

Short communication

# Optimizing synthesis of silicon/disordered carbon composites for use as anode materials in lithium-ion batteries

Z.P. Guo<sup>a,\*</sup>, D.Z. Jia<sup>b</sup>, L. Yuan<sup>a</sup>, H.K. Liu<sup>a</sup>

<sup>a</sup> Institute for Superconducting & Electronic Materials, University of Wollongong, NSW 2522, Australia

<sup>b</sup> Institute of Applied Chemistry, Xinjiang University, Urumqi, Xinjiang 830046, China

Available online 26 May 2006

## Abstract

Pyrolysis conditions for the production of silicon/disordered carbon (Si–DC) nanocomposites using PVA as the carbon source were optimized in this work. It was found that the optimum sintering temperature for the Si–DC nanocomposites is 800 °C. In order to achieve good cell performance, a high argon gas flow rate and a slow heating rate are preferred in sample preparation. The morphology of the carbon source (PVA) affects the electrochemical performance of the Si–DC nanocomposites as well. The key point to obtain Si–DC nanocomposites with good electrochemical performance is to reduce the chances of pyrolysis gases (especially CO<sub>2</sub>) to react with carbon, thereby preventing carbon burnoff during the sintering process.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Silicon/disordered carbon nanocomposites; Optimizing synthesis; Lithium-ion batteries

## 1. Introduction

Recent work by many research groups has demonstrated that silicon/carbon composite anodes can combine the advantageous properties of carbon (long cycle life) and silicon (high Li storage capacity) to improve the overall electrochemical performance of the anode for lithium-ion batteries [1–3]. Li et al. [4] prepared nano-Si–carbon composites by hand mixing nano-Si and carbon black, which delivered a high reversible capacity of 1700 mAh g<sup>-1</sup>. Wilson et al. [5] have synthesized nanodispersed silicon in carbon using chemical vapor deposition (CVD) and achieved a reversible capacity of 500 mAh g<sup>-1</sup>. Yoshio and co-workers [6,7] reported that carbon-coated silicon synthesized by the thermal vapor deposition (TVD) method shows better cyclic characteristics when compared with conventional silicon anodes. Niu and Lee [8] dispersed crystalline silicon in a sol–gel graphite matrix by ball milling and demonstrated a reversible capacity of 832.2 mAh g<sup>-1</sup> in the first cycle. More recently, carbon gel microspheres containing silicon [9] have been prepared by adding silicon powder to the water phase during the inverse emulsion polymerization of resorcinol with formaldehyde, followed by freeze–drying and carbonization in

an inert atmosphere. It is assumed that the carbon component in the composition acts as a buffering matrix, which relieves the morphological changes of silicon occurring during charging/discharging, thereby reducing the mechanical stress within the electrode and preventing disintegration.

In our previous work [10], we demonstrated that carbon distribution on the Si particles in Si–disordered carbon (DC) nanocomposite using PVA as the carbon source, is more uniform than when using sugar as the carbon source under the same preparation conditions. The carbon content and the starting polymers significantly affect the electrochemical performance of the Si–DC nanocomposites. In this work, we describe pyrolysis conditions for the production of Si–DC nanocomposites using PVA as the carbon source, and their resulting electrochemical properties. Our experiments were designed to search for the optimum pyrolysis conditions for the preparation of Si–DC nanocomposites.

## 2. Experimental

### 2.1. Preparation of Si–DC nanocomposites

It was found in our previous studies that the Si–DC nanocomposites made from 10% Si–90% PVA under constant pyrolyzing conditions, showed the best electrochemical performance.

\* Corresponding author. Fax: +61 2 4221 5731.  
E-mail address: [zguo@uow.edu.au](mailto:zguo@uow.edu.au) (Z.P. Guo).

