

Electrochemical studies of the Si-based composites with large capacity and good cycling stability as anode materials for rechargeable lithium ion batteries

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Abstract

The Si–C and Si–M–C (C, the disordered carbon) composites prepared from pyrolysis reaction and high-energy mechanical milling process have a significant enhancement in the electrochemical cycling stability over pure silicon. The introduction of the hard co-milling components (M, such as TiB₂ and TiN) in the Si–C composite before pyrolysis reaction brings an improvement in the charging rate and cycling performance, but it leads to a slight loss in the reversible capacity. The full cell with the composite anodes and the LiCo_{0.2}Ni_{0.8}O₂ cathode was fabricated to show large anode capacity over 600 mAh g⁻¹ within a potential range of 2.3–3.9 V that might result in a high energy density. The Si-based composites appear to be the promising anode candidates for Li-ion batteries.

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1. Introduction

Recently, various anode materials with the improved capacity density and thermal stability over commercial graphite have been highly proposed for lithium ion batteries [1]. Silicon shows promising prospects for the largest capacity among all known host materials. However, silicon undergoes a rapid capacity fading upon cycling due to the morphology deterioration in the electrochemical alloying process [2–5]. An effective approach to overcome this detriment is to create a composite microstructure comprising active silicon uniformly dispersed in an inert matrix. The previous examples of the Sn–Fe–C nano-composites proposed by Dahn and co-workers suggest that high-energy mechanical milling (HEMM) could be an appropriate process to build such a composite microstructure [6]. For instance, under ballmilling with the hard TiB₂ or TiN, silicon can be significantly decreased to nano scale and homogeneously doped within the electron-matrix [7,8]. This, in turn, leads to an enhancement in the

cycling stability. The milled Si–TiB₂ and Si–TN composites had a stable capacity of ca. 400 mAh g⁻¹ for about 15 cycles, but they suffered from a low capacity utilization of Si and low first cycle efficiency. Dispersing silicon within a carbonaceous matrix by means of thermal pyrolysis reaction also showed an effective way to suppress the volume effects of silicon. Dahn and co-workers reported that the composites prepared by pyrolysis of organic compounds, containing silicon, had attractive electrochemical behavior but low initial faradaic yield [9,10]. Recently, it was found that pyrolysis of pitch or poly(vinyl chloride) (PVC) embedded with silicon showed large capacity and comparable cyclability [11–13]. The enhanced cyclability is attributed to the small volume expansion of carbon on lithium intercalation (ca. 9% for graphite) and the ability of the ductile carbonaceous matrix to accommodate the volume change of silicon, reducing mechanical strain within the electrode and consequent electrode disintegration. Although this type of pyrolyzed carbon has a large potential hysteresis between Li-insertion and -extraction, it may, mostly, function as an elastic network with electron/ion conductivity that permits the silicon in the carbon matrix to operate while maintaining electrode integrity.

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However, a single pyrolysis step was insufficient for ensuring homogeneous Si-distribution and good interface affinity between the silicon and the matrix. In addition, high porosity arising from the pyrolysis carbon may cause a low initial coulombic efficiency and an aggravated mechanical stress with the penetration of electrolytes [13]. Because inert TiB_2 and TiN were reported to show high electron conductivity and tend to form nano-composite with good Si distribution by means of HEMM [7,8], we tried to introduce the hard commilling components in the Si-C composite before pyrolysis reaction. The combination of pyrolysis reaction and HEMM treatment in the preparation for the composites can track the shortages from the pyrolysis reaction and the HEMM step alone, resulting in large capacity and good capacity retention [13–15]. Some key factors determining the electrochemical behavior of the Si-composites are presented and discussed in detail.

2. Experimental

The preparation of the Si-C composite was as follows: poly(vinyl chloride) (Aldrich) and silicon particles ($<1\ \mu\text{m}$, $>99.8\%$) were homogeneously mixed and the weight ratio of silicon versus PVC was 3:7. The mixture was heated at $900\ ^\circ\text{C}$ in an Ar atmosphere for 1 h at a heating rate of $5\ ^\circ\text{C}\ \text{min}^{-1}$ and allowed cool down to room temperature normally. The products were further treated by high-energy mechanical milling (HEMM) in a sealed bowl in Ar at a rotational speed of 500 rpm for 2–10 h. The resulting samples were mixed with PVC again (Milled product versus PVC was 3:7 wt.%). The mixture was processed by a pyrolysis reaction following the same procedures as the first heating process. For preparing the Si-M-C ($M = \text{TiB}_2$, TiN) composites, mixture of silicon particles ($<1\ \mu\text{m}$, $>99.8\%$) and TiB_2 (ca. $2\ \mu\text{m}$), or TiN (ca. $1.5\ \mu\text{m}$) with a weight ratio of 1:1 was treated by HEMM in a sealed bowl in Ar at a rotational speed of 500 rpm for 2–10 h. The milled product was followed a pyrolysis reaction similar to that for the Si-C composite. The final SiC and Si-M-C samples were ground and sieved.

