Comprehensive Approach to Investigate the De-/Lithiation Mechanism of Fe-Doped SnO₂ as Lithium-Ion Anode Material

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Iron-doped tin oxide (Sn₀.₉Fe₀.₁O₂), and specifically carbon-coated Sn₀.₉Fe₀.₁O₂-C (Sn₀.₉Fe₀.₁O₂-C) provides high reversible capacity and a reasonably low de-/lithiation potential owing to the combined conversion and alloying mechanism. The initial (quasi-)amorphization during the first lithiation, however, renders the initial (quasi-) amorphous nature of the active material after the initial lithiation.

1. Introduction

Lithium-ion batteries (LIBs) are the electrochemical energy storage technology of choice to power portable electronic devices and increasingly also (hybrid) electric vehicles.[1,2] Specifically for the latter application, however, further improvement is needed with respect to the energy and power density of LIBs—especially the potential for fast charging remains an unsolved issue.[3,4] The major limiting factor in this regard is the graphite-based negative electrode owing to the limited lithiation kinetics and the risk of lithium metal plating at high currents and low temperatures.[5] Besides Li₄Ti₅O₁₂ as high-power, but low-energy alternative,[6,7] the majority of potential candidates follows either an alloying mechanism (e.g., Si or Sn[8–10]), a conversion mechanism (e.g., Fe₂O₃ or CoO[11–13]), or a combination of these two mechanisms in one single material, also referred to as conversion-alloying materials (CAMs).[14] A family of CAMs that shows potentially high specific capacities of more than 1000 mAh g⁻¹ and a reasonably low de-/lithiation potential is based on SnO₂. Pure SnO₂, however, suffers from an essentially irreversible conversion reaction, which limits its theoretically available reversible capacity to about 782 mAh g⁻¹, i.e., the theoretical capacity of the alloying reaction. The electrochemical performance of SnO₂-based materials can be improved, for instance, by designating materials with a high amount of oxygen vacancies[15] or the utilization of SnO₂-x/Fe₂O₃ heteronanocrystals.[16] Another strategy is, to dope tin oxide with a small amount (e.g., 10%) of a transition metal (TM), with Sn₀.₉Fe₀.₁O₂ being presumably the most investigated compound of this kind.[17–21] The presence of the TM dopant leads to the formation of much smaller Sn₀ nanograins during the conversion reaction, which is important for the reversibility of the conversion, as it allows for the formation of a percolating conductive network. Further improvement of the cycling stability can be achieved by applying a carbonaceous coating, which raises the electronic conductivity, prevents particle agglomeration, and stabilizes the solid electrolyte interphase (SEI).[22,23] Although significant knowledge on the structural changes during cycling on the performance of Sn₀.₉Fe₀.₁O₂-C has been obtained, a detailed understanding of the reaction mechanism is, however, still missing. Investigations, were limited so far to the application of electrochemical methods and operando X-ray diffraction (XRD) experiments.[24]
Specifically, the latter technique is limited in providing in-depth insights due to the (quasi)amorphous or nanocrystalline nature of the reaction products in the fully lithiated state. In addition, the initial crystalline (or any well-crystallized) structure is not recovered upon delithiation. Nonetheless, the fundamental understanding of the reaction mechanism, also upon delithiation, is of utmost importance to overcome the remaining challenges such as the improvement of the Coulombic efficiency and the reduction of the pronounced voltage hysteresis at elevated potentials.[23]

Herein, we report the comprehensive investigation of the reaction mechanism by combining highly complementary characterization techniques, including a set of in/ex situ spectroscopic techniques, namely ⁵⁷Fe Mössbauer, ¹¹⁹Sn Mössbauer, ⁷Li magic angle spinning (MAS) nuclear magnetic resonance (NMR), and X-ray absorption spectroscopy (XAS), coupled with operando XRD and operando isothermal microcalorimetry (IMC) of Li₅[Sn₀.₉Fe₀.₁O₂]₅-C coin cells as well as of single Sn₀.₉Fe₀.₁O₂-C electrodes. Especially the calorimetric techniques may provide fundamental insights into the parasitic side reactions with the electrolyte and polarization effects, i.e., the origin of the Coulombic inefficiency and (part of) the voltage hysteresis, by following the irreversible and reversible heat evolution during discharge and charge.

2. Results and Discussion

2.1. Physicochemical Characterization of (Fe-doped) SnO₂

The XRD patterns of the three active materials SnO₂, Sn₀.₉Fe₀.₁O₂, and Sn₀.₉Fe₀.₁O₂-C are presented in Figure 1a. The comparison of the XRD patterns with the powder diffraction file (PDF) reference reveals that the reflections are matching well with the reference for tetragonal cassiterite-structured SnO₂ (space group: P₄₂/mnm with the lattice parameters a = 4.737 Å and c = 3.185 Å[24,25]) and no additional reflections were observed, indicating that all materials were phase-pure, that the iron dopant was successfully introduced into the tin oxide lattice, and that the carbon coating did not have an impact on the crystal structure, in line with previous studies.[20,21] All three diffraction patterns show rather broad reflections, pointing at a small crystallite (and potentially particle) size and/or a low crystallinity. By using the Scherrer equation, an average crystallite size of about 10 nm was calculated for pure SnO₂. For Sn₀.₉Fe₀.₁O₂, this value is slightly reduced to around 6 nm, suggesting that the iron doping results in a slightly reduced crystallite size and/or a slightly lower crystallinity. The same crystallite size was obtained for Sn₀.₉Fe₀.₁O₂-C, showing that the thermal treatment during the carbon coating does not lead to the sintering of the particles. The morphology

