Study of silicon/polypyrrole composite as anode materials for Li-ion batteries

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Abstract

Silicon and polypyrrole composites were synthesized using high-energy mechanical milling. The polypyrrole acts as a matrix to hold the active silicon grains as they repeatedly alloy with lithium during the operation of a lithium battery. Polypyrrole decreases the initial irreversible capacity loss of the silicon anode due to the reduction in the thickness of the solid electrolyte interface (SEI) layer formed. The composite containing 50 wt% silicon obtained after milling for 4 h exhibits a good reversibility, higher coulombic efficiency and better cycle life than the bare silicon.
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1. Introduction

Graphitic or graphitization carbons have been used extensively as the negative electrode materials for lithium-ion batteries. However, this has placed a limit on the anode specific capacity at 372 mAh g^{-1}. To increase the specific energy of lithium-ion batteries, alternative anode materials with higher capacity are needed. Besenhard et al. have evaluated different lithium alloys as anode materials for lithium-ion batteries [1]. Among the many matrices for lithium alloying, Si stands out because of its high capacity to accommodate lithium (with the maximum uptake of Li$_{4.4}$Si, corresponding to 4200 mAh g^{-1}) [2]. Unfortunately, most lithium alloys are brittle, and hence, easily pulverized by the large volume change in charge and discharge reactions. The resulting loss of connectivity with the conducting additive particles causes poor cyclability in practice [3]. To circumvent this problem, several research efforts have been carried out to disperse fine Si particles within a solid, mixed conducting host matrix by mechanical milling. Considerable improvement in cyclability has been obtained.

An electrically conducting polymer, polypyrrole, has been used in various applications such as batteries and supercapacitors. It has been used within LiMn$_2$O$_4$ cathode powder, in which it serves the dual-purpose of a binder and a conducting additive [4,5]. Since the polymer can form a conducting matrix, which provides a conducting backbone for the batteries, it could also be used as a host matrix to prevent large volumetric changes during charge/discharge cycles. The purpose of this paper is to improve the electrochemical properties of Si anode by exploring silicon/polypyrrole (Si/PPy) composite as an anode material. To the best of our knowledge, there have been no reports to date on this composite used as an anode in lithium-ion batteries. The basic premise of this work is to demonstrate the usefulness of polypyrrole as a host matrix in the presence of an electrochemically active phase of Si.

2. Experimental

2.1. Materials preparations

Polypyrrole (PPy) film was galvanostatically deposited at 0.15 mA cm^{-2} on stainless steel plate from 0.06 M pyrrole + 0.05 M TBAPF$_6$/PC for 100 min. After deposition, the film was washed with de-ionised water and peeled off the

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stainless steel plate. The film was dried in a vacuum oven at 50 °C for 8 h. Si/PPy nanocomposites were prepared using a Retsch MM301 high-energy mechanical mill. Si nanopowder was used as received from Nanostructured & Amorphous Materials Inc. A measured amount of synthetic PPy was mixed with Si nanopowder, and the mixture was loaded into a hardened steel vial containing hardened steel balls inside an argon filled glove box. The morphology of the composite obtained was analysed using a Leica scanning electron microscope (SEM). SEM measurements were also conducted on the pure Si sample for comparison.

2.2. Electrochemical tests

The electrochemical characterizations were performed using coin cells and Teflon cells. The anode was prepared by mixing Si/PPy powder with 10 wt% carbon black and 5 wt% PVDF (polyvinylidene fluoride) solution. The Si/PPy composite and carbon black powders were first added to a solution of PVDF in *N*-methyl-2-pyrrolidinone (NMP) to make a slurry with appropriate viscosity. Copper foil was then used to coat the mixture. After the electrode was dried at 100 °C for 2 h in vacuum, it was compressed at a rate of about 150 kg cm^{-2}. Coin cells and Teflon test cells were assembled in an argon filled glove box, where the counter electrode was Li metal and the electrolyte was 1 M LiPF$_6$ dissolved in a 50/50 vol% mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). These cells were cycled between 0.02 and 1.2 V at a constant current density of 0.25 mA cm^{-2} at room temperature to measure the electrochemical response. In this paper, the discharge capacity of the negative electrode refers to the lithium intercalation capacity while the charge capacity refers to the lithium de-intercalation capacity. AC impedance measurements were carried out utilizing an EG&G Model 6310 electrochemical impedance analyser. Electrochemical impedance software (Model 398) was used to control a computer for conductivity and stability measurements. After the electrode attained a steady-state potential, electrochemical impedance measurements were carried out by applying an AC voltage of 5 mV over the frequency range from 1 mHz to 100 kHz.

