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Carbon Coated Mesoporous Si Anode Prepared by a Partial Magnesiothermic Reduction for Lithium-Ion Batteries

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Abstract

Owing to its high theoretical capacity, Si based anode materials have been regarded as the most promising alternative anode materials for lithium-ion batteries. Unfortunately, the commercial application of Si based anode materials has been greatly hindered, due to the large volume change of Si materials during their lithiation/delithiation process, which results in severe pulverization, loss of electrical contact and rapid capacity fading. To address these issues, we reported a partial magnesiothermic reduction method by adjusting the proportion of added Mg powder to convert SiO_2 into Si/SiO_2 and subsequently to coat such a composite with a carbon layer. After removing unreacted SiO_2 using HF, carbon-coated mesoporous Si (p-Si@C) can be obtained. The internal pores could accommodate the volume changes of Si and the carbon coating layer could effectively stabilize the interface during cycling. With this design, the as-prepared p-Si@C shows superior electrochemical performance compared with bare Si. When the p-Si@C electrode evaluated at a rate of 0.5 A g⁻¹, a reversible capacity of 1146 mAh g⁻⁴ could still be maintained after 100 cycles.

Keywords: Mesoporous silicon; Carbon coating; Partial magnesiothermic reduction; Lithium-ion battery

1. Introduction

The ever-increasing demands for high-performance rechargeable batteries for use in various consumer electronics, electric vehicles and energy storage power stations, have stimulated tremendous research focus on developing lithium ion batteries (LIBs) with high energy density and long cycle life.[1-3] To date, the low theoretical capacity of commercialized graphite anode cannot meet the demands of high performance LIBs.[4, 5] Silicon (Si) has been widely regarded as one of the most promising anodes for high-performance LIBs because of its high theoretical capacity (3579 mAh g⁻¹), which is 10 times higher than that of graphite.[6-8] However, Si anodes would face the crush of active material and rupture of the solid–electrolyte interface (SEI) layer, due to the huge volume changes during cycling.[9-11]

These critical problems could be alleviated by combining conductive coatings layers and designing nano-sized construction. Yolk-shell structure with void space has been regarded as an effective method to address these problems, because the void space can effectively alleviate the stress strain caused by volume changes.[12-14] Typically, to produce void space for Si@void@C anodes, SiO₂ has been used as a sacrificial layer, produced between the Si core and the carbon coating layer, and then etched with HF. The formation of a SiO₂ sacrificial layer can be achieved by hydrolysis of TEOS or partial oxidation of Si.[13, 15, 16] Even with the improved cycling performance for yolk-shell Si-based anodes, practical application of such a designed anode at a low-cost remains a severe challenge.[17-20] First, most procedures involving these nano-Si particles are expensive and require complicated

synthesis processes, such as chemical vapor deposition (CVD). Second, the formation of void space requires an additional sacrificial SiO_2 layer, which increases the difficulty and cost of the synthesis process.

Recently, magnesiothermic reduction of SiO₂ has been regarded as an effective method to obtain nano-Si.[21, 22] To get a high reduction yield, the added Mg powder was usually excessive (the theoretical mass ratio SiO₂:Mg=1:0.8). However, the excessive Mg powder would lead to the formation of Mg₂Si, which could react violently with HCl to produce combustible gas, causing interference in subsequent treatment processes. Considering the reduction degree of SiO₂ can be controlled by adjusting the proportion of added Mg powder.[23, 24] Here, we present a partial magnesiothermic reduction method to convert SiO₂ into Si/SiO₂ and subsequently to coat such a composite with a carbon layer. After removing unreacted SiO₂ by the use of HF, carbon coated mesoporous Si can be obtained. The internal pores could accommodate the volume changes of Si and the carbon coating layer could effectively stabilize the interface during cycling. As a result, the as-prepared p-Si@C sample as an anode exhibits a reversible capacity of 1146 mAh g⁻¹ at 0.5 A g⁻¹ after 100 cycles and a capacity around 560 mAh g⁻¹ at 10 A g⁻¹.

