

鳥取大学研究成果リポジトリ

Tottori University research result repository

タイトル Title	Effect of Silicon Crystallite Size on Its Electrochemical Performance for Lithium-Ion Batteries
著者 Author(s)	Domi, Yasuhiro; Usui, Hiroyuki; Sugimoto, Kai; Sakaguchi, Hiroki
掲載誌・巻号・ページ Citation	ENERGY TECHNOLOGY , 7 (5)
刊行日 Issue Date	2019-05
資源タイプ Resource Type	学術雑誌論文 / Journal Article
版区分 Resource Version	著者版 / Author
権利 Rights	<p>This is the peer reviewed version of the following article: Domi Yasuhiro, Usui Hiroyuki, Sugimoto Kai, et al. Effect of Silicon Crystallite Size on Its Electrochemical Performance for Lithium-Ion Batteries. ENERGY TECHNOLOGY. 2019. 7(5), which has been published in final form at https://doi.org/10.1002/ente.201800946. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.</p>
DOI	10.1002/ente.201800946
URL	https://repository.lib.tottori-u.ac.jp/9136

Effect of Silicon Crystallite Size on its Electrochemical Performance for Lithium-Ion Batteries

Yasuhiro Domi,^[a,c] Hiroyuki Usui,^[a,c] Kai Sugimoto,^[b,c] and Hiroki Sakaguchi*^[a,c]

Abstract: It has been reported that Si anodes with smaller crystallite size show better electrochemical performance in lithium-ion batteries; Si particles with different diameters have also been used. However, it has not yet been clarified whether the better performance is attributed to crystallite size or particle diameter. Here, we investigate the effect of Si crystallite size on its anode performance using Si particles having same diameter and different crystallite size. Longer cycle life was obtained for smaller crystallite size, due to the small amount of amorphous Li-rich Li-Si phase formed during charging. The phase is likely to form in greater amount in Si particles with larger crystallite size, leading to degradation of the Si electrode at an early stage. Furthermore, Si electrodes with larger crystallite size show superior rate performance because of the high Li diffusion rate into the broader grain boundary; on the other hand, Si with smaller crystallite size should limit Li diffusion due to the narrower grain boundary. Therefore, smaller crystallite size helps improve the cycle life, but deteriorates the rate performance of lithium-ion batteries.

Silicon (Si) is promising candidate as an anode active material for lithium-ion batteries (LIBs) due to its high theoretical capacity of 3579 mA h g⁻¹ and a negative working potential close to that of lithium metal.^[1] Si expands and contracts significantly during the lithiation and delithiation reactions, respectively. An expansion rate per Si corresponds to 280%, which generates both large stress and strain in the active materials. The accumulated strain under repeated charge-discharge cycling results in severe pulverization and/or cracking of Si, leading to electrical contact loss between the active material and the current collector, and collapse of the surface layer formed on Si electrode via reductive decomposition of the electrolyte. Therefore, Si electrode shows poor cycle stability. To mitigate Si electrode degradation, nanostructured Si materials, such as nanoparticles,^[2,3] nanowires,^[4,5] and nanorods,^[6,7] have been utilized as the active material. It has also been reported that Si anodes with smaller crystallite size show better electrochemical performance for LIBs, and Si with different particle diameters has been used in the previous reports.^[8,9] However, it has not yet been clarified whether the better performance is attributed to crystallite size or diameter. It should be noted that a Si particle consists of some crystallites. Herein, we determine the effect of

Si crystallite size on the anode performance in LIBs using Si particles having the same diameter and different crystallite sizes. We also discuss the difference in performance based on phase transition of Si during the lithiation and delithiation processes.

The crystallite and particle sizes of different Si powders (Si-30, Si-80, Si-90 and Si-100; each numeric value represents crystallite size), which were determined using X-ray diffraction and particle size distribution analyzer (inset in Figure 1, Figures S1 and S2). Here, we defined mode diameter as particle size. Si electrodes were prepared by a gas deposition method without using a binder and a conductive agent, unlike conventional slurry-based electrodes.^[10] The thickness of the Si active material layers has been estimated to be about 1.6 μm;^[11,12] thus, Si particles should undergo fracture and/or plastic deformation during the GD process, as shown in Figure S3. We can confirm a number of fine particles with sub-μm size on Si-30 and Si-80 electrodes and the particles larger than 1 μm on Si-90 and Si-100 electrodes; the size of Si particles was not maintained after the GD process. However, the particle size distribution should be almost the same before and after the process.