3. Results and discussion

SEM analysis was conducted on the Si/PPy composite containing 90 wt% Si obtained after milling for 4 h to analyse the microstructure. Fig. 1 compares the microstructures of nano-Si and Si/PPy powders. As can be observed from the micrograph of the nano-Si in Fig. 1(a), many fine Si particles are agglomerated and the agglomerates are porous. However, the micrograph of the Si/PPy composite shown in Fig. 1(b) indicates that the polypyrrole glues the Si particles together, and the size of the agglomerates is in the range of 0.3–3 μm. Although Si particles in both samples are agglomerated, the agglomerates in nano-Si are not as dense as in Si/PPy composite.
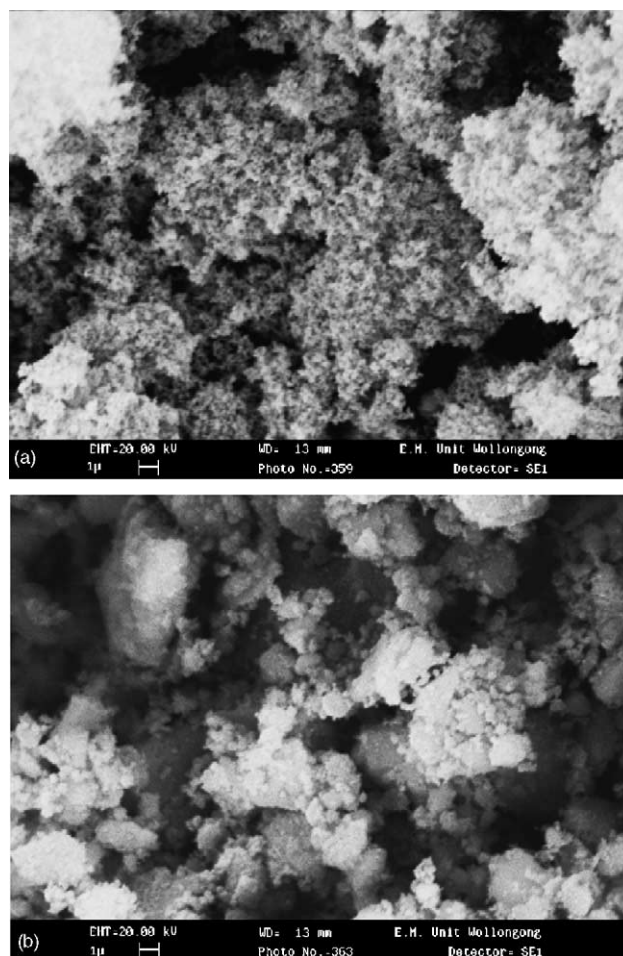

Fig. 1. SEM images of: (a) nano-Si powder and (b) Si/PPy (9:1) composite.

Fig. 2 shows the specific discharge capacity of the electrodes prepared with Si/PPy composite and bare nano-Si upon cycling. Although an initial capacity of about 3500 mAh g^{-1} can be attained for the pure nano-Si anode, it shows poor retention characteristics. This is mainly due to the very large
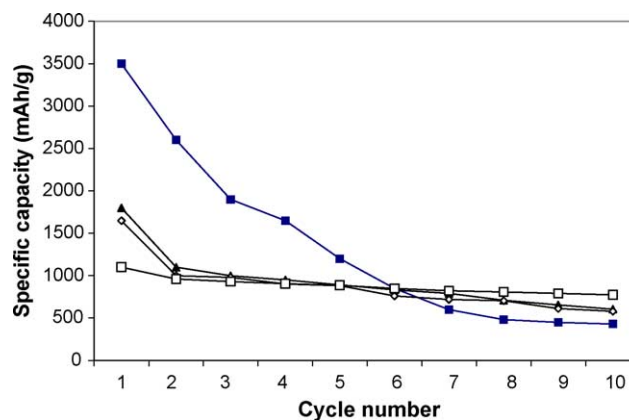

Fig. 2. Capacity as a function of cycle number for: (■) bare nano-Si; (▲) 4 h ball-milled Si/PPy (9:1) composite; (◇) 8 h ball-milled Si/PPy (9:1) composite and (□) 4 h ball-milled Si/PPy (1:1) composite.

change in volume during charge/discharge cycles, resulting in cracking or crumbling of the anodes [6]. A less active (carbon) or inactive conducting matrix (TiN, SiC, TiC, etc.) has been used to overcome this problem [7–9]. In this work, electrochemically synthesized polypyrrole was used as the host matrix. It has been reported that polypyrrole has no electrochemical activity towards lithium intercalation in the potential range of 1.6–0.01 V versus Li/Li$^+$, although some activity has been reported for polypyrrole prepared through electrochemical means in the potential range typical for cathodes (2.5–4.2 V versus Li/Li$^+$) [10].

