

Improved Electrochemical Performance of $\text{Ge}_x\text{Si}_{1-x}$ Alloy Negative Electrode for Lithium-Ion Batteries

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$\text{Ge}_x\text{Si}_{1-x}$ alloy electrode is useful to cover shortcomings of Si negative electrode for lithium-ion batteries. To improve the electrochemical performance of $\text{Ge}_x\text{Si}_{1-x}$ negative electrode much further, film-forming additive and composite with LaSi_2 were applied. $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode exhibited better cyclability with discharge capacity of 1240 mA h g^{-1} at 400th cycle in the additive-containing electrolyte. The cycle performance of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ composite electrode was also superior to that of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode.

Silicon (Si) is an attractive candidate as a negative electrode material for lithium-ion batteries (LIBs) because it has high theoretical capacity of 3580 mA h g^{-1} ($\text{Li}_{15}\text{Si}_4$) compared to that of graphite (372 mA h g^{-1}), which is used currently.¹ Si is also an abundant resource and relatively inexpensive. However, a tremendous pulverization of Si occurs as a result of large change in volume of Si during the alloying (charge) and dealloying (discharge) reactions with Li, which leads to an initial capacity fading. These limitations hinder the practical application of Si active material as a negative electrode for LIBs. We have previously reported that the electrochemical performance of composite electrode consisted of elemental Si and silicide such as VSi_2/Si and $\text{Fe-Si}/\text{Si}$ is superior to that of a Si electrode.²⁻⁴ In particular, LaSi_2/Si composite electrode has exhibited remarkably improved electrochemical performance. The silicide ought to release the stress generated by the large volumetric change in Si during charge-discharge cycle, which results in the improvement of the performance. In addition, it has been reported that film-forming additives, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), help to improve the electrochemical performance of a Si electrode.⁵⁻⁷

Germanium (Ge) has high theoretical capacity of 1384 mA h g^{-1} ($\text{Li}_{15}\text{Ge}_4$) as with Si and both Ge and Si belong to a same group XIV. The electrochemical performance of a Ge electrode is superior to that of Si due to the specific characteristics of Ge; isotropic lithiation, fast Li diffusion, low electrical resistivity, and so on.⁸ $\text{Ge}_x\text{Si}_{1-x}$ alloy electrodes were also prepared and their electrochemical performance was investigated with various ratio of x . It has been reported that all $\text{Ge}_x\text{Si}_{1-x}$ electrodes show an improved capacity retention compared to Si electrode, and that the cyclability is improved with an increase in x .⁹ A $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode especially exhibits the best compromise from a viewpoint of performance/price with reversible capacity of ca. 1000 mA h g^{-1} at 100 cycles.⁹

To improve the electrochemical performance of $\text{Ge}_x\text{Si}_{1-x}$ electrode much further, in the present study, we attempted to prepare the composite electrode consisted of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and LaSi_2 . In addition, the effect of VC on the cyclability of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode was investigated.

$\text{Ge}_{0.1}\text{Si}_{0.9}$ and LaSi_2 powders were synthesized by a mechanical alloying (MA) method.⁴ The stoichiometric mixture of elemental Ge and Si powders for $\text{Ge}_{0.1}\text{Si}_{0.9}$ or of elemental La chip and Si powder for LaSi_2 was put in a zirconia container together with balls. The weight ratio of the balls to the sample was about 15:1. The vessel used was sealed to keep an atmosphere of dry Ar gas. The MA for $\text{Ge}_{0.1}\text{Si}_{0.9}$ and LaSi_2 was performed using a high-energy planetary ball mill (P-5, Fritsch) for 10 and 8 h with a rotary speed of 380 and 300 rpm, respectively. The composite of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt.%) was prepared by mechanical milling for 2 h with a rotary speed of 150 rpm and for another 1 h with a rotary speed of 250 rpm.