2. Experimental

2.1 Preparation of the materials

The SiO₂ nanoparticles were prepared using a modified Stöber method reported before.[25, 26] Then the as-prepared SiO₂ nanoparticles were mixed with Mg powder,

NaCl with a mass ratio of 1:0.7:10 and sealed into an argon gas filled stainless autoclave. After heated to 650 °C for 6 h, the resulting powder was immersed into 1M HCl solution for 6 h to remove MgO. After that, the obtained Si/SiO₂ and phenolic resin (mass ratio=1:1) were mixed in ethanol and stirred at 80 °C until the solution was dried. The obtained precursor was calcined at 800 °C for 2 h under argon atmosphere. Finally, the resulting powder was immersed into 5wt% HF for 30 min to remove the residual SiO₂.

2.2 Characterization

The crystal structure of the samples was characterized on Rigaku-TTRIII. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) mapping were performed using a Nova NanoSEM230 and a JEOL JEM-2100F. Nitrogen adsorption and desorption (Quantachrome Nova Win 2) was used to determine the Brunauer-Emmett-Teller (BET) surface areas and pore size distributions samples. X-ray photoelectron of the spectroscopy (XPS. ThermoFisher-VG Scientific) was used to analyze the surface element of samples. Thermogravimetric analysis (TGA, SDTQ600) was used to estimate the weight percentage of Si and C in p-Si@C.

2.3 Electrochemical characterization

The obtained samples were mixed with carbon black and sodium alginate (mass ratio=8:1:1) using water as solvent to form a slurry and then coated on the Cu foil and dried in an oven at 60°C. The working electrodes were obtained by cutting electrode into disks (mass loading of the active material is around 0.5 mg cm⁻²). Coin cells were

fabricated in an Ar filled glovebox with lithium foil and Celgard 2400 separator. The used electrolyte was 1M LiPF₆ in 1:1 v/v ethylene carbonate/diethyl carbonate with 10wt% fluoroethylene carbonate additives. The electrochemical performance of these coin cells were conducted on battery-testing instruments (LAND-CT2001A). All the cells were tested between 0.01-1.2 V.

3. Results and discussion

Fig.1 shows the preparation procedure for the mesoporous Si with carbon coating (p-Si@C). Typically, SiO₂ nanoparticles synthesized via the modified Stöber method were uniformly mixed with Mg powders with the mass ratio of 1:0.7. Then the mixed powders were heated to 650 °C in an argon-filled reactor. During the heating process, SiO₂ was partially converted into Si (SiO₂(s) + 2Mg(g) \rightarrow Si(s) + 2MgO(s)), and the reaction temperature is much lower than the traditional carbothermic reduction of silica (over 2000 °C). Usually, to get a high reduction yield, the added Mg powder for magnesiothermic reduction was used in excess. However, excessive Mg powder would lead to the formation of Mg₂Si, which would cause interference in subsequent treatment processes. Therefore, the partial magnesiothermic reduction method could not only avoid the formation of Mg₂Si, but also reserve void space. After removing MgO, the composite of Si/SiO₂ can be obtained. In addition, according to the mass ratio of silica and Mg, we can infer that the content of Si in Si/SiO₂ sample is around 75wt% and the content of SiO_2 in Si/SiO_2 sample is around 25wt%. After that, the phenolic resin was used as carbon resources to wrap the as-formed Si/SiO₂, and

core-shell $Si/SiO_2@C$ can be obtained. After etching the residual SiO_2 from $Si/SiO_2@C$, void space was formed inside the Si core.

To compare the structure morphology clearly, SEM and TEM images of SiO₂, Si/SiO₂, bare Si and p-Si@C are displayed in Fig.2. The as-prepared SiO₂ nanoparticles have spherical structures with a diameter around 200 nm (Fig. 2a and e). After partial magnesiothermic reduction and following HCl etching, most of the Si/SiO₂ maintained the original morphology. According to the TEM image, the Si/SiO₂ sphere consisted of many interconnected nanoparticles with particle size around 10-20 nm, which is a common phenomenon for magnesiothermic reduction in the literature.[27-29] For bare Si (Fig. 2c and g), after etching residual SiO₂ from Si/SiO₂ composite, the porous structure of bare Si became more apparent, which can be even observed from the SEM image. Fig 2d and h exhibit the mesoporous Si wrapped with carbon layer, and the p-Si@C has a much smoother surface compared with the bare Si. According to the high-resolution TEM (HRTEM) acquired from the edges of p-Si@C, the lattice fringe of 0.31 nm can be ascribed to the (111) crystal plane. As a result of removing SiO₂ from the composite, void spaces were generated inside the Si core and covered with the carbon layer. In addition, EDX mapping was performed to characterize the element distribution of Si and C as shown in Fig. 2j-l. Besides the uniform distribution of the Si core in the carbon layer, it can be easily founded that many pores with diameter around 20 nm are uniformly distributed in the Si core. The internal pores and wrapped carbon layer are believed to be effective in accommodating the volume change, easing the stress strain and improving the cycling stability.

