 + 3 \text{Li} \leftrightarrow \text{Bi}^{0} + 3 \text{LiF} \]

Only the tysonite form of BiF3 is observed at the end of the delithiation on the X-ray data presented in Fig. 11b. As shown by means of in situ XRD of the BiF3/C nanocomposite in a LiClO4 EC/DMC electrolyte after a 1st lithiation at 2 V. The experiment was conducted at room temperature at a current density of 7.58 mA/g. (a) Galvanostatic curve with integrated intensities of the Bi0 (012) and tysonite BiF3 (111) peaks and (b) XRD patterns.

Another striking feature of the in situ XRD patterns of Fig. 11b is that the BiF3 Bragg reflections begin to be visible only at an advanced state of completion of the delithiation, at an x in “Li,BiF3” in the order of 1.3. As can be seen in Fig. 10a, this x value matches well the x value at which the first delithiation plateau ends and the voltage increases sharply before reaching the second plateau at 3.7 V. The identical result was obtained in the in situ XRD of the BiF3/C nanocomposite (cf. Fig. 12) and in the in situ XRD analysis performed on the BiF3/C nanocomposite in a LiClO4 EC/DMC electrolyte. Hence, based on the XRD results, it would seem that the only bismuth compound present in the nanocomposite along this first plateau is Bi0 and that the actual reconversion reaction begins only at the second plateau at higher voltage.

As the first delithiation plateau covers approximately two thirds of the delithiation and the capacity on the second discharge is almost identical to the capacity on the first discharge, there can nevertheless be no doubt that some if not the majority of the reversibility comes from this first plateau. Furthermore, as seen in Fig. 11a and 12a, the integrated intensity of the Bi0 Bragg reflection clearly decreases along the first delithiation plateau, indicating that the amount of Bi0 in the material decreases continuously along this 3.3-V plateau.

In order to provide a fundamental understanding of the origin of the redox reaction on the first delithiation plateau, XAS was used to monitor the evolution of the electronic and atomic structure of Bi under in situ conditions. The discharge and charge capacities are summarized in Table I. The cell was discharged and charged within the potential range of 2.0–4.5 V vs Li/Li+. The X-ray absorption near edge structure (XANES) data, collected during the first cycle of charging, are shown in Fig. 13 as a function of state of charge and vs Bi0 and Bi13+ standards. The data suggest the direct oxidation of metallic Bi0 to Bi13+ in BiF3 during the charging of a discharged BiF3 cathode. Structurally, this conclusion is also supported by the Fourier transform EXAFS data displayed in Fig. 14, as a function of state of charge, along with those for metallic Bi and BiF3 as reference standards.

The Fourier transform of EXAFS data for metallic Bi displays a doublet at 2.499 and 3.148 Å, which corresponds to contributions from 3 Bi atoms at the crystallographic distance of 3.073 Å and 3 Bi atoms at 3.527 Å, respectively. The Fourier transform of BiF3, on the other hand, displays mainly a single peak at 1.549 Å, which corresponds to contributions from 8 F atoms. For the discharged cathode, as expected, the Fourier transform mainly shows the presence of metallic Bi. During charge the Fourier transforms display both the Bi-F and Bi-Bi contributions, the Bi-F contribution in

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and delithiated to 3.35 V vs Li/Li⁺ after a 1st lithiation at 2 V. The current density was 7.58 mA/g and the electrolyte LiPF₆ EC/PC/DEC/DMC. The (reconverted) tysonite BiF₃ rings can clearly be identified.

creasing and the Bi–Bi contribution decreasing with the state of charge in a distinct two-phase manner. Finally, the Fourier transform for the charged cathode is consistent with that of BiF₃.

The in situ XAS study therefore suggests that the reconversion reaction to t-BiF₃ does indeed commence from the beginning of the delithiation. The data also reveal that there is no intermediate bismuth fluoride compound forming in which the oxidation state of the bismuth is lower than 3, which is a rare but distinct and plausible possibility. The presence of reformed tysonite BiF₃ along the first delithiation plateau at lower voltage has also been confirmed by SAED, as shown in Fig. 15. This SAED pattern has been collected on the BiF₃/C nanocomposite delithiated to the end of the first plateau at 3.35 V after a first lithiation down to 2 V. All the diffraction rings on this pattern could be indexed on the basis of the BiF₃

Figure 15. SAED on the BiF₃/C nanocomposite high-energy milled for 1 h and delithiated to 3.35 V vs Li/Li⁺ after a 1st lithiation at 2 V. The current density was 7.58 mA/g and the electrolyte LiPF₆ EC/PC/DEC/DMC. The (reconverted) tysonite BiF₃ rings can clearly be identified.

Figure 14. Phase-uncorrected Fourier transforms of k³-weighted EXAFS data collected during the 1st cycle of charging a fully discharged BiF₃ cathode at 0.25 mA (as a function of state of charge). The vertical arrow indicates the progression of spectra during the charge cycle. Fourier transform range is 2.85–10.0 Å.