![Figure 1. a) X-ray diffraction (XRD) patterns of SnO₂ (in purple), Sn₀.₉Fe₀.₁O₂ (in black), and Sn₀.₉Fe₀.₁O₂-C (in blue); in the bottom the powder diffraction file (PDF) reference for tetragonal cassiterite-structured SnO₂ (PDF 00-005-0467) is provided. b–d) High-resolution transmission electron microscopy (HRTEM) images of b) SnO₂ (with an image at lower magnification as inset), c) Sn₀.₉Fe₀.₁O₂, and d) Sn₀.₉Fe₀.₁O₂-C.](#)
and crystallinity of the active materials were analyzed via high-resolution transmission electron microscopy (HRTEM). The HRTEM images of pure SnO₂, Sn₀.₉Fe₀.₁O₂, and Sn₀.₉Fe₀.₁O₂-C are displayed in Figure 1b–d, respectively. All three materials are characterized by a very small particle size in the range from 10 to 20 nm, with a trend to slightly smaller particles in the case of Sn₀.₉Fe₀.₁O₂-C (Figure 1c,d) in agreement with the XRD data. In fact, all particles are single-crystalline, i.e., the crystallite size determined by XRD is equal to the average particle size. For Sn₀.₉Fe₀.₁O₂-C (Figure 1d), the primary particle agglomerates are covered by an amorphous carbon layer with a thickness of about 5–10 nm in agreement with a previous study.²¹ Furthermore, TEM EDX mapping of Sn₀.₉Fe₀.₁O₂-C (Figure S1, Supporting Information) shows a homogeneous dispersion of Fe in the sample, along with Sn.

In order to further investigate the impact of the Fe doping on the electronic and local structure, XAS was performed at the Sn L₃-edge and Fe K-edge. As illustrated in Figure 2a, pure SnO₂ shows a tetragonal cassiterite structure, with six oxygen atoms (represented by the red spheres; lattice parameters: \(a = 4.737 \text{ Å} \) and \(c = 3.186 \text{ Å}\); modified from ref. [24]). b) X-ray absorption near edge structure (XANES) spectrum of Sn₀.₉Fe₀.₁O₂-C at the Sn L₃-edge. c) XANES spectra of Sn₀.₉Fe₀.₁O₂ (in black) and Sn₀.₉Fe₀.₁O₂-C (in blue) at the Fe K-edge. d) Close-up of the absorption edge of the two XANES spectra shown in (c). e) Ab initio calculated XANES spectrum for the Fe K-edge of Sn₀.₉Fe₀.₁O₂ in comparison with the measured XANES spectrum of Sn₀.₉Fe₀.₁O₂.
The L$_2$-edge of Sn$_{0.9}$Fe$_{0.1}$O$_2$-C is presented in Figure 2b and is in good agreement with the spectrum reported for commercial SnO$_2$.[26] According to this earlier study on SnO$_2$, the indicated peaks (A), (B), and (C) in the near-edge region of the X-ray absorption edge can be assigned to certain electron transitions to empty or quasi-bound states. Metallic tin has the electron configuration [Kr]$4d^{10}5s^25p^3$, while Sn$^{4+}$ in SnO$_2$ shows the electron configuration [Kr]$4d^{10}$. As a consequence, the 5s orbital is empty and can accommodate electrons, and the transitions (A) and (B) are assigned to the transition from 2p$_{3/2}$ → 5s$^1$.[26] Although it would commonly be expected that this transition results in only one peak. However, Fracchia et al.[26] for instance, ascribed the appearance of two peaks to the covalent character of the Sn–O bond in SnO$_2$. This means that the Sn 5s and 5p states are showing some degree of hybridization with the O 2p states from the ligands, which leads to an additional electronic configuration, likely leading to the second peak (B). Most important, though, for the present study is the finding that the tin in Sn$_{0.9}$Fe$_{0.1}$O$_2$-C has the same oxidation state, lattice position, and coordination as in SnO$_2$. To get comparable information about the iron (in the absence and presence of the carbon coating), XANES spectra of both Sn$_{0.9}$Fe$_{0.1}$O$_2$ and Sn$_{0.9}$Fe$_{0.1}$O$_2$-C were recorded at the Fe K-edge (Figure 2c). Overall, the two spectra reveal very similar features and both pre-edge features and the main edge positions are qualitatively in line with octahedrally coordinated Fe$^{3+}$,[27] which is in line with an earlier study by X-ray photoelectron spectroscopy (XPS) on noncoated Sn$_{0.9}$Fe$_{0.1}$O$_2$.[21] When having a closer look at the Fe K-edge in the XANES spectra (Figure 2d), though, it is observed that the absorption edge of Sn$_{0.9}$Fe$_{0.1}$O$_2$-C is slightly shifted toward lower X-ray photon energies. This indicates that iron is partially reduced to a slightly lower oxidation state during the carbon coating process, as also found for Fe-doped ZnO.[28] and Mn-doped ZnO.[29] In both cases, however, the experimentally recorded spectrum qualitatively match the ab initio calculated XANES spectrum of Sn$_{0.9}$Fe$_{0.1}$O$_2$ (Figure 2e), indicating that iron is octahedrally coordinated by six oxygen as the Sn site in SnO$_2$, and that the coordination environment is asymmetric.

We may note at this point that the introduction of aliovalent iron into the tin oxide structure is presumably accompanied by the formation of oxygen vacancies and/or interstitial cationic sites. As we cannot safely exclude one or the other, neither quantify the amount of oxygen vacancies, we may continue referring to this material as Sn$_{0.9}$Fe$_{0.1}$O$_2$-C in the following.

2.2. Investigation of the Reaction Mechanism

For the investigation of the reaction mechanism of Sn$_{0.9}$Fe$_{0.1}$O$_2$-C, we firstly conducted an operando XRD experiment. The results are displayed in Figure S2 (Supporting Information) and are discussed in detail in the Supporting Information. The findings are well in line with a previous operando XRD investigation on Sn$_{0.9}$Fe$_{0.1}$O$_2$[21] and generally confirm an initial Li$^+$ insertion, followed by the reduction of the oxide to metallic tin upon further lithiation and eventually the formation of the Li$_x$Sn alloy. Nevertheless, owing to the (quasi-)amorphous nature of the compounds formed in the discharged (i.e., lithiated) state and the fact that the material remains (quasi-)amorphous also upon delithiation, little information can be gained beyond the initial lithiation and the iron dopant is essentially invisible in the XRD patterns.

