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Amorphous silicon dioxide-based composites for high-performance Li-ion battery anodes

Seung-Su Lee, Cheol-Min Park*

School of Materials Science and Engineering, Kumoh National Institute of Technology, 61 Daehak-ro, Gumi, Gyeongbuk 39177, Republic of Korea

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ABSTRACT

To design high performance SiO_2-based anodes for Li-ion batteries (LIBs), an amorphous SiO_2-FeSi-graphite (*a*-SiO_2/FeSi/G) composite was synthesized by a simple solid state synthetic method using SiO, Fe, and graphite powders. The *a*-SiO_2/FeSi/G composite was comprised of well dispersed amorphous SiO_2 and tiny (5–10 nm sized) FeSi inactive matrices within the graphite buffering matrices. The *a*-SiO_2/FeSi/G composite electrode showed excellent electrochemical performance featuring high initial charge capacity of 729 mAh g^{-1}, with high initial Coulombic efficiency of approximately 74%, and long capacity retention of 93.7% after 200 cycles, with a highly reversible capacity of 683 mAh g^{-1}.

1. Introduction

Recently, the demand for high capacity Li-ion batteries (LIBs) has been continuously increasing owing to the rapid development of mobile devices and electric vehicles. Therefore, many studies are currently underway to increase the capacity of the LIB anodes [1–3]. Among the various efforts to increase the capacity of LIB anodes, Si-based materials are a niche as representative candidates for the anode materials because it has a high theoretical capacity of 3578 mAh g^{-1} ($Li_{15}Si_4$) at room temperature [4–6]. However, Si-based materials suffer from large volume change during repeated Li insertion/extractions, which results in poor cycling behaviors. To alleviate the large volume changes during cycling when Si-based materials were used as LIB anodes, various Si-based approaches such as nano-architectures, C-modified composites, and binary compounds, have been dedicated to the application of Si-based anodes [7–12].

Since the discovery of our research group that amorphous SiO_2 can react reversibly with Li [13], high-capacity amorphous SiO_2-based anodes for LIB have been actively investigated [14–25]. However, they still suffer from a poor initial Coulombic efficiency caused by the formation of irreversible Li_2O or Li-Si-O compounds during the Li reactions.

The microstructure of SiO is known to have two representative structural models, the random bonding (RB) model with a continuous random network of Si(2+) and oxygen in silicon monoxide, and a random mixture (RM) model with Si(0) and SiO_2(4+) [26–28]. Recently, several reports have demonstrated that the RM model is more reasonable because SiO is thermodynamically unstable at high temperature and, thus, is disproportionated into Si and SiO_2 [29–31]. Among the compounds composed of Si and transition metals, FeSi can be synthesized well by a high-energy ball milling (HEBM) process using Fe and Si [32,33]. Considering the RM model of SiO and easy generation of FeSi, the following reaction is possible:

$$2SiO + Fe \rightarrow \text{amorphous } SiO_2 + FeSi \quad (1)$$

In this study, nanostructured amorphous SiO_2-FeSi-graphite (a-SiO_2/FeSi/G) composite was synthesized using a simple solid-state HEBM process referenced in reaction (1) to enhance the electrochemical performance of SiO_2. The synthesized *a*-SiO_2/FeSi/G composite was tested as an anode material in LIBs to circumvent the problems associated with amorphous SiO_2 when it is used solely as an electrode.

2. Experiment

First, the amorphous SiO_2-FeSi (*a*-SiO_2/FeSi) composite was synthesized by the following solid-state HEBM (Spex-8000)

* Corresponding author.
E-mail address: cmpark@kumoh.ac.kr (C.-M. Park).

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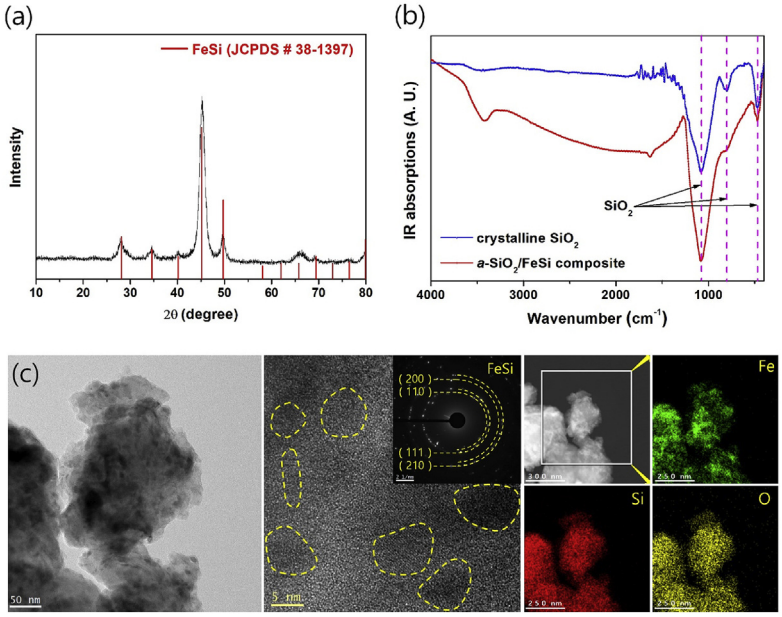

