多孔锂-硅薄膜锂离子电池负极材料的电沉积制备及其电化学性能

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摘要: 采用多步恒电流沉积技术, 在铜箔上电沉积制备了多孔锂-硅薄膜电极(LSF). 用X射线衍射(XRD)和扫描电镜(SEM)测试手段研究了该电极的结构和表面形貌. 作为锂离子电池负极材料, 电化学测试结果表明锂-硅薄膜电极具有较好的循环稳定性, 通过改变电沉积条件, 可有效调控该电极的嵌脱锂容量及首次循环效率. 譬如, 在 $0.5 \text{ mol} \cdot \text{L}^{-1}$ 四氯化硅+ $0.7 \text{ mol} \cdot \text{L}^{-1}$ 高氯酸锂的碳酸丙烯酯电解液中, 首先以 $-3.82 \text{ mA} \cdot \text{cm}^{-2}$ 的恒定电流密度沉积 600 s, 再将电流密度恒定为 $-1.27 \text{ mA} \cdot \text{cm}^{-2}$, 继续电沉积 7200 s, 制得锂-硅薄膜电极(LSF-3), 该电极以 $12.7 \mu\text{A} \cdot \text{cm}^{-2}$ 的电流密度预循环 2 次, 其首次循环库仑效率高达 97.1%. 预循环 2 次后, 电流密度增加到 $25.5 \mu\text{A} \cdot \text{cm}^{-2}$, 此时, 锂-硅薄膜电极充电质量比容量和面积比容量分别为 $1410 \text{ mAh} \cdot \text{g}^{-1}$ 及 $240.6 \mu\text{Ah} \cdot \text{cm}^{-2}$; 50 次循环后充电比容量为 $179 \mu\text{Ah} \cdot \text{cm}^{-2}$ ($1049 \text{ mAh} \cdot \text{g}^{-1}$), 容量保持率为 74.4%. 锂-硅薄膜电极中的活性锂组分可补偿首次循环时不可逆容量损失, 同时薄膜电极中的多孔结构可缓解电极材料的体积效应并改善其循环性能.

关键词: 多孔锂-硅薄膜; 电沉积; 库仑效率; 负极材料; 锂离子电池

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Electrodeposition and Electrochemical Property of Porous Li-Si Film Anodes for Lithium-Ion Batteries

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Abstract: Porous Li-Si thin films (LSFs) were prepared by a multi-step constant current electrodeposition onto Cu foil. The structure and morphology of the electrodeposited films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). As anodes for Li-ion batteries, Li-Si films give high cycling stability, adjustable Li-storage capacity and initial coulombic efficiency under different electrodeposition conditions. For instance, LSF-3 was electrodeposited in an electrolyte of $0.5 \text{ mol} \cdot \text{L}^{-1}$ SiCl_4 + $0.7 \text{ mol} \cdot \text{L}^{-1}$ LiClO_4 +propylene carbonate (PC) under certain conditions ($i_1=-3.82 \text{ mA} \cdot \text{cm}^{-2}$, $t_1=600 \text{ s}$; $i_2=-1.27 \text{ mA} \cdot \text{cm}^{-2}$, $t_2=7200 \text{ s}$). LSF-3 showed the first coulombic efficiency of 97.1% at a current density of $12.7 \mu\text{A} \cdot \text{cm}^{-2}$. After the two initial pre-cycles, it delivered gravimetric and geometric charge capacities of $1410 \text{ mAh} \cdot \text{g}^{-1}$ and $240.6 \mu\text{Ah} \cdot \text{cm}^{-2}$ at $25.5 \mu\text{A} \cdot \text{cm}^{-2}$. After 50 cycles, its charge capacity was $179.0 \mu\text{Ah} \cdot \text{cm}^{-2}$ ($1049 \text{ mAh} \cdot \text{g}^{-1}$), retaining 74.4% of its initial capacity. The porous structure in LSFs can accommodate a part of the volume change during Li insertion/extraction and this favors the structural stability.

Key Words: Porous Li-Si film; Electrodeposition; Coulombic efficiency; Anode material; Lithium-ion battery