Therefore, in this study, we focus on the Si–DC nanocomposite using 10% Si/90% PVA as precursor. Si powder (average particle size: 80 nm) and PVA (Aldrich) with weight ratios of Si:PVA = 1:9 were mechanically milled for 10 h to obtain Si–polymer composites with Si particles coated with polymer. The Si–PVA precursors (5 g) were put in an alumina ( $\text{Al}_2\text{O}_3$ ) boat, and then inserted into a quartz tube, which was placed inside a horizontal tube furnace. Experiments were first designed to search for an optimum sintering temperature,  $T_{\text{st}}$ , which would result in the best cycling performance for lithium intercalation/deintercalation. The precursors were heated under an argon atmosphere at a heating rate of  $5^\circ\text{C min}^{-1}$  from room temperature to  $T_{\text{st}}$ , kept at  $T_{\text{st}}$  for 2 h, and then cooled to room temperature. The sintering temperature,  $T_{\text{st}}$ , was changed from 600 to 1000  $^\circ\text{C}$  for different runs. After an optimal  $T_{\text{st}}$  was determined, the effect of heating rate and argon flow rate on the Si–DC nanocomposites were investigated. Samples were heated from room temperature to 800  $^\circ\text{C}$ , kept at 800  $^\circ\text{C}$  for 2 h, then cooled down to room temperature at a rate of  $20^\circ\text{C min}^{-1}$ . Here the sintering temperature, 800  $^\circ\text{C}$ , was chosen based on the results of the previous experiments. For the heating rate experiments, samples were heated from room temperature to  $T_{\text{st}}$  with different heating rates; 1, 5, 10 and  $20^\circ\text{C min}^{-1}$ , while the argon flow rate was kept constant, at  $50\text{ ml min}^{-1}$ . For the argon flow rate experiments, different argon flow rates (20, 50, 100,  $200\text{ ml min}^{-1}$ ) were used for different runs, while a constant heating rate of  $5^\circ\text{C min}^{-1}$  was applied.

The as-prepared Si–DC nanocomposites were characterized by scanning electron microscopy (JEOL, JSM-6460A). The precise DC concentration in Si–DC nanocomposites was determined using Thermogravimetric Analysis (TGA/DTA) via a Setaram TGA/DTA apparatus.

## 2.2. Electrochemical testing

Teflon-type and coin cells were assembled for electrochemical characterization of Si–DC nanocomposite electrodes. In order to exclude other influences, such as poor conductivity and active materials peeling off the substrate, high contents of carbon and binder have been used in our experiments. The testing electrodes were made by dispersing 70 wt.% active materials, 20 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry. The slurry was then spread onto a copper foil and dried in a vacuum oven. The electrodes were  $\varnothing$  12 mm disks. The cells were assembled in an argon filled glove-box (MBraun, Unilab, USA). The electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by Merck KgaA, Germany). The cells were galvanostatically charged and discharged at  $50\text{ mA g}^{-1}$  over the voltage range 0.02–1.2 V versus  $\text{Li/Li}^+$ . AC impedance measurements were carried out utilizing an EG&G Model 6310 Electrochemical Impedance Analyzer. Electrochemical Impedance software (EG&G Model 398) was used to control a computer for conductivity and stability measurements. The technique used in the experiment was Single Sine EIS  $Z(f)$ . Other experiment parameters are as follows—condition time: pass (0 s); condi-

tion potential: pass (0 V); initial delay: 20 s; equilibration time: pass (0 s); DC potential: 0 V versus open circuit; AC amplitude: 5 mV; initial frequency: 100 kHz; final frequency: 0.01 Hz; and points/decade: 6 points.

## 3. Results and discussion

$\text{Li}_{4.4}\text{Si}$  has a theoretical capacity of  $4200\text{ mAh g}^{-1}$ . However, 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. It was found that the carbon component in the Si–C composition could act as a buffering matrix, which relieves the morphological changes of silicon occurring during charging/discharging, preventing disintegration of Si electrodes to some extent, thereby improving the cyclability of Si anodes [10].

A typical scanning electron micrograph (SEM image is not shown here) of the Si–DC nanocomposites obtained in this work shows that calcined powders are loosely bound agglomerates of semi-spherical particles. The particle size distribution is apparently narrow, and the average is about 150 nm. Lithium-ion reversible and irreversible capacities of Si–DC nanocomposites were estimated from charging/discharging tests. A large irreversible capacity and a large hysteresis between charging and discharging curves can be observed from the typical charging/discharging curves of the Si–DC nanocomposites, which is typical for silicon-based electrodes. It is found that the electrochemical performance of the Si–DC nanocomposites is significantly influenced by the pyrolysis conditions of the sample production. The sintering temperature, the heating rate, the argon flow rate and the morphology of the PVA all affect the final products. The details are discussed below.

