Fabrication of Si/SiO_x Anode Materials by a Solution Reaction-Based Method for Lithium Ion Batteries

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Abstract: Si/SiO_x composite anodes were prepared using a facile solution reaction-based method. Their initial capacity was significantly improved to 1.3 times that of SiO_x by incorporating 3 wt% silicon nanoparticles into the SiO_x. The capacity retention of the Si/SiO_x anodes after 50 charge-discharge cycles was significantly enhanced, to 99%, compared with 8% retention for the pristine silicon anode. These improved results were achieved by combining the advantages of silicon, for high capacity, with SiO_x, for cyclic stability. Our current results suggest that this simple solution reaction-based approach is a promising method for fabricating low cost Si/SiO_x composite anode materials for lithium ion batteries, which exhibit high electrochemical performance, of more than 1000 mAh/g capacity, and cyclic stability.

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1. INTRODUCTION

Not only has the market size for lithium ion batteries (LIBs) become larger, but their application area has also been expanding, from conventional consumer electronics such as mobile phones and notebooks to products that require high capacity, such as electric vehicles and energy storage systems (ESS), etc [1,2]. To meet the new demands for lithium ion batteries with high energy density, stability, and long life times, extensive studies have been conducted [3,4]. Carbon-based materials have been popularly employed as anodes for lithium ion batteries, due to their excellent stability and cyclic performance resulting from structural characteristics favorable for the intercalation-deintercalation of lithium ions [5]. However, their low theoretical specific capacity of 372 mAh/g (LiC₆) remains an issue that needs to be resolved. As a way of improving the capacity, stability, and the lifetime of the anode materials, an approach of alloying with lithium has been widely applied [6-12]. Among the extensively studied Li-Si alloys (Li_{4.4}Si: 4212 mAh/g), Li-Sn (Li₁₇Sn₄: 959.5 mAh/g), Li-Sb (Li₃Sb: 660 mAh/g),

[12-16] Si-based anode materials have been found to be promising due to their large theoretical capacity and a low reaction potential of about 0.4 V Li⁺/Li⁰ [17,18]. However, the materials' initial high capacity has also been shown to drastically decrease due to microstructural distortions or disintegrations caused by large volume changes during the intercalation-deintercalation of lithium ions [19-22]. To address these issues, nanostructured [22,23] and hollow Si [24,25] materials have been extensively studied. However, Si/C compounds with a small amount of Si still seem to be the most practical approach for high volume production [26,27].

SiO_x (silicon suboxide, x<2), which is composed of nano-sized Si particles dispersed in a matrix of SiO₂, is considered to be a promising candidate anode material to replace conventional carbon anode materials [28,29]. Li₂O and Li₄SiO₄, which are produced during early reactions in LIBs with the SiO₂-based anode structure, are considered responsible for the reduction in reversibility [30-33]. However, they are considered to play a positive role in restraining the volume expansion of the anode by reducing the agglomeration and alloying between Si particles and Li [34,35].

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To improve the performance of the SiO_2 -based anode, various approaches have been studied and suggested to reduce the volume expansion and improve the performance of the electrode. These include a hollow porous SiO_2 which was synthesized with crevices on the surface to alleviate volume expansions and reduce the diffusion lengths of Li ions [32,36]. Carbon has also been coated on SiO_2 to improve conductivity and act as a buffer to the mechanical stress generated by volume expansions [34,37]. Nano-sized and core-shell structured particles have been synthesized and studied [28,38]. However, most of the approaches described above employ complicated and multiple processes not suitable for economical and high volume production systems.

In the present study, to synthesize Si/SiO_x , a chemical mixture of silicon nanoparticles-dispersed SiCl_4 was used as a source material. Ethylene glycol (EG) was employed to control the hydrolysis reactions of the chemicals involved. In order to synthesize Si/SiO_x , instead of using the conventional evaporation method at high temperature (above 1400°C) in a vacuum [29,39], our group adopted a solution reaction-based approach utilizing chemical and hydrolysis reactions. Our method demonstrates a facile and economical way to synthesize Si/SiO_x through simple chemical reactions, and using heat treatment at a relatively low temperature of about 725°C . The electrochemical performance of the synthesized Si/SiO_x composite was also investigated and presented for application as an anode material to LIBs.