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1 Introduction

Silicon has been extensively investigated for use as anode material due to its low discharge potential (vs Li/Li^+) and high theoretical lithium storage capacity of $4200 \text{ mAh} \cdot \text{g}^{-1}$. However, Si electrodes show poor electrochemical reversibility upon cycling for a drastic volume change of Si ($>300\%$) during the lithium insertion/extraction process. To accommodate the absolute volume change and further enhance the cycling stability, various Si nanostructures have been proposed.²⁻⁷ Among them, Si and Si-based alloy thin films become one of the important objects of study. These thin films were prepared by various physical or chemical evaporation/deposition techniques. Takamura *et al.*⁸ reported that a phosphor-doped *n*-Si film with thickness of 50 nm vacuum-deposited on a Ni foil showed a reversible capacity as high as $3000 \text{ mAh} \cdot \text{g}^{-1}$ for 1000 cycles in a lithium-ion battery. Sanyo Electric Company⁹ applied a novel amorphous Si film on a roughened Cu foil surface prepared by an argon radio-frequency (RF) sputtering process. After the first charge-discharge cycle, the Si film was broken into parallel micro-columns with gaps and these columns were still well connected to the Cu substrate. The peculiar morphology of the Si thin film generated excellent electrochemical performance. Seong *et al.*¹⁰ prepared Si-Sn nanocomposite electrodes by an RF-magnetron sputtering technique. The capacity could retain $560 \mu\text{Ah} \cdot \text{cm}^{-2} \cdot \mu\text{m}^{-1}$ after 15 cycles, and the available capacity was dependent on the amount of the incorporated Sn. It was also noticed that most Si or Si-based thin films have unsatisfactory coulombic efficiency at the first cycle.⁸⁻¹³

Many attempts have been made towards Si electrodeposition in molten halides¹⁴⁻¹⁶, organic electrolytes¹⁷⁻²¹, and ionic liquids²²⁻²⁴. Compared with the above-mentioned techniques for film preparation, electrochemical procedure is simple and efficient. Electrodeposition does not need a high vacuum apparatus or a high temperature furnace. It is able to control the morphology and thickness of the deposits by optimizing the electrodeposition conditions. In this paper, porous Li-Si thin films (abbreviated as LSFs) were electrodeposited on Cu foil by a multi-step constant current (MSCC) technique and directly used as anodes for lithium-ion batteries.

2 Experimental

A conventional three-electrode cell was employed for the experiments of linear sweep voltammetry (LSV) and electrodeposition. All experiments were carried out in an Ar-filled glove box at room temperature. Cu wire was used as a working electrode in LSV studies and 25- μm thick Cu foil as working electrode for Li-Si film electrodeposition. Platinum wire served as a quasi-reference electrode (Pt Q.R.E.), and all potentials in LSV and electrodeposition experiments were quoted with respect to the platinum wire. A polished graphite plate was used as the counter electrode for electrodeposition and LSV studies. Cu foil, Cu wire, and graphite plate were ultrasonically cleaned in acetone, subsequently washed with oxalic acid ($0.1 \text{ mol} \cdot \text{L}^{-1}$)

and distilled water, and dried for 6 h under vacuum at 50°C .

LSV studies and MSCC electrodeposition were performed on an electrochemical workstation CHI660C (Chenhua Co., China). The LSV studies of Si, Li, and Li-Si deposition were carried out in different solutions with propylene carbonate (PC) as the solvent, (a) $0.5 \text{ mol} \cdot \text{L}^{-1}$ tetrachlorosilane (SiCl_4 , 99.9999%) + $0.1 \text{ mol} \cdot \text{L}^{-1}$ tetrabutylammonium chloride (TBACl, $\geq 99.0\%$, Fluka); (b) $0.7 \text{ mol} \cdot \text{L}^{-1}$ lithium perchlorate (LiClO_4 , 99.5%); (c) $0.5 \text{ mol} \cdot \text{L}^{-1} \text{SiCl}_4 + 0.7 \text{ mol} \cdot \text{L}^{-1} \text{LiClO}_4$.

Li-Si thin films (LSFs) were deposited on one side of the Cu foil by MSCC electrodeposition technique. The geometric surface area of Cu foil substrate contacting electrolyte was 0.785 cm^2 ($\phi 1.0 \text{ cm}$). The detailed conditions of the MSCC are listed in Table 1. Freshly deposited LSFs were rinsed with PC, and then directly used for tests of charge and discharge.

The LSFs were characterized by scanning electron microscopy (SEM, Hitachi S-3400N, Japan) and energy dispersive X-ray (EDX, Bruker). The composition of the electrodeposited LSF was determined by inductively coupled plasma (ICP) measurements (Hitachi P-4010, Japan).

Electrochemical behaviors were evaluated using CR2016 coin cells assembled in an Ar-filled glove box (Mbraun, Germany). The test cell was composed of the LSF working electrode and Li foil counter electrode. The electrolyte solution contained LiPF_6 ($1 \text{ mol} \cdot \text{L}^{-1}$) in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (volume ratio of 1:1). ENTEK ET20-26 served as membrane separator. The charge-discharge tests of the cells were performed using LAND CT2001A system. The cells were charged (delithiation) and discharged (lithiation) in a galvanostatic mode and pre-cycled at a current density of $12.7 \mu\text{A} \cdot \text{cm}^{-2}$ during the two initial cycles, followed by the current density of $25.5 \mu\text{A} \cdot \text{cm}^{-2}$ between 0.01 and 1.4 V (vs Li/Li^+).

