



Morphology changes and long-term cycling durability of Si flake powder negative electrode for lithium-ion batteries

Masakazu Haruta^{a, *}, Ryuya Hioki^a, Takashi Moriyasu^a, Akira Tomita^b, Toshio Takenaka^b, Takayuki Doi^a, Minoru Inaba^a

^a Doshisha University, Tatara-Miyakodani, Kyotanabe, Kyoto 610-0321, Japan

^b OIKE & Co., Ltd., Kamitoba, Minami-ku, Kyoto 601-8121, Japan



ARTICLE INFO

Article history:

Received 17 November 2017

Received in revised form

9 February 2018

Accepted 10 February 2018

Available online 12 February 2018

Keywords:

Lithium-ion battery

Silicon negative electrode

Li-Si alloy

Flake powder

Solid electrolyte interface

ABSTRACT

Silicon flake powder (Si LeafPowder[®], Si-LP) with the thickness and lateral dimension of 100 nm and 3–5 μm, respectively, demonstrated superior cycle performance as a negative electrode in lithium-ion batteries. A multi-folded layered structure with many voids was spontaneously formed in Si-LP composite electrodes by morphology changes of Si-LP sheets in repeated charge and discharge cycles. The multi-folded layered structure accommodated volumetric changes of the Si active material and prevented exfoliation of the active material from the current collector, which led to the superior long-term cyclability of the Si-LP electrode. The main factor for capacity fading in long-term cycling was a gradual loss of conduction pathways between Si-LP sheets due to the accumulation of electrolyte reduction products in the electrode. The film-forming additives, vinylene carbonate and fluoroethylene carbonate, effectively suppressed the electrolyte decomposition and remarkably improved the cycle performance of the Si-LP electrode.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Demand for advanced lithium-ion batteries (LIBs) with high energy densities for electric vehicles and large-scale stationary energy storages has increased. Li-Si alloys are promising negative electrode materials for next-generation LIBs with high energy densities because of high gravimetric capacity and volumetric capacity (3578 mAh g⁻¹ and 2194 mAh cm⁻³, respectively, for Li₁₅Si₄), and relatively low discharge potentials (c.a. 0.4 V vs. Li/Li⁺ on average) [1–5]. However, the Li-Si alloy electrodes have encountered a serious problem, i.e. poor capacity retention in repeated charge and discharge (lithiation and de-lithiation, respectively) cycles.

Poor cyclability of Si electrodes is attributed to crack formation and pulverization of Si active material due to a large volume expansion and contraction during charging and discharging, respectively. It is important to suppress the physical stress induced by the large volume changes to improve the cyclability of Si electrodes. A variety of nanostructured Si materials have been reported

such as nanopowders [6,7], nanowires [8–10], core-shell and hollow shaped structures [11–14], and thin-films [15–17]. We designed a Si powder with a flake shape (Si LeafPowder[®], Si-LP, OIKE & Co., Ltd.) that was 100 nm thick with a 3–5 μm lateral dimension and reported high initial discharge capacity (ca. 2500 mAh g⁻¹) with good cyclability [18–20]. The Si-LP has a one-dimensionally nano-sized, simple structure and a specific surface area smaller than that of conventional nano-sized Si powders, and thus the contents of the conductive agent and binder in composite electrodes can be reduced. The cyclability of the Si-LPs were improved with film-forming additives such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), which assisted the formation of a stable solid electrolyte interface (SEI) that functioned as a passive layer against further electrolyte decomposition [21].

We investigated the effects of SEI forming additives, VC and FEC, on long-term cyclability (up to 500 cycles) of the Si-LP negative electrode in detail. We focused on microstructural changes of the composite electrodes with cycling and clarified the capacity fading mechanism of the Si-LP electrode by scanning electron microscope (SEM) observation of the surface and the cross-section of the electrode as well as electrochemical impedance spectroscopy (EIS) measurements. The superior cycle performance of Si-LP originated from unique microstructural changes of the Si-LP

* Corresponding author.

E-mail address: mharuta@mail.doshisha.ac.jp (M. Haruta).

electrode upon long-term cycling.

2. Experiments

The Si-LP was prepared by an electron-beam evaporation method with a roll-to-roll process. A Si thin film of approximately 100 nm thickness was deposited on a polymer-coated metal sheet. The Si film was peeled from the metal sheet and crushed into micro-flakes with a lateral dimension of 3–5 μm to form Si-LP. The amorphous structure of the Si-LP was confirmed by X-ray diffraction and Raman spectroscopy.

Composite electrodes were prepared using Si-LP, Ketjen Black (KB, Lion Corp.) as a conductive agent, and carboxymethyl cellulose sodium salt (CMCNa, Nippon Paper Industries Co., LTD.) as a binder. They were mixed in distilled water to obtain a slurry, where the weight ratio of the solid contents was Si-LP:KB:CMCNa = 83.3:5.6:11.1. The slurry was coated on a Cu foil current collector with a thickness of 20 μm by the doctor blade method and dried overnight in an oven at 80 $^{\circ}\text{C}$ under vacuum. The loading of the Si-LP composite on the Cu foil was typically 0.3 mg cm^{-2} . The thickness of the composite electrode without pressing was 3–4 μm . A coin-type half-cell was assembled with the Si-LP composite electrode as a working electrode, a separator (Celgard[®] 2400, Celgard, LLC.), and a Li foil (Honjo Metal Co., Ltd.) as a counter electrode in an Ar-filled glovebox (Miwa MFG Co., Ltd.) with a dew point under -70°C . The electrolyte solution of 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (3:7 by volume) was purchased from Kishida Chemicals Co. Ltd. (Lithium Battery Grade). VC (Kishida Chemicals Co. Ltd.) or FEC (Kishida Chemicals Co. Ltd.) additives were added by 10 wt% to the electrolyte in subsequent experiments.

