鳥取大学研究成果リポジトリ
Tottori University research result repository

Improved Electrochemical Performance of Ge_xSi_{1-x} Alloy Negative Electrode for Lithium-Ion Batteries

Yasuhiro Domi,[1,2] Hiroyuki Usui,[1,2] Yuya Takemoto,[1,2] Kazuki Yamaguchi,[1,2] and Hiroki Sakaguchi*[1,2]

[1]*Department of Chemistry and Biotechnology, Graduate School of Engineering, and* [2]*Center for Research on Green Sustainable Chemistry, Tottori University, Minami 4-101, Koyama-cho, Tottori 680-8552, Japan*

Ge_xSi_{1-x} alloy electrode is useful to cover shortcomings of Si negative electrode for lithium-ion batteries. To improve the electrochemical performance of Ge_xSi_{1-x} negative electrode much further, film-forming additive and composite with $LaSi_2$ were applied. $Ge_{0.1}Si_{0.9}$ 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 $Ge_{0.1}Si_{0.9}/LaSi_2$ composite electrode was also superior to that of $Ge_{0.1}Si_{0.9}$ 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} ($Li_{15}Si_4$) 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 Fe-Si/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} ($Li_{15}Ge_4$) 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 lithiuation, fast Li diffusion, low electrical resistivity, and so on.[8] Ge_xSi_{1-x} alloy electrodes were also prepared and their electrochemical performance was investigated with various ratio of x. It has been reported that all Ge_xSi_{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 $Ge_{0.1}Si_{0.9}$ 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 Ge_xSi_{1-x} electrode much further, in the present study, we attempted to prepare the composite electrode consisted of $Ge_{0.1}Si_{0.9}$ and $LaSi_2$. In addition, the effect of VC on the cyclability of $Ge_{0.1}Si_{0.9}$ electrode was investigated.

$Ge_{0.1}Si_{0.9}$ and $LaSi_2$ powders were synthesized by a mechanical alloying (MA) method.[4] The stoichiometric mixture of elemental Ge and Si powders for $Ge_{0.1}Si_{0.9}$ 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 $Ge_{0.1}Si_{0.9}$ 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 $Ge_{0.1}Si_{0.9}/LaSi_2$ (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 μm in thickness. The weight and thickness of the deposited active material on the substrate were estimated to be 22 – 40 μg and ca. 2 μm, 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 $Ge_{0.1}Si_{0.9}$ and $Ge_{0.1}Si_{0.9}/LaSi_2$ (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 $Li_{15}Si_4$ and 1384 mA h g^{-1} for $Li_{15}Si_4$.[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 $Ge_{0.1}Si_{0.9}/LaSi_2$ (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 $Ge_{0.1}Si_{0.9}$, XRD measurement was performed. Figure 1 shows XRD patterns of Ge_xSi_{1-x} (x = 0.1, 0.5, 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 $Ge_{0.1}Si_{0.9}$ 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%.
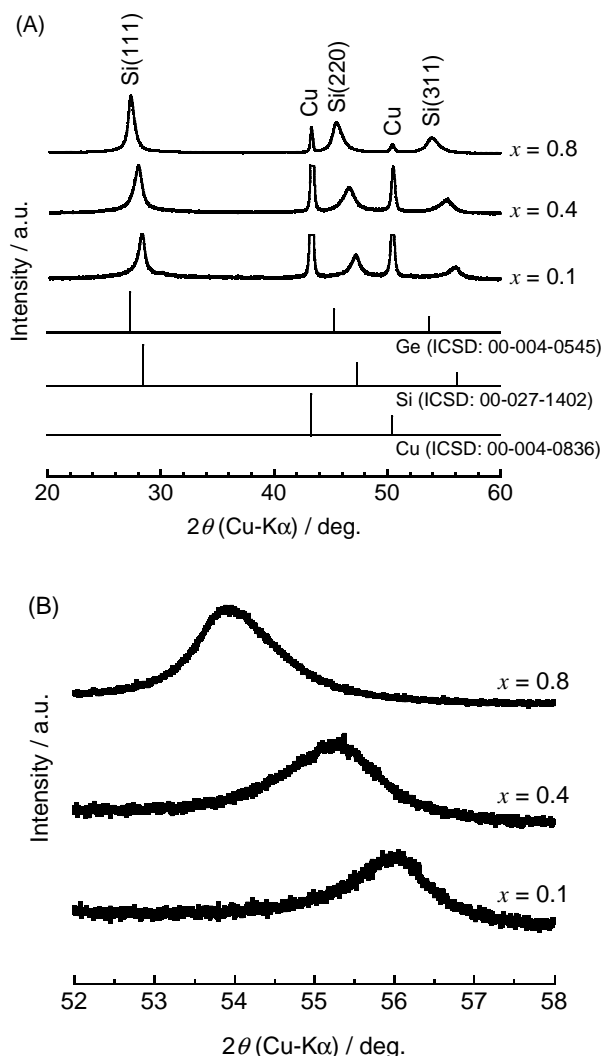
Figure 1 (A) XRD patterns of Ge$_x$Si$_{1-x}$ alloy powders and (B) magnified view of part A between 52 and 58°. Cu powder was used as an internal standard.