The electrode containing 8 wt.% acetylene black (AB), 80 wt.% active materials and 12 wt.% poly(vinylidene fluoride) was prepared by a normal casting. The active powders and AB were homogeneously mixed in a $0.02\ \text{g}\ \text{mL}^{-1}$ PVDF/1-methyl-2-pyrrolidone (NMP) solution, and the viscous mixture was cast onto a $300\text{-}\mu\text{m}$ thick Ni foam, which served as a current collector. The electrode was further dried at $120\ ^\circ\text{C}$ under vacuum for 2 h until NMP solvent was entirely removed. After pressing, the geometric area of the electrodes was $1.0\ \text{cm}^2$, and the typical thickness was $190\text{--}200\ \mu\text{m}$. To evaluate the electrochemical properties of the electrodes, a half-cell containing LiClO_4 /ethylene carbonate plus diethyl carbonate as 1:1 in volume electrolyte was used, and lithium metal was utilized as the counter electrode. All the three layers, including test electrode, separator and lithium metal, were stacked in a 2025 coin type cell in a

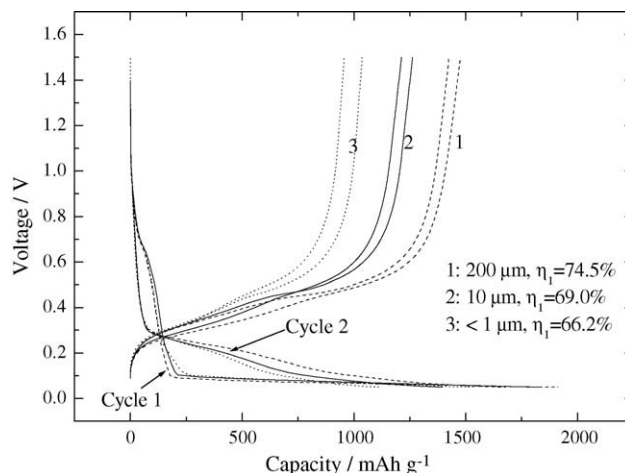


Fig. 1. Charge and discharge profiles of the silicon with different particle size at the first and second cycle.

glove box. Unless stated elsewhere, cycling was carried out at a constant current density of $0.18\ \text{mA}\ \text{mg}^{-1}$ and a voltage cutoff at 1.5/0.05 V versus Li/Li^+ . Charge and discharge of the cell refer, respectively, to lithium extraction from, and insertion into, the active hosts. The electrode capacity was calculated according to the weight of active materials.

3. Results and discussion

The electrochemical characterization of the silicon with different particle size was investigated and compared in Fig. 1. All the silicon electrodes are reactive to lithium that results in large capacities. A decrease in the particle size enhanced the solid electrolyte interface (SEI) film formation on the surface of the active hosts; thereby it increased the capacity loss in the first cycle. There was an obvious shift in the discharge potential plateau from the first cycle to the second cycle, which could relate to the irreversible phase transformation of silicon from crystalline to amorphous state in the first electrochemical alloying process [2,16]. After the initial Li-intercalation, the electrodes possessed a reactive potential plateau at average 0.1–0.4 V versus Li/Li^+ . However, all silicon electrodes suffered from poor capacity retention during cycling, indicating that decrease in the active hosts is insufficient for holding good morphology stability.

