Title: Silicon anode materials for Li-ion batteries

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Abstract:

The development of more efficient rechargeable lithium-ion batteries with higher energy and power density is of great importance for applications in portable electronics, electric vehicles, and renewable energy storage. Silicon is considered as one of the most promising anode materials for the next generation Li-ion batteries because of its high theoretical specific capacity (4200 mAh/g), wide elemental abundance, and low discharge potential (∼0.4 V vs Li/Li+). The remarkable theoretical capacity of silicon is ∼10 times higher than that of a graphite anode (372 mAh/g) used in commercial Li-ion batteries [1]. However, silicon anode materials have not yet been commercialized in Li-ion batteries due to the slow diffusion rate of lithium, rapid expansion of the volume of silicon by more than 300%, and significant storage capacity decrease during charge and discharge cycles [2]. The large volume expansion and associated stress in silicon electrode materials affect the battery performance in many ways. It causes fracture and pulverization of electrode materials, resulting in serious structural degradation and the loss of electrical contact to the current collector [1,2]. Recent studies have shown that the silicon stability problem can be overcome using solid-state battery design [3-5]. However, the reversible lithiation of Si anodes has been reported only at high pressures using sulfide-based electrolytes, typically above 50 MPa [3], which significantly restricts practical applications of silicon anodes in commercial Li-ion batteries.

The aim of this Ph.D. thesis is to study the mechanism of stress accommodation and interface changes in silicon-based anode materials in contact with quasi-solid and solid electrolytes in Li-ion batteries. Unique nanoengineered silicon materials will be prepared using scalable and low-temperature plasma-enhanced chemical vapor deposition (PECVD). New approaches will be pursued for silicon interface engineering using different (i) silicon and nanosilicon structures, morphologies and composites, (ii) doping, (ii) pre-lithiation, and (iv) external pressure. The effects of these approaches will be explored in half cells and full cells using advanced structural, chemical, and electrochemical characterization techniques, including *operando* X-ray diffraction and *operando* Raman spectroscopy. These experiments will shed light on the fundamental principles of lithiation and delithiation processes occurring at the interfaces between novel silicon and solid or quasi-solid electrolytes. The experiments will also allow us to identify suitable conditions for avoiding long-term capacity fading and obtaining highly reversible lithiation of silicon anode materials in Li-ion batteries. Mastering the fabrication of silicon materials will enable the creation of stress-tolerable interfaces with low energy barriers for lithium diffusion and ultra-high capacity, paving the way for the future generation of all-solid-state lithium batteries.

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