The working electrode was fabricated by a gas deposition (GD) method.² The GD thick-film was prepared on a current collector of Cu foil substrate with $20 \mu\text{m}$ in thickness. The weight and thickness of the deposited active material on the substrate were estimated to be $22 - 40 \mu\text{g}$ and ca. $2 \mu\text{m}$, respectively.⁵ A galvanostatic charge-discharge test was carried out with a 2032-type coin cell and an electrochemical measurement system (HJ-1001SM8A Hokuto Denko Co., Ltd. or BS2506 KEISOKUKI) in the potential range between 0.005 and 2.000 V vs. Li^+/Li at 303 K under constant current density of 1 C. 1 C for $\text{Ge}_{0.1}\text{Si}_{0.9}$ and $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt. %) was calculated to be 3360 and 1680 mA h g^{-1} , respectively, based on the theoretical value of 3580 mA h g^{-1} for $\text{Li}_{15}\text{Si}_4$ and 1384 mA h g^{-1} for $\text{Li}_{15}\text{Si}_4$.^{8,10} The capacity of LaSi_2 is vanishingly small.⁵ Both the counter and reference electrodes consisted of Li metal sheets (Rare Metallic, 99.9% thickness; 1mm). The electrolyte solution used was 1 M lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) in propylene carbonate (PC, Kishida chemical Co., Ltd.) with or without 5 vol. % VC. Backscattered electron (BSE) image of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt.%) powder was observed using field-emission scanning electron microscopy (JSM-6701F, JEOL Co., Ltd.). The beam acceleration voltage and working distance were set at 20 kV and 8 mm, respectively.

To confirm the solid solution formation of $\text{Ge}_{0.1}\text{Si}_{0.9}$, XRD measurement was performed. Figure 1 shows XRD patterns of $\text{Ge}_x\text{Si}_{1-x}$ ($x = 0.1, 0.5, \text{ and } 0.8$) powders. Peaks which assigned to Si (111), Si (220), and Si (311) were observed in Figure 1A. As shown in Figure 1B, XRD peak of Si (311) shifted toward a lower angle with an increase in x , which indicates an increase in the lattice spacing with x . It is considered that some of the Si atoms can be replaced by Ge atoms and that $\text{Ge}_{0.1}\text{Si}_{0.9}$ can be a substitutional solid solution because the atomic radius of Ge (0.122 nm) is larger than that of Si (0.111 nm), but still within 15%.

