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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLETYPE

Hedgehog-like polycrystalline Si as anode material for high performance Li-ion battery

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⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Hedgehog-like Si nanomaterial has been prepared by metal assisted chemical etching method with polycrystalline Si powder as raw materials and used as anode for lithium-ion batteries. The cycle stability and impedance are greatly enhanced compared with pristine silicon powder, and the columbic efficiency (CE) keeps above 99.5% up to 200+ cycles. The improved electrochemical characteristics are attributed to its volume buffering and effective conductance due to the unique structure, which combines nanowires on the surface and a core inside. The additives in electrolyte and suitable conductive materials help to stable the anode as well.

Introduction

To meet the demand by electric and hybrid vehicles, Li-ion batteries with high energy and power densities have received considerable attention. Silicon with merits, including high theoretical capacity (4200 mAh g⁻¹, ten times higher than graphite), [1] low lithium alloying/dealloying potential (about 370 mV vs. Li/Li⁺), [2] long discharge plateau [3] and abundance has been considered as a promising anode material for Li-ion battery with high energy density. In spite of these significant advantages, issues, such as poor cycle stability caused by huge volume expansion (400% in maximum) [4] and low conductivity remain to be addressed before its commercial application. There have been many efforts to overcome this fracture feature of Si electrode materials. The introduction of nanostructures including nanofilm, [5] nanoparticle, [6-8] nanoporous structures [9, 10] and nanowire [4, 11, 12] to Si materials are considered as one of the most effective methods to address these issues and are attracted much attention. Among these materials, nanowire (NW) structure offers a short electron transfer path and exhibit excellent cycle stability in Li-ion battery. Cui and coworkers [4] have fabricated high-performance Si based Li-ion battery possessing a charging capacity of 4277 mAh g⁻¹, using Si nanowires grown directly on stainless steel. The nanowires etched from the crystalline Si by metal assisted chemical etching (MACE) are also used for the high capacity Li battery. [13, 14] However, the high cost, low product yield or poor stability limits its applications.

Herein, cheap polycrystalline Si powders were used as a start material and hedgehog-like nano-Si were prepared through a MACE process. By optimizing the electrolyte and conductive additives, the nano-Si prepared exhibits stable cycle performance. The CE remains above 99.5% up to 200+ cycles with a set discharge capacity of 700 mAh g⁻¹.

Experimental Section

Preparation

Nanostructured silicon powders were synthesized by metal assisted chemical etching process. Polycrystalline silicon

particles (3N) with a diameter of about 5-10 μm were added in an etching solution of AgNO₃ (0.06 M) and HF acid (5.0 M). After stirred for 3 h, NH₄NO₃ (10%) and H₂O₂ were added drop-wisely to supply extra oxidant agent.

The etched nanostructured Si particles were filtered from solution and washed in deionized water. After removing the Ag on the surface using 50 mL HNO₃ (5 M), the particles were separated from the suspension in a centrifuge and dried at 80 °C for 10 h.

Scan electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the morphology of the etched Si, and X-ray diffraction (XRD) was used to confirm the crystallization of the material.

Electrochemical measurements

Nanostructured polycrystalline-Si, conductive materials (graphite: super P carbon black: vapor growth carbon fiber (VGCF) = 1:1:1) and polyacrylic acid (PAA) binder (weight ratio of 6:3:1) were thoroughly mixed with deionized water (DI water) by a magnetic stirrer for 6 h. Mixed slurry was then coated onto copper foil with a thickness of 150 μm. After heated at 110 °C for 20 h in vacuum drying oven, it is ready for cell assembling.

The coin-type half cells (2025R type), with lithium foils as counter electrodes, were assembled in a glove box (Mikrouna Super 1220/750) in the atmosphere of Argon. The electrolyte was LiPF₆ (1.0 M) in ethylene carbonate/methyl ethyl carbonate (EC/EMC, 30:70 vol%), with vinylene carbonate (VC, 5 wt%) and fluoroethylene carbonate (FEC, 30 wt%) as additives. Glass fiber filter or nickel foam were used to stabilize the coin system.

The coin-type half cells were cycled at a rate of 0.2C (= 700 mAh g⁻¹) on land battery test system. The cyclic voltammetry (CV) curves (in the range of 0.02 to 2.7 V and at a rate of 0.1 mV s⁻¹) and electrochemical impedance spectroscopy (EIS, in the range of 100000 to 0.01 Hz at a magnitude of 0.05 mV) were measured with an electrochemical workstation (PGSTAT302N, Autolab). The scanning electron microscope (SEM) was utilized to investigate the morphology of etched Si particles and the uniformity of anode.

