

Short communication

High capacity Si/C nanocomposite anodes for Li-ion batteries

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Abstract

Nanocomposites of Si/C were synthesized from Si and polystyrene (PS) resin using high-energy mechanical milling (HEMM) followed by subsequent heat-treatment. The resultant nanocomposites are comprised of amorphous carbon and nanocrystalline silicon as verified by X-ray diffraction (XRD). The XRD results also indicate the presence of iron silicide (FeSi) arising as a contaminant during HEMM. The Si/C nanocomposite corresponding to Si:C = 1:2 composition obtained after milling in two stages of 12 h each for a total time period of 24 h shows a capacity as high as ~850 mAh/g with reasonable capacity retention (~1.1% loss/cycle). The increase in either heat-treatment temperature or milling time renders the nanocomposites more stable at the expense of capacity. Transmission electron microscopy (TEM) analysis shows that the HEMM derived Si nanocrystallites <50 nm in size are distributed homogeneously within the amorphous carbon matrix.

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1. Introduction

There is considerable research being conducted to develop alternative anode systems to carbonaceous materials for Li-ion batteries and active/inactive nanocomposites containing electrochemically active Si and Sn has attracted significant interest due to their potential to generate high capacity [1–6]. However no systems to date have attained any commercial status mainly due to the crucial problems related to the structural instability, caused by the large volume changes associated with alloying and dealloying of lithium during electrochemical cycling [2–9]. The large volumetric change and the resulting stresses associated with it results in cracking and crumbling of the electrodes causing abrupt failure of the electrode. Hence there is an imminent need for identifying systems and developing strategies for generating composites that can exhibit high reversible capacities.

Our group has demonstrated the potential of Si/TiN, Si/TiB₂, Si/SiC and Sn/C active/inactive nanocomposites for use as anodes in Li-ion batteries synthesized using high-energy mechanical milling (HEMM) and chemical synthetic approaches [10–15]. Although these systems appear promising exhibiting reasonably high capacity with stability, some limitations arise due to the synthetic methods

used for generating the nanocomposites. Nanocomposites of Si/TiN, Si/TiB₂ and Si/SiC derived using HEMM exhibit significant capacity loss caused by the embedding of active species of Si during milling [16]. On the other hand, Sn/C composite generated using the chemical approach shows loss of Sn during heat-treatment, thus resulting in loss of capacity. HEMM though promising as an inexpensive approach for generating nanocomposites appears to be limited with regards to the use of high strength transition metal non-oxide as a matrix for enduring the volume expansion of brittle elements such as Si. The milling action for a prolonged period of time leads to embedding of Si within the non-oxide matrix causing a large increase in charge-transfer resistance thus rendering the system inactive. In the case of tin containing systems, chemical methods though effective, however necessarily require a pyrolysis step that invariably results in loss of tin due to its low melting point. Alternative approaches and modification of the current systems are thus sorely needed.

The objective of this research is to improve the performance of the anodes further by combining the two synthetic approaches together in order to overcome the limitations mentioned above. The embedment of Si can be accelerated by milling with hard materials. Hence the use of a soft precursor that transforms to an electrochemically inactive component is necessary. Since polystyrene (PS) resin derived carbon has demonstrated potential as shown by our previous study on Sn/C composite, PS-resin was chosen as a

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precursor for generating carbon with the objective of generating nanocomposites containing Si. In the case of Sn/C as shown by our earlier work, encapsulation of Sn by carbon during heat-treatment is a key step necessary to obtain the high capacity and also improve the capacity retention [14]. Hence the rationale for the present work was to explore the milling of PS-resin with Si to generate a composite mixture that after pyrolysis would largely be composed of silicon encapsulated by a thin film of carbon. Carbon could thus offer the desired mechanical stability while also contributing to the conductivity. In addition, PS-resin does not react with Si to form SiC while carbon does, preventing any capacity loss caused by the formation of the undesirable SiC inactive phase.

Hence Si/C nanocomposites were synthesized by HEMM followed by appropriate heat-treatments. Experimental studies and results of the electrochemical responses are presented. X-ray diffraction (XRD) and transmission electron microscopy (TEM) have been conducted to identify the phase and microstructural morphology of the resultant nanocomposites.