2. EXPERIMENTAL PROCEDURE

An agglomerated, sponge-like, white gel-type SiO_x precursor powder was synthesized by pouring and vigorously stirring 13 ml of EG (99.9%, Samchun Co.) into a mixed solution of 20 mL SiCl_4 (99%, Wako Co.) and 50 ml Benzene (99.5%, Daejung Co.). Before pouring the EG, three different kinds of SiCl_4 solution, with 1, 3, and 9 wt% ratios of dispersed silicon (Si) nanoparticles (99%, APS ≈ 100 nm, Alfa Aesar Co.), had been prepared under continuous stirring. The white gel-type SiO_x precursor which contained Si nanoparticles was heat treated at 725°C for 1 hr in vacuum. The Si/SiO_x composite powders, which turned black after

heat treatment, were crushed by 5 mm zirconia balls using a 3D-mixer (TurbulaMixer, DM-T2, Daemyoung Co.) at 50 rpm for 24 hrs to achieve uniform particle distribution.

The morphology and microstructure of the as-prepared Si/SiO_x composite powders were characterized using Field Emission Scanning Electron Microscopy (FE-SEM; S-4700, Hitachi Co.), Brunauer–Emmett–Teller (BET) analyzer (Nanoporosity-HQ, Mirae SI Co.). The crystallinity of the Si/SiO_x composites prepared with different amounts of Si nanoparticles were examined using X-ray diffraction (XRD; D/MAX 2500, Rigaku Co.) with $\text{Cu-K}\alpha$ radiation. Electrochemical characterization for the as-prepared Si/SiO_x electrode was done with 2032 coin-type cells, in which a metal lithium foil was used as the counter electrode.

All of the electrodes in the cells were prepared by mixing 70 wt% Si/SiO_x powder with 20 wt% conductive carbon blacks of Super-P (SP, TIMCAL, Super P Li), 10 wt% Na-CMC (Sodium Carboxymethyl Cellulose, Sigma Aldrich Co.) binder, and an appropriate amount of water to form a slurry. Here, conductive carbon blacks were added to facilitate the insertion/extraction of lithium ions during the charge/discharge processes. A solution of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate and dimethyl carbonate (3:7 v/v, Panaxetec) was used as the electrolyte. The electrodes were dried in a vacuum oven at 80°C for 24 hr before being transferred into an Ar-filled glove box for cell

Fig. 1. XRD patterns of as-synthesized SiO_x and Si/SiO_x composites with a different amount of Si added to SiO_x .

Fig. 2. FESEM images of the samples: (a) as-synthesized SiO_x , (b) magnification of (a), (c) crystalline Si, (d) Si/SiO_x composite with 1 wt% Si added to SiO_x, (e) Si/SiO_x composite with 3 wt% Si added to SiO_x, (f) Si/SiO_x composite with 9 wt% Si added to SiO_x.

assembly. The coin cells were charged and discharged between 0.01 and 1.5 V by applying a constant current of 100 mA/g at 25 °C for electrochemical characterization. By using electrochemical impedance spectroscopy (EIS, Bio-Logic Co, VMP3), we carried out impedance analyses with Nyquist plots in the frequency ranges of 1×10^6 Hz to 1×10^{-3} Hz with an AC amplitude of 10 mV, and tested the samples for various cycles.

3. RESULTS And DISCUSSION

First, the synthesized Si/SiO_x powders were characterized with X-ray diffraction patterns. XRD data for the Si/SiO_x powders with varying Si amounts of 1, 3, and 9 wt% are shown in Fig. 1. For the comparison, patterns for only Si and SiO_x are also presented. A typical amorphous peak of SiO_x is observed for all the Si/SiO_x samples at near $2\theta=20\text{--}25^\circ$ [29,30]. Based on the diffraction patterns, Si peaks corresponding to the (111), (220), (311), (400), and (331)

Fig. 3. Voltage profiles of the pristine Si, as-synthesized SiO_x, and the Si/SiO_x composites with a different amount of Si added to SiO_x.

planes are observed to become prominent with the increased Si amount in Si/SiO_x samples.

The morphology and surface structure of synthesized SiO_x and silicon powders were observed under FE-SEM. From the observation, the SiO_x particle was found to be irregular shaped with a size of approximately $1\sim 2\ \mu\text{m}$ (Fig. 2a). A close examination of the surface of the SiO_x revealed that it is structured with nanosized particles of 30-50 nm, as shown in Fig. 2b, implying a high surface area. A relatively high specific surface area of $34.01\ \text{m}^2/\text{g}$ was measured and confirmed by BET analysis [32], and is believed to contribute to the high charging capacity of the sample. Silicon powder was observed to be spherical shaped with diameters of approximately 100 nm (Fig. 2c). Fig. 2d, 2e, and 2f correspond to SiO_x particles incorporated with 1 wt%, 3 wt%, and 9 wt% Si, respectively.

