Facile and Efficient Synthesis of SiO_x@C Core−Shell Particles as an Anode Material for Lithium Ion Batteries

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1. Introduction

Core−shell particles have attracted broad interests in recent years for their remarkable properties and a wide range of potential applications, but the precise design and control of their structure remains a significant challenge.

In this work, we propose a strategy to synthesize carbon coated SiO_x (SiO_x@C) core−shell particles via a sol−gel method using the simultaneous hydrolysis−condensation of tetramethyl orthosilicate (TMOS) and polymerization of 3-aminophenol and formaldehyde. The synthetic process was conducted in the presence of ammonia as a basic catalyst and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant in a mixed water/methanol solution followed by the carbonization process. Results from this study provide new insight into the design of core−shell particles by using TMOS as an effective silica precursor for the first time with a well-controlled reaction rate and spherical morphology. To demonstrate the benefits of core−shell structure in energy storage, the performance of SiO_x@C as an anode material for lithium ion batteries (LIBs) is evaluated.

2. Experimental Method

In a typical procedure synthesis of SiO_x@C particles, an aqueous solution was prepared by stirring 3-aminophenol, ammonia solution, and ultrapure water at room temperature. CTAB dissolved in methanol was added to the above solution. TMOS and formaldehyde were simultaneously added to the solution. The reaction mixture was subjected to microwave irradiation with the temperature set at 70ºC and kept for 75 min. The obtained particles were separated from the solution by centrifugation and washed with ultrapure water and ethanol to remove impurities. After drying, the particles were carbonized by heat treatment in a nitrogen atmosphere for 3 h at 1200ºC.

3. Results and Discussion

The SiO_x@C core−shell particles with highly uniform spherical morphology were successfully formed as shown in the TEM result (Fig. 1(a)). For a better understanding of the characteristics of SiO_x@C particles, different characterizations were carried out. The Si 2p spectrum (Fig. 1(b)) showed that the average valence state of Si was 2.8, which corresponded to the chemical formula of $SiO_{1.4}$. The result indicated that there were different chemical states of Si in SiO_x, which was probably caused by the carbothermal reduction occurring between silica and carbon during the heating process. The TGA result (Fig. 1(c)) demonstrated

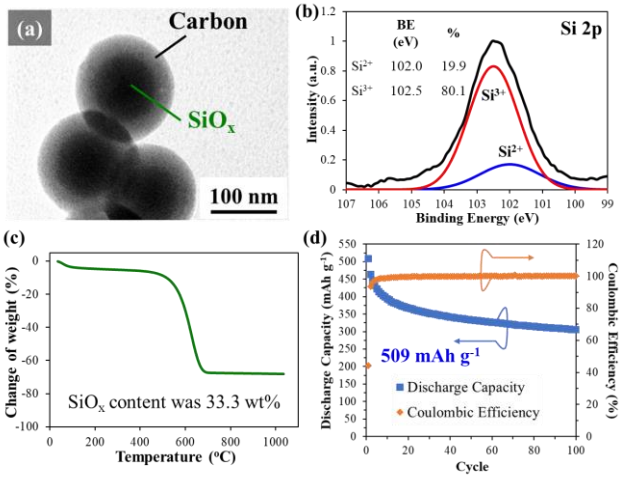

Fig. 1. (a) TEM image, (b) XPS spectra of Si 2p, (c) TGA curve, and (d) Cyclic performance of SiO_x@C particles.

that the SiO_x content in the SiO_x@C particles was approximately 33.3 wt%.

The electrochemical activity of SiO_x@C particles in lithium storage was investigated as the anode material for LIBs (Fig. 1(d)). The obtained SiO_x@C particles delivered a reversible capacity of 509 mAh g^{-1} at 100 mA g^{-1} and the capacity retention was approximately 80% after 100 cycles. The significantly improved electrochemical performance in comparison with that reported in our previous paper can be explained by the structure of material. The SiO_x@C particles with core−shell structure guarantee optimum contact with the carbon matrix, and the round shape of carbon shell is highly resilient toward stress. These will contribute to improving the conductivity of SiO_x and exerting the function of carbon.

References

1) Ogi, T. *et al.*, Nanostructuring Strategies in Functional Fine-Particle Synthesis towards Resource and Energy Saving Applications, Adv. Powder Technol, **25**, 3−17 (2014).
2) Izawa, T. *et al.*, Improving the Performance of Li-Ion Battery Carbon Anodes by *in-situ* Immobilization of SiO_x Nanoparticles, Mater. Res. Bull., **112**, 16−21 (2019).
3) Cao, K. L. A. *et al.*, Controllable Synthesis of Carbon-Coated SiO_x Particles through a Simultaneous Reaction between the Hydrolysis−Condensation of Tetramethyl Orthosilicate and the Polymerization of 3-Aminophenol, Langmuir, **35**, 13681−13692 (2019).

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