Figure 1 shows the cycle life of various Si electrodes in 1 mol dm⁻³ (M) lithium bis(fluorosulfonyl)amide (LiFSA) dissolved in *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide (Py13-FSA) with a charge capacity limit of 1000 mA h g⁻¹. Although the discharge capacity of a Si-100 electrode fades after about 600 cycles, other electrodes exhibit long cycle life beyond 1000 cycles. Particularly, a Si-30 electrode retains a reversible capacity of 1000 mA h g⁻¹ over 1400 cycles. Better cycle performance of Si-80 electrode than Si-100 electrode is attributed to particle size because their crystallite sizes are almost the same. If a Si-100 particle assumes the discharge

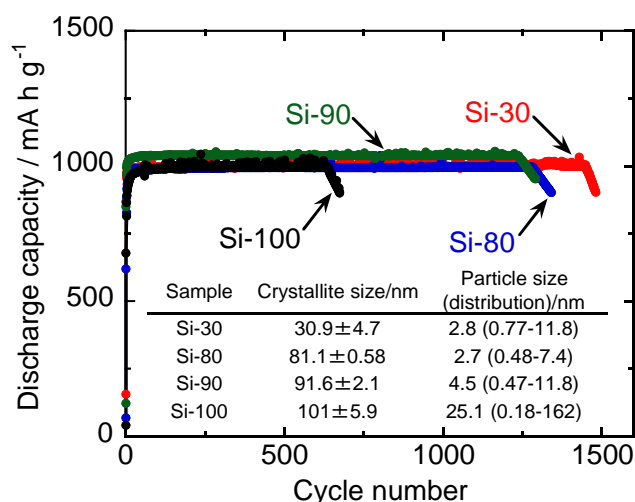


Figure 1. Cycle life of various Si electrodes in 1 M LiFSA/Py13-FSA at a constant current density of 0.36 A g⁻¹ (0.1 C) during the first cycle and of 1.44 A g⁻¹ (0.4 C) after the second cycle with a charge capacity limit of 1000 mA h g⁻¹.

[a] Dr. Y. Domi, Dr. H. Usui, Prof. H. Sakaguchi
Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan
E-mail: sakaguch@tottori-u.ac.jp

[b] Kai Sugimoto
Department of Engineering, Graduate School of Sustainable Science, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan

[c] Dr. Y. Domi, Dr. H. Usui, K. Sugimoto, Prof. H. Sakaguchi
Center for Research on Green Sustainable Chemistry, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan

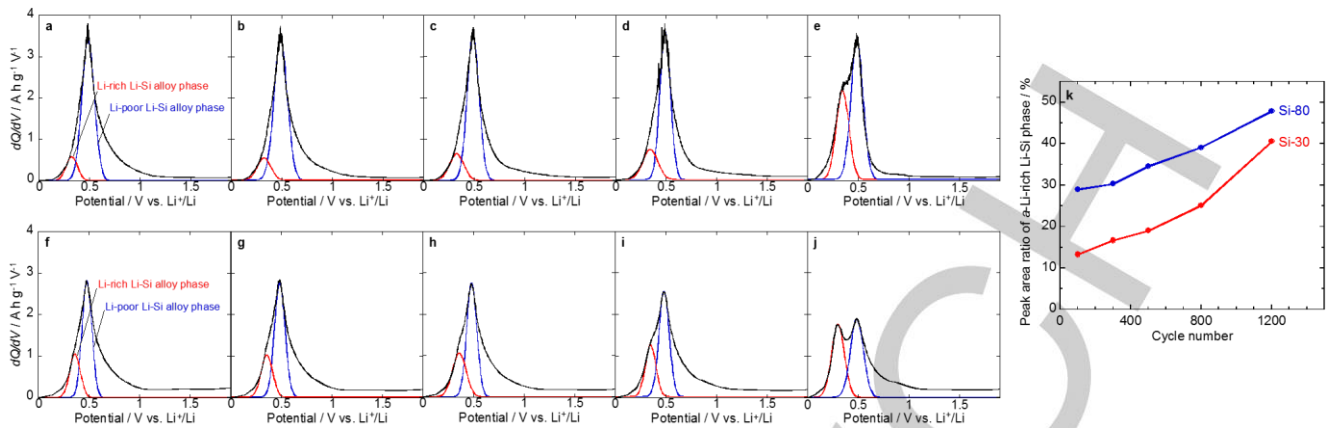


Figure 2. dQ/dV plot of (a-e) Si-30 and (f-j) Si-80 electrodes for discharge reaction after the (a and f) 100th, (b and g) 300th, (c and h) 500th, (d and i) 800th, and (e and j) 1200th cycles. Part (k) represents the correlation between the peak area ratio of the a-Li-rich Li-Si phase and the cycle number. The ratio is calculated by dividing the peak area of a-Li-rich Li-Si phase by the area of a-Li-rich and a-Li-poor Li-Si phases.

