Reduced Graphene Oxide Wrapped Ultra-thin Silicon Nanowires for Lithium Ion Battery Anodes

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Abstract. Nowadays, silicon is becoming a promising kind of material for lithium ion batteries (LIBs) because of its high theoretical capacities. In this paper, we developed a new Bi-metal assisted chemical etching (BACE) method to fabricate ultrathin silicon nanowires (UTSiNWs) with an average diameter of 30 nm, and fabricate reduced graphene oxide wrapped UTSiNWs (UTSiNWs@rGO). The UTSiNWs and UTSiNWs@rGO anode have a discharge capacity of 1011.6 mAh/g and 2013.1 mAh/g under the current density of 300 mA/g. Retention rate of the UTSiNWs and UTSiNWs@rGO anode are 93.3% and 76.6% respectively. Although the discharge capacity decreased due to the side reactions caused by the increased interface, the discharge capacity of UTSiNWs@rGO anode is still higher that of UTSiNWs anode because of the electron conductivity of the anode is improved.

1. Introduction

Nowadays, lithium ion batteries (LIBs) are highly used for portable electronics and new energy vehicles. Developing high capacity anodes is an extremely significant issue for advanced LIBs. However, traditional graphite anode only has a capacity of 372 mAh/g[1], which is unsuitable for building high energy density LIBs system. In comparison, silicon, which has a theoretical capacity of 4200 mAh/g[2], is considered as the most promising anode for LIBs. However, two main problems impede silicon from being used as the next generation LIBs anode. The first problem is the large volume expansion (400%) during cycling, and the second problem is the low electronic conductivity. Two main types of methods are used to solve these problems. The first method is building silicon nanoscale structures, such as 0D silicon nanoparticles[3], 1D silicon nanowires[4] and 2D silicon nanofilms[5]. The second method is mix silicon with stress-releasing or high conductivity materials, such as oxygen containing materials[6], metals[7], and carbon materials[8].

Since graphene was developed in 2004, it has attracted numerous attractions by researchers because of its unique 2D carbon structures, high electrical conductivity and excellent mechanical strength [9][10]. Hence, graphene has been used as a promising stress releasing and conductivity improving material for LIB anodes, by mixing graphene with other materials, such as silicon[11], Sn[12], Fe₂O₃[13], etc. Moreover, the large specific area, increased intersheet spacing also enables Li⁺ to absorb and diffuse faster, and makes graphene achieve a high rate property[14].

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Building silicon nanostructures is also a method to fabricate high capacity and stability LIB anode. Silicon nanowires (SiNWs) is considered as an excellent LIB anode because of its facile strain relaxation and efficient 1D electron transportation. There are mainly two types of method to prepare SiNWs. The first one is the bottom-up method, such as chemical vapor deposition (CVD) method[15] and physical vapor deposition (PVD) method[16]. The second one is the top-down method, such as the metal assisted chemical etching (MACE) method[17]. MACE method, which is a low-cost and mass-producing to fabricate silicon nanowires, is considered as a suitable method to produce silicon anodes for LIB. However, it is hard to get SiNWs with an average diameter for less than 50 nm, because of the anisotropic growth of Ag nanoparticles tend to from island-like film rather than film with nanopores. During the following etching process, stripe-like SiNWs are formed based on the Ag film. Fabricating SiNWs with a super thin diameter through MACE method is an significant issue for developing the next generation silicon-based LIB anodes. Recently, an ion beam assisted chemical etching (IBCE) is developed by researchers to fabricate ultrathin silicon nanowires (UTSiNWs) through Au film deposition and Ag ion beam implantation[18].

In this work, we developed a new Bi-metal assisted chemical etching (BACE) method to fabricate UTSiNWs. Briefly, Au film with nanopores were deposited on silicon wafer, and then Pt particles was deposited on Au film. After that, the silicon wafer was etched in HF/H2O2 solution to obtain UTSiNWs. In addition, UTSiNWs were mixed with reduced Graphene Oxide (GO) through freeze-drying and thermal reduction to synthesis reduced Graphene Oxide wrapped UTSiNWs (UTSiNWs@rGO). The UTSiNWs and UTSiNWs@rGO anode have a discharge capacity of 1011.6 mAh/g and 2013.1 mAh/g under the current density of 300 mA/g based on the total mass of active material, with a retention rate of 93.3% and 76.6% respectively. The high cycling stability of the UTSiNWs is because of its smaller average diameter, which prevent UTSiNWs from broken and pulverization. Although the discharge capacity decreased due to the side reactions caused by the increased interface when UTSiNWs are wrapped in rGO, the electron conductivity of the anode is increased, so the discharge capacity is increased in UTSiNWs@rGO anode.