Figure 3 shows the initial charge-discharge performance of SiO_x, and Si/SiO_x with different amounts of silicon. Pristine Si was also included for comparison purposes. The charge-discharge curves of the samples were obtained at a current density of 100 mA/g over a potential window of 0.01-1.5 V (versus Li⁺/Li₀). Near and below 0.2 V the potential plateau during charging corresponds to the intercalation of lithium ions for silicon. Meanwhile, a potential plateau near 0.5 V in the discharge cycle indicates

Table 1. Electrochemical properties of the Pristine Si, SiO₂, as-synthesized SiO_x, and Si/SiO_x composites with a different amount of Si added to SiO_x.

Samples	1st charge Capacity /mAhg ⁻¹	1st discharge Capacity /mAhg ⁻¹	1st Columbic Efficiency /%	Capacity After 50 cycles /mAhg ⁻¹	Capacity retention 2~50 cycles /%
Pristine Si	3495	3008	86	206	8
9 wt% Si to added to SiO _x	2221	1441	65	463	30
3 wt% Si to added to SiO _x	2550	1342	53	1079	80
1 wt% Si to added to SiO _x	2029	992	49	998	99
SiO _x	1922	851	44	781	95
SiO ₂	97	27	28	29	95

Fig. 4. Cycling performances of the pristine Si, SiO₂, as-synthesized SiO_x, and Si/SiO_x composites with a different amount of Si added to SiO_x at discharge/charge current densities of 100 mA g⁻¹.

the deintercalation of lithium ions for silicon [35-38]. The 0.5 V plateau increases with the amount of silicon added to SiO_x, which is reasonable from the viewpoint of capacity variation with silicon.

Pristine Si was measured to have a specific capacity of 3495 mAh/g, and a relatively high reversibility of 0.86. On the other hand, SiO_x had a lower capacity of 1922 mAh/g with a reversibility of 0.44. The specific capacity of SiO_x was gradually improved as silicon was incorporated into SiO_x, reaching 2550 mAh/g with 3 wt% silicon as shown in the graph. However, it decreased to 2221 mAh/g with 9 wt% silicon in Si/SiO_x. This decrement of initial charge capacity with increased silicon amount, contrary to expectation, seemed to be caused by unstable electrochemical reactions during the initial cycle. The electrochemical reactions became gradually stabilized after the initial cycle, as shown and

confirmed by Figs. 4 and 6, where variation in specific capacity and differential capacity (vs. potential) was monitored with charge-discharge cycles, respectively.

Meanwhile, the initial reversibility of SiO_x was found to be continuously enhanced, up to 0.65, with the addition of silicon up to 9 wt%. The reversibility and stability of Si/SiO_x can be negatively affected by the LiO₂ and Li₄SiO₄ produced through the irreversible reactions expressed (as Eqs. 1, 2) below, [31] and the Li_xSi formed by the reversible reaction (Eq. 3) with the addition of silicon to SiO_x, [9] respectively. However, the LiO₂ and Li₄SiO₄ play a role in improving the cyclic stability of the anode by accommodating volume change during the charge-discharge cycles.

Following the initial charge-discharge measurements, the cyclic performance of the samples was investigated to examine how the amount of Si in Si/SiO_x affected the stability of the anode. Fig. 4 shows the variation in the specific capacity of the samples for cycle numbers up to 50. Even though the pristine Si had a high initial capacity and coulombic efficiency, the capacity decreased gradually with each cycle, resulting in the low capacity retention of 8% after 50 cycles. The gradual deterioration in capacity is attributed to large volume changes in the Si anode during the intercalation-deintercalation of lithium ions.

Fig. 5. Nyquist plots of the SiO_2 , as-synthesized SiO_x and Si/SiO_x composites with a different amount of Si added to SiO_x

On the other hand, SiO_x maintained 99% of its initial capacity by the end of 50th cycle. The Si/SiO_x samples were also found to have a capacity retention of 30-99%, and the capacity retention was inversely proportional to the amount of Si (1-9 wt%) added to the SiO_x . These results are consistent with the well-known adverse effect of Si on capacity reversibility, resulting from its large volume changes during charge and discharge cycles. Our data suggest that an optimized amount of silicon added to SiO_x could play a critical role in improving capacity while maintaining high capacity retention of the SiO_x anode. The selected important data in Figs. 3 and 5 are tabulated in Table 1.