X-ray diffraction (XRD) patterns of these samples are provided in Fig. 3a. Five distinct peaks located at 28.4°, 47.3°, 56.1°, 69.1° and 76.4° can be indexed to the cubic phase of Si (JCPDS No. 77-2111). After carbon coating, a weak peak at around 22° can be ascribed to the amorphous carbon layer.[30] X-ray photoelectron spectroscopy (XPS, Fig. 3b) result could also demonstrate the existence of carbon outside the Si core. As we know, XPS can only detect the surface elements (~5 nm), the enhanced C1s peak and reduced Si signal of p-Si@C can be attributed to the carbon coating layer. While the oxygen signal detected from XPS result can be attributed to the SiO_x layer outside the Si nanoparticles, which have been commonly recognized in previous report.[31, 32] To further evaluate the mesoporous structures of Si/SiO₂, bare Si and p-Si@C, nitrogen adsorption-desorption measurements were carried out. The nitrogen adsorption curves of all samples are displayed in Fig. 3c, and each shows typical type IV isotherms, indicating the mesoporous character of these samples. The BET surface area of p-Si@C (573 m²g⁻¹) is much higher than that of bare Si and Si/SiO₂ (383 and 108 m²g⁻¹, respectively), which can be ascribed to the amorphous carbon layer and inter porous Si core. Moreover, the distribution of pore size of these samples was calculated based on the Barret-Joyner-Halenda (BJH) method as shown in Fig. 3d. Each samples shows peak centered around 3 nm, which could be attributed to the pores between interconnected nanoparticles of Si spheres as we mentioned above. However, after remove the residual SiO₂, broad peaks at around 20 nm can be observed for bare Si and p-Si@C samples. This result indicates that HF

etching of SiO_2 is an effective method to obtain mesoporous Si, and the pore diameters can be consistent with the speculation of EDX analysis.

To investigate p-Si@C sample as an anode material for LIBs, thermogravimetric analysis (TGA) measurement was carried out to determine the weight percentage of Si in the sample. As shown in Fig. 4a, the weight percentage of Si in the p-Si@C sample was determined to be around 49.4%. As anode materials for LIBs, the as-prepared bare Si and p-Si@C samples were tested within a voltage window between 0.01 and 1.2 V. Fig. 4b shows the discharge-charge curves of p-Si@C electrode at typical cycles tested at a current density of 0.5 A g⁻¹. During the initial discharge cycle, a distinct plateau profile below 0.1 V can be ascribed to Si lithiation process.[33] The first discharge and charge capacities of p-Si@C electrode are 1854 and 1287 mAh g⁻¹ respectively, with an initial columbic efficiency of 69.4%. The irreversible capacity loss of p-Si@C electrode during the first cycle could be attributed not only to the formation of SEI layers, but also to the irreversible lithiation of SiOx layer and carbon layer.[34-36] In the subsequent cycles, the capacity of p-Si@C electrode decreased slowly and the voltage profiles are almost identical, indicating a stable electrochemical behavior of p-Si@C electrode.

Fig. 4c shows the cycling stability of bare Si and p-Si@C electrodes evaluated at a rate of 0.5 A g^{-1} . It is clear that the p-Si@C electrode has a much stable cycling performance. And when cycling up to 100 cycles, the p-Si@C electrode maintains a reversible capacity of 1146 mAh g^{-1} (89.1% of its initial reversible capacity), which is almost 3 times higher than graphite anode. While the capacity of bare Si electrode

decreased rapidly from 2147 to 732 mAh g⁻¹, with capacity retention of 34.1%. To clearly understand the outstanding cycling performance of p-Si@C electrode, TEM measurement was performed to observe the morphology of p-Si@C electrode after 100 cycles. As shown in Fig. 4d, the composite could still maintain its sphere structure, which indicates that the well-organized structure could effectively alleviate the volume change and prevent the pulverization of active material. The cycling stability of p-Si@C electrode could be ascribed to the mesoporous Si core inside the carbon layer, which could provide void space for the expanded lithiated Si material.