The highest first discharge capacity observed for a Li/Si–PPy cell is about 1800 mAh g^{-1}, indicating a reduction in the amount of the active phase of silicon. The capacity fading of Si was suppressed to some extent. There are two reasons for the capacity reduction: the fact that the net amount of silicon was reduced in the composite compared with that in the pure Si sample; and the embedding of Si or the diffusion of Si into the PPy matrix. Although the capacity of the composites can be increased by increasing the fraction of Si phase in the composites or decreasing the ball-milling time (below 4 h), the capacity retention is not as good as that shown here. On the other hand, in order to improve the cycling stability of Si/PPy nanocomposite electrode, decreasing the Si powder content in the Si/PPy and extended ball-milling methods (above 4 h) were used to optimise the Si/PPy nanocomposites. It was found that extended ball-milling did not improve the cycling stability much, however, decreasing the amount of Si in the Si/PPy composite achieves better cyclability (Fig. 2). Due to the viscosity of PPy, it is very hard to coat PPy on the Si powder uniformly just by increasing the ball-milling time. This is why the capacity and cyclablity of Si/PPy composites were not significantly affected by the extended ball-milling. To further increase the efficiency of the PPy host matrix, we are now preparing nano-Si powder coated with chemically polymerized PPy. The results will be published elsewhere.

Fig. 3 compares the charge/discharge curves of the first three cycles for the composite and pure silicon. It was found that the irreversible capacity loss for 4 h ball-milled Si/PPy (9:1) composite during the first cycle due to electrolyte decomposition/SEI layer formation [11] was much lower than that of bare Si anode. The reasons for this are: (1) the polypyrrole in Si/PPy composites is a conducting polymer, which could increase the conductivity of the samples and (2) PPy forms a matrix in which Si particles are bound together, therefore, the particle-to-particle resistance will be decreased, thus reducing the irreversible reactions with the electrolyte. A careful examination of the voltage profile of the Si/PPy (9:1) composite shows a close similarity to that of the bare Si. This suggests that the reaction mechanisms in these electrodes are very similar and are based only on reactions of lithium with small grains of Si, while the polypyrrole in the composite acts as an inert matrix for the alloy reaction.

It also should be noted that in the case of the Si/PPy composite, the coulombic efficiency is higher when compared to the bare Si anode. It is well known that polypyrrole serves
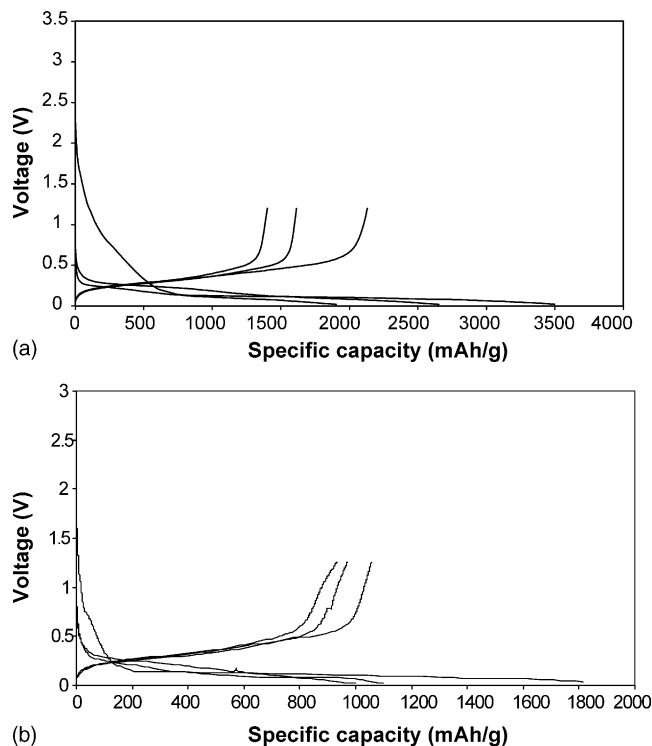

Fig. 3. The first three-cycle discharge and recharge curves of: (a) nano-Si anode and (b) Si/PPy (9:1) composite.

the dual-purpose of a binder and a conducting additive when used with cathode powders such as MnO_2, $LiMn_2O_4$ and V_2O_5 [12–15]. In our studies, it could also act as an efficient host matrix to prevent cracking and pulverization of the Si electrode due to phase transitions, thus improving the cyclability of the Si-based electrode. A schematic diagram of the Si/PPy composite is shown in Fig. 4, where the Si works as the active phase and PPy acts as the inactive phase. The Si lattice expansion during charging/discharging could be buffered by the presence of PPy. At the same time, PPy can also act as a conductive binder, increasing the contact between particles. To verify this concept, AC impedance measurements were conducted. The Nyquist plots obtained for
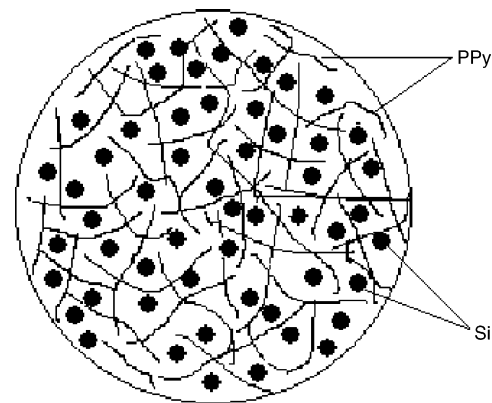