2. Experimental

The general procedure for generating the nanocomposite consists of milling and subsequent pyrolysis of the as-milled powders. Commercially obtained materials poly(styrene) (PS) resin (Purolite Co., USA, MN-200, Mw = 100,000 g/mole, >25% of Divinylbenzene, bead size: 0.3–1.2 mm) and silicon (Aldrich, 99.5%, 325 mesh) were used for generating the composites. All the powders were weighed and batched in a vial inside an argon filled glove box (VAC atmosphere, Hawthorne, CA, O₂ and moisture content < 10 ppm) and milled subsequently using a SPEX-8000 high-energy mechanical mill with a charge ratio of 12:1 employing 15 hardened steel balls. Since fine Si cannot be easily obtained using milling with soft materials such as PS-resin, a two step milling process was employed: 1.08 g of Si and 0.1 g of PS-resin were milled first for 12 h and then additional amount of PS-resin (2.46 g) was added again inside the glove box followed by another milling step for either 12 or 24 h. The nominal composition of the precursor was Sn:C = 1:2 based on the real weight of carbon residue obtained after pyrolysis of the PS-resin in ultra high purity (UHP) Ar containing 5% H₂. Hydrogen gas is used to reduce any possible oxidation of Si during heat-treatment. The as-milled powders were heat-treated subsequently at the desired temperature, 600, 800, and 1000 °C for 5 h, each in a furnace. The ramp rate was 300 °C/h and the flow rate of the UHP-Ar/H₂ (5%) used was 100 ml/min.

In order to evaluate the electrochemical characteristics, electrodes were fabricated using the as-heat-treated powder by mixing 87.1 wt.% of the active powder and 7.3 wt.% of acetylene black. A solution containing 5.6 wt.% polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidinone (NMP)

was added to the mixture. The as-prepared solution was coated onto a Cu foil (INSULECTRO, electro-deposited, thickness: 175 μm). A 2016 coin cell (Hohsen Corp.), cell-design was used employing lithium foil as an anode and 1 M LiPF₆ in EC/DEC (2:1) as the electrolyte. All the batteries tested in this study were cycled in the voltage range from 0.02 to 1.2 V employing a current density of 0.1 mA/cm² and, 60 s rest period between the charge/discharge cycles using a potentiostat (Arbin electrochemical instrument). The phases present in the as-milled and heat-treated powders were studied using X-ray diffraction (Philips X'PERT PRO system) and the microstructure was examined using a transmission electron microscope (JEOL 2000).

3. Results and discussion

The objective of this study as mentioned above is to improve the electrochemical performance of nanocomposite anodes using Si and carbon as the active and inactive components. Hence the primary goal is to explore the electrochemical response of Si/C nanocomposites synthesized using HEMM corresponding to a nominal composition of Si:C = 1:2. Fig. 1(a) shows the specific capacity versus cycle number for the Si/C nanocomposites synthesized from Si and PS-resin obtained after milling the precursor for an initial 12 h period followed by an additional 12 h milling step. The as-milled powders were then subsequently heat-treated at 600, 800 and 1000 °C for 5 h each in UHP-Ar/H₂ (5%), respectively. As discussed in our previous work [14], PS-resin will generate hard carbon that tends to encapsulate the active species after pyrolysis. The capacity retention of the nanocomposites as shown in Fig. 1(a) appears to improve with increase in heat-treatment temperature since a higher temperature treatment results in a dense structure of hard carbon, which maintains the structural stability and also possibly accommodates the volume change caused by the reaction of lithium during the charge and discharge cycles. However, the encapsulation of Si particles by hard carbon also results in loss in capacity since it is possible that some of the Si particles become inactive. This explains the decrease in overall capacity with increase in heat-treatment temperature. However, the first irreversible loss of the nanocomposites that is attributed to the disordered structure of the hard carbon is reduced, indicating that the higher temperature treatment is effective in minimizing the disorder of hard carbon. Nevertheless, the Si/C nanocomposite obtained after heat-treatment at 800 °C exhibits a high capacity of ~850 mAh/g with reasonable stability (~1.1% loss/cycle) and an irreversible loss of only ~23%. This irreversible loss is significantly less in comparison to the large values of ~45% observed in the Sn/C system reported by us in our prior work [14]. The differential capacity of the nanocomposite prepared after heat-treatment in UHP-Ar/H₂ (5%) at 800 °C for 5 h is shown in Fig. 1(b). The two broad peaks during charge and discharge cycles

