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Electrodeposited porous-microspheres Li–Si films as negative electrodes in lithium-ion batteries

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A B S T R A C T

A porous-microspheres Li–Si film (PMLSF) is prepared by multi-step constant current (MSCC) electrodeposition on Cu foil. Its structure and morphology are characterized using X-ray diffraction (XRD) and scanning electron microscope (SEM). As negative electrodes of lithium-ion batteries, the PMLSF electrode delivers the first gravimetric and geometric charge capacities of 2805.7 mA h g^{-1} and 621.9 μA h cm^{-2} at the current density of 25.5 μA cm^{-2}, and its initial coulombic efficiency is as high as 98.2%. When the PMLSF electrode is cycled in VC-containing electrolyte, the superior cycling performance can be obtained. After 50 cycles, 96.0% of its initial capacity is retained at the current density of 50.0 μA cm^{-2}. Electrochemical impedance spectra (EIS) research confirms the positive effect of VC additive on the behavior of the PMLSF electrode.

1. Introduction

Compact power sources are critical components of modern electronics. The thin-film lithium-ion battery is one of the most favorite options because it can provide a high energy and power density [1]. Recenly, they have been used in smartcards, implantable medical devices, microelectromechanical systems (MEMS), and others [2]. However, the theoretical Li-storage capacity of commercial carbon anodes is limited to 372 mA h g^{-1}; thus there is a great interest in developing alternative anode materials to carbonaceous. Silicon is a promising candidate for next-generation anodes due to its low discharge potential vs. Li/Li$^+$ and high theoretical Li-storage capacity of 4200 mA h g^{-1} [3]. Nevertheless, Si electrodes suffer from poor electrochemical reversibility upon cycling caused by a drastic volume change of Si (>300%) during the lithium insertion/extraction process.

To reduce the absolute volume change and improve the cycling stability of Si electrode, various Si nanostructures have been proposed and compatible electrolytes (e.g. vinylene carbonate (VC) as additive) have been studied [4–7]. Si and Si-based alloy thin films become one of the important objects of study. These thin films are generally prepared by physical or chemical evaporation/deposition techniques. Takamura et al. reported a vacuum-deposited phosphor-doped n–Si film with thickness of 50 nm on a Ni foil, which showed a reversible capacity as high as 3000 mA h g^{-1} for 1000 cycles in a lithium-ion battery [8]. Fleischauer and co-workers prepared porosity-controlled Si thin films by the glancing angle deposition (GLAD) technique. This film was composed of numerous Si columns with a uniform interspace. The peculiar morphology of the Si thin film led to good electrochemical performance. A 500-nm thick Si thin film with a porosity of ca. 80% presented a reversible capacity of over 90 μA h cm^{-2} and good capacity retention (75 μA h cm^{-2} after 70 cycles) [1]. The Seong group proposed Si–Sn nanocomposite electrodes fabricated by an RF-magnetron sputtering technique. The capacity could retain 560 μA h cm^{-2} μm^{-1} after 15 cycles, and the available capacity was dependent on the amount of the incorporated Sn [9]. It is also noticed that most of the Si or Si-based thin film electrodes have unsatisfactory coulombic efficiency at the first cycle, which mainly originatd from the formation of a solid electrolyte interphase (SEI) on the electrode surface [1,8–12].

The initial coulombic efficiency can be actually improved by preforming an artificial SEI layer (through chemical modification) on the active materials and/or prelithiating the active materials [13–16]. For example, Seong et al. studied lithiation of silicon monoxide using Li powders. Although the batteries showed enhanced initial reversibility and coulombic efficiency, the bulk distribution of Li powders in electrode was not uniform [15]. In this article, porous-microspheres Li–Si films (abbreviated as PMLSF hereafter) were first electrodeposited on Cu foil from propylene carbonate (PC) solution containing tetrachlorosilane ($SiCl_4$) and lithium perchlorate ($LiClO_4$) and exhibited high initial coulombic

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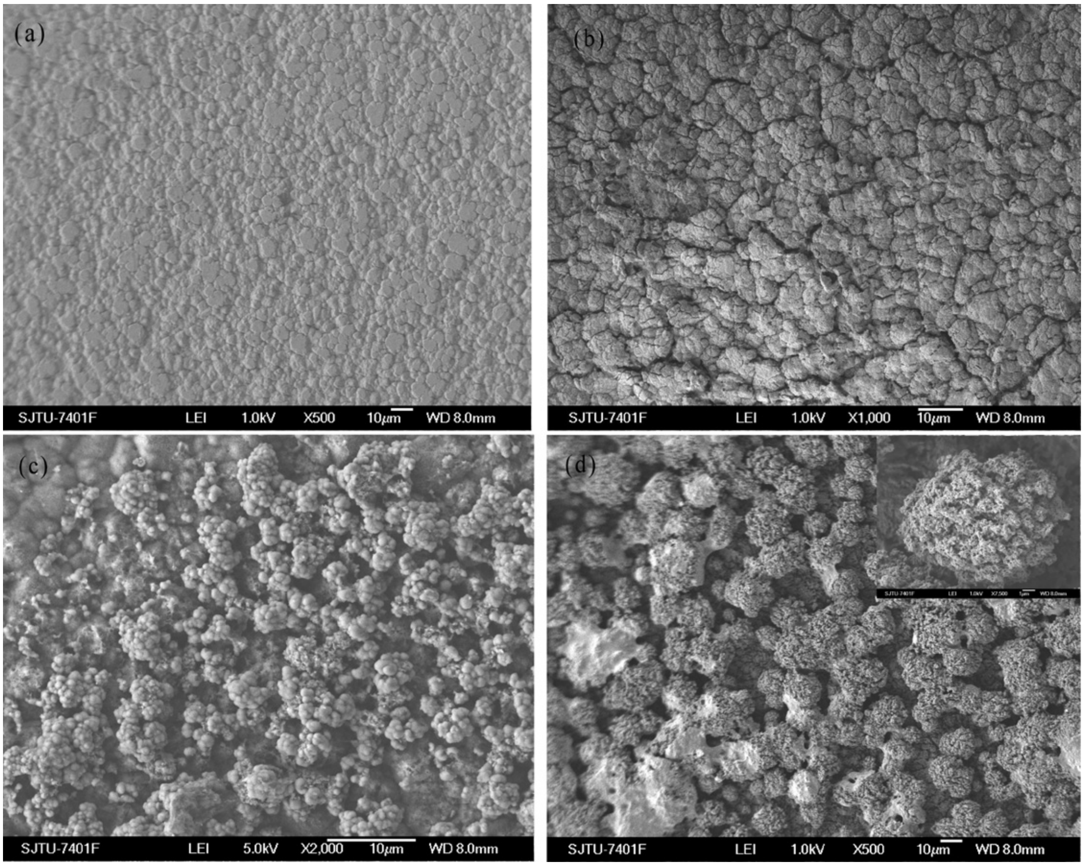