Results and discussion

Figure 1(a) shows the schematic diagram of a typical procedure for the preparation of the polycrystalline Si powder by MACE method. The formation of nanowire structure on the surface of powders can provide more space and flexibility for the volume change during insertion/extraction of lithium and improve the cycling performance of Li-ion battery, which was discussed in previous reports[15]. The size effect of nanomaterial can also hinder the crack of the material[16]. In the etching process, electrons are exchanged between Si and the oxidizing agent, e.g. H_2O_2 , catalyzed by Ag particles to form SiO_2 . Subsequently, the SiO_2 is removed by HF and the Ag particle sinks further into the Si powders forming hedgehog-like nano-Si. NWs on the surface are a good channel for electron and Li ions and the core inside is a hub that connects the channels. This structure ensures the good electron transport and could also avoid the agglomeration like nanoparticles.[17, 18] The etched nanostructured Si particles were shown in Figure 1(b). Due to the non-uniformity of the etching process, hedgehog-like nano-Si was not the only shape of the product; some porous structured silicon was also formed. However, it would not do much detriment to our result, as the skeleton has an equivalent small size.

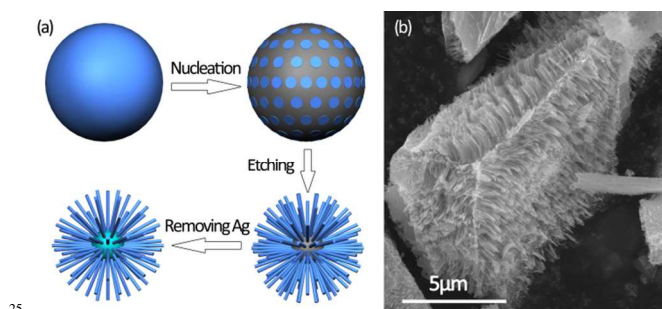


Figure 1. (a) Scheme of the etching process. (b) SEM of etched Hedgehog-like silicon particle.

HRTEM of the nanowire on the shell was shown in figure 2. It can be seen in figure 2 (a) that the diameter of the nanowire is about 100nm, which is meaningful in the size effect. The etched nanowire is polycrystalline as depicted in figure 2 (b), and is consistent with the pristine Si particle we used, which can also be illustrated in the XRD in figure 3.

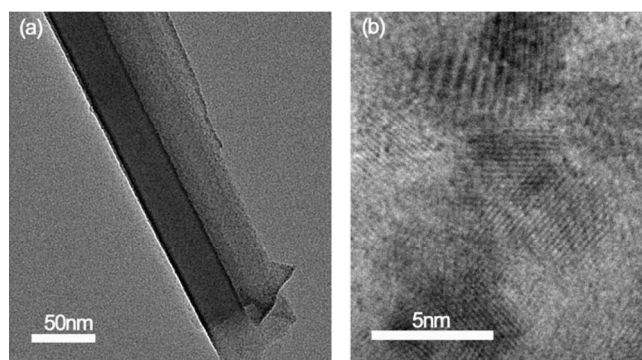


Figure 2. HRTEM of nanowire on the shell of etched hedgehog-like silicon particle.

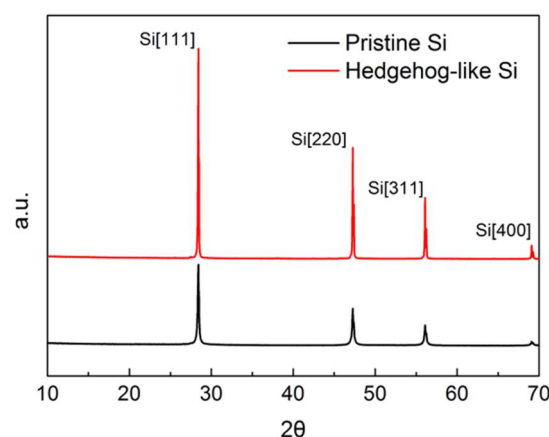


Figure 3. XRD of pristine Si and Hedgehog-like Si

Although Si materials possess the capacity of up to 4200 mAh g^{-1} , most of cathodes in lithium batteries cannot reach a comparatively high capacity so far. Therefore, the coin-type half-cell was cycled at a constant discharge capacity of 700 mAh g^{-1} to match the cathodes and to get better battery cycling performance. As it is confirmed that the volume expansion of silicon is related to the amount of lithium intercalating into silicon,[19] it will help to improve the life time of Li-ion battery by keeping the charge capacity at low value.