As reported previously, the morphology deterioration of silicon upon charge and discharge can be effectively conquered by comprising ultrafine silicon particles uniformly dispersed in a ductile carbonaceous matrix [13–15]. One of the advantages of this type composite is due to the high capacity utilization of Si. The Si-C and Si-M-C ($M = \text{TiB}_2$, TiN) composites made from combination of thermal pyrolyzed PVC reaction and HEMM process demonstrated high similarity in the capacity-potential curves upon Li insertion and extraction. Fig. 2 showed charge and discharge curves of the

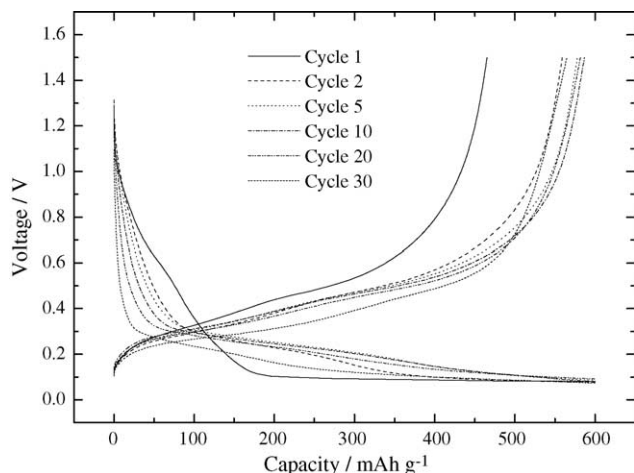


Fig. 2. Charge and discharge profiles of the Si-M-C composites at a controlled insertion level at 600 mAh g⁻¹ at different cycles, extraction potential is 1.5 V vs. Li/Li⁺.

typical Si-M-C composite electrodes under a controlled Li-insertion level at 600 mAh g⁻¹ at different cycles. In comparison with that of Fig. 1, the electrochemical behavior of the composite was obviously dominated by silicon insertion host, suggesting only small amount lithium storages in the pyrolyzed PVC. However, a sloping potential plateau appeared from 1.1 until 0.1 V in the first discharge, which was mostly attributed to Li intercalation into the disordered carbonaceous matrix and formation of the SEI film (ca. 0.8 V) on the surface of the active particles. The faradaic yield of extraction to insertion was 76%, which was close to that of the pure silicon with a particle size of 200 μm. The voltage profiles showed high coincidence from cycle to cycle indicating a good Li insertion and extraction reversibility.

The Si-C and Si-M-C composites had a remarkably enhanced morphology stability over silicon, as shown in Fig. 3. The capacity retention at the 35th cycle of the Si-C composite was ca. 80%, versus ca. 900 mAh g⁻¹ at the second cycle.

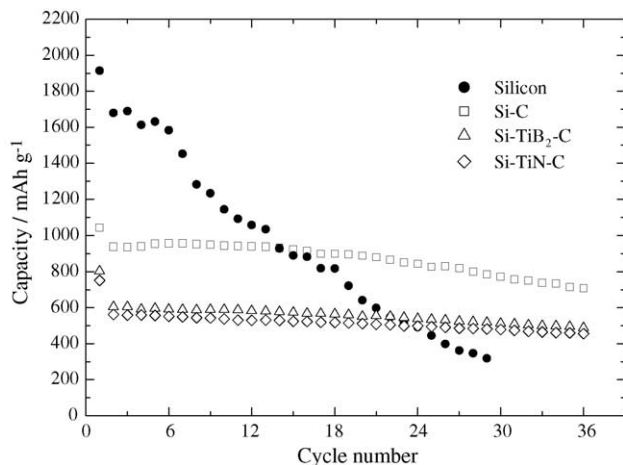


Fig. 3. Cycling performance of the Si, Si-C, Si-TiB₂-C and Si-TiN-C composites.

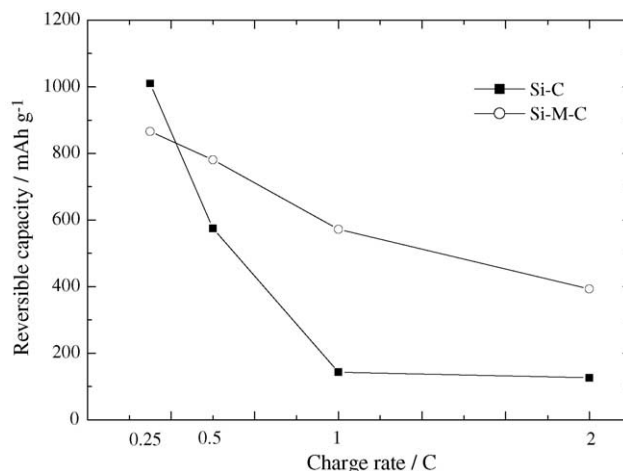


Fig. 4. Charging rate as a function upon the reversible capacity of the Si-C and Si-M-C composites.