To understand the improved electrochemical performance of the Si/SiO_x electrode, the variation in impedance during charge-discharge cycles was investigated by using the Nyquist plots of the samples. Fig. 5 shows the impedance

Fig. 6. Differential capacity plots (dQ/dV vs. potential) of the anodes of the SiO_x (a), (b) Si/SiO_x composite with 1 wt% Si added to SiO_x , (c) Si/SiO_x composite with 3 wt% Si added to SiO_x , (d) Si/SiO_x composite with 9 wt% Si added to SiO_x and (e) pristine Si

data of the samples in an uncharged state before charge-discharge cycles. By observing the diameter changes of each respective semicircle, the resistance of the SiO_x electrode was found to decrease with the amount of silicon added to SiO_x . It is, however, noteworthy that the tendency of decreasing resistance was reversed with the addition of 9 wt% silicon to SiO_x . These data are in accord with the variations in the capacity of SiO_x with the amount of silicon added to SiO_x , as tabulated in Table 1. Our data suggest that an optimized amount of silicon incorporated into SiO_x could improve its capacity along with the conductivity of the electrode

The changes in capacity with increasing applied potential (vs. Li^+/Li^0) during the 1st, 2nd and 3rd charge-discharge cycles for the samples were measured, and are shown in Fig. 6. A small peak is observed at 0.75 V (versus Li^+/Li^0) in the charging curves, indicating SEI layer formation on the anode surface [38]. Several peaks are observed in the charging curves near and below 0.2 V (versus Li^+/Li^0) showing the intercalation of lithium ions for silicon as described in Fig. 3. The SiO_x in Fig. 6a had relatively low electrochemical activities, while silicon (Fig. 6e) showed much higher activities and characteristic peaks at 0.09, and 0.24 V (vs. Li^+/Li^0) during the charging process [20,40]. The characteristic peaks of Si became prominent in the SiO_x electrode with the addition of silicon (Fig. 6b-d). The characteristic silicon peak for the deintercalation of lithium ions at 0.43 V is observed to become sharper with increasing amounts of silicon, while SiO_x shows a broad peak. The variations in the peaks of the samples observed during the 1st, 2nd and 3rd charge-discharge cycles suggest that the electrochemical reactions of the samples became stabilized after the 2nd cycle.

4. CONCLUSIONS

Si/SiO_x composite anodes were fabricated by incorporating silicon powders with diameters of approximately 100 nm into SiO_x using a simple and economical solution reaction-based method utilizing SiCl_4 , EG and benzene chemicals. The SiO_x matrix was found to be structured with nanosized particles of 30-50 nm, which were favorable for accommodating more

lithium ions. The initial capacity of the anode was measured to be significantly improved by incorporating silicon nanoparticles into SiO_x , to 1.3 times that of as-synthesized SiO_x . The capacity retention of the Si/SiO_x was also found to be much improved, to 99%, compared to 8% for silicon. These improved results were achieved by combining the advantages of each anode component, namely, the high capacity of silicon and the cyclic stability of SiO_x , respectively. We strongly suggest the proposed approach enables not only the development of Si/SiO_x anode materials with high capacity and cyclic stability for LIBs, but can also help to significantly lower the cost of production of Si/SiO_x composites.

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REFERENCES

1. M. Armand and J.-M. Tarascon, *Nature* **451**, 652 (2008).
2. P. G. Bruce, B. Scrosati, and J.-M. Tarascon, *Angew. Chem. Int. Edit.* **7**, 2930 (2008).
3. J. B. Goodenough and Y. Kim, *Chem. Mater.* **22**, 587 (2010).
4. J.-M. Tarascon and M. Armand, *Nature* **414**, 359 (2001).
5. H. A. Choi, B. K. Ko, S. E. Shim, and S. H. Baeck, *Korean J. Met. Mater.* **52**, 277 (2014).
6. L. Ji, Z. Lin, M. Alcoutlabi, and X. Zhang, *Energy Environ. Sci.* **4**, 2682 (2011).
7. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J.-M. Tarascon, *Nature* **407**, 496 (2000).
8. J. E. Chae, J. M. Yang, K. J. Park, J. H. Yoo, Y. C. Park, M. S. Sung, H. J. Yu, and S. S. Kim, *Korean J. Met. Mater.* **51**, 429 (2013).
9. C.-M. Park, J.-H. Kim, H. Kim, and H.-J. Sohn, *Chem. Soc. Rev.* **39**, 3115 (2010).
10. M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novák, *Adv. Mater.* **10**, 725 (1998).
11. Churl Kyoung Lee, *Korean J. Met. Mater.* **52**, 527 (2014).
12. S. -H. Hong, Y. -M. Jin, and M. Y. Song, *Met. Mater. Int.* **20**, 793 (2014).
13. Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, and T. Miyasaka, *Science* **276**, 1395 (1997).
14. M. Winter and J.O. Besenhard, *Electrochim. Acta* **45**, 31 (1999).
15. C.-M. Park and H.-J. Sohn, *Adv. Mater.* **22**, 47 (2010).