Therefore, we combined the operando XRD analysis with ex situ $^{119}$Sn and $^{57}$Fe Mössbauer spectroscopy. In addition to the pristine Sn$_{0.9}$Fe$_{0.1}$O$_2$-C also partially (0.7 V) and fully lithiated (0.01 V) as well as fully delithiated (3.0 V) electrodes were studied. These three different voltage points are highlighted in the cyclic voltammogram in Figure S3 (Supporting Information). The corresponding $^{119}$Sn and $^{57}$Fe spectra are presented in Figure 3a,b, respectively, and the summaries of the fitting results are provided in Table S1, Supporting Information ($^{119}$Sn) and Table S2, Supporting Information ($^{57}$Fe). For the pristine sample, the $^{119}$Sn spectrum (Figure 3a) was fitted by a doublet with an isomer shift (IS) of 0.01 mm s$^{-1}$ and a small quadrupole splitting (QS) of 0.41 mm s$^{-1}$, and thus strongly overlapping lines. These values are characteristic of Sn$^{4+}$ in the cassiterite (SnO$_2$) structure.[30] The QS is caused by the intrinsic asymmetry of the SnO$_2$ octahedra. The partial lithiation to a cutoff voltage of 0.7 V (i.e., below the initial voltage plateau, see Figure S2a, Supporting Information) leads to a decrease of the singlet component of cassiterite tin oxide, accompanied by a slight change of the IS to 0.060 mm s$^{-1}$. According to the in situ $^{119}$Sn Mössbauer investigation by Sandu et al.[31] such a shift indicates the reinforcement of the SnO$_2$ lattice as a result of the initial Li$^+$ insertion, leading to the formation of new Li–O bonds without the destruction of the initial Sn–O bonds. The additionally observed doublet component centered at 1.344 mm s$^{-1}$ is assigned to the presence of metallic tin,[32] corroborating the assignment of the voltage plateau at ~1.0 V to the reduction of Sn$^{4+}$ to Sn$^0$. In fact, Sandu et al.[31] reported that the insertion and further reduction to metallic tin partially overlap, in agreement with the operando XRD data (Figure S2d, Supporting Information). Upon further lithiation to 0.01 V, the $^{119}$Sn spectrum reveals an additional peak at 1.127 mm s$^{-1}$, which has been assigned to metallic tin with metallic bonds to tin and lithium, while there is also still some interaction with oxygen.[32] Given the absence of any SnO$_2$-related reflection in the corresponding XRD data (Figure S2e, Supporting Information), we may assume that this is related to the interaction of the tin (alloy) surface with the surrounding Li$_2$O matrix and/or the reaction with oxygen traces during the ex situ sample preparation owing to the high reactivity of the fully discharged material. Most interestingly, though, with regard to the (quasi-)amorphous nature of the active material in the delithiated state, is the finding that tin is not fully re-oxidized at 3.0 V. The $^{119}$Sn spectrum is comparable to the spectrum recorded for the sample discharged to 0.7 V, indicating that only the alloying reaction is completely reversible, while the conversion reaction, i.e., the re-oxidation to tin oxide remains incomplete. Besides, both components, the one for oxidized tin centered at 0.132 mm s$^{-1}$ and the one for metallic tin centered at 1.599 mm s$^{-1}$, show increased QS values of 0.463 and 1.244 mm s$^{-1}$, respectively, as a consequence of the pronounced disorder of the local environment.

For the fitting of the $^{57}$Fe Mössbauer spectrum of pristine Sn$_{0.9}$Fe$_{0.1}$O$_2$-C (Figure 3b), two doublets were necessary to achieve a reasonable fit. This indicates two different Fe environments in the sample, either in one compound or in different phases. The main doublet (86%) with IS = 0.39 mm s$^{-1}$ and QS = 0.87 mm s$^{-1}$ is assigned to Fe$^{3+}$ in the octahedral positions of SnO$_2$,[33,34] which
is in good agreement with the XAS results and the partial substitution of Sn$^{4+}$ by Fe$^{3+}$. The second doublet with IS = 0.083 mm s$^{-1}$ and a rather small QS of 0.321 mm s$^{-1}$ indicates the presence of Fe with a different oxidation state, which is in agreement with the XAS results that showed that Fe is partially reduced during the carbon coating process. Two possible explanations for the IS close to 0 mm s$^{-1}$ are possible: (i) this component belongs to Fe$^{2+}$ in a low-spin configuration, or (ii) this component represents Fe$^{0}$ inside very small Fe metal clusters that are too small to be detected by XRD and to establish magnetic ordering, while even very minor traces can give a significant signal in the Mössbauer spectra. The HRTEM analysis presented herein (Figure 1d) and in previous studies,[20,21] however, revealed perfectly crystalline particles also after the carbon coating, suggesting that the signal observed is related to the formation of Fe$^{2+}$ in a low-spin state rather than a complete reduction to the metallic state. The evolution of the $^{57}$Fe spectra upon discharge (lithiation) shows that the doublet attributed to Fe$^{3+}$ is gradually shifting from 0.390 mm s$^{-1}$ (pristine state) to 0.346 mm s$^{-1}$ (0.7 V) and further to 0.183 mm s$^{-1}$ (0.01 V). This significant shift indicates a gradual reduction.[35] Notably, an IS of 0.0 mm s$^{-1}$, which would correspond to the α-Fe reference, was not reached, neither was the typical hyperfine splitting observed. Given that a preliminary analysis of ex situ XAS data revealed the reduction of the transition metal dopant to the metallic state (not shown herein), a possible explanation for the findings obtained by $^{57}$Fe Mössbauer spectroscopy might be the formation of iron metal nanodomains with a superparamagnetic rather than ferromagnetic behavior or the formation of an iron-tin alloy, which would also lead to superparamagnetic behavior.[33] In fact, an in-depth investigation of iron-doped zinc oxide revealed the formation of an iron-zinc alloy upon lithiation[36] and it appears likely that such reaction occurs also for iron-doped tin oxide. The subsequent delithiation to 3.0 V reveals a Fe$^{2+}$ component centered at 0.312 mm s$^{-1}$, indicating the re-oxidation to Fe$^{3+}$. This re-oxidation, however, remains incomplete, as apparent from the additionally observed doublet at 0.941 mm s$^{-1}$ with a significantly higher QS of 1.784 mm s$^{-1}$, which is assigned to the accommodation of Fe$^{3+}$ in an octahedral position.[33] In fact, an incomplete re-oxidation of the iron dopant was observed also for iron-doped zinc oxide,[37] suggesting that the two active materials behave similarly upon electrochemical de-/lithiation.

