Influence of Film Thickness on the Electrochemical Performance of $\alpha$-SiO$_x$ Thin-film Anodes

MENG Xiang-Lu$^{1,2,3}$, HUO Han-Yu$^{1,2}$, GUO Xiang-Xin$^{1,4}$, DONG Shao-Ming$^{1}$

(1. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. University of Chinese Academy of Sciences, Beijing 100049, China; 3. College of Material Science and Technology, ShanghaiTech University, Shanghai 201210, China; 4. College of Physics, Qingdao University, Qingdao 266071, China)

Abstract: SiO$_x$ anodes of lithium ion batteries have attracted considerable attention in recent years, due to their cycle stability, large capacity, and feasibility on composition manipulation. Many previous works have focused on clarifying the influences of oxygen contents on SiO$_x$ based anodes. However, the size effect is still far from understanding. Herein, the size effect on electrochemical properties of SiO$_x$ with thin-film type anodes in different thickness was investigated. It is found that the SiO$_x$ electrodes prepared by sputtering is of a Si/O ratio of 0.7 and exhibits the highest initial Coulombic efficiency (ICE) of 71.68% and the highest capacity retention of 92.01% when the film thickness being 450 nm, compared with those in other thickness. The best performance under such intriguing thickness-performance relationship is attributed to the low charge transfer resistance, formation of the reduced SEI layer and good electrode integrity upon cycling, as evidenced by SEM images and EIS collected during cycling. These results indicate that as anodes of LIBs, the SiO$_x$ anodes with controlled size can greatly improve the electrochemical performance.

Key words: SiO$_x$ thin-film anodes; film thickness; cycle stability; capacity; lithium-ion batteries

Recent years have witnessed the growing demand of high performance lithium ion batteries (LIBs) from portable electronics and electric vehicles. The increase in energy density and safety of LIBs has been the primary duty of the battery research community. In terms of novel anode materials, the specific capacity is a critical parameter to be considered. Si as an anode shows the highest theoretical gravimetric capacity of 3579 mAh·g$^{-1}$ (Li$_{15}$Si$_4$), which is approximately one order of magnitude higher than that of carbonaceous materials (372 mAh·g$^{-1}$), including graphite, pyrolytic carbon and meso-phase pitch$^{[1-3]}$. In addition, the electrode potential of Si is below 0.5 V (vs. Li/Li$^+$). As the second abundant element on earth, Si is likewise of great advantages in cost and environmental friendliness. However, the application of Si anodes in LIBs is retarded by the huge volume change (around 300%) appeared during lithiation and delithiation processes$^{[4]}$. The tremendous volume expansion incurs severe internal mechanical stress, which induces particles fracturing, delamination, and then loss of electrical connection. Consequently, the capacity of Si electrode fades sharply after limited cycles$^{[5-7]}$.

The silicon suboxides (SiO$_x$) as anodes have received much attention recently, owing to its high capacities and enhanced cycle stability$^{[8-15]}$. The improved cyclability of SiO$_x$ is ascribed to that the introduced oxygen can be lithiated into inert lithium oxide and other lithium silicate compounds, functioning as the elastic buffers to eliminate the huge structure change upon lithiation and delithiation. In previous study, many works focused on discovering the influence of oxygen contents on the electrochemical performance of SiO$_x$ based anode materials$^{[9,12,14-15]}$. As proven in previous research, the size of Si particles plays a critical role in cycle performance and rate capability. For the SiO$_x$ anode, the size effect has been scarcely discussed, thus calling for the thorough investigation.

In this study, we investigated the size effect of SiO$_{0.7}$ anodes on the performance by using the thin-film type electrodes. With changing the film thickness of SiO$_{0.7}$ anodes, the cycle stability, initial Coulombic efficiency (ICE) and reversible capacity obviously change. The optimized film thickness for SiO$_x$ anode in terms of reversible capacity, ICE and cyclability can be determined.
Such influence is analyzed from the evolution of electrode surface morphology, charge transfer property and physical structure upon long-term cycling.

1 Experimental

1.1 Synthesis of SiOx film materials

SiOx thin-film electrodes were prepared by direct current (DC) reactive magnetron sputtering with a n-type monocrystalline Si of a high purity of 99.999% as the target. The samples were deposited simultaneously on both Si wafer for thickness measurement and rough Cu foil with a thickness of 14 µm for morphology and electrochemical measurements. The distance between target and Si/Cu substrates fixed in 10 cm. Both Ar (99.999%) and O2 (99.999%) were introduced into the chamber after the base pressure below 3.0×10⁻⁴ Pa. The gas flow rate of Ar was 20 sccm and and O2 flow rate used here was 0.8 sccm for depositing SiOx. The SiOx thin-films were grown at pressure of 0.55 Pa with a constant DC power supply of 30 W under room temperature. The deposition rate was approximately 9 nm·min⁻¹. Before film depositing, the Si target was cleaned by a pre-sputtering. The samples were deposited simultaneously on monocrystalline Si of a high purity of 99.999% as the target surface morphology of the Cu foil substrate.