3 Results and discussion

Fig.1 shows the linear sweep voltammetry of Li, Si, and Li-Si deposition. Lithium starts to deposit on Cu wire from $\text{LiClO}_4\text{-PC}$ solution at a potential more negative than -3.0 V (Fig.1(b)).²⁵ Fig.1(a) presents the reduction peak of Si deposition from $\text{SiCl}_4\text{-TBACl-PC}$ solution locating at -3.8 V . The cathodic peak around -2.7 V corresponds to the reductive decomposition of quaternary ammonium cation (TBA^+) accompanying a passivation layer formation. This peak disappears from the subsequent LSV curves (inset in Fig.1) because the passiv-

Table 1 Conditions for preparing the Li-Si thin films by MSCC electrodeposition technique

	$\frac{c(\text{SiCl}_4)}{(\text{mol} \cdot \text{L}^{-1})}$	$\frac{c(\text{LiClO}_4)}{(\text{mol} \cdot \text{L}^{-1})}$	$i_1/(\text{mA} \cdot \text{cm}^{-2})$	t_1/s	$i_2/(\text{mA} \cdot \text{cm}^{-2})$	t_2/s
LSF-1	0.5	0.7	-3.82	600	-1.27	10800
LSF-2	0.5	0.7	-6.37	600	-1.27	10800
LSF-3	0.5	0.7	-3.82	600	-1.27	7200

i_1 and i_2 are the current densities for step 1 and step 2, respectively;

t_1 and t_2 are the times for step 1 and step 2, respectively.

Fig.1 Linear sweep voltammies (LSV) of Cu wire electrode in different solutions with PC as the solvent

(a) 0.5 mol·L⁻¹ tetrachlorosilane (SiCl₄)+0.1 mol·L⁻¹ tetrabutylammonium chloride (TBACl) (the inset is the third LSV of Si deposition based on Fig.1a); (b) 0.7 mol·L⁻¹ lithium perchlorate (LiClO₄); (c) 0.5 mol·L⁻¹ SiCl₄+0.7 mol·L⁻¹ LiClO₄

ation layer prevents a further decomposition of TBA⁺.¹⁷ However, the weak peak at -3.3 V remains at the third curve. It indicates that the reduction of SiCl₄ to Si is processed in a stepwise mode *via* Si²⁺ intermediate product.²⁶ For Li-Si electrodeposition in the electrolyte containing both SiCl₄ and LiClO₄, the main current response shifts to a more positive potential. It means that the electrochemical co-deposition of Li and Si may take place and the related underpotential effect is evident. MSCC plot for the LSF-1 electrodeposition is shown in Fig.2. With the initial large current step of -3.82 mA·cm⁻², the electrode potential quickly shifts to the negative direction at the beginning of electrolysis, and then reaches a steady potential of ca. -3.35 V. The followed second current step of -1.27 mA·cm⁻² makes the potential ascend to ca. -3.0 V and stabilize at this value during electroplating, which locates in the potential range for the co-electrodeposition of Li and Si.

During the electrodeposition process, a black film gradually formed on Cu foil. ICP composition analysis for the deposit indicates the presence of Li and Si, and the Si/Li atomic ratio of LSF-1, LSF-2, and LSF-3 was about 0.31, 0.62, and 0.45, respectively. The co-deposition of Li with Si improves the electronic conductivity of the deposited film, thus the deposit layer

Fig.2 Multi-step constant current (MSCC) plot of electrodeposition for the LSF-1 electrode

thickness increases. The thickness of the Li-Si film is very difficult to determine due to its high activity. The XRD analysis for the LSFs did not find any peaks related to Si, Li, or Li-Si alloy except weak peaks for LiCl, which indicates that the electrodeposited LSFs are in a amorphous or nano-crystalline state and contain a small amount of LiCl impurity. LiCl impurity may mainly ascribe to the reaction of freshly electrodeposited lithium or Li-Si alloy with a small amount of chlorine in the electrolyte diffusing from the anode.

The SEM image in Fig.3(a) shows that the LSF-1 is basically composed of fine grains with the size of several micrometers and exhibits an irregular porous structure. The possible mechanism of the pore formation on deposited film was revealed by Nishimura and Fukunaka.¹⁷ The energy dispersive X-ray (EDX) spectrum in Fig.3(b) demonstrates a strong Si response and relatively weak O and Cl responses. Element chlorine denotes LiCl impurity and non-cleaved Si-Cl bonds,¹⁷ and oxygen impurity was mainly from the oxidation of the LSF-1 electrode during the transportation into the SEM apparatus.

