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Investigation on silicon alloying kinetics during lithiation by galvanostatic impedance spectroscopy

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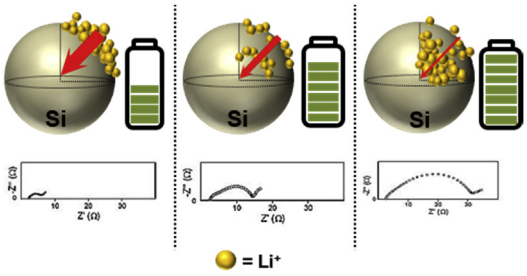
HIGHLIGHTS

- Si lithiation process was investigated by galvanostatic impedance spectroscopy.
- Kinetic parameters were obtained during galvanostatic lithiation.
- A fast charging strategy was designed to lithiate silicon anodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The parameters characterizing lithiation processes in silicon anodes of lithium ion batteries (LIBs) are compared between μm- and nm-sized silicon particles. Galvanostatic electrochemical impedance spectroscopy (GS-EIS) is used to investigate the silicon-lithium alloying reaction in a practical charging operation (galvanostatic lithiation). Effective kinetic parameters depending on lithiation C-rates are obtained along lithiation progress from a large body of impedance data. Nanosizing benefits of nanoparticles over micro-particles are confirmed such as lower polarization resistance (R_p) and thinner solid-electrolyte interphase layer (SEI layer) over the whole lithiation range. Based on the kinetic information obtained from the non-stationary conditions, a lithiation strategy consisting of multiple galvanostatic steps is designed to lithiate silicon anodes in a faster way. 75% of full capacity is lithiated by a galvanostatic sequence of 4C–2C–1C–0.5C within 20 min. However, only 43% and 21% are achieved by a single-rate galvanostatic lithiation at 1 C and 0.5 C, respectively.

1. Introduction

Silicon is one of the most promising anode materials of lithium ion batteries (LIBs) [1–4]. It offers large theoretical capacity of ~4200 mAh g^{-1}, being alloyed with lithium ions to $Li_{4.4}Si$ phase [5]. However, silicon has a drawback of >300% reversible volume expansion on complete charging [6] so that it is pulverized during repeated lithiation/delithiation cycles and subsequently cracks are developed on electrodes. Consequently, the capacity of silicon-based lithium ion cells decayed or faded with cycles [7,8]. Nanosizing and nanostructuring of silicon has been proposed to overcome capacity loss during cycling [9–11]. Reducing its particle size shortens lithium ion diffusion length resulting in faster kinetics and suppresses pulverization by keeping volume expansion within a critical dimension beyond which pulverization or crack development occurs.

When lithium ions are alloyed with silicon, a series of

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polarizations are involved. Lithium ions in electrolyte reach the surface of silicon wrapped with the solid electrolyte interface (SEI) layer, experiencing ohmic polarization represented by a solution resistance R_S. They enter the SEI layer from electrolyte and then move to silicon, overcoming activation polarizations relevant to each step (R_{SEI} and R_{CT}) [12,13]. After being alloyed with silicon, lithium ions are diffused throughout silicon mass along a concentration gradient (concentration polarization) [14,15]. The kinetic parameters of each step constituting an overall electrochemical process can be investigated by electrochemical impedance spectroscopy (EIS) because the EIS can deconvolute the overall process into its constituent steps by frequency. Impedance spectra are conventionally obtained at a fixed potential (by potentiostatic EIS or PS-EIS) after a stationary state is reached. However, the electrode-electrolyte interfaces in LIBs change dynamically during practically used galvanostatic lithiation and delithiation [13,16,17]. For this reason, the electrochemical parameters measuring polarization obtained by PS-EIS cannot describe the time-variant situations where the states of charge (SOC) cannot be defined only by corresponding potentials and the kinetic parameters depend on lithiation or delithiation rates. Therefore, impedance spectra should be obtained *in situ* by applying a current signal in which a sinusoidal current perturbation of a small intensity is overlapped to a fixed charge or discharge current (instead of a biased potential with a sinusoidal potential perturbation). The galvanostatic EIS (GS-EIS) successfully revealed the rate-dependent kinetics of lithium ion intercalation into graphite [18,19].

In this work, we compared the lithiation kinetics between nano-dimensional and micro-dimensional silicon particles in practical battery operation conditions by GS-EIS. The apparent kinetic parameters were highly dependent not only on SOC at a fixed rate but also on C-rates. Based on the kinetic information extracted from the *in situ* impedance spectra, a fast charging (lithiation) strategy was designed in a way that higher C-rates are preferred as far as lithiation kinetics can afford the rate.