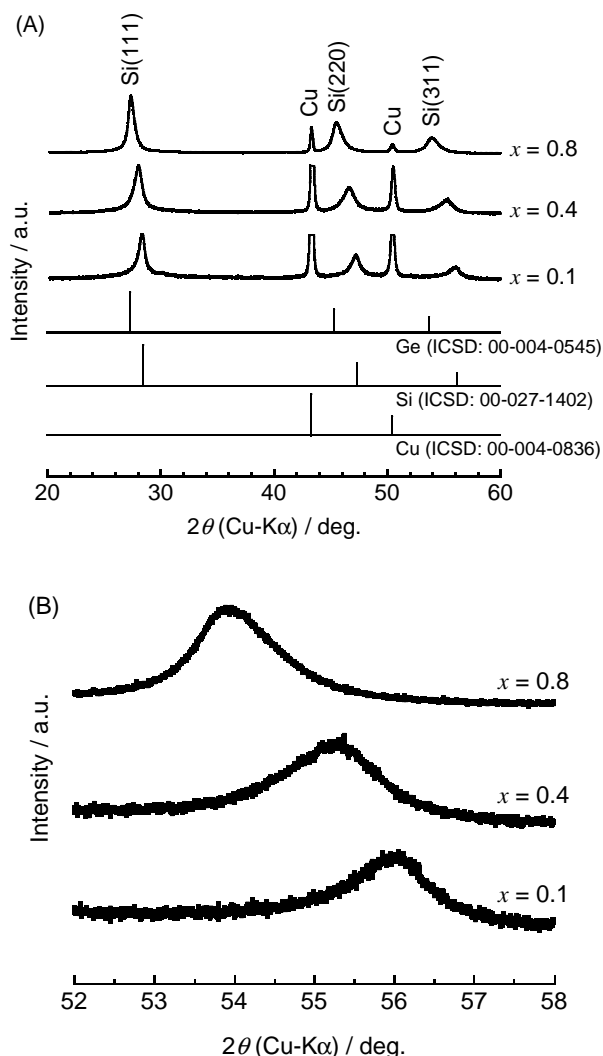


Figure 1 (A) XRD patterns of $\text{Ge}_x\text{Si}_{1-x}$ alloy powders and (B) magnified view of part A between 52 and 58°. Cu powder was used as an internal standard.

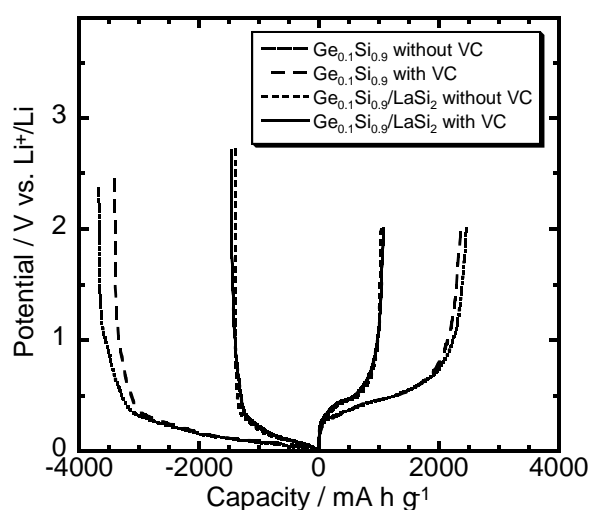


Figure 2 First charge-discharge curves of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt.%) thick-film electrodes in 1 M LiTFS/PC with and without 5 vol.% VC at 1 C rate.

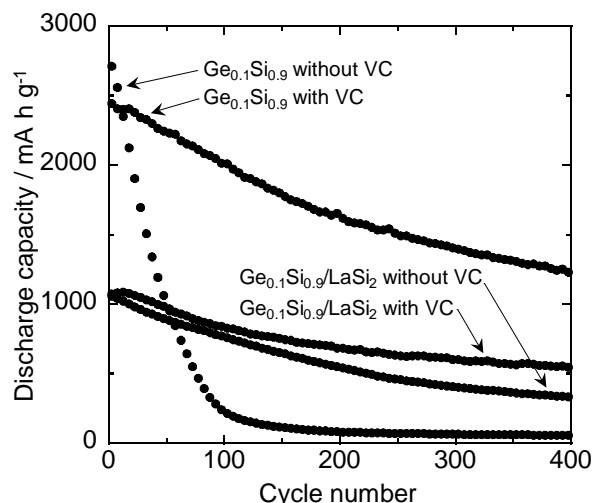


Figure 3 Cycle performance of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ in 1 M LiTFS/PC with or without 5 Vol.% VC at 1 C rate.

Figure 2 shows the first charge-discharge curves of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50/50 wt.%) electrodes in 1 M LiTFS/PC with and without 5 vol.% VC, respectively. In every case, potential plateaus were observed at 0.1 and 0.4 V vs. Li^+/Li on charge and discharge curves, respectively, which are attributed to the alloying and dealloying reactions of Si with Li. $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode showed almost the same first capacity in spite of the presence or absence of VC. The Coulombic efficiency was 70 and 67% in the electrolyte with and without VC, respectively; the efficiency was also almost the same. First capacity of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ composite electrode in VC-containing electrolyte was almost the same as that in VC-free electrolyte. While the first capacity of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ electrode was about half of that of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode, the capacity would be almost the same as that of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode when it is converted to capacity per mass of $\text{Ge}_{0.1}\text{Si}_{0.9}$ since the capacity of LaSi_2 can be ignored. In addition, the Coulombic efficiency of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ electrode was 75% in spite of the presence or absence of VC, which was higher than that of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode. The improved Coulombic efficiency should be attributed to the presumption that LaSi_2 releases the stress generated by the large volumetric change occurring in $\text{Ge}_{0.1}\text{Si}_{0.9}$ particle and the pulverization of $\text{Ge}_{0.1}\text{Si}_{0.9}$ is suppressed, and that reductive decomposition of the electrolyte does not occur on the newly formed surface.

