Materials Science & Engineering Doctoral Defense

Experimental and Theoretical Investigation of Tetrel Clathrates for Li-ion Batteries:Electrochemistry, Structure and Applications

School for Engineering of Matter, Transport and Energy

Andrew Dopilka

Advisor: Candace K. Chan

Abstract

Current Li-ion battery technologies are limited by the low capacities of the electrode materials and require developments to meet stringent performance demands for future energy storage devices. Electrode materials that alloy with Li, such as Si, are one of the most promising alternatives for Li-ion battery anodes due to their high capacities. Tetrel (Si, Ge, Sn) clathrates are a class of host-guest crystalline structures in which Tetrel elements form a cage framework and encapsulate metal guest atoms. These structures can form with defects such as framework/guest atom substitutions and vacancies which result in a wide design space for tuning materials properties. The goal of this work is to establish structure property relationships within the context of Li-ion battery anode applications. The type I Ba8AlyGe46-y clathrates are investigated for their electrochemical reactions with Li and show high capacities indicative of alloying reactions. DFT calculations show that Li insertion into the framework vacancies is favorable, but the migration barriers are too high for room temperature diffusion. Then, guest free type I clathrates are investigated for their Li and Na migration barriers. The results show that Li migration in the clathrate frameworks have low energy barriers (0.1-0.4 eV) which suggest the possibility for room temperature diffusion. Then, the guest free, type II Si clathrate (Na1Si136) is synthesized and reversible Li insertion into the type II Si clathrate structure is demonstrated. Based on the reasonable capacity (230 mAh/g), low reaction voltage (0.30 V) and low volume expansion (0.21 %), the Si clathrate could be a promising insertion anode for Li-ion batteries. Next, synchrotron X-ray measurements and pair distribution function (PDF) analysis are used to investigate the lithiation pathways of Ba8Ge43, Ba8Al16Ge30, Ba8Ga15Sn31 and Na0.3Si136. The results show that the Ba-clathrates undergo amorphous phase transformations which is distinct from their elemental analogues (Ge, Sn) which feature crystalline lithiation pathways. Based on the high capacities and solid-solution reaction mechanism, guest-filled clathrates could be promising precursors to form alloying anodes with novel electrochemical properties. Finally, several high temperature (300-550 °C) electrochemical synthesis methods for Na-Si and Na-Ge clathrates are demonstrated based on a Na β''-alumina solid electrolyte.

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