capacity of 1000 mA h g⁻¹, many Si-80 particles are necessary to obtain the same capacity. Thus, a large strain intensively accumulates in the Si-100 particle, leading to the electrode disintegration at an early stage. In contrast, the stress should disperse when the Si-80 particles are used, suppressing the disintegration. The Si-80 and Si-90 electrodes have approximately equal cycle life, indicating that moderate difference in diameter has no influence on the cycling performance. Some groups have reported that the Si electrode consisting of smaller particle show an improved cyclability.^[13] However, these reports have not mentioned whether the Si crystallite sizes are the same in the studied electrodes. Therefore, here we demonstrate that smaller Si particle contributes to improvement of the cyclability using Si particles having same crystallite size. It has been reported that the electrolyte influences the surface film properties and the electrochemical performance.^[14,15]

The Si-30 electrode, having smaller crystallite size than and the same particle size as the Si-80 electrode, exhibits longer cycle life by about 200 cycles. When the Li-rich Li-Si alloy phase forms during lithiation, large strain accumulates in the active material, and the capacity fades due to the electrode disintegration. Thus, the difference in cycle life should be attributed to the amount of Li-rich phase. Figure 2 shows the differential capacity (dQ/dV) plot of the Si-30 and Si-80 electrodes for delithiation with the charge capacity limit of 1000 mA h g⁻¹ and includes the peak fitting results. In both cases, two peaks appear at around 0.33 and 0.48 V vs. Li⁺/Li, corresponding to delithiation from amorphous Li-rich (a-Li-rich, including amorphous Li_{3.5-3.75}Si) and amorphous Li-poor (a-Li-poor, including amorphous Li_{2.0}Si) Li-Si alloy phases, respectively.^[16,17] A peak area ratio of the a-Li-rich phase gradually increases with increasing cycle number regardless of the electrode material. The peak area ratio is lower for the Si-30 electrode than for the Si-80 electrode over all the cycles. Therefore, the above expectation appears to be valid; longer cycle life is obtained for smaller crystallite size, due to the small amount of a-Li-rich phase.

Next, we discuss the relationship between the crystallite size and the amount of the a-Li-rich phase. Figure 3 illustrates a process of Li storage in each of the different Si powders. Herein, we assume that grain boundary work as Li⁺ diffusion pass but not Li storage space. We also hypothesize that grain boundary of Si-80 is broader than that of Si-30 (Figure 3a and 3d). It can be seen by imagining that a difference in interspace between golf and soccer balls when they are filled in a box. At the beginning of Li storage, Li should preferentially diffuse into the grain boundary because diffusion energy of Li into the boundary is lower than that into the crystallite (Figure 3b and 3e). An a-Li-poor phase forms along the boundary. As lithiation proceeds, Li diffuses from the grain boundary into the crystallite without considering Li diffusion from the particle surface. Simultaneously, the a-Li-rich phase should form easily in Si-80 due to higher Li concentration around the grain boundary (Figure 3c, 3f, and 3g), resulting in greater strain accumulation. Consequently, the Si-80 electrode with larger crystallite size degrades at a relatively early stage. In contrast, Si-30 with smaller crystallite size suppresses the a-Li-rich phase formation, resulting in the improved cycle life. We also confirmed the Si crystallinity after 100 cycles with a charge capacity limit of 1000 mA h g⁻¹ by XRD (Figure S4). Decreasing ratio of Si (111) peak intensity is 0.80 and 0.40 at Si-30 and Si-80, respectively, indicating that Si-30 maintains higher

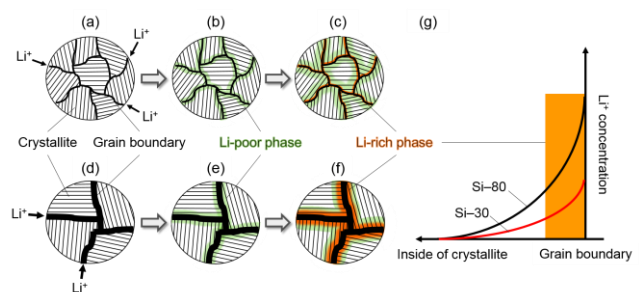


Figure 3. Schematic of a Li storage process into (a-c) Si-30 and (d-f) Si-80 powders. Part (g) represents a difference in the Li concentration gradient around the grain boundary.