To gain further insights into the reaction mechanism, also ex situ $^{7}$Li MAS NMR spectroscopy was conducted at the same states of dis-/charge (Figure 3c). For the pristine Sn$_{0.9}$Fe$_{0.1}$O$_{2}$-C, no lithium is found, as expected. In the spectrum recorded for the partially lithiated material (0.7 V), a peak at 0 ppm appears. This peak is assigned to lithium in a diamagnetic environment, i.e., Li$_2$O,[36,38] which is formed along with the formation of metallic tin. Upon further lithiation to 0.01 V the peak intensity is increasing as a result of the ongoing reduction of the initial oxide. These results are in good agreement with the findings obtained by ex situ Mössbauer spectroscopy. In addition, a broad shoulder is observed in the fully lithiated state at 0.01 V, revealing the presence of a second lithium-containing compound, presumably the lithium-tin alloy.[38] During the subsequent delithiation, this broad shoulder vanishes, confirming the complete reversibility of the alloying reaction, but the peak related to Li$_2$O remains. While the presence of Li$_2$O also in the fully delithiated state might in part originate from the formation of the SEI,[39] the pronounced intensity suggests that the conversion reaction is incomplete, in agreement with the ex situ Mössbauer spectroscopy investigation.

In sum, the ex situ Mössbauer and $^{7}$Li NMR spectroscopy analysis reveals the following findings: (i) In the pristine state, Fe$^{3+}$ is located in the octahedral position of the cassiterite crystal structure, partially replacing tin. (ii) The alloying reaction is

Figure 3. a) $^{119}$Sn Mössbauer spectra, b) $^{57}$Fe Mössbauer spectra, and c) $^{7}$Li MAS NMR spectra of the pristine Sn$_{0.9}$Fe$_{0.1}$O$_{2}$-C and Sn$_{0.9}$Fe$_{0.1}$O$_{2}$-C discharged (disc.) and charged (char.) to different states of de-/lithiation, i.e., 0.7 and 0.01 V upon discharge and 3.0 V upon charge.
fully reversible, while the conversion reaction and re-oxidation of tin and iron remain incomplete.

To complement the operando XRD and ex situ Mössbauer spectroscopy and \(^7\)Li MAS NMR study, operando IMC was performed in order to gain additional insights into the de-/lithiation mechanism. The recorded heat flow and the corresponding voltage profile of the \(Li||Sn_{0.9}Fe_{0.1}O_2-C\) cell are presented in Figure S4 (Supporting Information). A more detailed analysis following a normalization of the recorded heat flow to the mass of the Sn\(_{0.9}Fe_{0.1}O_2-C\) active material is presented in Figure 4a–c. The initial discharge is displayed in Figure 4a. Generally, the heat flow profile reveals three distinct peaks at 3\% (see Figure 4b for a magnification of the first part of the discharge), 7\%, and 34\% state of discharge (SOD), which is in accordance with the inflection points of the corresponding voltage profile. Additionally, an increase in heat flux is observed starting from about 80\% SOD. Following the three distinct peaks, the heat flow, and voltage profile are separated into three regions, i.e., Region (A)–(C). The first peak in Region (A) at 3\% SOD is assigned to the initial insertion of lithium into the cassiterite host structure,\(^{[31]}\) in accordance with the previous findings. The second peak at 7\% SOD appears just ahead of the voltage plateau at around 1.0 V. Hence, the peak in the heat profile is attributed to the nucleation of the second phase, i.e., metallic tin and Li\(_2\)O, which is formed along the voltage plateau.\(^{[36]}\) Finally, Region (C) is attributed to the formation of the lithium-tin alloy (along with a further reduction of the oxide to metallic tin, as observed from the previous experiments) and the eventual increase in heat flow starting from about 80\% SOD is assigned to the decomposition of the electrolyte.

During the subsequent delithiation (Figure 4c) the heat flow is generally much lower, which very well reflects the voltage hysteresis. Besides, the delithiation heat flow reveals an essentially continuous increase, though with a varying slope, and is roughly divided into two regions, i.e., Region (D) and Region (E), according to the peak observed for the heat flow and the inflection point of the charge profile that occur at the same state of charge (SOC). In Region (D), the heat flow increases only very slowly up to about 35\% SOC. The corresponding part of the voltage profile has been assigned to the dealloying reaction, which appears to be a kinetically favorable process. The subsequent Region (E) commences with a peak at about 42\% SOC along with the inflection point of the charge profile. Hence, this peak is attributed to the onset of the reconversion reaction.
of metallic tin and iron to the corresponding oxides. The further course of the graph shows a steep increase in heat flow, finally reaching around ~59 mW g⁻¹ at the cut-off voltage of 3.0 V. In other words, the reconversion reaction is characterized by a substantially larger heat flow than the dealloying reaction.

