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Short communication

Influence of mechanical grinding on lithium insertion and extraction properties of iron silicide/silicon composites

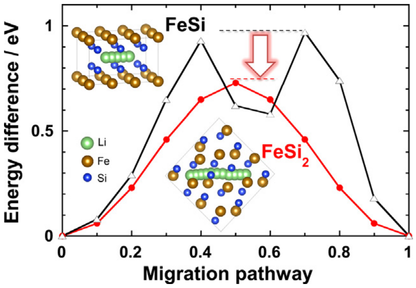
Hiroyuki Usui [a, b], Kazuma Nouno [a, b], Yuya Takemoto [a, b], Kengo Nakada [c], Akira Ishii [c], Hiroki Sakaguchi [a, b, *]

[a] Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan
[b] Center for Research on Green Sustainable Chemistry, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan
[c] Department of Applied Mathematics and Physics, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan

HIGHLIGHTS

- Anode performances of iron silicide/Si composites were studied for Li-ion battery.
- We prepared the composites by mechanical grinding for mixture of ferrosilicon and Si.
- Crystal phase changed from FeSi to $FeSi_2$ with increasing mechanical grinding time.
- Better performances were obtained for electrodes of the composites of $FeSi_2$ and Si.

GRAPHICAL ABSTRACT



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ABSTRACT

We prepared composite electrodes of iron silicide/Si by using mechanical grinding for mixtures of ferrosilicon and Si followed by gas-deposition, and investigated their electrochemical properties as Li-ion battery anode. With increasing the mechanical grinding time, the phase transformation from FeSi to $FeSi_2$ took place more significantly, and the composite electrode showed better cycle stabilities. There was no remarkable difference in mechanical properties and electronic conductivity between FeSi and $FeSi_2$. On the other hand, the $FeSi_2$ electrode exhibited about three times larger capacities in comparison with the FeSi electrode. In addition, a result of our first principle calculation indicates that Li-ion can diffuse more easily in $FeSi_2$ lattice than in FeSi lattice. It is suggested that the better cyclability of the composite electrodes was attributed to the moderate reactivity of $FeSi_2$ with Li and the smooth Li-ion diffusion in it.

1. Introduction

Li-ion battery has been extensively studied in these days not only for portable electronic devices but also for electric vehicles. In particular, much larger energy density is required for the electric vehicles. Based on this requirement, Si has attracted much attention as a high-capacity anode material in the next-generation Li-ion battery. It can accommodate 3.75 Li-ions per Si atom at room temperature [1–5]. This accommodation leads to a theoretical capacity of about 3580 mA h g^{-1}, which is approximately ten times higher than the theoretical capacity of a graphite anode in practical use. On the other hand, Si has critical disadvantages of a low

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[*] Corresponding author. Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan. Tel./fax: +81 857 31 5265.
E-mail address: sakaguch@chem.tottori-u.ac.jp (H. Sakaguchi).

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electronic conductivity, a slow kinetics of Li-ion diffusion, and significant volume changes during Li-insertion and Li-extraction. The volume changes are a very serious problem as anode material because those cause a huge mechanical stress and a loss of electrical contact between active material and current collector. The electrode performance, consequently, drastically degrades with increasing charge–discharge cycles. Many researchers have studied various composite electrodes consisted of elemental Si and other active materials compensating for the silicon's disadvantages.

Since about 2003, the authors have intensively investigated various anode materials of intermetallic compounds [6–9], Si-based composites [10–20], and elemental Si [21–23]. As a part of these results, it has been revealed that silicon's high capacity can be effectively exerted for a long term charge–discharge cycle by a combination of elemental Si and suitable other active materials. We have reported that four kinds of properties are mainly required for the active materials as follows [10–20]:

1. Mechanical properties suitable for relaxation of the stress from Si
2. High electronic conductivity
3. Moderate reactivity with Li^+
4. High thermodynamic stability

As for the fourth factor, transition metal silicides are promising as the active materials because they have generally high thermodynamic stabilities. The authors have succeeded in improving anode performances of composite electrodes consisted of elemental Si and rare-earth metal silicides such as $LaSi_2$/Si [11], mischmetal silicide ($MmSi_2$)/Si [15], and Gd–Si/Si [25]. On the other hand, we have investigated Li-insertion/extraction properties for composite electrodes of Si and base metal silicide such as $FeSi_2$/Si [15,24], $NiSi_2$/Si [24], and VSi_2/Si [15,24]. From the viewpoint of abundance and cost, it is very important to utilize iron silicides for an electrode material of large size Li-ion battery for electric vehicles and stationary batteries.