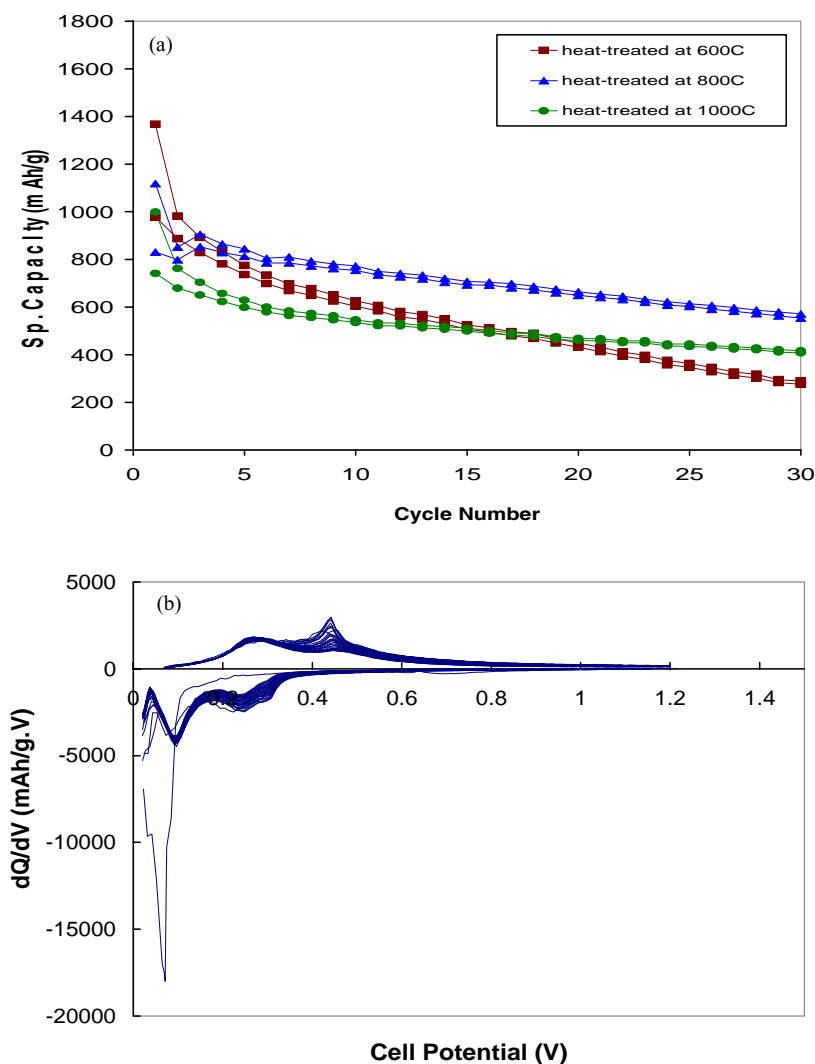


Fig. 1. (a) Capacity as a function of cycle number for Si/C nanocomposites containing 33 mol.% Si obtained after milling for 12 + 12 h followed by subsequent heat-treatment in UHP-Ar/H₂ (5%) for 5 h each at 600, 800 and 1000 °C. (b) Differential capacity vs. cell potential curves of the nanocomposite obtained after heat-treatment at 800 °C for 5 h in UHP Ar/H₂ (5%) (current rate: 100 μ A/cm², potential: 0.02–1.2 V).

($\cong 0.08$ V, 0.2 V; $\cong 0.3$ V, 0.45 V) are attributed to the reaction of nanocrystalline Si with Li. The slow decrease in peak intensity is attributed to the gradual loss of capacity.

The XRD spectra collected on nanocomposite before and after heat-treatment at 800 °C is shown in Fig. 2. The main broad peaks shown in Fig. 2(a) correspond to nanocrystalline Si, marked as hollow circles which do not appear to change much after heat-treatment at 800 °C for 5 h (see Fig. 2(b)). Hence the first milling step of Si with small amount of PS-resin appears to be effective in generating nanocrystalline Si. The small peaks marked with asterisks correspond to the iron silicide phase, the formation of which is caused by the contamination from Fe arising from the steel balls and vial used for milling. Although the peaks become sharp after the heat-treatment, the presence of this phase and its effect on the electrochemical response may not be significant since EDX analysis on the nanocomposite exhibits that the incorporation of Fe is not severe (<1 at.%) as shown in Table 1.