Generally, the total heat flux caused by the electrochemical dis-/charge process consists of three contributions: (i) a reversible contribution $Q_{\text{rev}}$, that reflects the entropy change during the electrochemical processes, which changes its sign when the direction of the electrochemical processes, i.e., the current direction is inverted; (ii) an irreversible contribution $Q_{\text{pol}}$, which always leads to the evolution of heat owing to the deviation from equilibrium during current flow; and (iii) the Joule heat that is caused by the current flow through the electrolyte and which also always produces heat. For a further evaluation of these different contributions to the overall heat flow, the galvanostatic intermittent titration technique (GITT), including a variation of the temperature during the open circuit voltage (OCV) step, was used. During the intermittence of the dis-/charge process, the cell voltage relaxed from the cell voltage with current flow $E_{\text{load}}$ to the (close-to) equilibrium open cell voltage $E_{\text{OCV}}$. For the determination of the irreversible, polarization-related heat flow $Q_{\text{pol}}$, $E_{\text{load}}$ and $E_{\text{OCV}}$ were estimated from the voltage profiles during intermittent discharging and charging shown in the upper panels of Figure 4d,e. Note that only the sections with current flow are depicted. During the discharge process in Figure 4d the cell voltage drops to its value for steady current flow $E_{\text{load}}$, while during the intermittence periods (not shown) the cell voltage relaxes positive toward $E_{\text{OCV}}$. The difference $E_{\text{load}} - E_{\text{OCV}}$ corresponds to the overpotential, i.e., the deviation from equilibrium. Multiplying the overpotential with the applied specific current of 50 mA g⁻¹ yields the corresponding irreversible heat flux $Q_{\text{pol}}$. The entropic heat flow contribution $Q_{\text{entr}}$ corresponds to the reversible heat flow and was derived by measuring the change of the OCV upon temperature steps of $\Delta T = 10$ K, that is the temperature coefficient of the cell potential, which is proportional to the reaction entropy of the cell reaction. The Joule heat is estimated from the electrolyte resistance ($\approx 8 \Omega$) and amounts to about 0.03 mW g⁻¹, which is much smaller than the other two contributions and which is therefore neglected in the following discussion. The corresponding values of $Q_{\text{pol}}$ and $Q_{\text{entr}}$ for the de-/lithiation of the Li||Sn₀.₉Fe₀.₁O₂-C coin cells are presented in Figure 4d along with the GITT experiment. The polarization heat flow $Q_{\text{pol}}$ reveals an initial rapid decrease after a jump from the first to the second data point, followed by a small local maximum at approximately 35% SOD. The latter is in accordance with the second peak in Figure 4a that has been assigned to the onset of the alloying reaction. Similarly, the entropic heat flow $Q_{\text{entr}}$ shows a distinct peak at ~5% SOD, which is in line with the second peak at 7% SOD in Region (B) of the IMC experiment, given the resolution of the experiment. This large increase in $Q_{\text{entr}}$ with a minimum of ~18 mW g⁻¹ is attributed to the onset of the conversion reaction, i.e., the reduction of the oxide to the metals and the decay of the crystalline structure. Note that the entropic heat flux $Q_{\text{entr}}$ reflects the entropy change of the cell reaction, including both the lithiation/delithiation of the iron-doped tin oxide and the reaction at the counter electrode, i.e., the Li²⁺/Li bulk metal deposition/dissolution reaction. The entropic contribution of the half cell reaction will be explicitly discussed below. Subsequently, at higher SOD, $Q_{\text{entr}}$ decreases steadily until it reaches a constantly small value of less than 1 mW g⁻¹. In accordance with our earlier study on iron-doped zinc oxide,[46] it is concluded that overall $Q_{\text{pol}}$ and specifically $Q_{\text{entr}}$ show more pronounced variations for the conversion reaction.

Upon delithiation (Figure 4e), $Q_{\text{pol}}$ is constantly increasing until it reaches 36 mW g⁻¹ at the cut-off voltage of 3.0 V. There is a small step-like increase observed at about 40% SOC, which coincides with the peak in the overall heat flow (Figure 4c), indicating the onset of the reconversion reaction. $Q_{\text{pol}}$ remains generally rather small, never exceeding 2 mW g⁻¹. Nonetheless, there is a significant increase when the reconversion sets in, before it decreases again toward the end of the charge process. It is noteworthy that $Q_{\text{pol}}$, determined for the discharge and charge processes, coincides nicely for high Li contents, i.e., for SODs >40% and SOCs <60%, respectively, which signals high reversibility of the lithiation/delithiation process at higher Li contents. However, at lower Li concentrations rather pronounced deviations occur. In particular the rather steep peak of $Q_{\text{pol}}$ upon delithiation extending from 0% to 20% SOD becomes smeared out between 60% and 100% SOC upon delithiation. This may be attributed, e.g., to SEI formation and irreversible structural transformations, namely the incomplete recovery of the cassiterite structure during the first dis-/charge cycle, as discussed above.

To corroborate the above measurements of the reversible contribution to the heat flux $Q_{\text{rev}}$, and to obtain information about the timescale on which the reversible processes occur, we performed electrochemical microcalorimetric measurements of the reversible heat/cold evolution at the Sn₀.₉Fe₀.₁O₂-C electrode, i.e., of the half-cell electrode reactions. In the following, this method is abbreviated half-cell microcalorimetry (HCMC).[40-42] For this purpose, we measured the temperature at the back of a thin Sn₀.₉Fe₀.₁O₂-C electrode with a thin pyroelectric sensor, while the charging or discharging reaction is conducted for 10 ms by a small potential pulse, starting from a well-equilibrated rest potential. Such a 10 ms pulse duration is short enough to avoid heat dissipation into the bulk of the electrolyte and long enough that the electrode-sensor assembly becomes thermally equilibrated.

