Reaction mechanism of Sb-based negative electrode materials for Na batteries investigated by operando X-ray absorption spectroscopy: what can we really learn?

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In the search for efficient electrode materials for Na-ion batteries, *p*-block semi-metals were found to be viable alternatives to hard carbon, showing interesting performance with reversible capacities exceeding 400 mAh/g.[1] Among them, Sb seems to have a specific affinity for Na, showing excellent cycling stability even in the simplest form of bulk Sb powder despite a huge volume expansion during the alloying process.[2] The reason of this affinity has not been totally understood: while the electrochemical signature suggests the formation of several possible intermediates, the Na-Sb phase diagram indicates the existence of only one phase between the end member species formed during cycling, Sb and Na_3Sb. Moreover, such intermediates are amorphous and thus totally indistinguishable by diffraction. More recent results from other synchrotron-based methods suggested the formation of possible short-range structures and compositions for the intermediates formed with pure Sb.[3] In parallel, we studied the performance and the role of a second metal in binary antimonides such as $FeSb_2$ and SnSb.[4,5] With the goal of better understanding this specific affinity of Na for Sb, we have very recently undertaken a thorough study of the electrochemical reaction of Sb, $FeSb_2$ and SnSb with Na by *operando* XAS. Sb and Sn K-edge XAS data were analysed using adapted chemometric tools (PCA and MCR-ALS) in order to extract all information on the mechanisms of three compounds. The obtained results suggest that the sodiation reaction is similar in the three studied materials, a multi-step process clearly distinct from the reaction of these materials vs. Li. Na_3Sb is obtained by the sodiation of Sb, which is also irreversibly amorphised during further cycling. The activity of Sn and Fe-based species could also be followed in detail and related to the electrochemical signature. The results of this analysis show that, while it is possible to gather important information for the reconstruction of the reaction paths, it is intrinsically impossible to prove by XAS the formation of some of the intermediates proposed in the case of Sb.

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