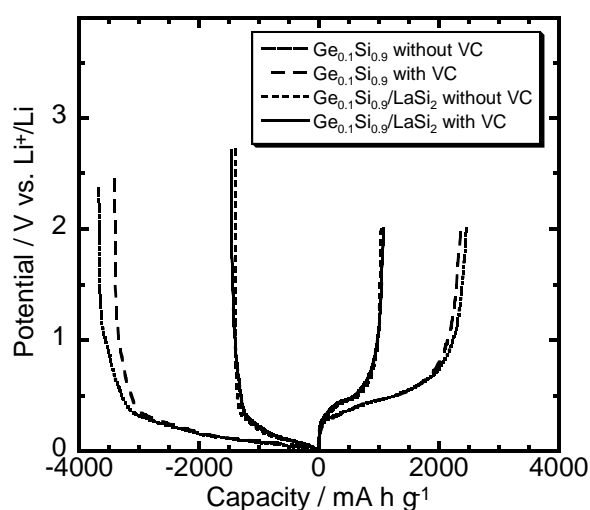Figure 2 First charge-discharge curves of Ge$_{0.1}$Si$_{0.9}$ and Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ (50:50 wt.%) thick-film electrodes in 1 M LiTFSA/PC with and without 5 vol.% VC at 1 C rate.
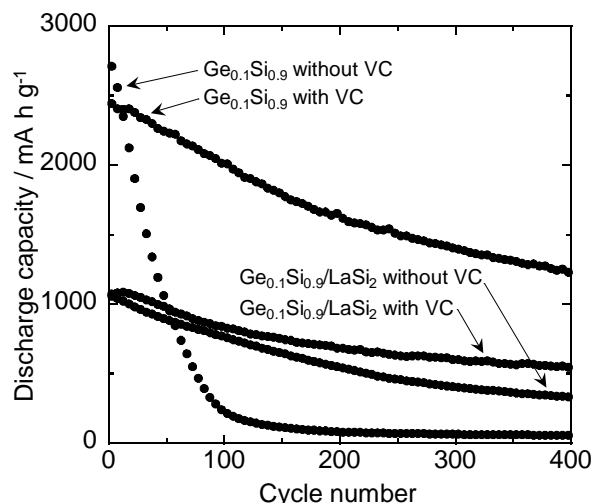

Figure 3 Cycle performance of Ge$_{0.1}$Si$_{0.9}$ and Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ in 1M TiTFSA/PC with or without 5 Vol.% VC at 1 C rate.