The microstructure of the Si/C nanocomposite obtained after milling for 12 + 12 h has been examined using transmission electron microscopy (TEM) combined with selected area diffraction. The selected area diffraction pattern (SADP) (see the inset of Fig. 3) exhibits a clear ring pattern, indicating the nanocrystalline nature of Si in an amorphous C matrix. The presence of spot(s) between rings appears to be caused by the FeSi phase, as identified in the XRD

Table 1
EDX elemental analysis^a of the nanocomposite containing Si:C = 1:2 obtained after milling for 12 + 12 h and subsequent heat-treatment in UHP-Ar/H₂ (5%) for 5 h at 800 °C

Si (at.%)	C (at.%)	Fe (at.%)
66.4	32.8	0.8

^a Average values were obtained from five different locations in the sample.

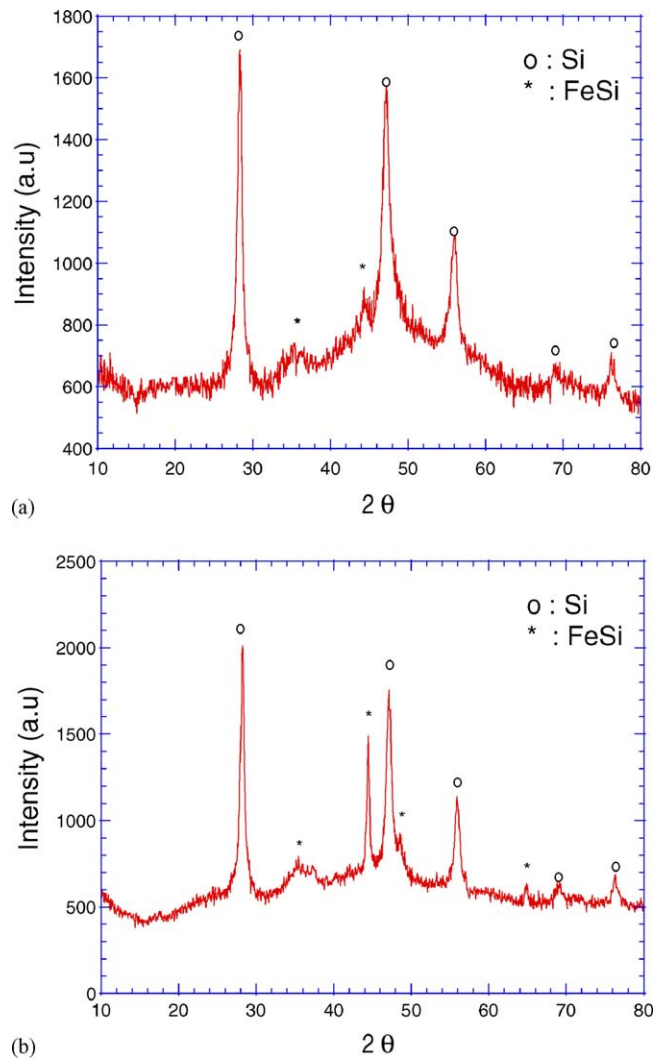


Fig. 2. (a) XRD patterns of the nanocomposite containing Si:C = 1:2 obtained after milling for 12 + 12 h (before heat-treatment), and (b) after subsequent heat-treatment in UHP-Ar/H₂ (5%) for 5 h at 800 °C.

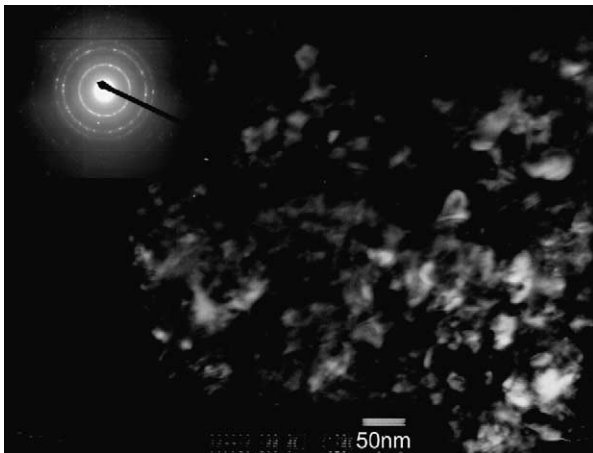


Fig. 3. The dark field image and the SADP of the nanocomposite containing Si:C = 1:2 obtained after milling for 12 + 12 h followed by subsequent heat-treatment in UHP-Ar/H₂ (5%) for 5 h at 800 °C (the SADP is shown in the inset has been collected with camera length = 80 cm, reduced to 33% of its original size).

pattern. The dark field TEM image of the Si/C nanocomposite suggest that fine (<50 nm) irregularly shaped Si particles are homogeneously distributed in the amorphous carbon matrix similar to the microstructure of Si observed in Si/SiC nanocomposites reported by us previously [15]. As discussed in our previous work [14], the specific microstructure where fine particles of active component are embedded within amorphous carbon plays an important role in maintaining the stability in capacity of the nanocomposite.

