Silicon and Germanium Nanowires for Lithium and Sodium Ion Batteries

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Abstract Silicon (Si) and Germanium (Ge) have both been explored as high storage capacity negative electrodes (or anodes) in lithium ion batteries as a replacement for graphite. Si has very high lithium storage capacity (of about an order of magnitude greater than graphite); however, Si-based electrodes usually require the addition of carbon because of the low electrical conductivity of Si. We have recently shown that carbon addition can be minimized by using Si nanowires with a thin layer of carbon coating,[1,2] or completely avoided using Si nanowires containing high concentrations of tin (Sn, 8-10 mol%).[3] The Sn-containing Si nanowires can be cycled in LIBs with very high capacity (~1,000 mA h g^{-1} for more than 100 cycles at a current density of 2.8 A g^{-1} (1 C). Capacities exceeding graphite (of 373 mA h g^{-1}) could be reached at rates as high as 2 C. Ge nanowire LIB electrodes have lower charge capacity (1,624 mA h g^{-1}) than Si, but perform better than Si at high cycle rates (without the addition of carbon). One approach that we have been exploring for achieving high capacity and high rate capability in batteries is to combine Si and Ge nanowires into one electrode. Using this approach, a capacity of 900 mA h g^{-1} could be obtained at extremely fast delithiation rates of 20 C (37.16 A g^{-1}). Using in situ TEM, we have been studying the lithiation/delithiation mechanisms of Si and Ge nanowires and observe that fast rates lead to pore formation in both Si and Ge, which should be considered when designing electrolytes and electrode formulations.[4] We have also been studying nanowire materials for energy storage concepts beyond the lithium ion battery that use alternatives like Na, Ca or Mg. We have found that Ge nanowires are a very good electrode material for Na-ion batteries (NIBs). Crystalline Ge does not sodiate; however, a pretreatment process of lithiation to amorphize the nanowires then leads to very efficient sodiation. We have performed in situ TEM studies of the sodiation and desodiation of Ge nanowires and find that sodiation rates are actually quite fast, similar to the typical rates observed for lithiation of Ge nanowires. The current state-of-the-art of Si and Ge nanowire materials for LIB and NIBs will be discussed.

References

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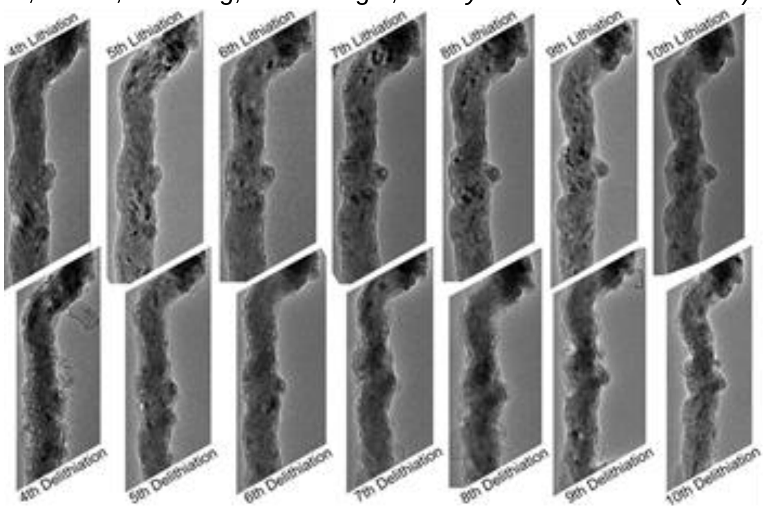

Figure. TEM images of an Si nanowire after several lithiation/delithiation cycles. The nanowire shrinks in diameter and develops pores after each delithiation event. Relithiation causes the nanowire to swell and the pores are filled in.