2. Experimental
2.1 Fabrication of UTSiNWs@rGO anode
Synthesis procedure of UTSiNWs@rGO were shown in figure 1. In order to fabricate the UTSiNWs, the Au film was deposited on the Si Wafers (p type, (100) oriented, 1-10 Ω·cm) using a direct-current (DC) sputtering source with target-substrate distance of 30mm, deposition current and deposition time of 10 mA, 30 s, and then, Pt film was deposited on the Au film with a deposition current and deposition time of 10 mA and 10 s, respectively. After that, Silicon wafers with Au and Pt Bi-metal film were etched in a mixed solution consist of 12 ml 40% HF, 1ml 30% H2O2 and 37 ml H2O to obtain UTSiNWs. 100nm SiNWs was synthesized through MACE method and set as the controlled group. The UTSiNWs and 100 nm SiNWs were peeled off from Si wafers and then dispersed in deionized water by ultrasonic with Sodium laurylsulfonate as the dispersant. The SiNWs with an average diameter of 100 nm were produced by the MACE method[17], and set as the contrast group.

GO produced by the Improved Hummers method[19] was mixed evenly with the UTSiNWs dispersion liquid through magnetic stirring and ultrasonic. The mixed liquid with UTSiNWs and GO was then freeze by liquid nitrogen and dried through freeze drying for 48 h to get the UTSiNWs and GO composite (UTSiNWs@GO). After that, UTSiNWs@GO was reduced into UTSiNWs@rGO through thermal reduction at 600 °C for 2 h under the protection of nitrogen.

The anode was prepared by mixed the UTSiNWs@rGO with carbon black (Super P) and Carboxymethyl (CMC) followed by stirring the composite in deionized water for 1 h to obtain the electrode slurry. The anodes were obtained by coating slurry on a 16 mm Cu foils and dried for 12 h at room temperature.

2.2 Material Characterization
The Field Emission Scanning Electron Microscopy (Hitachi S-4800) at an accelerating voltage of 10 Kv and the Transmission Electron Microscopy (TECNAI, G2 F20) was used to studied the morphology of the materials. The X-ray photoelectron spectroscopy was tested by Thermofisher, ESCALAB 250Xi.

2.3 Electrochemical Tests

2025 coin half cells where the samples were applied as cathode and the lithium metals were used as anode were assembled in the glove box (MBRAUN UNI lab plus) for electrochemical tests. The two electrodes were separated by a polypropylene membrane separator, and 1M LiPF6 solution mixed with ethylene carbonate (EC) /dimethyl carbonate (DMC) was used as electrolyte. Battery test system (CT-3008) with a voltage range from 0.01 V to 1.5V was used to test the charging and discharging properties of the cells, and cyclic voltammetry (CV) curves and EIS were tested by an electrochemical station (CHI660E). The scan rate of the CV curves was 0.05 mV/S. The frequency range of the EIS varied from 0.01 Hz to 106 Hz, with amplitude of 5 mV.

Figure 1. The schematic diagram of the synthesis procedure of UTSiNWs@rGO anode

2. Results and Discussion

The SEM image of the Au and Pt template is shown in figure 1 a). There is nanopores with channel-like structure on the Au and Pt template. Figure b) shows the SEM image of the UTSiNWs. The UTSiNWs have a weed-like morphology and tend to agglomerate with each other because of the Van Der Waals interaction. The average diameter of UTSiNWs is about 30 nm, which was calculated by the statistic diameters of 50 UTSiNWs. The cross sectional SEM images is shown in figure 2 c). The UTSiNWs in figure 2 c) also have a weed-like morphology due to their high specific ratio, which indicate that the UTSiNWs have an excellent flexibility. The high flexibility of the UTSiNWs could prevent them from crack and pulverization during the LIB cycling, which is beneficial for the cycling properties of the LIB testing. Figure 2 d) shows the TEM images of a single UTSiNW which is selected randomly from the UTSiNWs array, and the [100] direction is shown in the red arrow. This UTSiNW have a diameter of 31 nm, which coincides with the average diameter of the UTSiNWs. The high resolution TEM images of the single UTSiNW is shown in the inset. The lattice fringe spacing is 0.324 nm which ascribe to the (111) plane of silicon according to the formal literature[20].
Figure 2. a) The SEM image of the Au template with nanopores on it, b) The SEM image of the UTSiNWs, c) The cross sectional SEM images of the UTSiNWs and d) The TEM image of a single UTSiNW which is selected randomly from the UTSiNWs array (inset show the high resolution TEM image of the UTSiNW)