2. Experimental

2.1. Cell preparation

A slurry of 60:20:20 mixture Silicon nanoparticular silicon (nSi; Alfa Aesar, average particle size = ~50 nm) or microparticular silicon (μSi; Shanghai chemical, average particle size = 3–8 μm), a conducting agent (Super P) and PAA/CMC (1:1 polyacrylic acid: carboxymethyl cellulose) binder was coated in 18 μm thickness on a current collector (18 μm thick copper foils) and then dried at 150 °C for 2 h in a vacuum oven. Loading densities of silicon mass were fixed at ~0.63 mg cm^{-2}. Capacity densities were 2.0 mAh cm^{-2} for nSi and 1.3 mAh cm^{-2} for μSi, which were calculated from the capacities measured at 0.05 C. 2032-type half coin cells were assembled in Argon-filled glove box. Lithium foil was the counter electrode and 1.3 M LiPF6 in 3:7 (v/v) ethylene carbonate (EC): diethyl carbonate (DEC) with 10% fluoroethylene carbonate (FEC) was the electrolyte. A micro-porous polyethylene film (Asahi NH716, 20 μm thick) was used as the separator. The cells were galvanostatically charged/discharged in a voltage range of 0.01 V–1.2 V vs. Li/Li^+ at 0.05 C three times for stabilizing before experiments by using a battery cycler (WonATech/WBCS 3000). The currents for 1 C were defined as 3000 mA g^{-1} (2.0 mA cm^{-2}) for nSi and 2000 mA g^{-1} (1.3 mA cm^{-2}) for μSi.

2.2. Impedance measurement by GS-IES

After the cells were conditioned by three repeated cycles of charge/discharge, the impedance spectra of cells containing delithiated silicon anodes were measured by GS-EIS during galvanostatic lithiation. The input signals were synthesized by superimposing sinusoidal alternating current waves of small amplitude (10 μA) at 200 kHz to 1 Hz onto a fixed direct current determined by the C-rate we chose. One channel in a multi-channel potentiostat (BioLogic/VSP-300) was used for generating sinusoidal waves and measuring outputs for impedance spectra while the other channel synthesized the inputs, applied them to cells and recorded voltages for voltage profiles. The impedance spectra were measured every 10 min for 0.1 C, 5 min for 0.5 C and 1 C, and 3 min for 2 C. Kinetic parameters were obtained by fitting experimental impedance data with an equivalent circuit model (ZSimpWin).

2.3. Lithiation by C-rate switching (CRS)

All cells were kept at 1.5 V vs. Li/Li^+ using a battery cycler before C-rate switching (CRS) experiments. The experiments were carried out galvanostatically in four different conditions. Two cells, as controls, were continuously lithiated to Si with 1 and 0.5 C respectively. The test cell was lithiated in CRS-mode using an automatically controlled computer program. The current was applied to the cell with a series of 4 C, 2 C, 1 C and 0.5 C, consecutively.

3. Results and discussion

Lithiation processes of μSi and nSi were investigated *in situ* by

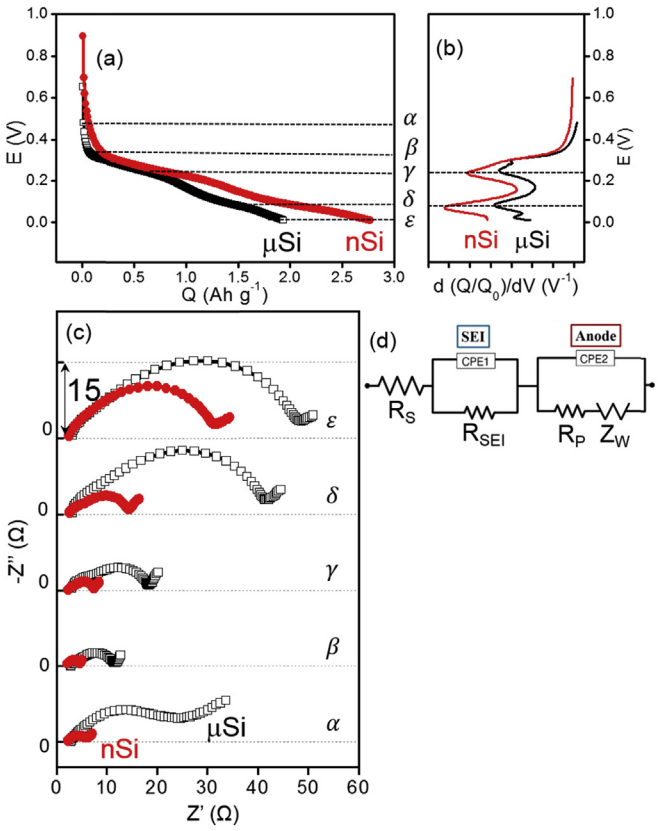

Fig. 1. Lithiation of μSi (black square) and nSi (red circle) at 0.1 C as a slow rate. Charge transfer is supposed to be limited. (a) Voltage profiles. (b) Differential capacity with respect to voltage calculated from (a). (c) Impedance spectra obtained at Greek letters in (a). (d) The equivalent circuit to describe the experimental data shown in (c). The impedance data in Warburg region were excluded for fitting so that the circuit for fitting did not include the Warburg element (Z_W). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).