1.2 Materials characterization

The surface morphology and film thickness of the pristine α-SiOx films were examined by field emission scanning electron microscopy (FESEM, Magellan 400). The crystalline phase of α-SiOx was determined by X-ray diffraction (XRD, Bruker D8 Phaser with Cu Kα radiation, λ = 0.15406 nm) within the range of 10°-60°. The structure of α-SiOx films were analyzed by Raman spectrum and the chemical state of α-SiOx films were analyzed using X-ray photoelectron spectroscopy (XPS, ESCAlab 250).

1.3 Cells assembly and electrochemical measurements

The coin cells in type of 2025 were assembled in an Ar-filled glove box with both the O2 and H2O contents below 0.1×10⁻⁶. Each cell consisted of α-SiOx film deposited on rough Cu as the working electrode and with a counter electrode. The electrolyte and lithium foil with a diameter of 10 mm as the separator, the electrolyte and lithium foil with a diameter of 10 mm as the counter electrode. The electrolyte was 1 mol/L LiPF6 dissolved in a 1 : 1 (V/V) mixture solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1wt% vinylene carbonate (VC) additive. Galvanostatic charge/discharge measurements were carried out with a multichannel battery testing system (LAND CT2001A) in the potential range from 0.01 to 1.5 V at different current densities. The cyclic voltammetry (CV) of SiOx/Li was performed from 0.01 V to 1.5 V at a scan rate of 0.05 mV·s⁻¹ by Arbin BT-2000. Electrochemical impedance spectroscopy (EIS) tests were conducted with a frequency range from 0.1 Hz to 10⁵ Hz by an electrochemical workstation (Autolab PGSTAT302N). All the electrochemical measurements were performed at 25℃.

2 Results and discussion

2.1 Characterizations of as-deposited SiOx film electrodes

The morphology and thickness of SiOx thin films were examined by FESEM. As shown in Fig. 1(a), the surface of pristine SiOx film appears rough structure with polygonal particles in size of several microns, which depends on the surface morphology of the Cu foil substrate. This morphology is similarly observed in the MnO thin-film anodes deposited on Cu foils, exhibiting a columnar crystal growth mode[16]. Fig. 1(b) shows a cross-sectional SEM image of SiOx thin film deposited on a Si wafer, which is used for determining the growth rate of SiOx thin films[17]. It is found that the thickness of SiOx thin-film deposited for 20 min is 180 nm corresponding to a growth rate of 9 nm·min⁻¹. Fig. 1(c) shows the XRD patterns of the as-deposited SiOx thin films deposited on rough Cu foil. Two broad peaks centered at 2θ values of 18° and 30° were observed. All the diffraction peaks are assigned to the Cu foil[9,16], and no characteristic peaks of crystalline Si and SiO2 appear. This indicates that the as-deposited SiOx films are amorphous. This amorphous feature of SiOx films is consistent with that characterized in previous reports[8-10]. Fig. 1(d) shows the Raman spectra of as-prepared SiOx films. In the spectral region between 100 cm⁻¹ and 700 cm⁻¹, the spectrum mainly comprises of two broad bands at 160 cm⁻¹ and 480 cm⁻¹, which corresponds to the characteristic transverse-acoustic (TA) and transverse-optic (TO) phonon modes of amorphous silicon respectively[18-19]. In addition, no peaks at 520 cm⁻¹ corresponding to the characteristic crystalline Si are detected in the spectra of α-SiOx films[20], further confirm the amorphous feature of the as-prepared SiOx thin films. Fig. 1(e) shows the XPS Si 2p spectra of the as-deposited SiOx films near-surface depth profile that was obtained after sputtering with Ar⁺ ions for 20 s to remove the surface oxygen layer. To determine the precise valance of Si, The peak shape of Si2p3/2 spectra were fitted to a superposition of five peaks with an energy difference of 1 eV, corresponding to the different Si oxidation states, namely Si⁰, Si⁺, Si²⁺, Si³⁺ and Si⁴⁺[15]. In the curve-fitting process, the position...
MENG Xiang-Lu, et al: Influence of Film Thickness on the Electrochemical Performance of α-SiO_x Thin-film Anodes 1143