The SEM and EDS images of UTSiNWs@rGO is shown in Figure 3 a). The yellow and cyan part show the distribution of C and Si respectively, which is conformable with the SEM image of UTSiNWs@rGO. The SEM and EDS images indicate that UTSiNW is wrapped in rGO. By this method, the cycling property of LIB is improved because UTSiNWs can be hardly separated from the rGO during charge and discharge cycling. Also, the electron conductivity of UTSiNWs anode is improved after being mixed with rGO. The XPS C1s spectra of UTSiNWs@GO and UTSiNWs@rGO were investigated to understand the reduction degree of GO (Figure 3 b) and c)). The intensities of the C–O bond at 286.9 eV and O–C=O bond at 288.4 eV are decreased after the thermal reduction of 600 °C for 2h, which indicate that the oxygen contained group in GO is largely reduced by the thermal reduction procedure.

Figure 4 a) shows the Cycling performance of UTSiNWs@rGO, UTSiNWs, 100 nm SiNWs and rGO. The 2nd discharge capacities of UTSiNWs@rGO, UTSiNWs, 100 nm SiNWs and rGO are 2013.1 mAh/g, 1101.6 mAh/g, 1409.6 mAh/g and 246.2 mAh/g respectively under a current density of 300 mA/g based on the total mass of active material (Table 1). The 50th discharge capacities of UTSiNWs@rGO, UTSiNWs, 100 nm SiNWs and rGO are 1542.1 mAh/g, 954.1 mAh/g, 216.2 mAh/g and 156.3 mAh/g respectively. Both the 2nd discharge capacity and 50th discharge capacity of UTSiNWs@rGO are larger than that of 30 nm UTSiNWs and SiNWs, because of the addition of rGO, which increase the electron conductivity of the UTSiNWs@rGO anode. The capacity retention of the 4 kinds of anodes are 76.6%, 93.3%, 15.4%, 63.6%, respectively. The capacity retention of 30 nm UTSiNWs anode is far larger than that of the 100 nm SiNWs. It is because that the smaller average diameter of the 30 nm UTSiNWs prevent it from pulverization and separation form current collector during cycling. The capacity retention of UTSiNWs@rGO is lower than that of UTSiNWs anodes because of the side reactions caused by the increased interface, where Li+ reacted with Si and SiO2 and formed Li2O and lithium silicates [22]. Moreover, the structural stability caused by the defects of rGO and the decreased number lithium
insertion sites caused by the irreversible stacking of rGO sheets also induce the capacity degradation of UTSiNWs@rGO in the following cycles. However, the discharge capacity of the UTSiNWs@rGO (1542.1 mAh/g) is still larger than that of UTSiNWs (954.1 mAh/g).

Figure 3. a) The SEM and EDS images of UTSiNWs@rGO b), c) The XPS C1s spectra of UTSiNWs@GO, UTSiNWs@rGO respectively.

The galvanostatic discharge-charge profiles of the 1st, 2nd, 25th and 50th of UTSiNWs@rGO are shown in figure 4 b). There is a long discharge flat plateau during the first discharge, which is attributed to the reaction between crystalline Si and Li to form amorphous Li$_x$Si, the formation of SEI layer and the decomposition of the electrolyte. The plateau in discharge-charge profiles of the following cycles correspond to the reaction between amorphous Si and Li. Figure 4 b) also illustrate that the discharge capacities of UTSiNWs@rGO are 3288.2 mAh/g, 2013.1 mAh/g, 1714.2 mAh/g and 1542.1 mAh/g in the 1st, 2nd, 25th and 50th cycle respectively. During the first discharge process, there is a long plateau caused by the decomposition of the electrolyte the formation of the SEI layer and the lithiation process from Silicon to unsaturated Li-Si alloy. During the following discharge and charge cycles, the plateaus are caused by the transition from Si and Li$_x$Si. Figure 4 c) shows the rate properties of UTSiNWs@rGO. The discharge capacities of UTSiNWs@rGO are 1907.2 mAh/g, 1569.1 mAh/g, 1383.0 mAh/g and 1518.0 mAh/g, with the current density of 300 mA/g, 600 mA/g, 1200 mA/g and 300 mA/g based on the mass of active material. With the addition of rGO, the insertion and de-insertion process of Li$^+$ becomes easier.
Figure 4. a) Cycling performance of UTSiNWs@rGO, UTSiNWs, 100 nm SiNWs and rGO, b) Galvanostatic discharge-charge profiles of UTSiNWs@rGO c) Rate performance of UTSiNWs@rGO.

