Electrochemical Mechanism of $TiMnSn_4$ as Anode Material for Li-ion Batteries

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Li-ion batteries are widely used in portable electronic devices, electric vehicles or energy storage systems for intermittent energy sources, due to their high energy density, light weight and long cycle life. However, the performances must be continuously improved, which requires the development of new electrode materials. Carbon is commercially used for the anode but its specific capacity is limited to 372 mAh g^{-1} due to the electrochemical insertion mechanism involving only 1 Li per 6 C. In order to increase the specific capacity, Sn was considered as electrochemically active element although it is about ten times heavier than C. This is due to the alloying/dealloying mechanism with up to 4.4 Li per Sn, providing a theoretical capacity of 992 mAh g^{-1}. However, the $Sn \leftrightarrow Li_{4.4}Sn$ reversible transformations are associated with large volume variations responsible for capacity fading.

Tin intermetallic compounds of the form MSn_x, where M is a transition metal, were proposed to overcome this problem. The first lithiation transforms the pristine material into Li_7Sn_2/M nanocomposites where the M nanoparticles are expected to buffer the volume variations [1]. However, the delithiation process is more complex involving a possible back reaction of M with Sn, which could play a crucial role in the cycling stability. Such reaction was observed for Ni_3Sn_4 [2] and $MnSn_2$ [3] but not for $FeSn_2$ [4]. In addition, $TiSn_x$ intermetallics show very poor electrochemical activity [5].

The present work concerns the tin based ternary phase $TiMnSn_4$ as new anode material for Li-ion batteries. This compound is of particular interest because it contains two different transition metals that are expected to react differently with Sn during delithiation, if we consider the previous results obtained for $MnSn_x$ and $TiSn_x$. $TiMnSn_4$ was obtained by mechanosynthesis to optimize the microstructure and characterized by different experimental tools and DFT (density functional theory) calculations. We propose an analysis of the reaction mechanism based on operando X-ray diffraction and ^{119}Sn Mössbauer spectroscopy combined with a DFT interpretation of the electrochemical potential curve.

References

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