



Effects of lithium fluoride coating on the performance of nano-silicon as anode material for lithium-ion batteries



Yong Yang, Zhixing Wang*, Rong Zhou, Huajun Guo, Xinhai Li

School of Metallurgy and Environment, Central South University, Changsha 410083, PR China

ARTICLE INFO

Article history:

Received 17 June 2016

Received in revised form

1 August 2016

Accepted 3 August 2016

Available online 3 August 2016

Keywords:

Lithium-ion batteries

Silicon

Lithium fluoride

Nanoparticles

Interface

ABSTRACT

To overcome the capacity fading issue of Si particle upon repeated cycle process, in this study, lithium fluoride (LiF) is introduced to coat commercial nano silicon to form an artificial solid electrolyte interface (SEI) film. After a facile spray drying process, Si nanoparticles are aggregated to form spheres and the LiF is homogeneously coated on the surface of Si nanoparticles. Compared with the bare nano-Si, Si/LiF composite shows a huge increase in capacity retention, increasing from 0.8% to 31.2% after 30 cycles. Such improvement results from artificial formation of a stable LiF-based SEI film on the Si surface, reducing the parasitic reaction and thus minimizing the capacity loss during the first lithiation process.

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1. Introduction

Lithium-ion battery (LIB) is an attractive energy storage device because of its high energy and power density [1]. To increase the energy density for further demanding applications, new electrode materials with higher capacity and lower cost are required [2,3]. Silicon is one of the most promising anode materials for LIBs because of the high theoretical capacity (3580 mAh/g) [4]. Unfortunately, Si suffers from the large volume expansion (up to 300%) during lithiation, which leads to structural degradation and instability of the solid electrolyte interphase (SEI) during cycling [5]. In order to improve the performance of Si anode, it is proved to be a successful route to use the electrolyte additives to optimize SEI composition and structure. For example, fluoroethylene carbonate (FEC) has been successfully introduced to improve the cycle life of silicon anode. The kinetically fast reduction of FEC to neutral radical carbonate and fluoride anion lead to rapid formation of LiF in the SEI that is stable during cycling [6,7].

Inspired by the function of FEC to produce LiF in SEI, herein, LiF is employed to coat Si nanoparticles to form an artificial SEI to enhance the surface stability of Si anode. The LiF coating process is carried out by spray drying method. The introduced LiF is expected to act as a stable SEI to reduce the side reaction at the anode side, thereby to improve the electrochemical performance of Si anode.

2. Material and methods

The Si/LiF composite was prepared as follows. Firstly, 2 g nano-Si (~30 nm, Shuitian ST-NANO Science & Technology Co., Ltd, Shanghai, China) powders were dispersed into 100 mL absolute ethyl alcohol by ultrasonic treatment for 30 min. Secondly, 0.463 g lithium acetate ($\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$) was dissolved into a certain amount of deionized water to form the 1 wt% aqueous solution and then added into the nano-Si suspensions with stirring for 30 min. Thirdly, 17.5 g of 1 wt% ammonium fluoride (NH_4F) solution was added dropwise under continuously stirring for 60 min. Finally, the mixture was further diluted by 400 mL and underwent spray drying to obtain Si/LiF microspheres.

The samples were characterized by X-ray diffraction (XRD, Rint-2000, Rigaku) with $\text{Cu K}\alpha$, field emission scanning electron microscopy (FESEM, Nova NanoSEM 230), transmission electron microscopy (TEM, FEI Tecnai G220), and X-ray photoelectron spectroscopy (XPS, K-Alpha 1063).

The electrochemical performance was evaluated in CR2025 coin cells with lithium foil as counter and reference electrode. Each working electrode was composed of 80 wt% active material, 10 wt% Super P and 10 wt% LA-132 binder (Chengdu Indigo Power Sources Co., Ltd, China). The cells were assembled in an Ar-filled glovebox using a polypropylene micro-porous film as a separator and 1 M LiPF_6 in EC/DMC/EMC (1:1:1, in volume) as electrolyte and cycled between 0.01 and 2.0 V at room temperature with a battery tester (Neware, Shenzhen). Cyclic voltammetry (CV, 0.1 mV s^{-1}) and electrochemical impedance spectroscopy (EIS, AC voltage

* Corresponding author.