Figure 5 a) shows the cyclic voltammetry (CV) curves of UTSiNWs@rGO during the first three cycles. During the first discharge cycle, there is a broad reduction peak around 0.8 V because of the formation of SEI layer, the decomposition of the electrolyte and the irreversible first cycle capacity of graphene. The cathodic peak 1 at 0.18 V and peak 2 at 0.01 V indicate the lithiation process from Silicon to unsaturated Li-Si alloy and then to saturated Li-Si alloy respectively. Anodic peak 3 at 0.30 V and peak 4 at 0.48 V indicate the delithiation process from saturated Li-Si alloy to unsaturated Li-Si alloy and then to Silicon respectively. Due to the polarization of cells, there is voltage difference between the cathodic peaks and the anodic peaks. The CV results are coincident with formal literatures[23][24]. In addition, Due to the activation of the active materials, the current intensity of the peaks increase in the 2nd and 3rd cycles.

Table 1. Discharge capacity and capacity retention of UTSiNWs@rGO, UTSiNWs, 100 nm SiNWs and rGO

| Anodes     | 2nd discharge capacity (mAh/g) | 50th discharge capacity (mAh/g) | Capacity Retention (50th cycle) |
|------------|--------------------------------|---------------------------------|---------------------------------|
| UTSiNWs@rGO | 2013.1                         | 1542.1                          | 76.6%                           |
| UTSiNWs    | 1011.6                         | 954.1                           | 93.3%                           |
| SiNWs      | 1409.6                         | 216.2                           | 15.4%                           |
| rGO        | 246.2                          | 156.3                           | 63.6%                           |

In order to further understand the electrochemical reaction of the two types of anodes during cycling, Figure 5 b) is used to show the Nyquist plots (shown in the red and black plots) and fitting results (shown in the red and black curves) of the UTSiNWs and UTSiNWs@rGO in the 50th cycle, and the equivalent circuit model is also shown in figure 5 b). In the equivalent circuit model, Rs, R-SEI, Rint and Rct are the solution resistance, SEI film resistance, interphase electronic contacts resistance, charge-transfer resistance respectively[25][26]. Fitting parameters for the Nyquist plots of UTSiNWs@rGO and UTSiNWs is shown in table 2. Generally, Rint is the largest resistance, followed by Rct, R-SEI and Rs is the smallest. The Rs, Rint and Rct of UTSiNWs@rGO are 4.28 Ohm, 20.99 Ohm and 10.73 Ohm respectively, which are smaller than that of UTSiNWs (4.66Ohm, 100.40 Ohm, 61.99 Ohm respectively), which indicates that in UTSiNWs@rGO anode, the electrons transformation from silicon to Cu current collector easier and the electrical contact is more compact. This is because of the addition of rGO, which not only improved the conductivity of anode materials, but also formed continuous conducting networks. However, the R-SEI of UTSiNWs@RGO (4.86 Ohm) is larger than that of UTSiNWs (2.99 Ohm), which demonstrate that the SEI layer is thinner and more stable in the UTSiNWs anode than the UTSiNWs@rGO anode, as there are more interface reactions caused by rGO.
Figure 5. a) The Cyclic voltammetry (CV) curves of UTSiNWs@rGO during the first three cycles, b) Nyquist plots (showed in the red and black plots) and fitting results (showed in the red and black curves) of the UTSiNWs and UTSiNWs@rGO in the 50th cycle

| Table 2. Fitting parameters for the Nyquist plots of UTSiNWs@rGO and UTSiNWs |
|-----------------|-----------------|-----------------|-----------------|
|                 | Rs (Ohm)        | R-int (Ohm)     | Rct (Ohm)       |
| UTSiNWs@rGO    | 4.28            | 20.99           | 10.73           |
| UTSiNWs        | 4.66            | 100.40          | 61.99           |

3. Conclusion
In conclusion, we developed a new BACE method to produce UTSiNWs with an average diameter of 30 nm, and fabricated UTSiNWs@rGO composites. The UTSiNWs@rGO anode have a capacity of 2013.1 mAh/g under the current density of 300 mA/g based on the total mass of active material, with a retention rate of 76.6%. We also discussed the electrochemical reaction mechanism based on the results of CV curves and EIS plots.

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