Figure 3 shows the cycle performance of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt.%) electrodes in 1 M LiTFS/PC with and without 5 vol.% VC. While the initial discharge capacity of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode rapidly faded in 1 M LiTFS/PC, it was significantly suppressed in VC-containing electrolyte; the discharge capacity was 1240 mA h g^{-1} at 400th cycle with VC. The capacity retention of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode was 52 and 2 % at 400th cycle in 1 M LiTFS/PC with and without VC, respectively. At 800th cycle, in addition, the discharge capacity was 700 mA h g^{-1} , which was about twice as much as that of currently used graphite negative electrode. These results indicate that a VC-derived stable surface film forms on the surface of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode in VC-containing

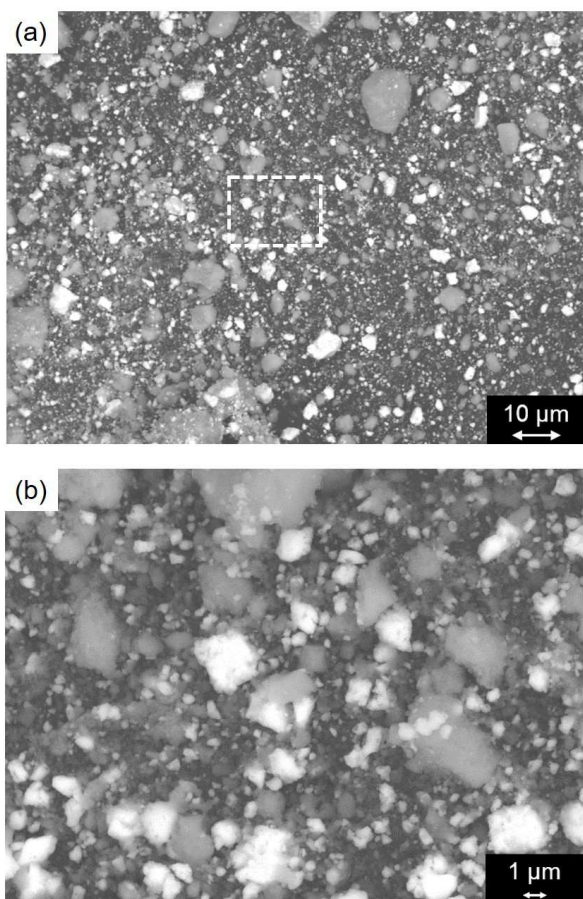


Figure 4 Backscattered electron images of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ powder. Magnification is (a) 1000 X and (b) 5000 X.

electrolyte, which the effectiveness of VC-derived surface film was confirmed on graphite and Si electrodes.^{5,7,11,12}

$\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ composite electrode also exhibited better cycle performance in VC-free electrolyte solution compared to $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode. Discharge capacity and capacity retention of the composite electrode were 332 mA h g^{-1} and 32% at 400th cycle, respectively. The reason for improved cyclability of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ electrode should be attributed to the electrical and mechanical properties of LaSi_2 . The electrical resistivity of pressed $\text{Ge}_{0.1}\text{Si}_{0.9}$ powder was estimated to be $130 \Omega \text{ cm}$, while LaSi_2 showed the resistivity of $2.2 \Omega \text{ cm}$; LaSi_2 has better electrical conductivity compared to $\text{Ge}_{0.1}\text{Si}_{0.9}$.² In addition, LaSi_2 should work as a matrix, which reduces the stress induced by the volumetric change in $\text{Ge}_{0.1}\text{Si}_{0.9}$. In addition, the cycle performance of $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ in VC-containing electrolyte solution was superior to that in VC-free electrolyte solution; the discharge capacity and the capacity retention were 543 mA h g^{-1} and 51% at 400th cycle, respectively. The discharge capacity was $1086 \text{ mA h g}(\text{Si}_{0.9}\text{Ge}_{0.1})^{-1}$ which is even equal to that of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode in VC-containing electrolyte solution.

