

Materials Science & Engineering

Master's Defense

Synthesis And Electrochemical Characterization Of Silicon Clathrates As Anode Materials For Lithium Ion Batteries

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abstract

Novel materials for Li-ion batteries is one of the principle thrust areas of current research in energy storage. One of the major limiting factors in a Li-ion battery's performance is the low specific capacities of the active materials in the electrodes. Anode materials based on silicon have generated much interest of late. Both cubic and amorphous silicon can reversibly alloy with lithium and have a theoretical capacity of 3500 mAh/g, making silicon a potential high density anode material. However, a large volume expansion of 300% occurs due to changes in the structure during lithium insertion, often leading to pulverization of the silicon. To this end, a class of silicon-based cage compounds called clathrates are studied for electrochemical reactivity with lithium. Silicon-clathrates consist of silicon covalently bonded in cage structures comprised of face sharing Si_{20} , Si_{24} and/or Si_{28} clusters with guest atoms occupying the interstitial positions in the polyhedra. In this work, the synthesis and electrochemical characterization of two categories of silicon clathrates – Type-I $\text{Ba}_x\text{Al}_y\text{Si}_{46-y}$ and Type-II $\text{Na}_x\text{Si}_{136}$, are explored.

The Type-I clathrate, $\text{Ba}_x\text{Al}_y\text{Si}_{46-y}$ consists of an open framework of aluminium and silicon, with barium (guest) atoms occupying the interstitial positions. X-ray diffraction studies show that a crystalline phase of clathrate is obtained from synthesis. Electrochemical measurements show that capacities comparable to graphite can be obtained for up to 10 cycles and lower capacities can be obtained for upto 20 cycles. The clathrate structure undergoes minimal volume change on lithium intercalation, and therefore, the crystal structure is morphologically stable over many cycles. X-ray diffraction of the clathrate after cycling showed that crystallinity is intact, indicating that the clathrate does not collapse during reversible intercalation with Li-ions. Electrochemical potential spectroscopy data showed an absence of lithium-silicide, which is the product of lithium alloying with Si.

Type-II silicon clathrate, $\text{Na}_x\text{Si}_{136}$, consists of silicon making up the framework structure and sodium (guest) atoms occupying the interstitial spaces. These clathrates showed very high capacities during their first lithiation, in the range of 3,500 mAh/g, but deteriorated during subsequent cycles. X-ray diffraction after one cycle showed the presence of lithium-silicide, indicating the disintegration of clathrate structure.



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