Fig. 1. Synthesis of *a*-SiO_2/FeSi composite. (a) XRD data of the fabricated *a*-SiO_2/FeSi composite. (b) FT-IR data of crystalline SiO_2 and the fabricated *a*-SiO_2/FeSi composite. (c) BF- and HR-TEM images with corresponding DPs and EDS mappings.

process. Stoichiometric amounts of SiO, Fe, and stainless steel balls (diameter: 3/8 in. and 3/16 in) were placed in a hardened steel vial (80 cm^3) with a ball-to-powder ratio of 20:1, and the HEBM process was applied under an Ar atmosphere for 6 h. Subsequently, to obtain the *a*-SiO_2/FeSi/G composite, the HEBM process was applied for additional 10 min to the mixture of *a*-SiO_2/FeSi and graphite (mesocarbon microbead, MCMB) powders with the optimal amounts of *a*-SiO_2/FeSi 70 wt% and graphite 30 wt %. The average particle size of the *a*-SiO_2/FeSi and *a*-SiO_2/FeSi/G composites was 5.9 and 7.9 μm, respectively (Fig. S1), which was analyzed using particle size analyzer (Mastersizer-2000) and scanning electron microscopy (SEM, JSM-6701F, JEOL).

The structure of the synthesized materials was characterized by X-ray diffraction (XRD, DMAX2500-PC, Rigaku), Fourier-transform infrared spectroscopy (FT-IR, Vertex 80v, Hyperion 2000), high-resolution transmission electron microscopy (HR-TEM, FEI F20, operating at 200 kV), energy-dispersive spectroscopy (EDS, attached to the HR-TEM) and extended X-ray absorption fine structure (EXAFS, Fe K-edge at the Pohang Light Source 7D-XAFS beamline in South Korea, acceleration voltage: 3.0 GeV).

The *a*-SiO_2/FeSi and *a*-SiO_2/FeSi/G composite electrodes consisting of the active materials (70 wt%), carbon black (Denka, 15 wt %) conducting agent and polyvinylidene fluoride (15 wt%), dissolved in N-methyl-2-pyrrolidone as a binder were fabricated. Coin-type electrochemical cells were assembled in an Ar-filled glove box using the Celgard 2400 separator, Li foil was used as the counter and reference electrodes, and 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 by volume) was the electrolyte. All the cells were galvanostatically tested between 0 and 3 V (vs. Li^+/Li) at the current density of 100 mA g^{-1} using a Maccor automated tester. Cyclic voltammetry (CV, ZIVE MP2A) was also conducted within the voltage range 0–3 V (vs. Li^+/Li) at the scan rate of 0.05 mV s^{-1}.

3. Results and discussion

The XRD pattern of the synthesized *a*-SiO_2/FeSi composite shows only crystalline FeSi without other phases (Fig. 1a). However, FT-IR results show that the same peaks comprising of Si-*O*-Si rocking vibrational mode (468 cm^{-1}), O-Si-O bending mode (808 cm^{-1}), and Si-O asymmetric stretching mode (1082 cm^{-1}) in

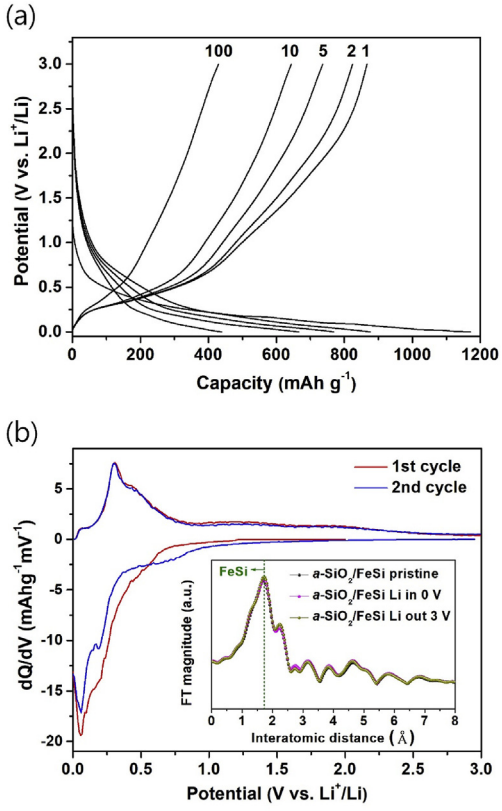

Fig. 2. Electrochemical performance of *a*-SiO_2/FeSi composite electrode. (a) Voltage profiles from the 1st to 100th cycles for the *a*-SiO_2/FeSi composite electrode. (b) DCPs of the *a*-SiO_2/FeSi composite electrode and Fe K-edge EXAFS result of the FeSi electrode during Li reactions.