Microstructures of nanoporous-Si composite anodes in sulfide-based all-solid-state lithium-ion batteries

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Abstract. Nanoporous-Si composite anodes with different dispersibility were prepared to compare the electrochemical performances of sulfide-based all-solid-state lithium-ion batteries. Ball-milled anode with higher dispersibility exhibited the capacity retention of 80% at 150th cycle. The structure and composition were accurately analyzed using field emission scanning electron microscope with energy dispersive x-ray spectrometer. The both of the pores in Si particles and the elastic deformation of solid electrolyte effectively relieved the stress derived from the volume change of highly dispersed nanoporous Si, resulting in the high capacity retention.

1. Introduction

All-solid-state lithium-ion batteries (LIBs) with high safety and reliability are the dominant power source for electric and hybrid vehicles. To meet the energy demands of near-future automobile technology, the anode materials should possess the enhanced storage capacity, high energy density, and long cycle life. Though Si is the most attractive choice because of its high theoretical capacity (4200 mAh g\textsuperscript{-1}), there are few applications for the all-solid-state LIBs [1,2]. In contrast, significant problems prevent the practical use of Si in the LIBs using liquid electrolytes. The large volumetric fluctuation (>300%) in lithiation/delithiation causes the mechanical fracture of Si-based anodes and repeats the formation of surface electrolyte interface (SEI). These behavior result in the poor cycle life, drastic irreversible capacity loss, and low coulombic efficiency (CE). To overcome these issues, nanosizing (e.g., nanowire, nanotube, hollow nanosphere) is effective to relieve the structural stress [3,4]. Despite the superior performance, these promising candidates have disadvantages such as the high manufacturing costs and handling difficulty.

Our interest focuses on porous particles, because the pores are expected to act as the buffer region for volume change. Very recently, we have found that all-solid-state LIB with nanoporous-Si composite anode exhibited high capacity retention [5]. In general, the performance of LIBs strongly depends on the microstructural features of electrodes. Therefore, it is important to optimize the systematic design of porosity, dispersibility, particle size and shape. In the present study, the nanoporous-Si composite anodes with different dispersibility were prepared by ball milling and mortar milling to elucidate the cause of the observed stable cyclability. We report here the results of structural, compositional, and electrochemical studies on the sulfide-based all-solid-state LIBs with nanoporous-Si composite anodes.
2. Experimental procedures

2.1. Preparation
Nanoporous-Si particles were prepared through air-oxidation demagnesiation of Mg$_2$Si using Qian's method [6]. Mg$_2$Si (1000 mg) and Mg (30 mg) were mechanically milled at 1800 rpm for 15 min. The mixture was oxidized in air at 700 °C for 12 hrs. All of the following procedures were performed under dry Ar atmosphere. Si particles were collected by centrifugation after washing the oxidation product with HCl, followed by deionized water and ethanol three and two times, respectively. Solid electrolyte (SE), Li$_3$PS$_4$ glass, was prepared by mechanical milling of Li$_2$S and P$_2$S$_5$ [7]. Anode composite material was comprised of the nanoporous-Si particles (36wt%), SE powder (55wt%), and acetylene black (AB: 9wt%). We adopted two mixing methods, ball milling and mortar milling, to vary the dispersion degree of Si particles. Mechanical ball milling was conducted by using high speed mixer (CM-1000, EYELA) equipped with ZrO$_2$ balls (φ 4 mm and φ 1 mm) under rotation speed of 1800 rpm for 60 min. Mortar milling was carried out for 10 min.

All-solid-state half-cells were fabricated as follows. In an electric insulation tube with 10 mm diameter, the SE powder (80 mg) and anode composite material (2 mg) were pressed under 330 MPa to make two-layered pellet. As the counter electrode, Li-In foil was attached on the SE side. Finally, the three-layered pellet was compressed at 70 MPa using stainless-steel disks.

2.2. Structural, compositional, and electrochemical measurements
XRD patterns of the nanoporous-Si particles were measured with Rigaku SmartLab using CuKα radiation. To accurately analyze the cross section of the nanoporous-Si composite anodes, the samples were transferred to a polishing machine (IB-19520CCP, JEOL) using vacuum vessel. The surface was carved with 4 keV Ar$^+$ ion beam, the ion current being 70–80 µA. The structure and composition were evaluated using field emission scanning electron microscope (FE-SEM: JSM-7800F, JEOL) with energy dispersive x-ray spectrometer (EDX).

By a charge/discharge measurement device (BTS-2004, Nagano), the electrochemical tests were conducted in the constant current mode of 0.127 mA cm$^{-2}$ for initial 3 cycles and 0.3 mA cm$^{-2}$ for the following cycles at 30 °C. The cut-off voltages were 0.88 and -0.58 V vs Li-In, corresponding to 1.50 and 0.04 V vs Li$^+$/Li.