E-mail address: zxwang.csu@hotmail.com (Z. Wang).

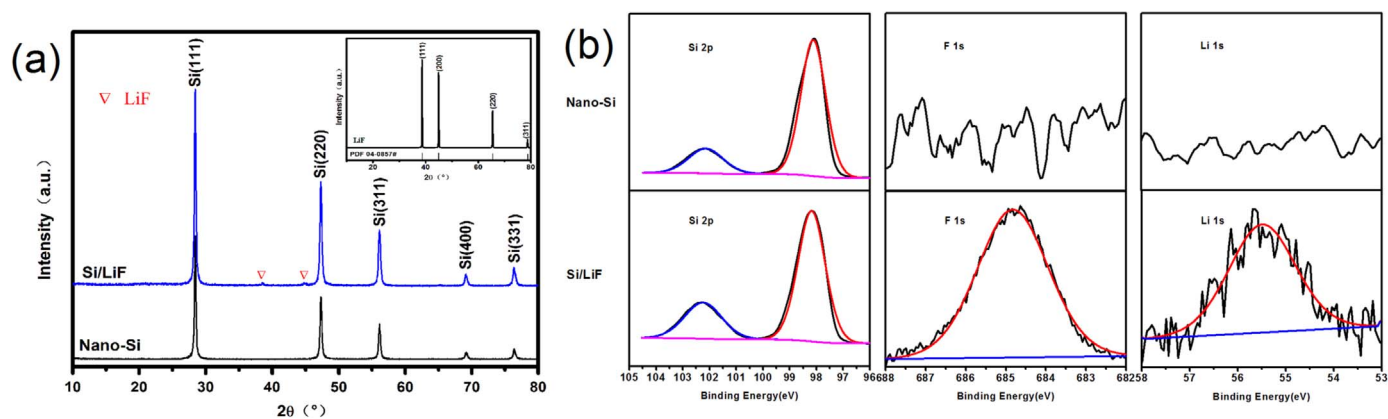


Fig. 1. (a) XRD patterns and (b) X-ray photoelectron spectra of nano-Si and Si/LiF composite, (XRD of LiF is shown in the inset of Fig. 1a).