Figure 5 shows typical potential, current, and temperature transients for the lithiation and delithiation at a rest potential of 0.07 V, corresponding to a SOD of about 90%, which is well in the lithium-tin alloy phase. When the potential pulse is applied, at $t = 10$ ms, the current peaks and the temperature at the electrode start to fall for the negative potential pulse (lithiation), while it begins to rise for the positive pulse (delithiation), signaling cold or heat evolution, respectively, caused by the electrochemical electrode processes. At $t = 20$ ms the cell was switched to open cell conditions and the outer current flow ceased. The potential slightly relaxed on a timescale of roughly 100 ms. Shortly after the current ceased, the temperature transients reached a minimum for the delithiation and a maximum for the lithiation process. After reaching its extremum the temperature relaxed toward the temperature before the application of the pulses by dissipation of cold/heat into the electrolyte. From simulations and the pyroelectric coefficients of the sensor we estimate that the overall temperature change is well below 1 mK. Thus our measurements proceeded quasi-isothermal.
The symmetric behavior of the current and temperature transients in Figure 5a,b under potential pulse inversion already signals a high degree of reversibility of the electrochemical dis-/charge processes in the pulse experiments. Note that the electrochemical conversion during each pulse amounted to only $\approx 7 \text{ mC g}^{-1}$ in the depicted experiments, which has to be compared with the theoretical capacity of the material ($\approx 4300 \text{ C g}^{-1}$) and therefore corresponds to only $\approx 1.6 \times 10^{-2} \%$. A closer inspection of the results reveals that the absolute value of the temperature variation upon cooling is about half of that during warming, although the absolute amount of charge, which flowed during the potential pulses, is about the same for both pulse directions (with a deviation of about 9%). This reflects irreversible contributions to the total heat, which do not change their sign upon current reversal, while the entropic contributions to the heat change their sign. In other words, due to irreversibly exchanged heat, the electrode becomes less cold upon lithiation and warmer upon delithiation than it would be expected for a purely reversible behavior. The irreversible contribution can be directly removed from the temperature transients by subtracting temperature transients obtained from the positive and negative potential pulses. This results in an (averaged) temperature transient, representing the reversible warming or cooling of the electrode during the electrode reaction. By this procedure also experimental artifacts such as long-term temperature drifts or heat from ongoing background reactions are removed. The closer inspection of the temperature transients in Figure 5 for longer times indeed reveals that the temperature relaxation upon cooling (Figure 5a) is faster than that upon warming (Figure 5b), indicating background heat evolution, probably due to side reactions such as an ongoing SEI formation and electrolyte decomposition. Note that we are extremely sensitive to background processes, since their continuous heat evolution adds to the potential-pulse driven heat evolution of only 10 ms duration. Indeed, ongoing heat evolution due to background processes rendered it impossible to measure the heat during the first discharge step. Only after conditioning the electrode by a slow voltammetrically controlled dis-/charge cycle (1 mV s$^{-1}$; 3.0 V $\rightarrow$ 0.01 V $\rightarrow$ 3.0 V) background heat evolution becomes sufficiently small for the reliable determination of the pulse-driven heat evolution. From the averaged reversible temperature transients, absolute values for the reversible heat exchange were derived (see the Experimental Section for more details on the procedure). To include also reversible heat exchange during the relaxation period, we integrated the reversible heat flux up to 100 ms after the onset of the potential pulse.

Figure 6 depicts the reversible molar heat of the discharge process at the Sn$_{0.9}$Fe$_{0.1}$O$_2$-C electrode, i.e., for the cathodic process direction (red circles). The right axis gives the corresponding reaction entropy for the discharge process. We plotted the data versus the SOD, as obtained from the voltage profile of the second dis-/charge cycle (Figure S5, Supporting Information). Since the HCMC experiments started at well relaxed rest potentials, this procedure disregards the polarization overpotential, which is included in the voltage profile and may thus lead to an underestimation of the SOD. For the comparison with the GITT experiment, we included the corresponding reversible molar heat for the half-cell reaction at the Sn$_{0.9}$Fe$_{0.1}$O$_2$-C electrode in Figure 6 (black crosses), as calculated from the entropic heat flux in the lower panel of Figure 4d. For this purpose, the entropic heat flux data were divided by the specific current, yielding the reversible molar heat of the lithium metal deposition at the Li counter electrode, which we determined in a previous work to be 48 kJ mol$^{-1}$, corresponding to a reaction entropy of 160 J mol$^{-1}$ K$^{-1}$.[43,44] This value is indicated as a dashed horizontal line in Figure 6. Both datasets, the GITT data from the first discharge and the HCMC data obtained for the second discharge process, nicely coincide. In particular for high SODs $\geq 20\%$, both datasets reach the same high reversible molar heat or reaction entropy for the lithiation process of approximately 48 kJ mol$^{-1}$ or 160 J mol$^{-1}$ K$^{-1}$. At low SOD ($\leq 20\%$) both measurements exhibit a minimum of only about 15 kJ mol$^{-1}$ (50 J mol$^{-1}$ K$^{-1}$), whereas at the very beginning of the charge process a steep decrease of the reaction entropy is observed with an increasing SOD.

The differences between both datasets, namely the broader minimum of the HCMC data for SODs $\leq 20\%$ and the lower molar heat at the very beginning of the discharge process, are not too surprising when considering that the HCMC data were measured during the second dis-/charge cycle, where the original cassiterite structure of the iron-doped tin oxide...
The entropy of Li in the alloy phase is close to that of Li metal without pronounced influence of the disorder of the alloy. Indeed, assuming ideal solution behavior, the expected increase of the entropy of Li in the alloy phase upon diluting the Li concentration by a factor of 10 amounts to only 19 J mol⁻¹ K⁻¹, which would result in a decrease of the reversible molar heat of the lithiation process by only 5.7 kJ mol⁻¹. Therefore, at intermediate to high lithium contents in the lithium-tin alloy no significant variation of the molar heat is expected with a variation of the SOD, and the plateau of the molar heat between 25% < SOD < 100% can be well assigned to the desolvation and reduction of Li⁺ and subsequent alloying into the lithium-tin alloy phase. Only below ~25% SOD the molar heat steeply decreases by roughly 30 kJ mol⁻¹ and reaches a minimum at around 10% SOD. This strong decrease cannot be explained by gradual dilution effects of Li in the metal phase, but rather indicates a change in the discharge process. The low entropy values strongly suggest that there is no significant desolvation of Li⁺ ions involved in the electrochemical processes in this SOD range. This is compatible with pure reduction of the iron-doped tin oxide. For very low SODs, the reversible molar heat for the discharging process increases up to 30 kJ mol⁻¹ for the HCMC data and even higher for the GITT experiments. Although the definite assignment of a particular reaction mechanism is not possible at this stage, the high reaction entropy at very low SODs is compatible with the desolvation of Li⁺ ions and an initial insertion-type reaction prior to the reduction of the oxides to the metallic state.