3. Results and discussion

3.1. Structural and compositional characteristics
FE-SEM image of the grain comprising nanoporous-Si particles is shown in figure 1. The disordered nanometer pores were clearly observed on the grain surface. By applying the Scherrer equation to XRD data, the average crystallite size of Si particles was estimated to be about 55 nm. Figure 2 shows EDX mapping images of the nanoporous-Si composite anodes. Si and SE are colored in white and black, respectively. In the ball-milled anode, nm-sized Si particles were highly dispersed in the SE. On the other hand, some Si particles were aggregated in the mortar-milled anode. Since the both anodes contain the same quantity of nanoporous-Si particles, the observed difference is caused by the mixing methods. Namely, the dispersibility in the ball-milled anode is concluded to be higher than that in the mortar-milled anode.
Figure 1. FE-SEM image of nanoporous-Si grain.

Figure 2. Cross-sectional EDX mapping images of (a) ball-milled and (b) mortar-milled nanoporous-Si composite anodes. Si and SE are colored in white and black, respectively.

3.2. Electrochemical characteristics

Figure 3(a) shows the first charge/discharge curves of the half-cells with ball-milled and mortar-milled nanoporous-Si composite anodes. The former possessed the initial charge and discharge capacities of 2543 and 1240 mAh g$^{-1}$, respectively, resulting in CE of 49%. In the latter, their values were 3259 and 2300 mAh g$^{-1}$, corresponding to 71% CE. Figure 3(b) shows the cycle characteristics of ball-milled and mortar-milled anode cells. It is worthy to note that the discharge capacity was maintained in the former, resulting in the capacity retention of 80% at 150th cycle. In contrast, the lower capacity retention, 44% at 150th cycle, was obtained in the latter. To precisely estimate the capacity retentions, they were calculated from the maximum discharge capacities at 15th and 4th cycles for the former and latter, respectively. Previously, non-porous nano-Si composite anode cells have exhibited the poorer electrochemical performances with the discharge capacity less than 1000 mAh g$^{-1}$ at scant 20th cycle [2]. Hence, the retained capacities are extremely high in the nanoporous-Si composite anode cells.

Figure 3. (a) Charge/discharge curves during the first cycle and (b) plot of discharge capacity versus cycle number of sulfide-based all-solid-state half-cells with ball-milled and mortar-milled nanoporous-Si composite anodes.
3.3. Microstructures

To consistently explain the structural, compositional, and electrochemical features described above, we propose the microstructural models for the nanoporous-Si composite anodes. Specifically, the nanoporous-Si particles are highly dispersed in the ball-milled anode (figure 4(a)), while µm-sized Si aggregates exist in the mortar-milled anode (figure 4(b)).

![Figure 4. Microstructural models of (a) ball-milled and (b) mortar-milled nanoporous-Si composite anodes.](image)

Since a lot of pores on the surface of Si particles are exposed to SE in the ball-milled anode, SEI should be easily formed at the first cycle, leading to the large amount of irreversible Li consumption. This finding successfully explains that the initial CE is smaller than that of the mortar-milled anode cell. However, SEI is hard to become thick with the increase of charge/discharge cycle. This is because SE possesses high stability and low fluidity in comparison with liquid electrolytes [8].

In regards to the capacity retention, we note the contact state between SE and Si particles/aggregates. Though the volumetric expansion is buffered by the shrinkage of pores, the nanoporous-Si particles slightly become large during lithiation. In the case of highly dispersed Si particles (figure 4(a)), the stress arising from the expanded Si particles should be relieved by the elasticity of surrounding SE. During delithiation, elastically deformed SE returns to the original shape and maintains the contact with Si. In contrast, the µm-sized nanoporous-Si aggregates should give larger stress to the surrounding SE, leading to the plastic deformation of SE (figure 4(b)). Thus, in the delithiation process, voids are formed between the Si aggregates and plastically deformed SE, resulting in the lower capacity retention.

4. Summary

Sulfide-based all-solid-state LIB with ball-milled nanoporous-Si composite anode exhibited the capacity retention of 80% at 150th cycle. Composition mapping analysis indicated that nm-sized Si particles were highly dispersed in the SE-AB matrix. Based on the comparative results with the mortar-milled cell, the highly dispersed nanoporous-Si particles form the intimate contact with SE due to the buffer effect of pores and elastic deformation of surrounding SE. In these respects, we currently make effort to compare the structure and composition between the before and after charging/discharging by high-resolution FE-SEM/EDX system.

Acknowledgments

The authors gratefully acknowledge Visiting Professor Yutaka Fujiwara and Yasuyuki Agari (Nara Inst. Sci. Tech.) for their valuable discussions. This work was partially supported by JSPS KAKENHI Grant Numbers JP16K06787, JP16K05949.
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