Highly Stable Mesoporous Ge@C Sphere Anodes for Lithium-ion Batteries

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Abstract. The Mesoporous Ge@C sphere has been designed via a modified Stöber method and an in-situ solution deposition. Compared with the pure Ge nanoparticles, the as-synthesized Mesoporous Ge@C sphere nanocomposites show much better cycling stability and rate capability. That as-prepared anode material can maintain a reversible capacity of 708.8mAhg⁻¹ after 200 cycles at a rate of 0.2C, and even at 5C, it also exhibits a high discharge capacity of ~522.4mAhg⁻¹. The superior comprehensive electrochemical performance of the electrode is ascribed to the synergic effects of the porous structure and hollow carbon sphere, which can effectively alleviate the structural strain and suppress large volume changes, additionally, can reduce electrolyte diffusion path length beneficial to allow rapid electron transportation and let more Li⁺ flux across the interface.

Introduction

Of late, high energy density and long cycle life lithium-ion batteries (LIBs) are widely applied in electric vehicles driven by a rising demand for new energy vehicles. Extensive research has been devoted to developing new electrode materials capable of delivering high energy density and cycling stability as alternates to traditional graphite electrodes[1-3]. Germanium (Ge) has been considered as promising anode materials for LIBs due to a high theoretical capacity of 1600 mAhg⁻¹ and a superior intrinsic kinetics (high electrical conductivity and Li diffusion coefficient), making it more appropriate for high-power Li-ion batteries.

However, Ge suffers tremendous volume expansion during the Li-ion insertion and extraction processes, resulting in pulverization of the electrodes and degrading the capacity consequently. Fortunately, it has documented that nanoscale Ge with variously designed morphologies could improve cycling stability and rate capability because of its shorter lithium-diffusion distance and more reaction sites, such as nanoparticles[4], nanowires[5, 6], nanotubes[7]. Other alternate approaches to increase cyclability involve porous structure[8, 9] and hybridizing with carbon materials[10, 11] or other components[12]. Over the last few years, large amounts of work combining germanium with carbon materials or other components are reported. Xiu Li et al[9] reported porous amorphous Ge/C composites, which can deliver a reversible capacity of 681mAhg⁻¹ after 350 cycles. Xuanwen Gao et al[12] prepared Nano-Germanium/polypyrrole composites. The electrode exhibits a lithium storage capacity of 1014mAhg⁻¹ after 50 cycles at 0.2 C rate.

Herein, we proposed mesoporous Ge@C sphere composites through a modified stöber method[13] and an in-suit solution deposition[14]. When used as anode material, the mesoporous Ge@C sphere electrode exhibits high cycling stability and superior rate capability. The mesoporous Ge@C sphere composites could maintain a reversible capacity of 708.8mAhg⁻¹ after 200 cycles at a rate of 0.2C, and even at 5C, it also exhibits a high discharge capacity of ~522.4mAhg⁻¹.

Result and Discussion

Scheme1. Schematic illustration of the synthesis route for the mesoporous Ge@C sphere

The synthesized route for the mesoporous Ge@C sphere was shown in Scheme1. RF@SiO₂ nanospheres were prepared using a modified Stöber method (a typical process shown in the first step). Consequently, RF@SiO₂ transformed to hollow carbon sphere (HCS) through the carbonization of RF resin at 900 °C for 2h and etching SiO₂ with HF overnight. Importantly, the nanopores on the surface of HCSs were introduced by the HF etching process. At last, a mesoporous Ge@C sphere was synthesized by an in-situ solution deposition method. Ge was introduced by the reduction of GeO₂ precursor, and then deposited on the surface of HCSs.

Figure.1 SEM images of (a) Ge nanoparticles, (b) RF@SiO₂ nanospheres, (c) HCS and (d)(e)(f) TEM images of the mesoporous Ge@C sphere

Fig.1a reveals the pristine Ge particle size is extremely small and these primary particles have clustered into large agglomerates. The smooth surfaces nanospheres with diameters of about 100~130 nm uniformly dispersed, shown in Fig.1b. After the carbonization and etching process, the HCS has a slightly shrunken diameter compared to RF@SiO₂ nanospheres and its surface becomes rough, due to the pyrolysis of the RF resins during high temperature calcination (Fig.1c). Fig.1d,e and f exhibit the TEM images of the mesoporous Ge@C sphere in different magnifications. Simultaneously, it gave visible evidence that the Ge nanoparticles uniformly cover on the surface of the HCSs. The HCSs could not only act as a barrier to reduce the severe aggregation of Ge nanoparticles during charge/discharge processes, but also could be beneficial to allow rapid electron transportation due to the improved conductivity of the whole electrodes. Additionally, the HCSs could effectively alleviate the structural strain and suppress large volume changes during the cycling processes. Owing to the synergistic effect of the HCSs and nano-sizes, the mesoporous Ge@C sphere anodes exhibit a high-capacity, high-rate and long-life performance.