Ferrosilicon (*Fe–Si*) is one of several ferroalloys used for desulfurization and deoxidation from molten steel in a steel process. The *Fe–Si* is less expensive than metal grade Si (4 N purity) because it is widely used in great quantities in steel industry. It consists of mostly $FeSi_2$ which shows charge–discharge capacities of about several 10 mA h g^{-1}. The capacities are considered an appropriate reactivity with Li^+ as the third factor. Moreover, $FeSi_2$ has a more ductile property, a higher electrical conductivity, and a higher thermodynamic stability compared with elemental Si. As a preceding study, Ai et al. reported that $FeSi_2$/Si/C nanocomposites were synthesized by a ball-milling method, and that the nanocomposite electrodes showed an excellent capacity retention of 92% at the 200th charge–discharge cycle in a conventional organic electrolyte [26]. On the other hand, Choi and Kim et al. prepared a sputtered $FeSi_{2.7}$ ($FeSi_2$/Si composite) thin-film delivering a good retention of 92% at the 100th cycle even in an ionic liquid electrolyte [27]. They have purchased, however, commercial source materials of Fe and Si for the $FeSi_2$ synthesis though the composites of $FeSi_2$ and Si were found to be excellent anode active materials. Therefore, it is expected that *Fe–Si* becomes a promising candidate to be combined with Si as a low-cost anode material. In this study, we applied *Fe–Si* to Si-based composite electrodes and investigated their electrochemical properties as Li-ion battery anode.

2. Experimental

As an active material, *Fe–Si* and Si powders (Silgrain® e-Si, Elkem AS) were used. The average particle sizes of the *Fe–Si* and Si powders were approximately 60 μm and 10 μm, respectively. A mechanical grinding (MG) was performed for a mixture of the *Fe–Si* and Si powders to obtain a composite active material of *Fe–Si* and Si (*Fe–Si*/Si). The mixture of the *Fe–Si* and Si powders was put in a zirconia vessel together with balls so that the weight ratios of *Fe–Si*:Si were 70:30, 50:50, and 30:70. The weight ratio of the balls to the active materials was 15:1. The vessel used was sealed to keep an atmosphere of dry argon gas. The MG was carried out by using a high-energy planetary ball mill (P-6, Fritsch) for 10, 20, and 30 h with a rotation speed of 380 rpm at room temperature, resulting in a formation of *Fe–Si*/Si composite powders. The particle sizes of the composite powders were measured by a using a laser diffraction particle size analyzer (SALD-2300, Shimadzu Co. Ltd.). The typical sizes of primary particles were confirmed to be about 0.1 μm. The crystal structure of the powders was confirmed by using X-ray diffraction (XRD, Ultima IV, Rigaku). A reference breaking strength of the powders was measured by a uniaxial compression test using a dynamic ultra-micro hardness tester (DUH-211S, Shimadzu Co. Ltd.). In this study, the reference breaking strength was defined as an applied pressure when a compressed particle of the powder showed 10% deformation compared with its original size. The electrical resistivity was measured for the powders under a uniaxial press of 55 MPa using a two probes method.

Thick-film electrodes of *Fe–Si*/Si composites were prepared by a gas-deposition (GD) method [9,23]. This method is a unique process in which thick-films thicker than 1 μm consisting of various metal, alloy, and oxide powders can be easily formed by a single deposition without any binder. Procedures and conditions of thick-film electrode preparation have been described in our previous reports [9–23]. In this study, we prepared *Fe–Si*/Si composite film electrodes by using a nozzle with 0.5 mm in diameter, an Ar carrier gas with a purity of 99.99% under a differential pressure of 7.0×10^5 Pa, and a current collector of Cu foil substrate with 20 μm in thickness. The active material weights in the electrodes were typically kept within the range of 46–79 μg.

Li-insertion/extraction properties of the composite electrodes were evaluated in a beaker-type there-electrode cell. We assembled the composite electrodes as a working electrode, Li metal sheets (Rare Metallic, 99.90%) as counter and reference electrodes, and $LiClO_4$ dissolved in propylene carbonate (PC; $C_4H_6O_3$, Kishida Chemical Co., Ltd.) at a concentration of 1 M as the electrolyte. Galvanostatic charge–discharge tests were carried out using an electrochemical measurement system (HJ-1001 SM8A, Hokuto Denko Co., Ltd.) at 303 K with potential ranges of 0.005–2.000 V vs. Li/Li^+. The current densities were set to be 1.0 A g^{-1}, corresponding to current rates of 0.40–0.93 C.

To investigate behavior of Li-ion migration in iron silicides, we performed first principle calculations based on density functional theory (DFT) using projector augmented wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [28,29]. The local density approximation (LDA) was also used as the term exchange correlation with a cutoff energy of 350 eV and all calculations performed nonmagnetically. The Brillouin zone sampling was done via a (6 × 6 × 6) *k*-point mesh within Gamma point centered mesh scheme. Structural relaxation was carried out to determine all atomic positions after Li was inserted into crystal lattices of $FeSi_2$ and FeSi. We calculated a formation energy E_f for Li-inserted $FeSi_2$ in a super cell consisted of six unit cells as an interstitial solid solution ($Li_{0.17}FeSi_2$) from a total energy E_{total}. The E_f of $Li_{0.17}FeSi_2$ was defined by

$$E_f(\mathrm{Li_{0.17}FeSi_2}) = E_{\mathrm{total}}(\mathrm{Li_{0.17}FeSi_2}) - 0.17E_{\mathrm{total}}(\mathrm{Li}) - E_{\mathrm{total}}(\mathrm{FeSi_2}).$$

As for Li-inserted FeSi, E_f of $Li_{0.06}FeSi$ in a super cell consisted of four unit cells was calculated by equation of