

High-performance self-organized Si nanocomposite anode for lithium-ion batteries

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Abstract

Silicon is being investigated extensively as an anodic material for next-generation lithium ion batteries for portable energy storage and electric vehicles. However, the large changes in volume during cycling lead to the breakdown of the conductive network in Si anodes and the formation of an unstable solid-electrolyte interface, resulting in capacity fading. Here, we demonstrate nanoparticles with a Si@Mn_{22.6}Si_{5.4}C₄@C double-shell structure and the formation of self-organized Si-Mn-C nanocomposite anodes during the lithiation/delithiation process. The anode consists of amorphous Si particles less than 10 nm in diameter and separated by an interconnected conductive/buffer network, which exhibits excellent charge transfer kinetics and charge/discharge performances. A stable specific capacity of 1100 mAh·g⁻¹ at 100 mA·g⁻¹ and a coulombic efficiency of 99.2% after 30 cycles are achieved. Additionally, a rate capacity of 343 mAh·g⁻¹ and a coulombic efficiency of 99.4% at 12000 mA·g⁻¹ are also attainable. Owing to its simplicity and applicability, this strategy for improving electrode performance paves a way for the development of high-performance Si-based anodic materials for lithium ion batteries.

Key words

cycling performance; self-organized; Si nanocomposite anode; lithium ion batteries

1. Introduction

Owing to the rapid development of portable electronics, electric vehicles and energy storage devices, the demand for the high-energy-density lithium-ion batteries (LIBs) (by weight and volume) has spurred research efforts to develop next-generation electrode materials that can be substituted for the currently available conventional ones [1–5]. Compared with graphite, which has a theoretical specific capacity of 372 mAh·g⁻¹, Si is considered one of the most promising anodic materials because of its high theoretical capacity (3579 mAh·g⁻¹), safe lithium-uptake potential, high availability and environmentally friendly nature [6–10]. Despite the significant advances made in the study of Si-based anode materials, their practical use in LIBs has been hindered by their poor cycle stability with applicable volume energy density. During the Li insertion/extraction process, the active

material in Si-based anodes undergoes significant volume expansion (>300%), which results in the disintegration of the electrode structure, including the pulverization of Si particles, the detachment of their surrounding electrical connections and electrode peel-off [11–15].

To overcome these issues, several different strategies have been proposed so that the materials that can help prevent the mechanical degradation of silicon electrodes and maintain the stability of the solid-electrolyte interface (SEI) film can be designed. These strategies revolve around several methods, from the use of nanosized Si particles [16–18], nanowires [19–23] and nanotubes [24–27], to the alloying of Si with metals [10,28,29]; from the use of porous Si structures [30–33] and Si/inactive-component composites [34–36] to coating Si with carbon [37–39]. However, many of these approaches are not suitable for large-scale production as they result in low-active-Si-content electrodes that exhibit poor practical capacities. In addition, the processes involved are complicated and costly

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and have low yields. Furthermore, the low tap density of nano-sized Si materials decreases the volumetric capacities of the anodes. Therefore, it is highly desirable to develop a low-cost strategy for the large-scale synthesis of Si anode materials that exhibit superior performances.

The use of Si nanoparticles coated with carbon shells can improve cycling performance. However, the electrical conductivity of carbon shells formed by pyrolysis is usually too low (approximately 10^{-3} S·cm⁻¹) to allow for high charge/discharge rates [40,41]. In addition, owing to the repeated volume changes of Si particles during electrochemical cycles, the carbon shells disintegrate and subsequently the SEI film cracks, with new SEI layers forming on the freshly exposed silicon surfaces. This causes the SEI film to increase in thickness as the lithiation/delithiation process progresses and leads to capacity fading. Therefore, the shells that are made of a mechanically rigid composite material and can play a buffering role and promote lithium ion and electron transport, are highly desirable as such shells should form stable SEI films. Such shells should also minimize the change in volume of Si particles and allow an electrical network to be maintained through a direct contact between the particles and the electrolyte. This strategy can also be extended to other electrode materials that exhibit similarly large volume changes.

