

**MS14-2-1 Structural changes during the sodiation of branch-like antimony-based anodes for Na-ion batteries  
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**Abstract**

Anode materials based on alloying-type reactions are a promising solution to improve the capacity of the Na-ion batteries. This electrochemical process is characteristic for elements of group 14 and 15 of the periodic table which form various Na-Me (Me - metal, metalloid) alloys reversibly. Among them, antimony stands out with its high electrical conductivity, as well as the high theoretical capacity of 660 mAh·g<sup>-1</sup>. However, it is not flawless: with volume changes up to 293% and severe microstructure degradation, poor cyclability is inevitable. The prospective strategy to overcome these obstacles is to synthesize sub-micron and nanosized antimony composites with carbon.

This work aims to elucidate the sodiation and desodiation mechanism of the antimony-carbon composite with branch-like microstructure synthesized via a solvothermal reaction. Such microstructure enables good reversibility of the electrochemical reaction. Operando and ex-situ measurements revealed processes hidden during the discharge and charge processes.

The crystal structure of the material was characterized by the X-ray diffraction (XRD) method combined with Rietveld refinement and Raman spectroscopy. The main phase of the as-obtained sample was found to be rhombohedral antimony (R-3m space group), with the second monoclinic phase of Sb<sub>4</sub>O<sub>5</sub>Cl<sub>2</sub> (P21/a space group). The phase contribution was defined by linear fitting of the X-ray absorption spectra compared with the spectra of pure materials. Scanning electron microscopy revealed the presence of an extraordinary branch-like microstructure with a sub-micrometre particle size. The as-obtained material was mixed with a carbon additive and an eco-friendly carboxymethyl cellulose (CMC) binder to prepare an electrode. To gain a deep understanding of the structural changes during (de)sodiation, operando XRD and Raman spectroscopy measurements were conducted. The qualitative change of results of the X-ray absorption spectroscopy (XAS) for the L<sub>1</sub> and L<sub>3</sub>-edge for Sb and the K-edge for Na as a function of sodium content (ex-situ measurements) in transmission mode, total electron and total fluorescence yields is also presented. Comparison of the three above-mentioned techniques allowed providing the detailed description of the processes occurring during first sodiation and desodiation into the antimony characterized by the remarkable microstructure. Moreover, numerous electrochemical measurements were performed: charge and discharge cycling, cycling voltammetry, and electrochemical impedance spectroscopy as a function of the state of charge.

The results confirm that during the alloying reaction, despite the application of a novel synthesis method, the Na<sub>3</sub>Sb phase was formed, similar to that of commercial antimony. Not only crystal structure, but also oxidation state has been changed during the sodiation, which was proven by XAS. The application of a broad range of different operando and ex-situ characterization methods revealed structural changes in the electrode depending on the stage of the reaction. The obtained results contribute to the development of post-lithium-ion technology for energy storage.

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