The nanocomposite obtained after milling for 12 + 12 h and subsequent heat-treatment at 800 °C for 5 h exhibits relatively good electrochemical performance compared to other two samples as shown in Fig. 1(a). However, there is still need for improvement and the current research is focused on the optimization of the Si/C system prepared from Si and PS-resin. One example of such an optimization will be to increase the second step milling time from 12 to 24 h and the experimental result is shown in Fig. 4. Although the overall capacity has been decreased to ~540 mAh/g by ex-

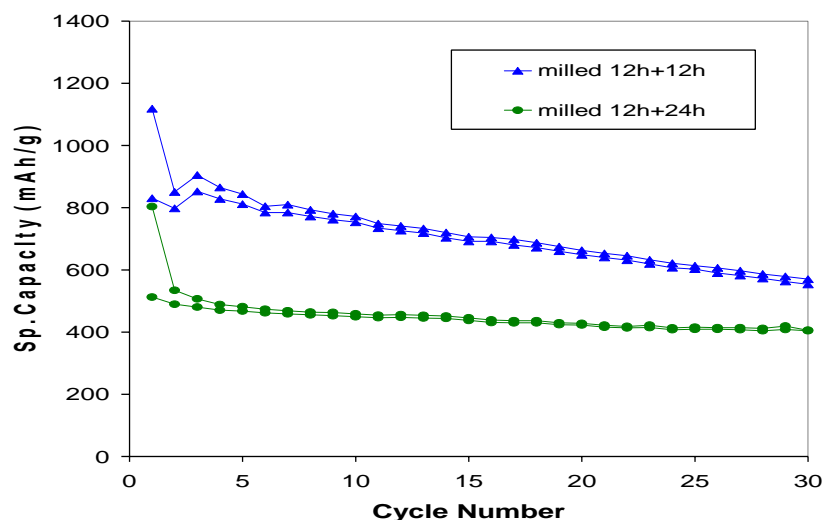


Fig. 4. Capacity as a function of cycle number for Si/C nanocomposites containing 33 mol.% Si obtained after milling for 12 + 12 h and 12 + 24 h followed by subsequent heat-treatment in UHP-Ar/H₂ (5%) for 5 h at 800 °C (current rate: 100 μ A/cm², potential: 0.02–1.2 V).

tended milling for 24 h, the stability in capacity has been improved significantly ($\sim 0.67\%$ loss/cycle). Efforts to optimize the electrochemical response of Si/C systems are still in progress and the results obtained will be reported subsequently. Nevertheless, the results from this study suggest that the nanocomposites of Si/C derived using HEMM of Si and PS-resin as the carbon source have the potential for generating nanostructured composites containing uniformly dispersed nanocrystallites of Si. The initial promising results obtained on these nanocomposites show their ability to be used as replacements anodes to carbon based on the encouraging high capacity (~ 540 – 850 mAh/g), good stability (0.67–1.1% loss/cycle) and low irreversible loss (23–36%) observed. Further studies could demonstrate the true long-range stability and retention of capacity of these nanocomposites.

4. Conclusion

Si/C nanocomposites are generated from Si and PS-resin using HEMM and subsequent heat-treatment. The composite containing 33 mol.% Si (Si:C = 1:2) obtained after milling for 12 + 12 h followed by heat-treatment at 800 °C for 5 h in UHP-Ar/H₂ (5%) exhibits high capacity (~ 850 mAh/g) with good stability ($\sim 1.1\%$ loss/cycle) up to 30 cycles. Based on the XRD and TEM analyses, the nanocomposites comprise nanosized Si particles (< 50 nm) in an amorphous carbon matrix. The EDX result indicates the slight contamination (0.8 at.%) of Fe, which results in the formation of the iron silicide phase as shown in the XRD pattern after heat-treatment. The nanocomposite exhibits better stability ($\sim 0.67\%$ loss/cycle) in capacity after increasing the milling time of for an additional 24 h thus corresponding to a total milling time of 36 h (12 + 24 h).

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