To confirm the mixing state of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and LaSi_2 , BSE image was observed, as shown in Figure 4. It is obvious that LaSi_2 and $\text{Ge}_{0.1}\text{Si}_{0.9}$ mixed in micrometer order because BSE image reflects electron density of sample; light and dark spots in Figure 4 correspond to LaSi_2 and $\text{Ge}_{0.1}\text{Si}_{0.9}$, respectively. It is considered that these mixing state of $\text{Ge}_{0.1}\text{Si}_{0.9}$ and LaSi_2 in micrometer order contribute to the

improvement in the electrochemical performance of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode.

In summary, the cycle performance of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode was improved in VC-containing electrolyte due to a stable surface film formed on the surface of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode. In addition, the $\text{Ge}_{0.1}\text{Si}_{0.9}/\text{LaSi}_2$ (50:50 wt.%) composite electrode exhibited better cyclability because LaSi_2 which was mixed with $\text{Ge}_{0.1}\text{Si}_{0.9}$ in micrometer order should release the stress generated by large volumetric change in $\text{Ge}_{0.1}\text{Si}_{0.9}$ during charge-discharge cycle. It is proved that the film-forming additive of VC and composite electrode with LaSi_2 , which are useful for the improvement in the electrochemical performance of Si negative electrode alone, improve the cyclability of $\text{Ge}_{0.1}\text{Si}_{0.9}$ electrode.

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References

- 1 T. D. Hatchard, J. R. Dahn, *J. Electrochem. Soc.* **2004**, *151*, A838.
- 2 Y. Domi, H. Usui, Y. Takemoto, K. Yamaguchi, H. Sakaguchi, submitted for publication.
- 3 H. Usui, K. Maehara, K. Nakai, H. Sakaguchi, *Int. J. Electrochem. Sci.* **2011**, *6*, 2246.
- 4 H. Sakaguchi, T. Iida, M. Itoh, N. Shibamura, T. Hirono, *IOP Conf. Series: Mater. Sci. Eng.* **2009**, *1*, 012030.
- 5 Y. Domi, H. Usui, M. Shimizu, K. Miwa, H. Sakaguchi, *Int. J. Electrochem. Sci.* **2015**, *10*, 9678.
- 6 V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching, D. Aurbach, *Langmuir* **2012**, *28*, 965.
- 7 I. A. Profatilova, C. Stock, A. Schmitz, S. Passerini, M. Winter, *J. Power Sources* **2013**, *222*, 140.
- 8 A. M. Chockla, K. C. Klavetter, C. B. Mullins, B. A. Korgel, *ACS Appl. Mater. Interfaces* **2012**, *4*, 4658.
- 9 D. Duveau, B. Fraisse, F. Cunin, L. Monconduit, *Chem. Mater.* **2015**, *27*, 3226.
- 10 P. R. Abel, A. M. Chockla, Y.-M. Lin, V. C. Holmberg, J. T. Harris, B. A. Korgel, A. Heller, C. B. Mullins, *ACS Nano* **2013**, *7*, 2249.
- 11 S. Tsubouchi, Y. Domi, T. Doi, M. Ochida, H. Nakagawa, T. Yamanaka, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* **2013**, *160*, A575.
- 12 C.-C. Chang, S.-H. Hsu, Y.-F. Jung, C.-H. Yang, *J. Power Sources* **2011**, *196*, 9605.

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