

Understanding the Lithiation/Delithiation Mechanism of $\text{Si}_{1-x}\text{Ge}_x$ Alloys

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Abstract : Lithium-ion batteries (LIBs) have an important place among energy storage devices due to their high capacity and good cyclability. However, the advancements in portable and transportation applications have extended the research towards new horizons, and today the development is hampered, e.g., by the capacity of the electrodes employed. Silicon and germanium are among the considered modern anode materials as they can undergo alloying reactions with lithium while delivering high capacities. It has been demonstrated that silicon in its highest lithiated state can deliver up to ten times more capacity than graphite (372 mAh/g): 4200 mAh/g for $\text{Li}_{22}\text{Si}_5$ and 3579 mAh/g for $\text{Li}_{15}\text{Si}_4$, respectively. On the other hand, germanium presents a capacity of 1384 mAh/g for $\text{Li}_{15}\text{Ge}_4$, and a better electronic conductivity and Li ion diffusivity as compared to Si. Nonetheless, the commercialization potential of Ge is limited by its cost. The synergetic effect of $\text{Si}_{1-x}\text{Ge}_x$ alloys has been proven, the capacity is increased compared to Ge-rich electrodes and the capacity retention is increased compared to Si-rich electrodes, but the exact performance of this type of electrodes will depend on factors like specific capacity, C-rates, cost, etc. There are several reports on various formulations of $\text{Si}_{1-x}\text{Ge}_x$ alloys with promising LIB anode performance with most work performed on complex nanostructures resulting from synthesis efforts implying high cost. In the present work, we studied the electrochemical mechanism of the $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy as a realistic micron-sized electrode formulation using carboxymethyl cellulose (CMC) as the binder. A combination of a large set of in situ and operando techniques were employed to investigate the structural evolution of $\text{Si}_{0.5}\text{Ge}_{0.5}$ during lithiation and delithiation processes: powder X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), Raman spectroscopy, and ^7Li solid state nuclear magnetic resonance spectroscopy (NMR). The results have presented a whole view of the structural modifications induced by the lithiation/delithiation processes. The $\text{Si}_{0.5}\text{Ge}_{0.5}$ amorphization was observed at the beginning of discharge. Further lithiation induces the formation of a- $\text{Li}_x(\text{Si/Ge})$ intermediates and the crystallization of $\text{Li}_{15}(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ at the end of the discharge. At really low voltages a reversible process of overlithiation and formation of $\text{Li}_{15+\delta}(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ was identified and related with a structural evolution of $\text{Li}_{15}(\text{Si}_{0.5}\text{Ge}_{0.5})_4$. Upon charge, the c- $\text{Li}_{15}(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ was transformed into a- $\text{Li}_x(\text{Si/Ge})$ intermediates. At the end of the process an amorphous phase assigned to a- Si_xGe_y was recovered. Thereby, it was demonstrated that Si and Ge are collectively active along the cycling process, upon discharge with the formation of a ternary $\text{Li}_{15}(\text{Si}_{0.5}\text{Ge}_{0.5})_4$ phase (with a step of overlithiation) and upon charge with the rebuilding of the a-Si-Ge phase. This process is undoubtedly behind the enhanced performance of $\text{Si}_{0.5}\text{Ge}_{0.5}$ compared to a physical mixture of Si and Ge.

Keywords : lithium ion battery, silicon germanium anode, in situ characterization, X-Ray diffraction

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