16. C.-M. Park and H.-J. Sohn, *Chem. Mater.* **20**, 3169 (2008).
17. H. Wua and Y. Cuia, *Nano Today* **7**, 414 (2012).
18. H. Jung, M. Park, Y.-G. Yoon, G.-B. Kim, and S.-K. Joo, *J. Power Sources* **115**, 346 (2003).
19. Jeannine R. Szczech and Song Jin, *Energy Environ. Sci.* **4**, 56 (2011).
20. M. N. Obrovac and L. J. Krause, *J. Electrochem. Soc.* **154**, A103 (2007).
21. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, and G. Yushin, *Nat. Mater.* **9**, 353 (2010).
22. H. -S. Lee and B. -J. Lee, *Met. Mater. Int.* **20**, 1003 (2014).
23. H. Li, X. Huang, L. Chen, Z. Wu, and Y. Liang, *Electrochem. Solid St.* **2**, 547 (1999).
24. H. Kim, B. Han, J. Choo, and J. Cho, *Angew. Chem. Int. Edit.* **47**, 10151 (2008).
25. Y. Yao, M. T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W. D. Nix, and Y. Cui, *Nano Lett.* **11**, 2949 (2011).
26. M. L. Terranov, S. Orlanducci, E. Tamburri, V. Guglielmotti, and M. Rossi, *J. Power Sources* **246**, 167 (2014).
27. S.-L. Chou, J.-Z. Wang, M. Choucair, H.-K. Liu, J. A. Stride, and S.-X. Dou, *Electrochem. Commun.* **12**, 303 (2010).
28. B. Guo, J. Shu, Z. Wanga, H. Yang, L. Shi, Y. Liu, and L. Chen, *Electrochem. Commun.* **10**, 1876 (2008).
29. M. K. Kim, B. Y. Jang, J. S. Lee, J. S. Kim, and S. Nahm, *J. Power Sources* **244**, 115 (2013).
30. P. Lv, H. Zhao, J. Wang, X. Liu, and T. Zhang, Q. Xia, *J. Power Sources* **237**, 291 (2013).
31. T. Kim, S. Park, and S. M. Oh, *J. Electrochem. Soc.* **154**, A1112 (2007).
32. B.-C. Yu, Y. Hwa, J.-H. Kim, and H.-J. Sohn, *Electrochim. Acta* **117**, 426 (2014).
33. J.-H. Kim, C.-M. Park, H. Kim, Y.-J. Kim, and H.-J. Sohn, *J. Electroanal. Chem.* **661**, 245 (2011).
34. Y. Yao, J. Zhang, L. Xue, T. Huang, and A. Yu, *J. Power Sources* **196**, 10240 (2011).
35. W.-S. Chang, C.-M. Park, J.-H. Kim, Y.-U. Kim, G. Jeong and H.-J. Sohn, *Energy Environ. Sci.* **5**, 6895 (2012).
36. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu, and Q. Chen, *Scientific Reports* **3**, 1568 (2013).
37. J.-Y. Kim, D. T. Nguyen, J.-S. Kang, S.-W. Song, *J. Alloys Compd.* **633**, 92 (2015).
38. P. Lv, H. Zhao, C. Gao, T. Zhang, and X. Liu, *Electrochim. Acta* **152**, 345 (2015).
39. S.-S. Suh, W. Y. Yoon, D.-H. Kim, S.-U. Kwon, J.-H. Kim, Y.-U. Kim, C.-U. Jeong, Y.-Y. Chan, S.-H. Kang, and J.-K. Lee, *Electrochim. Acta* **148**, 111 (2014).
40. J. Li and J. R. Dahn, *J. Electrochem. Soc.* **154**, A156 (2007).