Fig. 1. SEM images of Cu foil substrate (a), electrodeposited Si thin film (b), primary Li–Si deposit (c), and PMLSF electrode (d) (the inset shows its partial magnification).

efficiency and cycling stability as negative electrodes for lithium-ion battery.

2. Experimental

All experiments were carried out in an Ar-filled glove box at 30 ± 1 °C. $SiCl_4$ and $LiClO_4$ were added to the organic electrolyte as Si source and Li source, respectively. PC was chosen as an organic solvent because of its high $SiCl_4$ and $LiClO_4$ solubility. These chemicals were used without a further purification. The electrolyte composition was adjusted to $0.5\,mol\,L^{-1}$ $SiCl_4$ and $0.6\,mol\,L^{-1}$ $LiClO_4$ in PC. For a comparison, Si thin film was electrodeposited in PC solution containing $0.5\,mol\,L^{-1}$ $SiCl_4$ and $0.1\,mol\,L^{-1}$ tetrabutylammonium chloride as supporting electrolyte.

A conventional three-electrode cell was employed for the electrodeposition experiments. 25-μm Cu foil with a geometric surface area of $0.785\,cm^2$ ($\phi = 1.0\,cm$) was used as the substrate (cathode) for PMLSF electrodeposition. A polished graphite plate was employed as the counter electrode (anode). Cu foil and graphite plate were ultrasonically cleaned in acetone, subsequently washed with oxalic acid ($0.1\,mol\,L^{-1}$) and distilled water, and dried under vacuum at 50 °C. Platinum wire served as a quasi-reference electrode. PMLSF and Si thin films were electrodeposited on one side of the Cu foil on an electrochemical workstation CHI660C (Chenhua Co., China). Multi-step constant current (MSCC) electrolysis for PMLSF and Si thin films was conducted at the current density of $-3.82\,mA\,cm^{-2}$ for 10 min, followed by the current density of $-1.27\,mA\,cm^{-2}$ for 150 min. All freshly deposited samples were rinsed with PC, and then directly characterized and electrochemically evaluated.

The PMLSF before cycling and after 50 discharge–charge cycles were analyzed by X-ray diffraction (XRD) on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu K_α radiation. Parafilm covered the surface of a PMLSF to keep out the air during XRD experiments. The morphologies of the samples were observed by scanning electron microscopy (SEM) on a JEOL field-emission microscope (JSM-7401F). The composition was determined by inductively coupled plasma (ICP) measurements (Hitachi P-4010, Japan). The gravimetric capacity of PMLSF electrode was calculated according to the weight of silicon in the PMLSF obtained from the ICP analysis.

Electrochemical behaviors were evaluated using CR2016 coin cells assembled in an Ar-filled glove box (Mbraun, Germany). The test cell was composed of PMLSF or Si film working electrode and Li foil counter electrode. The electrolyte consisted of a solution of $1\,mol\,L^{-1}$ $LiPF_6$ in EC/DMC (1:1 vol%) with or without 2 wt% VC as additive. ENTEK ET20-26 served as membrane separator. The cells were charged (delithiation) and discharged (lithiation) using LAND CT2001A system in a galvanostatic mode between 0.01 and 1.4 V vs. Li/Li^+. For the first pre-cycle, the current density of $25.5\,\mu A\,cm^{-2}$ was adopted following by the current density of $50.0\,\mu A\,cm^{-2}$. Cyclic voltammogram (CV) of a PMLSF electrode was measured at the range of 0.01–1.5 V vs. Li/Li^+ at a scan rate of $0.2\,mV\,s^{-1}$. Electrochemical impedance spectra (EIS) were taken on CHI660C over the frequency range from 100 kHz to 0.01 Hz with ac amplitude of 5 mV.

3. Results and discussion

Due to the high activity, the deposited PMLSF electrodes were preserved under Ar before transporting to the SEM, XRD and ICP apparatus. ICP composition analysis for the deposit indicates the presence of Li and Si elements in PMLSF. The Si/Li atomic ratio of the deposit layer is about 1.51 (85.9 wt% for Si) at the first electrodepo-