Abstract

Tang, Jialiang. Ph.D., Purdue University, May 2018. Development of High-Capacity Anodes for Advanced Li-/Na- Ion Rechargeable Batteries. Major Professor: Vilas G. Pol.

Since the introduction of the first commercial lithium ion batteries (LIBs) by Sony in 1991, LIBs have dominated the rechargeable energy storage market owing to their high energy density, good cycling stability, and long cycle life. By 2020, the global LIBs market revenue is projected to reach $76 billion dollars, a five-fold increase from 2013. To better accommodate the rising demand, research efforts are intensifying to develop next-generation LIB chemistries (i.e., silicon anodes and sulfur cathodes) that offer much higher energy densities. At the same time, concerns over lithium shortage have prompted research into sodium ion batteries (SIBs), a potentially cheaper and more abundant supplementary system to LIBs. My research has been dedicated to solving challenges presented in these new systems, particularly in regards to the anode materials.

The conventional LIB anode, graphite, has a theoretical specific capacity of 372 mAh/g based on lithium intercalation reaction. Its practical specific capacity is already reaching this limit, leaving little room for improvement. Alternative anode materials based on alloying and conversion mechanisms have the potentials to achieve two- to ten-fold capacity increase. These materials however are plagued with technical hurdles that limit their immediate commercialization. For alloying materials such as silicon, volumetric expansion (up to 370%) upon lithiation destabilizes the solid electrolyte interphase (SEI) and electrode structure, leading to rapid capacity fade. To that end, I synthesized a carbon/silicon composite anode with built-in porosity in the carbon to accommodate volume expansion of silicon nanoparticles hence greatly improving the cycling stability. I also studied Fe_2O_3-based conversion anode and identified an interesting high-rate activation process that leads to significant capacity gains (greater than theoretical value). Taking inspiration from these studies, I designed and synthesized a series of iron oxide-silicon nanocomposites that yield substantial capacity improvement in comparison to the silicon control anode. I also carried out detailed characterization and electrochemical evaluation to reveal the synergetic interactions between iron oxide and silicon. Key findings from this study could provide important design guidelines for future development of similar conversion-alloying composite (CAM) anodes.

For the development of SIBs, the lack of suitable anode materials have greatly impeded its commercialization. The most promising anode material is hard carbon which could be derived from the pyrolysis of biomasses and petroleum coke. Challenges in production scalability, particle morphology control, and reduction of early-cycle irreversible capacity losses are frequently encountered during the early developmental stage. In collaboration with industrial partners, I evaluated the suitability of using carbon microsheets as a scalable SIB anode. While good cycling stability is demonstrated over 300 cycles, large early-cycle capacity losses severely limit energy density and reversible capacity of the cell. This motivated me to develop a pre-sodiation technology that could potentially be applied to all SIB anodes to reduce early-cycle losses. I employed pulse ultrasonication technique to synthesize sodium metal powders as the pre-sodiation agent. Subsequent half- and full-cell study confirms that sodium powders can effectively improve Coulombic efficiency, reversible capacity, and energy density.