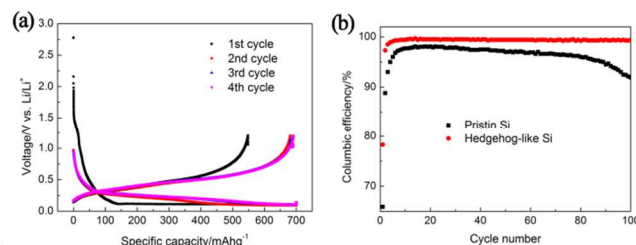


Figure 4. (a) Voltage vs. specific capacity profile of coin cell with the hedgehog-like nano Si powder as anode. (b) Columbic efficiency test of coin cell with hedgehog-like nano Si and pristine Si as anode.

From Figure 4 (a) we find there is a relative high irreversible capacity of 21.7% in the 1st cycle due to the formation of solid electrolyte interface (SEI) film, and the VGCF may also be a factor of the irreversible capacity. The followed cycles exhibit much higher CE and the curves behaved substantially the same. The charge capacity was relatively constant from the 2nd cycle onwards, indicating a high stability for the bare nanostructured silicon anode. It is also demonstrated in Figure 4 (b) that after an activation process of the first few cycles, the hedgehog-like nanostructured polycrystalline Si electrodes show good cycling stability with an average discharge capacity retention of more than 99.5% up to 200+ cycles (as shown in the red line of Figure 4b) with a charging capacity of 700 mAh g^{-1} (Figure 5(a)). The performance of battery can keep well when increasing the charge/discharge capacity while the CE decrease a little bit at higher rate (See figure 1s and 2s).

As a comparison, CE of Li-ion battery for pristine Si powders declined drastically (black line in Figure 4(b)). The high reversible capacity and the long cycle life of Li-ion battery based on nanostructured Si anode can be attributed to the unique hedgehog-like architecture that combining the advantages of volume flexibility of NWs and electrical conductance connection

of core inside. The conductive material and electrolyte additives also contribute to the stability of the cell. The applying of VGCF with a weight ratio up to 10% in anode materials helps form an effective electrical conductance network to transfer the electrons and reduce the internal resistance. Moreover, the additives of VC and FEC help form a flexible and stable SEI to adapt the volume change and avoid the fresh surface due to the expansion in discharging process. This greatly improves their cycle performance. From Figure 5 (b) we can clearly see that the cell without the additives of VC and FEC holds a lower CE and a shorter life time. At the higher mass loading, the batteries can also keep the well performance (Figure 3s).

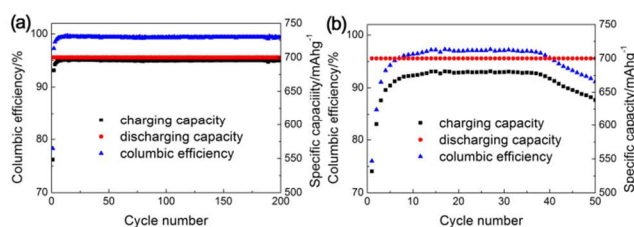


Figure 5. Specific capacity and CE of cells with (a) and without (b) VC and FEC as electrolyte additives.

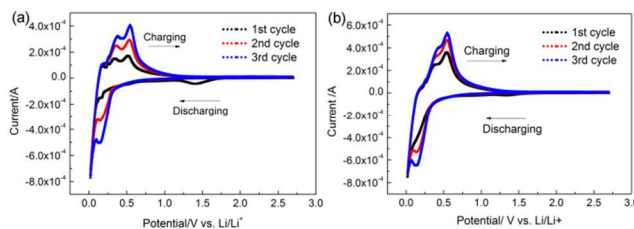


Figure 6. Cyclic voltammetry performance of coin cell with hedgehog-like nano Si powders as anode in different electrolyte. (a) with additives, (b) without additives.