The only possible way to reconcile the in situ XRD data, on which the reconstructed BiF₃ can be seen only on the second plateau at higher voltage, and the SAED and in situ XAS data, which shows that BiF₃ does indeed reform on the first plateau as well, is that the primary crystallite size of the reconstructed BiF₃ on the first delithiation plateau is too small to be resolved by XRD. Similar to the situation resolved during lithiation, the separation of the delithiation voltage profile in two plateaus at about 3.3 and 3.7 V is a pure kinetics effect and is due to a polarization increase.

A GITT experiment was performed on the BiF₃/C tysonite orthorhombic nanocomposites and the plots shown in Figs. 8 and 9, respectively, support our theory. It is clear that the voltage after relaxation is the same on both delithiation plateaus, indicating that the same reaction (i.e., the BiF₃ reconversion reaction) is taking place on both plateaus as opposed to an alternative phase formation. The same result has obviously been observed on the GITT curve of the t-BiF₃/C nanocomposite, because, as mentioned before, only the tysonite form of BiF₃ reforms during the delithiation, the two nanocomposites being therefore essentially identical at the end of the first lithiation. The fact that the sudden voltage increase during the delithiation is related to a polarization increase is further supported by Fig. 6 where the first cycle of the t-BiF₃ nanocomposite at different rate is presented. Hence, when the current density is increased the transition from the 3.3-V plateau to the 3.7-V plateau occurs at an earlier stage of the delithiation, as one would expect for a kinetically limited transition.

Analogous to what we have proposed for the lithiation reaction, the division of the delithiation plateaus due to kinetics effects can be understood in terms of transport mechanisms. Schematics of the two proposed transport mechanisms for the delithiation are depicted in Fig. 16. At the end of the lithiation, what were the BiF₃ nanoparticles in the initial nanocomposite are now aggregates of fine BiO⁺ and LiF nanoparticles arranged in a shell. When the oxidation reaction commences, the Li⁺ ions diffuse from the LiF nanoparticles near the surface of the aggregates directly into the electrolyte and the electrons are transferred from the BiO⁺ nanoparticles near the surface of the (LiF + BiO⁺) aggregates directly to the carbon matrix, inducing the oxidation of the bismuth metal into BiF₃ (transport mechanism A in Fig. 16). The kinetic hindrances for those electronic and ionic transport mechanisms are small, and therefore, the polarization is small (less than 0.1 V according to the GITT plot of Fig. 9), resulting in a plateau at 3.3 V vs Li/Li⁺. After

Figure 16. Schematics of the two different transport mechanisms suggested for the delithiation. Mechanism A (x in “LiₓBiF₃” > 1): the electrons are transferred to the carbon matrix from the BiO⁺ nanoparticles near the surface of the (BiO⁺ + LiF) aggregate and the Li⁺ ions diffuse to electrolyte from the LiF nanoparticles near the surface of the (BiO⁺ + LiF) aggregate, inducing the oxidation of BiO⁺ into BiF₃. Mechanism B (x in “LiₓBiF₃” < 1): all the surface of the (BiO⁺ + LiF) aggregate has been oxidized into BiF₃. For the delithiation reaction to proceed the electrons have to tunnel through the remaining BiO⁺ nanoparticles to the carbon matrix through the BiF₃ layer and the Li⁺ ions have to diffuse from the remaining LiF nanoparticles to the electrolyte through the BiF₃ layer.
although from the XRD patterns shown in Fig. 1 the BiF$_3$ crystallite size does not seem to decrease much when the milling time is increased, the distribution of crystallite size is probably different. Hence, the longer the milling time the more the nanocomposite has BiF$_3$ crystallites of extremely small dimensions and the less it has 30-nm BiF$_3$ crystallites. If the average particle size gets smaller when the high-energy milling time is increased, the surface over volume ratio of the BiF$_3$ particles becomes larger and the transition from transport mechanism A to transport mechanism B during the delithiation occurs later. This would explain why, as can be seen in the inset of Fig. 17, the t-BiF$_3$/C nanocomposite high-energy milled for 4 h does not exhibit the second plateau at 3.7 V during delithiation. The smaller average crystallite size may also justify the improved capacity retention when the milling time is increased.

**Conclusion**

The reversible conversion reaction occurring in the BiF$_3$/C nanocomposite when it is cycled against lithium metal has been studied by electrochemical methods, in situ XRD, in situ XAS, and SAED. All the results obtained confirm that BiF$_3$ is fully reduced to LiF during lithiation and is fully reformed during the following delithiation.

It has been demonstrated that both lithiation and delithiation reactions are two-phase reactions. No intermediate bismuth fluoride or lithium bismuth fluoride compounds where the oxidation state of the bismuth differs from 0 or 3 have been identified at any stage of the conversion or reconversion reactions.

It has been shown that regardless of the amount of orthorhombic BiF$_3$ in the initial nanocomposite, only the tysonite form of BiF$_3$ reforms during delithiation.

Finally, it has been demonstrated that the different voltage plateaus or pseudo plateaus occurring during lithiation and delithiation may stem from kinetic, as opposed to thermodynamic, effects. A model based on the variation of the electronic and ionic transport mechanisms with the composition has been proposed to explain those plateaus.

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