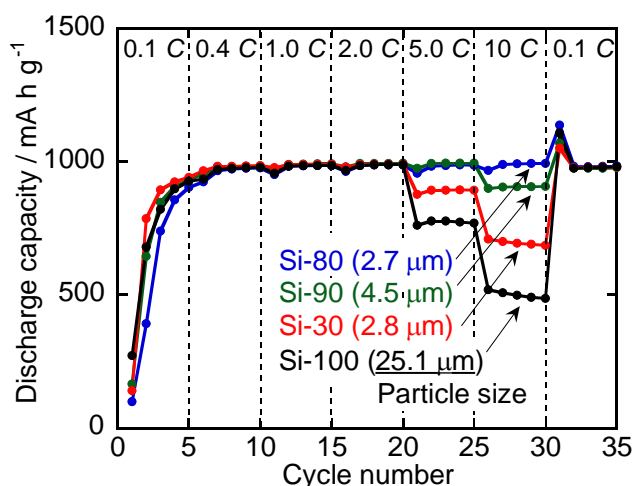


Figure 4. Rate performance of different Si electrodes in 1 M LiFSA/Py13-FSA with a charge capacity limit of 1000 mA h g⁻¹.

crystallinity after the 100th cycle and a phase transition from crystalline Si to amorphous Si easily proceeds at Si-80. While the detail of Li⁺ diffusion behavior in the grain boundary is still unclear, the obtained results can be rationalized by the assumptions.

Figure 4 shows the rate performance of each Si electrode with a charge capacity limit of 1000 mA h g⁻¹. The discharge capacity of Si-100 electrode begins to fade at 5 C. Capacity fading of the Si-30 and Si-90 electrodes also begins from 5 and 10 C, respectively. In contrast, the Si-80 electrode maintains a reversible capacity of 1000 mA h g⁻¹ over the entire C-rate range. As with the cycle life, rate performance of Si-90 electrode is almost the same as that of Si-80 electrode. Comparing the Si-30 and Si-80 electrodes, which have almost the same particle diameter and different crystallite sizes, Li diffusion into the grain boundary of Si-80 should proceed immediately at high C-rate due to its larger width. On the other hand, the narrower grain boundary of Si-30 should limit Li diffusion at high C-rate, leading to capacity fading. These results demonstrate that smaller crystallite size deteriorates the rate performance. Based on the particle size of the Si-80 and Si-100 powders, the volume of a Si-100 particle is equal to that of 800 Si-80 particles. In addition, the total surface area of 800 Si-80 particles is ~9-times larger than that of a single Si-100 particle, indicating greater reactivity between Si-80 and Li. Therefore, a Si utilization rate should be higher at the Si-80 electrode due to its shorter diffusion pathway: the inside of Si-100 does not react with Li.

In summary, we have investigated the effect of Si crystallite size on its electrochemical performance using Si particles having the same diameter and different crystallite sizes. Longer cycle life was obtained for smaller crystallite size, due to the small amount of a-Li-rich Li-Si phase formed during charging. The phase easily forms in greater amount in Si particles with larger crystallite size because the Si has broader grain boundary and greater strain accumulates in the Si, leading to degradation of the Si electrode at an early stage. Si electrodes with larger crystallite size show superior rate performance due to immediate

Li diffusion into the grain boundary. In contrast, Si with smaller crystallite size should limit Li diffusion due to the narrower grain boundary. While effect of silicon crystallite size on its electrochemical performance for LIBs has been treated as unimportant, we demonstrated smaller crystallite size helps improve the cycle life, but deteriorates the rate performance.

Experimental Section

Various Si powders (Si-30, Si-80, and Si-90) were supplied by Elkem. Si powder (Si-100) purchased from Wako Pure Chemical Industries, Ltd. was also used as an active material. The surface morphology of Si electrodes was observed by field-emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL Co., Ltd.). The beam acceleration voltage and working distance were set at 3 kV and 10 mm, respectively. We assembled a 2032-type coin cell using the prepared Si electrode as the working electrode. A Li metal sheet (Rare Metallic, 99.9%, thickness = 1 mm) and a glass fiber filter (Whatman GF/A) served as the counter electrode and the separator, respectively. The electrolyte used was 1 M LiFSA/Py13-FSA. We performed cell assembly and electrolyte preparation in an Ar-filled glovebox (DBO-2.5LNKPTS, Miwa MFG) with a dew point below -100°C and O₂ concentration below 1 ppm. Cycle life of the cell was investigated by a galvanostatic charge-discharge test using electrochemical measurement systems (HJ-1001SD8 or HJ-1001SM8, Hokuto Denko Co., Ltd.) in a potential range of 0.005–2.000 V vs. Li⁺/Li at 303 K. The peak fitting of the differential capacity (dQ/dV) plot was performed by using the Origin Pro 8.5.0J (Light Stone) software.