To study the electrochemical reactions in the coin cell further, cyclic voltammetry was characterized (see Figure 6 (a)). The battery was cycled between 0.02 and 2.7 V with a rate of 0.1 mV s⁻¹. In the first cycle of discharge, a distinct peak at 0.17 V corresponds to the initial formation of amorphous phase of Li_xSi, as discussed in previous report.[19] The sharp increase of current below 80 mV was due to the phase transformation to crystalline of Li₁₅Si₄. In the first charging cycle, the peaks at 0.33 V and 0.57 V are from the transitions between amorphous Li_xSi phases. However, the redox peak at about 1.37 V origins from the SEI formation due to decomposition of VC and FEC, which can be confirmed by figure 6 (b). The decomposition of additives can avoid the decomposition of electrolyte, and maintain the capacity. The disappearance of this redox peak in the latter cycles indicates that the SEI was relatively stable. It also reveals the stability of the nanostructured Si anode due to the unchanged peak position and shape in the followed cycling. Moreover, the successive increases of current with cycling can shed a light on the activation of Li-ion battery with a low charging/discharging rate for the first few circles.

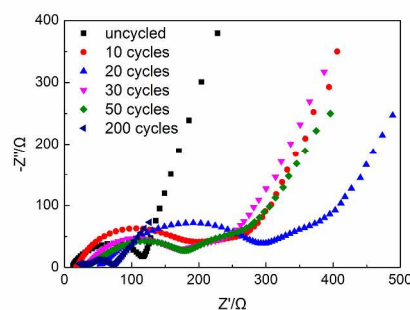


Figure 7. Electrochemical impedance for coin cell cycled for different circles.

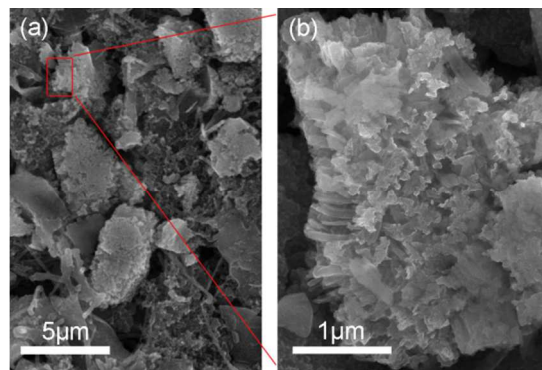


Figure 8. SEM of anode material cycled for 200 cycles.

The impedance performances of the battery are depicted in Figure 7. It is an important factor to reveal the electrochemical performance and longer life of battery. Clearly, two semi-circles and an inclined line were observed after cycling. It is known that the semi-circle in high frequency corresponds to the migration of Li⁺ in SEI film on the surface and the one in middle frequency is assigned to impedance of the charge-transfer reaction, whereas the line in low frequency is attributed to the diffusion of Li⁺ in Si anode material.[20] It can be seen that the impedance increases first and then decreases after fully activation. The volume increases greatly due to lithiation, so the SEI formed in the 1st cycle will crack and reform, which causes an irreversible capacity and increased impedance. The strong bondage between silicon atoms also increases the impedance in the beginning, which disappears in the followed cycles due to the decrystallization of anode. The change of impedance illustrates that the structure damage of anode only takes place in the beginning few circles and can be neglected afterwards. SEM of anode material after 200 cycles is shown in Figure 8. Clearly, nanostructured silicon particles did not aggregate after cycling (Figure 8 (a)). The NWs expanded obviously to form an amorphous status but without falling off the Si cores (Figure 8 (b)), which agree well with the impedance change with cycling.

Conclusion

Hedgehog-like nano-Si was prepared by metal assisted chemical etching method and used as anode material of lithium ion battery. The structure of anode was comparatively stable, leading to a long life and a columbic efficiency above 99.5% up to 200+ cycles. It is the distinctive structure that contributes to the improved electrochemical characteristics, which lead to volume buffering and effective conductance. Suitable additives in the

electrolyte and conductive material also help form a stable battery system.

Acknowledgements

This work was supported in part by National Thousand Talents Program of China, the bilateral collaboration project between Chinese Academy of Sciences and Japan Society for the Promotion of Science (Grant no GJHZ1316), the National Natural Science Foundation of China (Grant nos. 61176013 and 61177038), Beijing Natural Science Foundation (Grant no. 2142031), Beijing Municipal Science and Technology Commission project (Grant no. Z141100003814002), the Major State Basic Research Development Program of China (Grant nos. 2013CB632103 and 2011CBA00608), and the National High-Technology Research and Development Program of China (Grant nos. 2012AA012202 and 2011AA010302).

Notes and references

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