### 3.1. Effects of sintering temperature

Fig. 1 shows the cyclic performance of the reversible capacities of the Si–DC nanocomposites prepared at different sintering

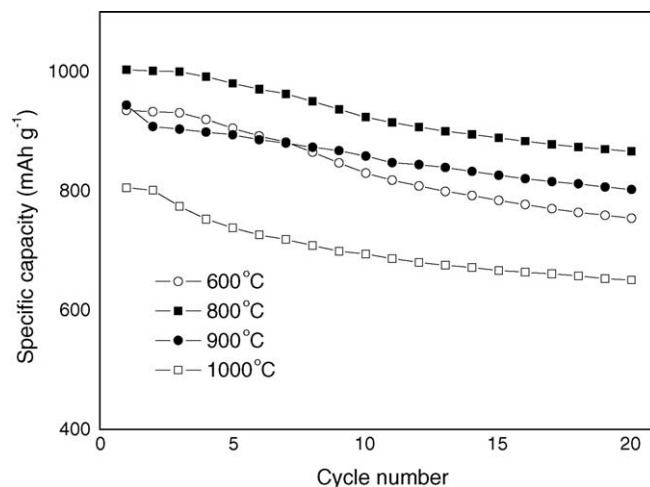


Fig. 1. Cycling performance of the reversible capacities of the Si–DC nanocomposites prepared at different sintering temperatures.

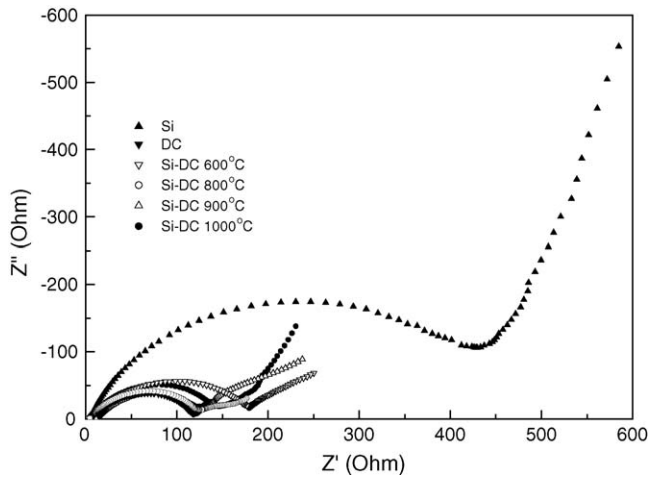


Fig. 2. Electrochemical impedance spectra of Si, disordered carbon, and the Si-DC nanocomposites obtained at different sintering temperatures.

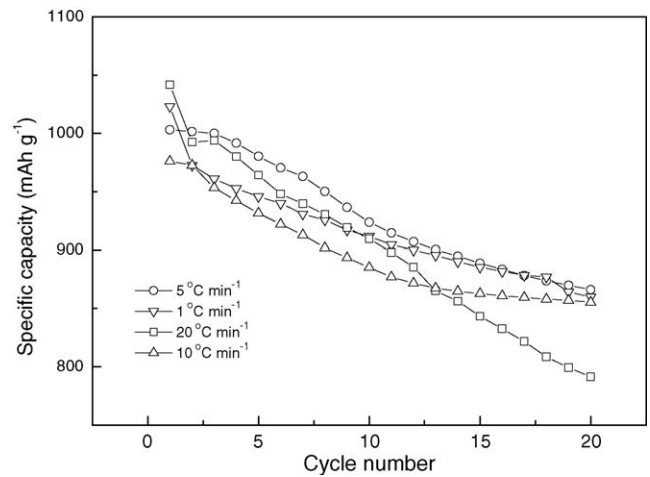


Fig. 3. Cell performances of the Si-DC nanocomposites heated at different heating rates.

temperatures. It can be seen that the reversible capacity initially increases as the sintering temperature ( $T_{st}$ ) increases from 600 to 800 °C. However, with  $T_{st}$  further increasing from 800 to 1000 °C, the specific capacities decrease, especially for the sample sintered at 1000 °C, for which the capacity fades much more quickly with cycling when compared to the other samples. To explore the reasons for this phenomenon, ac impedance experiments were performed on all as-assembled electrodes. A comparison of the EIS Nyquist complex plane plots (Fig. 2) shows that the pure Si electrode exhibits a much larger semicircle when compared to other electrodes, while the interfacial impedances of the Si-DC nanocomposites obtained at 800 and 900 °C are similar to that of the DC anode. These may indicate that the Si particles in the Si-DC nanocomposites have been effectively coated by a carbon layer. However, for the samples sintered at 600 and 1000 °C, the interfacial impedances are slightly larger than that of the DC anode. This may suggest that the Si particles in these samples are not uniformly coated by the disordered carbon. Therefore, the volume expansion of Si particles during charge/discharge cycling could not be effectively buffered by the carbon matrix, so that the cycling stability of the samples becomes worse compared with the samples obtained at 800 and 900 °C.

