Silicon-Carbon Nanocomposite Negative Electrode Architectures for Li-Ion Batteries

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Electrochemical energy storage has become a critical technology for a variety of applications, including grid storage, electric vehicles, and portable electronic devices [1]. Metal based anodes (Si, Ge, Sn, Al, Sb, etc.) have much higher Li storage capacity than the intercalation-type graphite anode that is currently used in Li-ion batteries. Among all the metal based anodes, silicon (Si) has the highest specific capacity. Silicon is considered as a promising anode material for rechargeable Li-ion batteries (LIB), owing to its high theoretical specific capacity (about 4200 mA h g^{-1}), high abundance in the earth's crust and its environmentally friendly nature [2]. A further benefit is that mass production of elemental silicon is already a mature technology in the semiconductor industry. Despite these advantages, graphite anodes still dominate the marketplace due to the fact that alloy anodes have two major challenges that have prevented their widespread use. However, the practical implementation of Si anodes is still blocked due to three major problems [3-6]. First, poor cycle-life of silicon materials results from pulverization during the huge volumetric fluctuations (>300 %) which accompany lithium ion intercalation and deintercalation [7]. Second, drastic irreversible capacity loss and low coulombic efficiency is caused by mechanical fracture of Si anodes during the alloying/dealloying process [8]. Finally, the solid electrolyte interphase (SEI) breaks as the nanostructure shrinks during delithiation [9]. This results in the exposure of the fresh silicon surface to the electrolyte and the reformation of the SEI, resulting in the SEI growing thicker with each charge/discharge cycle [10].

In order to prevent these challenges, most common and effective strategy to adopt nanoscale silicon materials with various morphologies, including nanoparticles [11] and [12], nanowires [13], nanotubes [14] and [15], and hollow spheres [16, 17]. Compared to bulk silicon, such nanostructured Si is able to accommodate elevated mechanical stress, resulting in prolonged cycling stability. Nanostructured silicon materials, however, still suffer from poor electric conduction [18]. Further optimization is achieved by incorporating nano-silicon materials with various conductive matrixes, such as graphene [19] and [20], carbon nanotubes [21], and carbon [22] and [23] to form core-shell and yolk-shell nanocomposites [24]. The most promising carbon coating strategy has been explored to promote the electrochemical performance [25-28]. The obvious advantage of carbon shells is intensive improving the overall electrical conductivity of the Si-based anodes. In addition, the introduction of such a carbon shell plays a key role in alleviating the agglomeration of nano-silicon particles [29] and [30]. However, the well-established carbon coating methods are based on the chemical vapor deposition, hydrothermal of carbohydrates and polymerization of phenolic resin from sol–gel process, all of them unfortunately result in the compact carbon shells without open and connecting mesopore channels for fast transport of Li^+ ions between the electrolyte and silicon. This could be the reason that Si particles covered with carbon layer matrix as an anode present unsatisfactory rate-capability [18, 29, 31]. Furthermore, the crucial impact of SEI is usually be neglected and the formation of SEI is hard to control. Importantly, if a stable and compact SEI is constructed, the electrolyte molecules would not penetrate through SEI layer into the active material for further growth, thereby avoiding continual lithium loss and ensuring higher Coulombic efficiency.

In this review, we summarized the recent progress in developments of Si anode materials

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in our laboratories. First, the electrochemical reaction and failure are outlined, and then, we summarized various methods for improving the battery performance, including those of nanostructuring, alloying and forming hierarchic structures. The synthesis of carbon-silicon electrodes with chemical reduction, sol-gel, spin coating, sputter coating, filtration and microwave hydrothermal techniques are introduced The electrochemical features are discussed in the core-shell, co-axial and yolk-shell structured negative electrodes in the half-cells. Studies are concentrated on the nanocomposite structures of carbon coated silicon nanoparticles reinforced with carbon fibres, carbon nanotubes and graphene.

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