Fig. 4. Schematic diagram of the Si/PPy composite. Si acts as the active phase and PPy as the inactive phase.
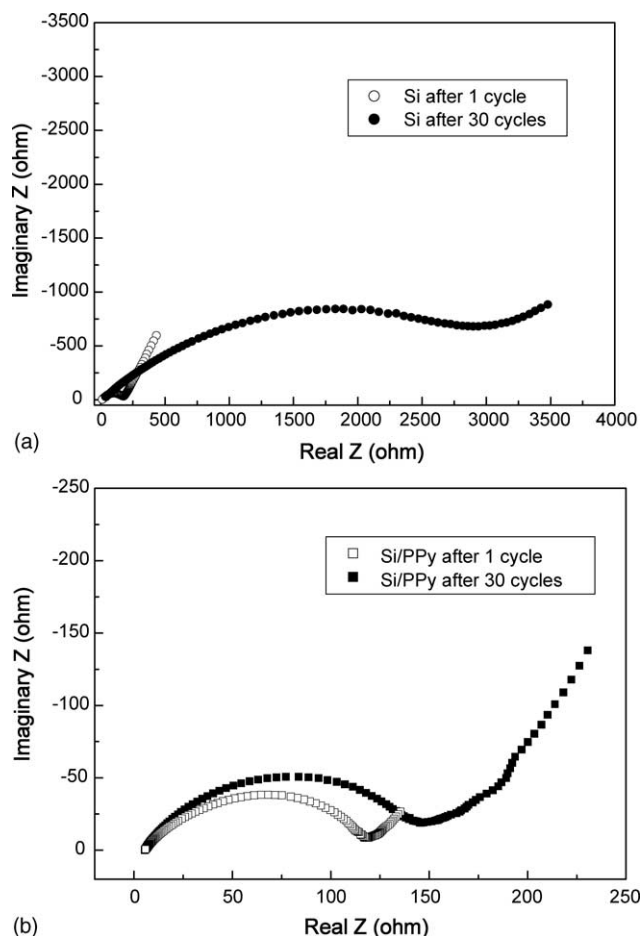
Fig. 5. Impedance plots for (a) the bare Si anode and (b) the Si/PPy (9:1) composite in the de-lithiated state.

Si/PPy (9:1) composite compared with Si after 1 and 30 cycles are shown in Fig. 5. The thickness of the electrodes was controlled at 50 μm, and the coated area of the electrodes at 1 cm^2. The impedance of the anode in the Li-ion cell depends strongly on the lithium content inside these electrodes. To maintain uniformity, electrochemical impedance spectroscopy (EIS) experiments were performed on working electrodes in the charged state (state of charge = 100%). Fig. 5(a) shows the EIS profiles of the bare Si sample, and Fig. 5(b) is the EIS of Si/PPy (9:1) composite. Just one semicircle was observed for all the samples. In the low frequency region, a straight line was obtained which represents a diffusion-controlled process in the solid electrode. Generally, all the semicircles shown in Fig. 5 were enlarged after 30 cycles at room temperature. However, when Fig. 5(b) is compared with Fig. 5(a), considerable differences are observed. The semicircle at high frequencies increased remarkably after 30 cycles in the case of bare Si relative to Si/PPy composite. Fan and Fedkiw [16] reported that the semicircle might contain a contribution due to the compaction of particles in the anode, i.e. the inter-particle contacts such as Si/PPy–carbon or

carbon–carbon contacts. Therefore, the reduction in the diameter of the semicircle in Si/PPy electrodes probably can be ascribed to a decrease in the inter-particle contact resistance. So, it can be speculated that the polypyrrole suppresses the cracking or crumbling of the anodes during charge/discharge cycles.

4. Conclusions

A series of novel Si/PPy composites, suitable as lithium-ion battery anodes, was prepared by high-energy mechanical milling techniques. These anode materials had high capacities characteristic of the Li–Si alloy system but with substantially improved cyclability compared to bare silicon anodes. The vast network of the PPy matrix is a suitable environment to cushion the volume change associated with Li$_x$Si alloying and dealloying reactions. The capacities of the composites were dependent on the amount of silicon added.

Acknowledgements

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