### 3.2. Effects of heating rate

Fig. 3 shows the cell performance for the Si-DC nanocomposites heated at different heating rates. The samples were heated from room temperature to 800 °C with different heating rates, 1, 5, 10 and 20 °C min<sup>-1</sup>, while the argon flow rate was kept constant at a constant rate of 50 ml min<sup>-1</sup>. The capacities of samples seem not to be sensitive to the heating rate in the range from 1 to 20 °C min<sup>-1</sup>. However, it is found by carefully comparing the curves, that the cycling performance of anodes obtained at a low heating rate is better than that of anodes made with a high heating rate. Especially when the heating rate is increased to 20 °C min<sup>-1</sup>, the cycling performance of the Si-DC nanocomposite becomes significantly worse, indicating that slow heat-

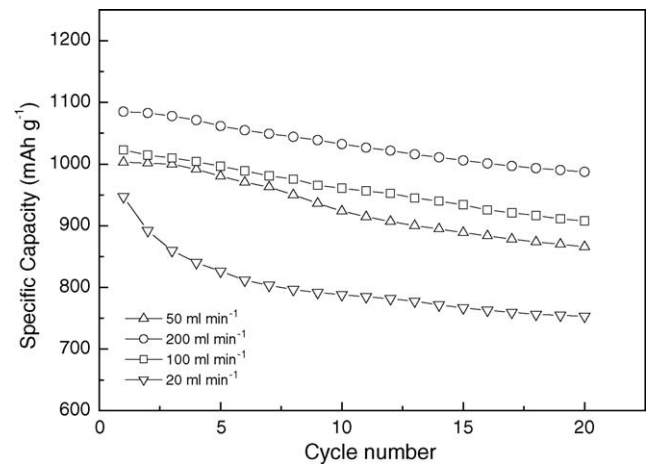


Fig. 4. Cycling performance of the Si-DC nanocomposites obtained by using different argon gas flow rates.

ing could help somewhat to improve the cycle stability of samples.

### 3.3. Effects of argon flow rate

Fig. 4 shows the cycling behaviour of Si-DC electrodes produced with different argon flow rates. A constant heating rate of 5 °C min<sup>-1</sup> was used. It is found that the cell performance of samples is very sensitive to the argon flow rate. With the argon flow rate increasing, the capacity and the cycle life both improved. The carbon contents in the Si-DC nanocomposites produced by using different argon flow rates are listed in Table 1.

Table 1  
Carbon concentration in Si/DC nanocomposites synthesized under different argon flow rates

	Argon flow rate (ml min <sup>-1</sup> )			
	20	50	100	200
Carbon (wt.%)	19.5	24.4	28.7	29.6

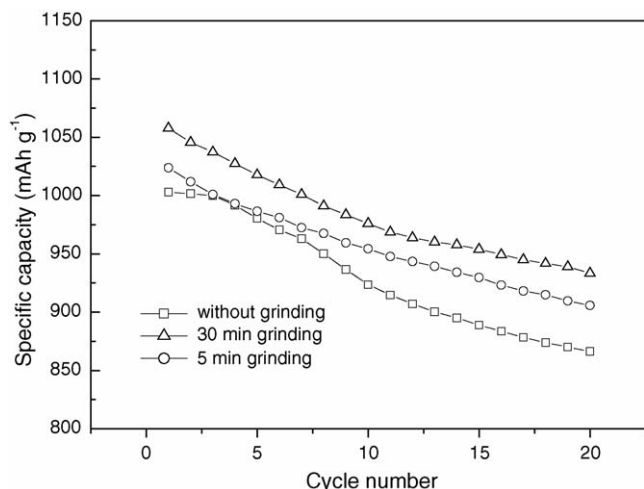


Fig. 5. Cycling performance of the Si–DC nanocomposites prepared by using different PVA as precursors.