For the Si-M-C composites, the capacity of ca. 600 mAh g⁻¹ in the second cycle was remained to over 90% at the 35th cycle. In the previous work, we have shown several possibilities for such a significant improvement in the cycling performance [13]. First, HEMM increases the Si distribution that can prevent silicon particles from the possible aggregation. Secondly, high adhesion strength between the silicon and the matrix treated under HEMM can hold a good electron-contacting. Finally, pyrolyzed PVC can function as an elastic network with electron/ion conductivity that permits the silicon in the carbon matrix to operate while maintaining electrode integrity. Compared with the Si-C composite, the decrease in the reversible capacities for the Si-M-C composites was remarkable. The difference in the silicon content, e.g., ca. 47 wt.% for the Si-C and ca. 35 wt.% for the Si-M-C composites, may take this consequence. Furthermore, it is probably attributed to a negative effect in the capacity utilization from the silicon caused by the co-ballmilling hard components [7,8,15]. It indicates that the silicon have a propensity in the capacity loss under co-milling with the hard components.

The introducing of the hard co-milling components, such as TiN, TiB₂, in the preparation for the Si-M-C composite brought an improvement in the charging rate over that of the Si-C composite, as shown in Fig. 4. The Si-C composite had a rapid loss in the reversible capacity with increasing the charging rate. This is probably due to poor electron-conductivity of silicon in the nature characteristic. When the charging rate was increased to 2C, the capacity of the Si-M-C composites under 1/4C still remained to be over ca. 50%. A remarkable decrease in the particle size of silicon may take this consequence. Observation from SEM and XRD indicates that the relatively hard co-balling components tend to significantly reduce the particle size of silicon during the HEMM treatment.

A comparison with mesocarbon microbead (MCMB, a kind of commercial graphitic carbon) in the charge and

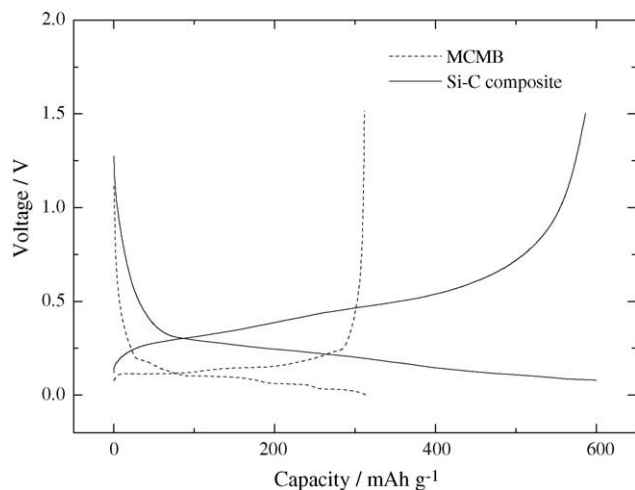


Fig. 5. Comparison of the charge and discharge curves between the MCMB and the Si-C composite electrodes. Voltage cutoff: MCMB, 1.5–0.01 V vs. Li/Li⁺; Si-C, insertion level at 600 mAh g⁻¹, extraction potential is 1.5 V vs. Li/Li⁺.

discharge profiles at the second cycle revealed that the Si-M-C (or Si-C) composite had a slight increase in the Li insertion and extraction potential plateau for about 0.12 V, as shown in Fig. 5. This, in turn, can prevent lithium dendrite formation at a high charging rate and therefore leads to an enhanced operation safety. However, the Si-based composite suffers from a loss in the volume capacity due to a low density (1.7 g cm⁻³, in case of Si-C) compared with that of MCMB (ca. 2.25 g cm⁻³). From this point of view, we suppose that the carbonaceous matrix with low porosity is in favor for the volume capacity.

A full cell using the Si-C composite anode and the LiNi_{0.8}Co_{0.2}O₂ cathode was fabricated to study its electrochemical characteristics, as shown in Fig. 6. For full utilization of lithium storage capacity of the Si-C composite anode, the weight of cathode has to be much over that of the