Acknowledgements

This work was partially supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI, Grant Numbers JP17K17888, JP17H03128, and JP16K05954.

Keywords: lithium-ion battery • silicon anode • crystallite size • particle size • gas deposition

- [1] S. Lai, *J. Electrochem. Soc.* **1976**, *123*, 1196-1197.
- [2] X. H. Liu, L. Zhong, S. Huang, S. X. Mao, T. Zhu, J. Y. Huang, *ACS Nano* **2012**, *6*, 1522-1531.
- [3] M. Nie, D. P. Abraham, Y. Chen, A. Bose, B. L. Lucht, *J. Phys. Chem. C* **2013**, *117*, 13403-13412.
- [4] J.-H. Cho, S. T. Picraux, *Nano Lett.* **2014**, *14*, 3088-3095.
- [5] F. Xia, S. Kwon, W. W. Lee, Z. Liu, S. Kim, T. Song, K. J. Choi, U. Paik, W. I. Park, *Nano Lett.* **2015**, *15*, 6658-6664.
- [6] Y. Yu, C. Yue, S. Sun, W. Lin, H. Su, B. Xu, J. Li, S. Wu, J. Li, J. Kang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 5884-5890.
- [7] J. Wang, X. Meng, X. Fan, W. Zhang, H. Zhan, C. Wang, *ACS Nano* **2015**, *9*, 6576-6586.
- [8] M. Gauthier, D. Mazouzi, D. Reyter, B. Lestriez, P. Moreau, D. Guyomard, L. Roué, *Energy Environ. Sci.* **2013**, *6*, 2145-2155.
- [9] X. Hou, M. Zhang, J. Wang, S. Hu, X. Liu, Z. Shao, *J. Alloys Compd.* **2015**, *639*, 27-35.
- [10] H. Sakaguchi, T. Toda, Y. Nagao, T. Esaka, *Electrochem. Solid-State Lett.* **2007**, *10*, J146-J149.
- [11] Y. Domi, H. Usui, M. Shimizu, Y. Kakimoto, H. Sakaguchi, *ACS Appl. Mater. Interfaces* **2016**, *8*, 7125-7132.
- [12] K. Yamaguchi, Y. Domi, H. Usui, H. Sakaguchi, *ChemElectroChem* **2017**, *4*, 3257-3263.

- [13] J. Zhang, C. Zhang, S. Wu, J. Zheng, Y. Zuo, C. Xue, C. Li, B. Cheng, *Electrochim. Acta* **2016**, *208*, 174-179.
- [14] Y. Domi, H. Usui, M. Shimizu, K. Miwa, H. Sakaguchi, *Int. J. Electrochem. Sci.* **2015**, *10*, 9678-9686.
- [15] Y. Domi, T. Doi, S. Tsubouchi, T. Yamanaka, T. Abe, Z. Ogumi, *Phys. Chem. Chem. Phys.* **2016**, *18*, 22426-22433.
- [16] K. Ogata, E. Salager, C. J. Kerr, A. E. Fraser, C. Ducati, A. J. Morris, S. Hofmann, C. P. Grey, *Nat. Commun.* **2014**, *5*, 3217.
- [17] K. Ogata, S. Jeon, D.-S. Ko, I. S. Jung, J. H. Kim, K. Ito, Y. Kubo, K. Takei, S. Saito, Y.-H. Cho, H. Park, J. Jang, H.-G. Kim, J.-H. Kim, Y. S. Kim, W. Choi, M. Koh, K. Uosaki, S. G. Doo, Y. Hwang, S. Han, *Nat. Commun.* **2018**, 9 479.

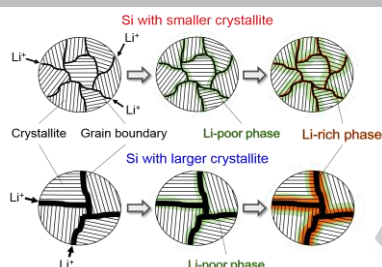
WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Effect of silicon crystallite size on its electrochemical performance for lithium-ion batteries has not yet been clarified. Here, we investigate the effect using Si particles having same diameter and different crystallite size. Smaller crystallite size helps improve the cycle life, but deteriorates the rate performance of lithium-ion batteries.



Yasuhiro Domi, Hiroyuki Usui, Kai Sugimoto, Hiroki Sakaguchi*

Page No. – Page No.

Effect of Silicon Crystallite size on its Electrochemical Performance for Lithium-Ion Batteries