Figure 2 shows the first charge-discharge curves of Ge$_{0.1}$Si$_{0.9}$ and Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ (50/50 wt.%) electrodes in 1 M LiTFSA/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. Ge$_{0.1}$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 Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ composite electrode in VC-containing electrolyte was almost the same as that in VC-free electrolyte. While the first capacity of Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ electrode was about half of that of Ge$_{0.1}$Si$_{0.9}$ electrode, the capacity would be almost the same as that of Ge$_{0.1}$Si$_{0.9}$ electrode when it is converted to capacity per mass of Ge$_{0.1}$Si$_{0.9}$ since the capacity of LaSi$_2$ can be ignored. In addition, the Coulombic efficiency of Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ electrode was 75% in spite of the presence or absence of VC, which was higher than that of Ge$_{0.1}$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 Ge$_{0.1}$Si$_{0.9}$ particle and the pulverization of Ge$_{0.1}$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 Ge$_{0.1}$Si$_{0.9}$ and Ge$_{0.1}$Si$_{0.9}$/LaSi$_2$ (50:50 wt.%) electrodes in 1 M LiTFSA/PC with and without 5 vol.% VC. While the initial discharge capacity of Ge$_{0.1}$Si$_{0.9}$ electrode rapidly faded in 1 M LiTFSA/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 Ge$_{0.1}$Si$_{0.9}$ electrode was 52 and 2 % at 400th cycle in 1 M LiTFSA/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 Ge$_{0.1}$Si$_{0.9}$ electrode in VC-containing
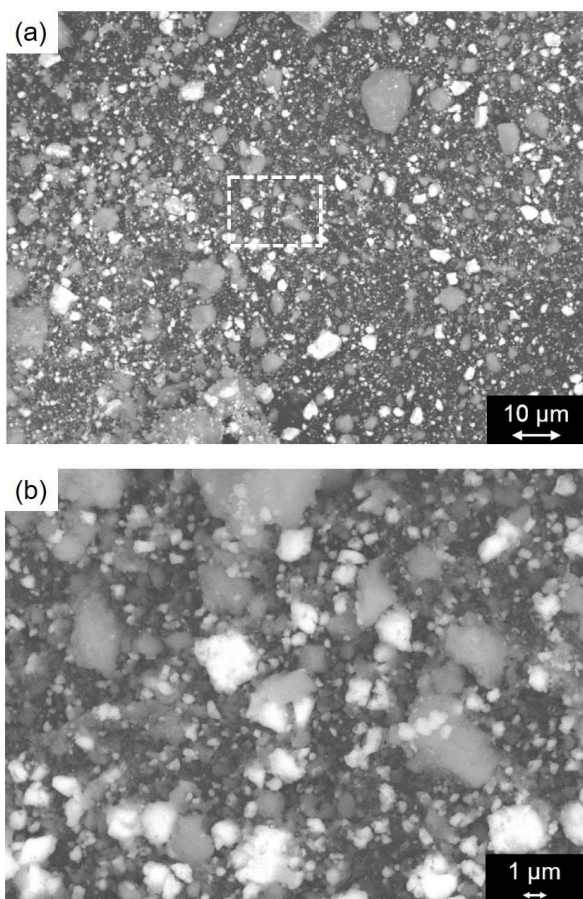
Figure 4 Backscattered electron images of $Ge_{0.1}Si_{0.9}$/$LaSi_2$ powder. Magnification is (a) 1000 X and (b) 5000 X.

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

$Ge_{0.1}Si_{0.9}$/$LaSi_2$ composite electrode also exhibited better cycle performance in VC-free electrolyte solution compared to $Ge_{0.1}Si_{0.9}$ 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 $Ge_{0.1}Si_{0.9}$/$LaSi_2$ electrode should be attributed to the electrical and mechanical properties of $LaSi_2$. The electrical resistivity of pressed $Ge_{0.1}Si_{0.9}$ powder was estimated to be 130 Ω cm, while $LaSi_2$ showed the resistivity of 2.2 Ω cm; $LaSi_2$ has better electrical conductivity compared to $Ge_{0.1}Si_{0.9}$.[2] In addition, $LaSi_2$ should work as a matrix, which reduces the stress induced by the volumetric change in $Ge_{0.1}Si_{0.9}$. In addition, the cycle performance of $Ge_{0.1}Si_{0.9}$/$LaSi_2$ 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 mA h $g(Si_{0.9}Ge_{0.1})^{-1}$ which is even equal to that of $Ge_{0.1}Si_{0.9}$ electrode in VC-containing electrolyte solution.

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

In summary, the cycle performance of $Ge_{0.1}Si_{0.9}$ electrode was improved in VC-containing electrolyte due to a stable surface film formed on the surface of $Ge_{0.1}Si_{0.9}$ electrode. In addition, the $Ge_{0.1}Si_{0.9}$/$LaSi_2$ (50:50 wt.%) composite electrode exhibited better cyclability because $LaSi_2$ which was mixed with $Ge_{0.1}Si_{0.9}$ in micrometer order should release the stress generated by large volumetric change in $Ge_{0.1}Si_{0.9}$ 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 $Ge_{0.1}Si_{0.9}$ electrode.

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. Maebara, 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.

Graphical Abstract

Textual Information

A brief abstract (required)	To improve the electrochemical performance of Ge_xSi_{1-x} negative electrode for lithium-ion batteries much further, vinylene carbonate (VC) and composite with $LaSi_2$ were applied. $Ge_{0.1}Si_{0.9}$ electrode exhibited better cyclability with discharge capacity of 1240 mA h g^{-1} at 400th cycle in the VC-containing electrolyte. The cycle performance of $Ge_{0.1}Si_{0.9}/LaSi_2$ composite electrode was also superior to that of $Ge_{0.1}Si_{0.9}$ electrode.
Title(required)	Improved Electrochemical Performance of Ge_xSi_{1-x} Alloy Negative Electrode for Lithium-Ion Batteries
Authors' Names(required)	Yasuhiro Domi, Hiroyuki Usui, Yuya Takemoto, Kazuki Yamaguchi, Hiroki Sakaguchi

Graphical Information