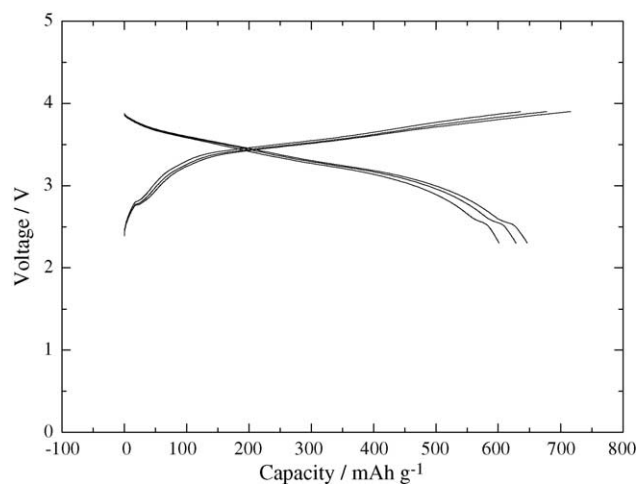


Fig. 6. Charge and discharge curves of the Si-C/LiCo_{0.2}Ni_{0.8}O₂ cell at the cycle 2, 3 and 5; potential cutoff: 2.3–3.9 V.

anode (7–8 times). The cell had a large anode capacity of ca. 600 mAh g⁻¹ within the working potential of 2.3–3.9 V that might result in a high energy density. After the first cycle, a high overlapping in the potential trends indicated good operation reversibility. We expect that further optimization of the composite anodes might lead to a practical lithium-ion battery with a more safety performance and high energy density over the current graphite-based batteries.

4. Conclusions

We reported studies of the electrochemical characterization of series Si-based composite materials with significantly improved cycling stability over silicon. The Si-C composite made from two PVC pyrolysis reactions, combined with an intervening high-energy mechanical milling (HEMM) step, presents a large capacity of 900 mAh g⁻¹ and good capacity retention. The Si-M-C composites prepared by ballmilling hard component (M, such as TiB₂ and TiN) with silicon, and a subsequent embedding with pyrolyzed PVC, also demonstrates both large capacity and good capacity retention. The introduced co-milling components (M) in the Si-C composite bring an increase in the charging rate and cycling performance, but it leads to a slight loss in the reversible capacity. A positive shift in the reactive potential for the Si-based composite causes an enhanced operation safety over the commercial graphite. However, low density for this material remains to be conquered. Furthermore, the full cell with the Si-based composites and the LiCo_{0.2}Ni_{0.8}O₂ cathode was found to show large anode capacities and high working potentials that might result in high energy density. The Si-composites shows promising properties as anode alternative for commercial graphite for Li-ion batteries.

Acknowledgements

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References

- [1] J.-M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] W.B. Xing, A.M. Wilson, K. Eguchi, G. Zank, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2410.
- [3] H. Kim, J. Choi, H.J. Sohn, T. Kang, *J. Electrochem. Soc.* 146 (1999) 4401.
- [4] H. Li, X.J. Huang, L.Q. Chen, G.W. Zhou, Z. Zhang, D.P. Yu, Y.J. Mo, N. Pei, *Solid State Ionics* 135 (2000) 181.
- [5] A. Netz, R.A. Huggins, W. Weppner, *J. Power Sources* 5271 (2003) 1.
- [6] O. Mao, R.L. Turner, I.A. Courtney, B.D. Fredericksen, M.I. Buckett, L.J. Krause, J.R. Dahn, *Electrochem. Solid-State Lett.* 2 (1999) 3.
- [7] I.-S. Kim, P.N. Kumta, G.E. Blomgren, *Electrochem. Solid-State Lett.* 3 (2000) 493.

- [8] I.-S. Kim, G.E. Blomgren, P.N. Kumta, *Electrochem. Solid-State Lett.* 6 (2003) 157.
- [9] A.M. Wilson, J.R. Dahn, *J. Electrochem. Soc.* 142 (1995) 326.
- [10] D. Larcher, C. Mudalige, A.E. George, V. Porter, M. Gharghouri, J.R. Dahn, *Solid State Ionics* 122 (1999) 71.
- [11] J. Yang, B.F. Wang, K. Wang, Y. Liu, J.Y. Xie, Z.S. Wen, *Electrochem. Solid-State Lett.* 6 (2003) A154.
- [12] Z.S. Wen, J. Yang, B.F. Wang, K. Wang, Y. Liu, *Electrochem. Commun.* 5 (2003) 165.
- [13] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, *Solid State Ionics* 168 (2004) 61.
- [14] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, *Electrochem. Solid-State Lett.* 7 (2004) A369.
- [15] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, *Electrochem. Solid-State Lett.* 7 (2004) A492.
- [16] L.Y. Beaulieu, T.D. Hachard, A. Bonakdarpour, M.D. Fleischauer, J.R. Dahn, *J. Electrochem. Soc.* 150 (2003) A1457.