Following a simplified energy balance model for batteries, which has been developed by Downie et al.,[45] the parasitic heat flow, e.g., due to irreversible phase transitions of the electrode material, SEI formation, and/or electrolyte decomposition, can be calculated by subtracting $Q_{\text{pol}}$ and $Q_{\text{entr}}$ from the total heat flow. Therefore, $Q_{\text{pol}}$ and $Q_{\text{entr}}$, which were determined by GITT,
were compared with the overall heat flow measured during the operando IMC experiment (Figure 7). Given the different experimental conditions for the two experiments this comparison is more qualitative than quantitative, but still provides interesting insights into the reaction mechanism. Generally, upon discharge (Figure 7a) the two main peaks for the onset of the conversion and alloying reaction are well apparent from both plots and the overall trend is the same, except beyond an SOD of about 80%, where the IMC-derived heat flow increases, while the GITT-derived heat contributions remain fairly constant. This indicates that at such low potentials, the contribution of the parasitic heat flow becomes increasingly relevant, thus, further corroborating the earlier assignment to reductive electrolyte decomposition. For the delithiation process (Figure 7b), the two profiles generally match each other very well, while the increase in heat flow toward the upper cut-off is more pronounced for the IMC-derived data than for the GITT-derived data, indicating that also the SEI reformation that occurs at such elevated potentials adds to the parasitic heat.[16,19,46] In combination with the generally higher heat flow for the conversion contribution, these findings provide an explanation for the beneficial impact of lower cut-off voltages on the energy efficiency in lithium-ion cells.[23]

4. Experimental Section

Materials Synthesis: \( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2 \) was synthesized in a similar manner as reported earlier.[29] In brief, 0.482 g (0.001 mol) iron(II) gluconate dihydrate (Alfa Aesar) and 10.262 g (0.030 mol) sucrose (Merck) were dissolved in 100 mL ultrapure water. Upon continuous stirring, 20 mL acetic acid (Sigma Aldrich) and 2.131 g (0.009 mol) tin(II) acetate (Alfa Aesar) were successively added to the solution, which was stirred for another 1.5 h. Subsequently, the solution was heated to 50 °C for 30 min, before evaporating the water at 180 °C for 5 h. The remaining black solid was further dried at 80 °C overnight and then manually ground in an agate mortar prior to the calcination at 450 °C for 3 h (heating rate: 3 °C min\(^{-1}\)) under ambient atmosphere. Pure tin(IV) oxide (SnO\(_2\)) was prepared accordingly, but without the addition of iron(II) gluconate dihydrate. For the carbon coating of \( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2 \) (\( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2\)-C), 1.200 g (0.007 mol) glucose (VWR Chemicals) was dissolved in 80 mL ultrapure water. Then, 800 mg of \( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2 \) was added. The resulting dispersion was transferred into a stainless steel autoclave (Berghof BR-100) and heated to 180 °C under continuous stirring for 13 h. The resulting precipitate was rinsed five times with 30 mL ultrapure water and two times with ethanol in a centrifuge before drying at 80 °C overnight. Finally, the powder was thermally treated at 500 °C for 4 h under an argon atmosphere (heating rate: 3 °C min\(^{-1}\)) to obtain the final product.

Physicochemical Characterization: The crystal structure of the synthesized samples was investigated via XRD using a Bruker D8 Advance diffractometer (Cu-K\(\alpha\) radiation, \( \lambda = 0.154 \) nm) within a 2\( \theta \) range from 20° to 100°. The carbon content in \( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2\)-C was determined by thermogravimetric analysis (TGA; Model Q5000, TA Instruments) under an oxygen atmosphere in a temperature range from 40 °C to 850 °C with a heating rate of 5 °C min\(^{-1}\), yielding 13 wt% of carbon. HRTEM was performed on an image Cs-corrected FEI Titan 80–300 kV at 300 kV and STEM-EDX measurements were recorded using a Thermofisher Talos 200X TEM equipped with a SuperX EDX detector at 200 kV. XAS was conducted at the XAFS beamline of the Elettra Synchrotron in Trieste, Italy. The storage ring was operated at

Figure 7. Comparison of the total heat flow measured by operando isothermal microcalorimetry (IMC; in red) and the sum of \( Q_{\text{pol}} \) and \( Q_{\text{entr}} \) (in blue), as determined by galvanostatic intermittent titration technique (GITT) for the electrochemical a) lithiation and b) delithiation of \( \text{Li|Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2\)-C in a coin cell (specific current: 50 mA g\(^{-1}\); cut-off voltages: 0.01 and 3.0 V).

3. Conclusions

In this work, the de-/lithiation mechanism of \( \text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2\)-C was comprehensively investigated by a combination of various complementary operando and ex situ characterization techniques. The findings reveal a three-step lithiation mechanism, including an initial Li\(^+\) insertion, followed by the reduction to the metallic phases and the eventual alloying reaction. These three steps, however, partially overlap—at least under the given experimental conditions. The subsequent delithiation occurs in two steps beginning with the dealloying, followed by the reconversion; the latter, though, remains partially incomplete, while the alloying reaction is fully reversible. This partially incomplete reconversion is accompanied by a significant heat release owing to the reformation of the SEI, highlighting the importance of lower cut-off voltages for such anode materials when employed in lithium-ion cells, which is also beneficial for achieving a high energy efficiency, i.e., a limited voltage hysteresis, and maintaining a high full-cell voltage also at decreasing SOC. Last but not least, this study highlights the need for a comprehensive approach to investigate the reaction mechanism of new electrode active materials via a set of complementary experimental methods, particularly if such materials are amorphous or turn amorphous during the initial lithiation.
2.0 GeV in top-up mode with a current of 280 mA. The experiments were performed at the Sn L3-edge and Fe K-edge in transmission mode by using three ionization chambers filled with appropriate mixtures of argon, nitrogen, and helium optimized to achieve the optimum level of absorption in each chamber. The white beam was monochromatized by using a fixed exit monochromator equipped with a pair of Si(111) crystals. Elemental Sn (L3 = 3929 eV) and Fe (K = 7112 eV) reference samples, placed between the second and the third chamber, were used for the energy calibration in each scan, which allowed for continuous monitoring of the energy. The absorption edge energy was determined as the first inflection point of the spectrum. The spectra were processed using the Demeter package. Normalization, background subtraction, energy calibration, and alignment were performed using the Athena software. The ab initio simulation of the XANES spectrum of the Fe K-edge was performed using the FDMNES software.[47] The Fe K-edge was calculated in the photoelectron energy range −5 < E < 120 eV with respect to the Fermi energy level using the Multiple Scattering Theory (MST). The Hedin–Lundqvist complex potential[48] was used to calculate the excited states, while the absorption cross-section was calculated within the dipolar approximation. A discrete FeO6 cluster with an asymmetric coordination environment was considered and the best agreement between experiment and calculation was obtained by fixing the Fe–O bond lengths to 2.12 Å (x3), similar to hematite, or contracted to 90% (x3) of that value.