Charge and discharge characteristics were measured at 30 $^{\circ}\text{C}$ using a battery test system (TOSCAT-3100, Toyo System Co., Ltd.). The electrodes were lithiated at a rate of C/2 to 20 mV, where it was kept until the current decayed to a value of C/20, and delithiated at C/2 to 1.5 V. EIS was performed using a three-electrode cell consisting of Si-LP working, Li counter, and Li reference electrodes. Impedance spectra were obtained by applying an AC voltage with an amplitude of 10 mV over the frequency range of 0.03 Hz–300 kHz using a potentiostat/galvanostat equipped with a frequency response analyzer (SP-150, Biologic). The EIS spectra were measured at 0.1 V in the charging process of the Si-LP electrodes.

After the charge and discharge tests, the cells were disassembled in the glovebox, and the Si-LP electrodes were rinsed with 1,2-dimethoxyethane to remove residual solvent and salt. The surface morphology of the composite electrodes before and after the charge and discharge tests was observed with a SEM (SU8220, HITACHI Ltd.) at an acceleration voltage below 1 kV to avoid irradiation damage from the electron beam. The rinsed electrodes were

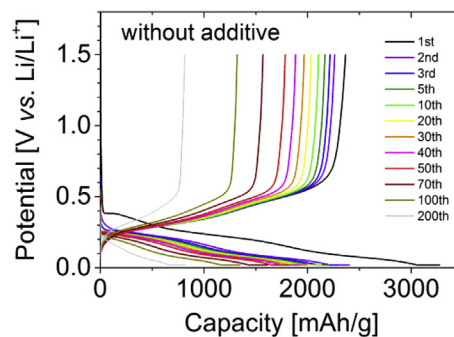


Fig. 2. Charge and discharge characteristics of the Si-LP electrode at a C/2 rate in 1 M LiPF₆/EC + DEC without additives.

dried in the glovebox and transferred to the SEM chamber using a transfer vessel without air exposure. For cross-sectional observation, a roughly cut cross-section of the electrode was polished with an Ar-ion milling system (IM4000 plus, HITACHI Ltd.) in which the specimen was cooled with liquid nitrogen to avoid damage from the Ar-ion beam. Elemental analysis was conducted by SEM equipped for energy dispersive X-ray spectroscopy (EDX, XFlash5060FQ, Bruker) at an acceleration voltage of 4 kV, in which the electron interaction depth was estimated to be approximately 200 nm.

3. Results and discussion

3.1. Electrochemical properties of Si-LP electrodes

A SEM image of the surface of the Si-LP composite electrode before cycling is shown in Fig. 1a. Si-LP sheets of 3–5 μm in the lateral dimension and highly dispersed KB particles (ca. 50 nm) were observed. From the cross-sectional SEM image (Fig. 1b), the uniformly stacked Si-LP sheets aligned parallel to the Cu current collector were confirmed. The thickness of the Si-LP composite electrode (t_{elec}) was typically 3 μm before cycling.

Charge and discharge characteristics of the Si-LP electrode up to 200 cycles without additives are shown in Fig. 2, and those with VC and FEC are shown in Fig. S1. The potential changed monotonously on charging and discharging without any clear potential plateaus, which indicates the absence of Li₁₅Si₄ formation [22,23]. Moreover, the Li₁₅Si₄ phase was not observed for the Si-LP electrode even in the case of a slow rate (C/100) even when charged to a lower potential (5 mV) as shown in Fig. S2. The initial discharge capacity was approximately 2400 mAh g^{-1} in the absence or presence of the additives. The addition of VC and FEC improved the capacity retention and suppressed an increase in overpotential upon cycling as shown in Fig. S1.

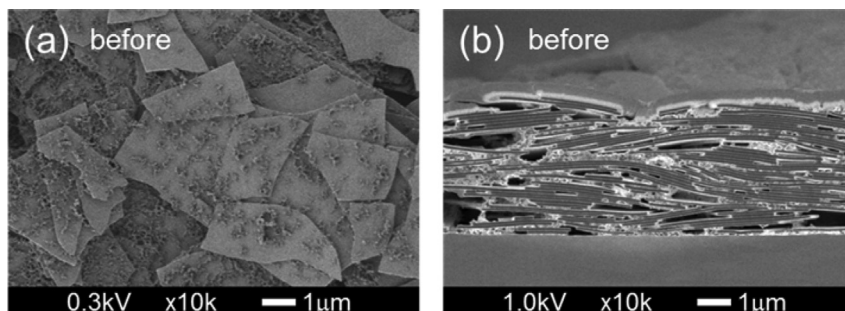


Fig. 1. SEM images of (a) surface and (b) cross-section for the Si-LP composite electrode before cycling.

Download English Version:

<https://daneshyari.com/en/article/6603900>

Download Persian Version:

<https://daneshyari.com/article/6603900>

[Daneshyari.com](https://daneshyari.com)