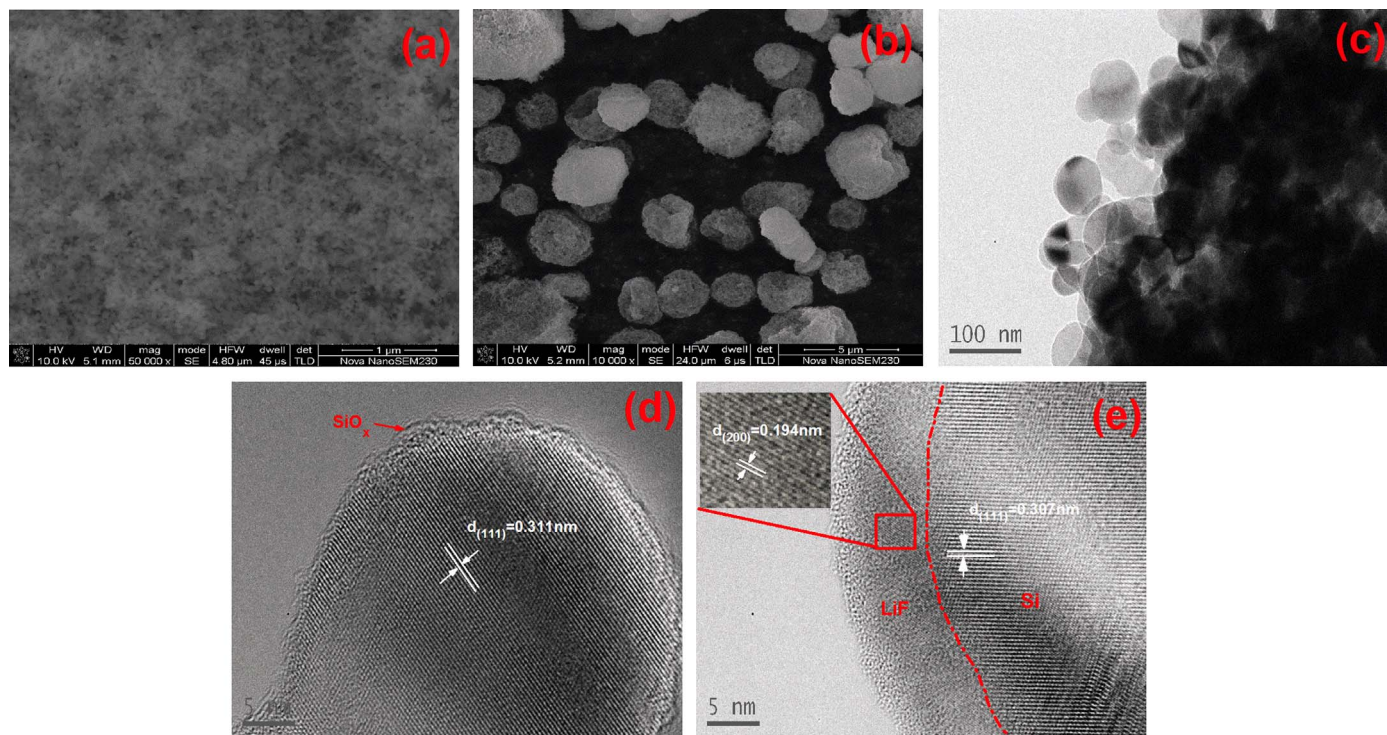


Fig. 2. SEM images of (a) nano-Si and (b) Si/LiF composite; (c) TEM images and (d) HRTEM of nano-Si; and (e) HRTEM of Si/LiF composite. The inset of (e) is a magnified HRTEM image of LiF coating layer.

amplitude: 5 mV; frequency range: 0.01–10⁵ Hz) measurements were conducted by an electrochemical workstation (CHI660A).

3. Results and discussion

In the inset of Fig. 1a, the XRD pattern of LiF prepared by CH₃COOLi and NH₄F reaction shows the diffraction peaks of LiF (PDF# 04-0857), indicating successful formation of LiF in this study. As shown in Fig. 1a, in the prepared Si/LiF composite, except the diffraction peaks of nano-Si, two weak peaks appearing around 2θ = 38.6° and 44.9° indicate the formation of LiF phase. The addition of LiF has no influence on the crystal structure of silicon, and no other impurity phase is detected in the Si/LiF material.

To further identify the coating layer, the XPS spectra of nano-Si and Si/LiF are presented in Fig. 1b. The peaks located at 98.3 and 102.2 eV of Si 2p spectra are associated with the spectrum of Si and SiO_x (0.6 < x < 2) [8,9], indicating silicon substrate status is not changed after coating with LiF. However, the appearance of

new peaks at 685 eV in the F 1s spectra and 55.5 eV in the Li 1s is visible from Si/LiF, which is attributed to the formation of LiF on the surface.

The morphology of the nano-Si and Si/LiF composite are observed by FESEM and TEM. As shown in Fig. 2a, nano-Si powders show a great agglomeration which would exacerbate the volume change of silicon particles in the discharge-charge process. The morphology of the Si/LiF material (Fig. 2b) presents sphere-like shape and shows a median particle size of 2–8 μm. Spray drying can reduce the specific surface area of the material and decrease the direct contact with the electrolyte. The TEM image of Si/LiF sample (Fig. 2c) demonstrates that the diameter of Si nanoparticles is about 30–60 nm and the composite is porous, which is helpful to accommodate the volume expansion of the Si nanoparticles during cycling. From the HRTEM image of Si in Fig. 2d, the lattice fringes ($d = 0.311$ nm, corresponding to (111) plane of Si) are clearly observed. In addition, about 1 nm of an amorphous layer on the surface nano-Si surface can be distinguished due to oxidation of Si. As shown in the Fig. 2e, the interface between crystal Si [(111)]

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