Figure.2 (a) XRD patterns of the Mesoporous Ge@C sphere and Pure Ge, (b) pore-size distribution of the Mesoporous Ge@C sphere

The X-ray diffraction (XRD) patterns of the as-synthesized pure Ge nanoparticles and mesoporous Ge@C sphere are presented in Fig.2a. Two broad diffraction peaks were present in the diffraction pattern of the pure Ge, suggesting the amorphous structure of Ge, which could be indexed to the standard cubic phase Ge (JCPDS No. 04-545). Simultaneously, the diffraction peaks of mesoporous Ge@C sphere were similar to that of pure Ge. However, there was no diffraction peak for carbon in the nanocomposites, which might be ascribed to the broad diffraction peaks overlapping the diffraction peak for carbon. In Fig.2b, the pore size distribution curve suggests that the nanocomposites have a large amount of mesoporous (the porous size ranging from 2nm to 10nm), which can mitigate the mechanical stress and buffer the volume changes during cycling.

Figure.3 Electrochemical tests of the electrode (a) cyclic voltammograms of the Mesoporous Ge@C sphere; (b) the cycling performance and the corresponding coulombic efficiency of the Mesoporous Ge@C sphere and pure Ge at 0.2 C; (c) the specific capacity at different rates of the two electrode; (d) Nyquist plots of the two electrodes at different cycles

Fig.3a shows the first four cyclic voltammetry (CV) curves of the Mesoporous Ge@C sphere electrode. Except for the little peak shift, the four CV curves overlapped with each other, which indicates the excellent reversibility and stability of the electrode. Fig.3b exhibits the cycling performance and the corresponding coulombic efficiency of the Mesoporous Ge@C sphere and pure Ge at 0.2 C ($1C=1600\text{mAhg}^{-1}$). The two electrodes deliver very high first charge/discharge capacities of $532.2\text{mAhg}^{-1}/1668.2\text{mAhg}^{-1}$ and $813.9\text{mAhg}^{-1}/1329.9\text{mAhg}^{-1}$ with an initial coulombic efficiency of 31.9% and 61.2%, respectively. The dramatic capacity loss was observed in the first 5 cycles, which was attributed to the formation of solid electrolyte interface (SEI) films. However, the Mesoporous Ge@C sphere electrode remains highly stable in the subsequent cycles and delivers a high reversible specific capacity of 708.8mAhg^{-1} after 200 cycles. For a comparison, the dramatic capacity fading of the pure Ge electrode existed throughout the 200 cycles and only a specific capacity of 159.4mAhg^{-1} was reserved.

Fig.3c reveals the specific capacity of the Mesoporous Ge@C sphere electrode was about 910.0, 776.5, 688.3, 587.2 and 522.4mAhg^{-1} at current rate from 0.1, 0.2, 1, 2 to 5C. When the rate goes back to 0.1 C, the specific capacity of the Mesoporous Ge@Csphere anode reversibly recovers to 757.2mAhg^{-1} , demonstrating superior electrochemical reversibility. However, after the high-rate measurements, the pure Ge delivers very low specific capacity of 72.9mAhg^{-1} , caused by the Ge nanoparticles lost contact to Cu collector in electrode pulverization process. Fig.3d displays Nyquist plots of the two electrodes at different cycles. After 200 cycles, the charge transfer resistance of the Mesoporous Ge@Csphere anode increased from 6Ω (as shown in the inset of Fig.3d) to 80Ω , much lower than that of pure Ge (from 50Ω to 220Ω). Low charge transfer resistance is beneficial to Li^+ transfer at the interface of the electrolyte/electrode for the good cycle performances.

Conclusion

In conclusion, the Mesoporous Ge@Csphere was synthesized via a modified Stöber method and an in-situ solution deposition. When used as anode material, the mesoporous Ge@C sphere electrode exhibits high cycling stability and superior rate capability. The mesoporous Ge@C sphere composites could maintain a reversible capacity of 708.8mAhg^{-1} after 200 cycles at a rate of 0.2C, and even at 5C, it also exhibits a high discharge capacity of $\sim 522.4\text{mAhg}^{-1}$.

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