The rate performance of these samples was also performed as shown in Fig. 4e. When the discharge/charge current density increased from 0.2 to 10 A g^{-1} , the reversible capacities of bare Si electrode decreased rapidly. While the p-Si@C electrode delivers reversible capacities of 1470, 1320, 1200, 1000, 780 and 560 mAh g^{-1} at 0.2, 0.5, 1, 2, 5, 10 A g^{-1} , respectively. Significantly, the carbon coating layer has a positive effect on the rate performance of electrode, which could be attributed to the enhanced electron transfer through the carbon network. Moreover, once the current density was returned back to 0.2 A g^{-1} , the capacity of p-Si@C electrode could recover back to 1410 mAh g^{-1} , corresponding to approximately 96% of the reversible capacity at the initial rate of 0.2 A g^{-1} . This result manifests that the p-Si@C sample has an excellent rate performance and reversibility.

In addition, to further evaluate the high-rate electrochemical performance of p-Si@C electrode, the cycling performance at 2 A g^{-1} after the activation process (cycled at 0.5 A g^{-1} for the initial 20 cycles) has been provided in Fig. 4f. The coin cell

shows a reversible capacity of 1035.1 mAh g^{-1} at the beginning of 2 A g^{-1} . During the first 100 cycles, the reversible capacity decreased rapidly to 817.2 mAh g^{-1} and then increased slightly to 872.5 mAh g^{-1} . This phenomenon can be considered a concentration polarization, which indicates that the rate of Li-ion migration is slower than that of electron and electrochemical reaction of Li-ions is in short supply.[10, 12, 37, 38] After cycling up to 500 cycles, the reversible capacity of graphite. We ascribed this excellent electrochemical performance to the existence of mesoporous inside the Si core, which in turn relieve the stress–strain during the volume change. Additionally, the carbon coating layer also contributed to the fast electron transfer and stabilization of SEI films.

4. Conclusions

In this study, we designed a carbon coated mesoporous Si structure using a partial magnesiothermic reduction method to convert SiO₂ into mesoporous Si. Etching of SiO₂ provided the Si core sufficient void space for the volume change. In addition, the carbon coating layer could provide fast electron diffusion and maintain the structure stability of the p-Si@C, thus leading to outstanding electrochemical performance for LIBs. As a result, the as-prepared p-Si@C sample as an anode exhibits a reversible capacity of 1146 mAh g⁻¹ at 0.5 A g⁻¹ after 100 cycles and a capacity around 560 mAh g⁻¹ at 10 A g⁻¹.

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Figure Captions:

Fig. 1. Schematic illustration of the synthesis processes of the bare Si and p-Si@C.

Fig. 2. SEM and TEM images of (a and e) SiO₂, (b and f) Si/SiO₂, (c and g) bare Si and (d and h) p-Si@C. Corresponding (i) HRTEM image and (j-l) EDX mapping of carbon and silicon distribution in the p-Si@C sample.

Fig. 3. (a) XRD patterns of the bare Si and p-Si@C samples. (b) Survey XPS spectra of the bare Si and p-Si@C samples. (c) Nitrogen adsorption-desorption curves and (d) pore size distribution of Si/SiO₂, bare Si and p-Si@C samples.

Fig. 4. (a) TGA curves of the p-Si@C sample measured at a heating rate of 10 °C min⁻¹ in air. (b) Voltage profiles of p-Si@C electrode at typical cycles tested at a current density of 0.5 A g⁻¹. (c) Cycling stability of the as-prepared bare Si and p-Si@C electrodes. (d) TEM image of p-Si@C electrode after 100 cycles. (e) Rate performance of the bare Si and p-Si@C electrodes. (f) Electrochemical performance of p-Si@C electrode at a current density of 2 A g⁻¹.



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Highlights

- A Partial Magnesiothermic Reduction Method is used to obtain mesoporous Si.
- The internal pores could accommodate the volume changes of Si.
- The carbon coating layer could effectively stabilize the interface during cycling.

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