**Operando XRD:** For the operando XRD measurements, a self-designed two-electrode cell was used.[49] The slurry, comprising the active material, conductive carbon (Super C65, IMERYS), and the binder (sodium carboxymethyl cellulose; CMC; Dow Wolff Cellulosics) in a weight ratio of 75:20:5, was homogenized using a planetary ball-mill (Pulverisette 4; Fritsch; milling conditions: 4 x 30 min at 400–800 rpm with 10 min rest in-between). The resulting dispersion was cast directly on a beryllium disc (25 mm diameter, 0.25 mm thickness; Materion), which served simultaneously as the current collector and “window” for the X-ray beam. The coated Be disc was dried for 4 h at room temperature and 60 °C under vacuum overnight. Metallic lithium (battery grade, Honjo) was used as the counter and reference electrode and two Whatman separators (d = 19 mm) drenched with 300 µL of the electrolyte (1 M LiPF6 in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC); UBE) served as the separator. Upon de-lithiation, the X-ray diffractograms were measured in a 2θ range of 22° ≤ 2θ ≤ 50°.

**Ex situ Li NMR and Mössbauer Spectroscopy:** For the ex situ Li NMR and Mössbauer spectroscopy investigation, Sn5F6O2-C was mixed with the conductive carbon in a ratio of 75:20 and dried overnight at 120 °C under vacuum. The resulting powder was transferred into an argon-filled glovebox (with an oxygen and water content below 0.1 ppm), in which pellets with a diameter of 8 mm and a mass of approximately 35 mg were pressed. These pellets were used as working electrodes in Swagelok-type T-cells with lithium metal foil (battery grade; Honjo) as counter and reference electrodes. A Whatman glass fiber sheet was used as the separator and 300 µL of the aforementioned electrolyte. The T-cells were cycled to specific cut-off potentials of 0.7 and 1.2 V upon lithiation and 3.0 V upon delithiation using a 400 mW laser pulse. The cell was allowed to rest for 4 h at OCV before it was dis-charged at a constant specific current of 50 mA g⁻¹ for 60 min. At the end of the current pulse, the cell voltage E°(cal) was measured. After 40 h of relaxation, the cell voltage was measured again to determine E°(OCV). Subsequently, the polarization was estimated from the difference between E°(OCV) and E°(cal). After each relaxation step, the temperature was ramped stepwise from the initial temperature of 20 °C to 10 °C, 20 °C, 30 °C, and back to 20 °C. Each temperature step was held constant for 2 h to allow the OCV to relax. Afterward, the entropic heat coefficient dE/dT was determined by the changes of the OCV values with respect to the temperature intervals. This procedure was repeated at different SODs and SOC to determine the polarization and entropic heat contributions as a function of the SOCC or SOC.

**Operando Isothermal Microcalorimetry (HCMC):** The microcalorimetric half-cell measurements were conducted in a home-built microcalorimeter[50,51] attached to a glove box under an argon atmosphere (O₂ < 5 ppm; H₂O < 5 ppm). As the working electrode (geometrical area of 0.2 cm²) a dendritic Cu foil was used, coated with the active material, as described above. On top of the working electrode, a propylene electrochemical cell was mounted, sealed with a Viton O-Ring. Li bands (approximately 15 × 2 × 1 mm³) were used as reference and counter electrodes. The cell contained about 400 µL of electrolyte (1 M LiPF6 in a 1:1 mixture of EC and DMC; UBE). For determining the heat flux during the electrochemically driven processes from the temperature transients, these were deconvoluted by employing the thermal response function of the electrode-sensor assembly, measured by illumination with a 2 mW laser pulse.[52] As discussed above, significant potential relaxation proceeds up to about 100 ms after the pulse. Thus, to include the reversible heat exchange during the relaxation processes, the heat flux was integrated up to 100 ms. To obtain absolute values for the reversible molar heat, the calorimeter was calibrated by measuring the electron transfer reaction in 0.5 M KFe(CN)₆/0.5 M K₄Fe(CN)₆, for which the corresponding molar heat is known from literature.[53] The data points in Figure 6 were obtained as the average from a total of 50 single temperature transient measurements at 10 different potential pulse amplitudes ranging from −300 to +300 mV. The absolute errors of the molar heat values were estimated to about 5 kJ mol⁻¹, mainly due to uncertainties from heat evolution of the rather strong background processes. The relative errors for the data points in Figure 6 are much smaller, as can be inferred from their rather smooth course. The reversible molar heat is referenced to the molar of elementary charges, which flowed in the outer cell circuit. It is given for the cathodic direction of the electrochemical processes, i.e., for the discharge (lithiation) process.

From the reversible molar heat, the reaction entropy of the investigated electrochemically driven processes can be directly derived. In principle, since the reversible molar heat of a half-cell reaction was considered,
entropic contributions from the ion transport in solution had to be included. However, due to the expected small entropy of transport of Li⁺ and PF₆⁻ in the organic carbonate-based electrolyte, such contributions were neglected here and the reaction entropy of the half cell process was obtained by dividing the reversible molar heat by the room temperature (300 K; see also the discussion and the references cited therein). The corresponding reaction entropy scale is plotted at the right axis in Figure 6. The reaction entropy is also given for the cathodic process direction.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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