Galvanostatic charge-discharge was conducted to evaluate the electrochemical lithium-storage behavior of the LSF electrodes. As shown in Fig.4(a), the sloping curves during the first discharge process of the LSF electrodes confirm the amorphous structure of LSF. For the LSF-1 electrode, the first discharge and charge capacities are 412.5 and 502.2 μAh·cm⁻² at the current density of 12.7 μA·cm⁻², respectively, indicating a coulombic efficiency of 121.7%. As the anodes for lithium-ion battery, pre-lithiation of silicon can compensate the irreversible capacity loss in the initial cycles.²⁷ The co-deposited active lithium can compensate the irreversible capacity caused by the formation of solid electrolyte interface (SEI) film related to electrolyte decomposition, the structural defects and reactive impurities in the deposit layer. Owing to the active lithium in the

Fig.3 SEM image (a) and EDX pattern (b) of the LSF-1

Fig.4 The first discharge and charge curves (a) and the cycle behaviors (b) of the LSF anodes in the potential range of 0.01–1.4 V (vs Li/Li^+)

In Fig.4(b), the current density of $12.7 \mu\text{A}\cdot\text{cm}^{-2}$ at the initial two pre-cycles, followed by the current density of $25.5 \mu\text{A}\cdot\text{cm}^{-2}$; hollow marks represent charge capacity, solid marks represent discharge capacity.

electrode, the open-circuit potential of the LSF-1 electrode before cycling is 0.286 V (vs Li/Li^+). For the LSF-2 and LSF-3 electrodes, the initial coulombic efficiency is 77.2% and 97.1%, respectively. The differences of the Si/Li atomic ratio among the three LSF electrodes led to the various coulombic efficiencies at the first cycle. These results indicate that the initial electrochemical reversibility of the Si-based electrode is adjustable by controlling the electrodeposition conditions (Table 1). Fig.4(b) shows the relationship of charge/discharge capacities vs cycle number of the three electrodes. As for the LSF-3 electrode, it delivered $240.6 \mu\text{Ah}\cdot\text{cm}^{-2}$ at the first charge capacity. According to the ICP result and EDX analysis, a mass of about 0.134 mg was estimated for LSF-3, thus educing the first gravimetric charge capacity of $1410 \text{ mAh}\cdot\text{g}^{-1}$. After 50 cycles, its charge capacity was $1049 \text{ mAh}\cdot\text{cm}^{-1}$ ($179.0 \mu\text{Ah}\cdot\text{g}^{-2}$), retaining 74.4% of its initial capacity. As for the LSF-1 electrode, the charge capacity also retains about 74.0% of its initial value after 50 cycles at $25.5 \mu\text{A}\cdot\text{cm}^{-2}$. The fairly good cycling performance of LSF electrodes partly attributes to the porous structure, which is beneficial to accommodate the volume change during lithium insertion/extraction. The relatively small geometric charge and discharge capacities for LSF-3 film are due to the thin film thickness related to the short electrodeposition time. By varying electrodeposition conditions, the atomic

ratio of Si/Li and the film thickness can be optimized. The Li-Si film anodes with variable coulombic efficiency at the first cycle can match the cathodes with different lithium contents to reach a high cell energy density. Further investigation is still in progress to enhance the purity of the deposited films.

4 Conclusions

In summary, the porous Li-Si thin films can be expediently prepared by a multi-step constant current electrodeposition technique. The SEM image exhibits the irregular porous structure of the Li-Si film, which can buffer the volume change during lithium insertion/extraction. By varying the electrodeposition conditions, the initial coulombic efficiency and the film thickness can be optimized. The obtained Li-Si film electrodes demonstrate good electrochemical reversibility for Li insertion/extraction and are promising for lithium-ion thin film batteries.

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第十六次全国电化学学术会议通知

由中国化学会电化学委员会主办的第十六次全国电化学学术会议定于2011年10月13–17日在重庆市重庆大学举行。本次大会由重庆大学承办。全国电化学学术会议是国内规模化、系列化的学术会议之一，每两年举办一次，以此推动国内电化学领域的学科发展和科技进步，促进科研合作和技术转化。这次会议是我国电化学界的又一次高水平、高信息容量的学术交流。会议将构筑高水平的学术交流平台，围绕电化学和技术发展中的基础问题，提出创新观点，交流学术思想，展示最新成果。

中国化学会电化学委员会热诚邀请大陆、港、澳、台地区从事电化学基础研究、应用研究、仪器开发以及产业界同仁聚会重庆，交流和展示最新成果，讨论电化学学科的前沿和基础问题，探索如何进一步推动电化学科学和技术在国民经济发展中的应用。

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