Reducing the size of Si particles to the nanoscale can help mitigate the physical stresses induced by the large changes in their volume that occur during the lithiation/delithiation process. Previous studies based on the calculated misfit stress energies of partially delithiated particles have suggested that the shells of particles with diameters less than 10 nm do not crack [9]. Furthermore, using the Griffith-Irwin equation, it has been found that the fracture strength of an isotropic material is related to its elastic modulus and Poisson's ratio [42]. In the case of uniformly distributed, isotropic Si particles, their small size and amorphous nature result in their elastic modulus being high and their Poisson's ratio being low; this, in turn, should lead to higher fracture strength. Therefore, amorphous Si particles with a diameter of less than 10 nm could be ideal as they would not undergo stress fractures during lithiation/delithiation process. In addition, their high fracture strength should result in a lower degree of cracking and particle pulverization and lead to high coulombic efficiency. However, to the best of our knowledge, there have not been any reports on the use of amorphous Si particles having a diameter less than 10 nm as an anodic material.

In this study, we design and fabricate nanoparticles with a Si@Mn_{22.6}Si_{5.4}C₄@C double-shelled structure and use them to form a self-organized nanocomposite Si anode. This nanocomposite Si anode has three attractive features. First, the double shell, which is composed of a mechanically rigid Mn_{22.6}Si_{5.4}C₄ phase and an amorphous nitrogen-containing carbon layer, does not undergo pulverization that usually results from repeated fractures and maintains intimate contact to form a highly interconnected conducting electrical network. By this approach, not only could the large volumetric expansion of silicon be accommodated and the integrity of the conductive network be preserved, but the stability of SEI

films is also enhanced. Second, the amorphous Si nanoparticles, which are less than 10 nm in diameter, are uniformly separated by the interconnected conductive/buffer network. This prevents further fracturing of Si nanoparticles which is resulted from the volume changes induced during lithiation/delithiation. Finally, the Si@Mn_{22.6}Si_{5.4}C₄@C double-shell nanoparticles could be readily realized by polymerization and pyrolyzation processes. The resulting sample, which has a tap density as high as 0.76 g·cm⁻³, can be produced on a large scale. When compared with anodes based on bare silicon and Si-C composite, the self-organized nanocomposite Si anode exhibits better electrochemical performance. Its reversible capacity is 1100 mAh·g⁻¹ after 30 cycles at 100 mA·g⁻¹ (97.8% capacity retention) and the coulombic efficiency is up to 99.2%. Given that such nanocomposite Si anodes can be fabricated on a large scale at low costs, they should be found wide application in LIBs.

2. Experimental

2.1. Synthesis

Si nanopowder (average particle size: 50 nm, 98%, 0.113 g) and manganese phthalocyanine (MnPc, 0.567 g) were mixed ultrasonically in N, N-dimethylformamide (DMF, 35 mL), while pyrazine (0.24 g) and sodium dodecyl sulfate (SDS, 0.0288 g), used as a bridge and a disperser, respectively, were added to the mixture. The resultant mixture was then transferred into a 50 mL Teflon-lined autoclave and heated at 160 °C for 4.5 h. During this process, the MnPc molecules polymerized and the Si nanoparticles became encapsulated within the polymer molecules. The autoclave was then allowed to cool to room temperature, and the precipitate was separated using a vacuum rotary evaporator. The Si-Mn-C composite was obtained by annealing the precipitate at 700 °C in an Ar atmosphere for 1 h. A metal-free composite (i.e., a Si-C composite) was also prepared using the Si nanopowder and phthalocyanine under the same conditions and used as a reference.

2.2. Characterization

The X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer using Cu K_α radiation. Raman spectroscopy was performed using a Renishaw RM-2000 CCD spectrometer with a 633 nm 5 mW HeNe laser; the spot size was approximately 1.5 μm. The X-ray photoelectron spectroscopy (XPS) spectra were obtained using an AXIS-Ultra instrument from Kratos Analytical and monochromatic Al K_α X-rays (1486.6 eV) at 15 kV and 15 mA (emission current); the base pressure within the chamber was approximately 10⁻⁸ Pa. The shift in the binding energy was corrected using the C 1s level at 284.8 eV as an internal standard. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a Hitachi S-4300 SEM system and a Hitachi H-9000 TEM system (ac-

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