The carbon contents were determined by TGA analysis, which was described in detail previously [10]. It is obvious that the carbon concentrations in the samples increase rapidly as the flow rate increases from 20 to 200 ml min<sup>-1</sup>. Different carbon contents in samples is probably the main reason for the difference in cell performance. Dahn and co-workers [11,12] have investigated the polymer pyrolyzing process by using thermal gravimetric analysis (TGA) and residual gas analysis (RGA). They found that carbon can react with carbon dioxide to form carbon monoxides during heating. They refer to this reaction as carbon burnoff. Combining the results on the carbon contents and the argon flow rates, we believe that the different carbon contents in samples are caused by carbon burnoff. Under a high argon gas flow, the inert argon could flush away the pyrolysis gases, thus substantially reducing the chances of reactions between released gas and carbon, i.e. preventing the carbon burnoff. However, when a low argon gas flow rate is applied, the gases released upon heating (CO<sub>2</sub>) cannot be removed immediately from the reaction furnace. It is very likely that pyrolysis gases have more chances to react with carbon. Therefore, the argon flow rate applied drastically influences the carbon content in the final products.

### 3.4. Effects of morphology of PVA

The effect of morphology of carbon sources (PVA) on the electrochemical performance of Si–DC nanocomposites was also investigated in our work. The PVA powders were ground in an agate mortar for 5 and 30 min, respectively, before mixing them with nano-sized Si powder. The same heating scheme was used for all samples shown in Fig. 5. From Fig. 5, we can see that the charge/discharge performance of samples improves as the grinding time increases. TGA analysis results show that the

carbon contents in the 30 min grinding, 5 min grinding and without grinding samples are 26.8, 24.9 and 24.4 wt.%, respectively. The results imply that the carbon burnoff in ground samples was reduced. Possible reasons for this are: when the PVA was ground into smaller particles, it became easier for the gases to be released upon heating. The easy escape of the pyrolysis gases reduces the chance for them to react with the carbon and thereby keeps more carbon in the final products, which provides a better buffering matrix for the Si particles and improves the cycling performance of the Si–DC anodes.

## 4. Conclusions

In this work, silicon–disordered carbon nanocomposites were pyrolyzed under various conditions. Experiments were carried out to optimize the pyrolyzing conditions. The electrochemical behavior of the Si–DC nanocomposites was found to be affected by the sintering temperature, heating rate, argon flow rate and morphology of the carbon source (PVA). To achieve Si–DC nanocomposites with good electrochemical performance, it is essential to have a suitable sintering temperature (800 °C), a high argon flow rate, a slow heating rate and loose powders with small particle sizes. The Si–DC nanocomposites synthesized under optimal conditions showed a large reversible capacity (above 1000 mAh g<sup>-1</sup>) with good cyclability. Si–DC nanocomposites are therefore promising candidates as anode materials in lithium-ion batteries.

## Acknowledgements

Financial support provided by the Australian Research Council (ARC), Sons of Gwalia Ltd., the OM Group and Lexel Battery Ltd. is gratefully acknowledged.

## References

- [1] M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, J. Electrochem. Soc. 149 (2002) 1598.
- [2] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, Solid State Ionics 168 (2004) 61.
- [3] X. Zhang, P.K. Patil, C. Wang, A.J. Appleby, F.E. Little, D.L. Cocke, J. Power Sources 125 (2004) 206.
- [4] H. Li, X.J. Huang, L.Q. Chen, Z.G. Wu, Y. Liang, Electrochem. Solid-State Lett. 2 (1999) 547.
- [5] A.M. Wilson, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 326.
- [6] N. Dimov, K. Fukuda, T. Umeno, S. Kugino, M. Yoshio, J. Power Sources 114 (2003) 88.
- [7] T. Umeno, K. Fukuda, H. Wang, N. Dimov, T. Iwao, M. Yoshio, Chem. Lett. CL-010828 (2001).
- [8] J. Niu, J.Y. Lee, Electrochem. Solid-State Lett. 5 (2002) A107.
- [9] T. Hasegawa, S.R. Mukai, Y. Shirato, H. Tamon, Carbon 42 (2004) 2573.
- [10] Z.P. Guo, E. Milin, J.Z. Wang, J. Chen, H.K. Liu, J. Electrochem. Soc. 152 (2005) A2211.
- [11] J.S. Xue, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 3668.
- [12] W. Xing, J.S. Xue, J.R. Dahn, J. Electrochem. Soc. 143 (1996) 3046.