2.2 Effect of film thickness on electrochemical performance of α-SiO_x thin film anodes

It is demonstrated that the SiO_{0.7} anodes possess good cycle performance with reduced capability sacrifice, due to the fact that the moderate oxygen contents enable the formation of sufficient insulated lithium oxide/silicates. This not only relieves the large volume change occurred on in situ formed Si particles, but also shields the electrolytes from further decomposition by suppressing electron leakages from electrode surfaces. Therefore, SiO_{0.7} are selected to study the relationship between the film thickness and the electrochemical performance of SiO_x anodes. Coin-type cells with SiO_{0.7} as anodes were assembled and cycled at the current density of 0.064 mA·cm^{-2} (~0.2C). Fig. 2 shows the 1st cycle charge-discharge curves of SiO_{0.7} thin-film anodes with the thickness range of 90 nm-630 nm. It is found that the discharge plateaus of all the SiO_{0.7} electrodes with different thickness lie at around 0.23 V, the electrode with different thickness delivers a similar discharge capacity. Upon recharge, the charge plateaus of all the SiO_{0.7} anodes with different thickness lie at the range of 0.2 V-0.75 V. As for the first cycle, the discharge/charge capacities of SiO_{0.7} with thickness of 90 nm, 270 nm, 450 nm and 630 nm are 639.4/410.4, 644.7/443.4, 647.3/464.0 and 641.8/424.9 μAh·cm^{-2}·μm^{-1}, with a corresponding initial Coulombic efficiencies (ICE) of 64.18%, 68.78%, 71.68% and 66.20%, respectively. It is clear that the SiO_{0.7} with a thickness of 450 nm shows the highest ICE. With increasing of film thickness in SiO_{0.7} anodes, the ICE initially increases and then decreases. Formation of solid electrolyte interphase (SEI) is beneficial for shielding the further decomposition of electrolytes on the surface of anodes during discharge but gives rise to extra irreversible capacity, resulting in a low ICE[23]. Beyond the formation of SEI layers, the formation of irreversible...
compounds like Li$_2$O and Li$_4$SiO$_4$ during the first few cycles is another important consideration causing the low ICE in SiO$_x$ anodes$^{[16,18,24]}$. The Li$^+$ insertion/extraction reactions between Li and SiO$_x$ film species were studied by cyclic voltammetry (CV). Fig. 3 shows the initial five CV scans of the SiO$_{0.7}$ film electrodes with a thickness of 90 nm (Fig. 3(a)) and 450 nm (Fig. 3(b)). In the first scanning cycle, there is a cathodic peak around 0.5 V, which disappears in the following cycles, indicating a nonreversible reaction (Fig. S1(b)). The reduction peak is associated with the formation of a stable solid electrolyte interphase (SEI) passivation layer on the surface of the SiO$_{0.7}$ film$^{[25]}$, which is the reason for low initial Coulombic efficiency (Fig. 2). In both 90 nm and 450 nm electrodes, four redox peaks are observed in all five cyclic voltammograms, including two cathodic peaks at 0.21 V and 0.08 V, and two anodic peaks at 0.45 V and 0.29 V. They are attributed to the electrochemical reaction of lithium ions insertion and extraction in SiO$_{0.7}$ films$^{[26]}$. It is observed that the four redox peaks are almost overlapped and little shift in the five cycles, indicating that an excellent cycling performance and a small polarization of the electrode.

Fig. 4(a) shows the cycle performance of SiO$_{0.7}$

![Fig. 3 Cyclic voltammograms of SiO$_{0.7}$ film electrode with thickness of (a) 90 nm and (b) 450 nm of the 1st, 2nd, 3rd, 4th and 5th cycle at a scan rate of 0.05 mV s$^{-1}$ in the potential range of 0.01 V-1.5 V](image)

![Fig. 4 Electrochemical performances of SiO$_{0.7}$ film anodes with different thickness](image)
anodes with various film thickness. It can be seen that there exists an optimum thickness in terms of SiO$_{0.7}$ anodes$^{[23]}$. As the thickness increases from 90 nm to 270 nm, 450 nm and then 630 nm, the SiO$_{0.7}$ based anodes deliver a discharge/charge capacity of 675.4/433.8, 647.4/445.1, 644.7/462.1 and 648.3/428.8 μAh·cm$^{-2}$·μm$^{-1}$, leading to a corresponding ICE of 64.23%, 68.75%, 71.68% and 66.14%. After 200 cycles, the discharge capacities for these electrodes are 286.0 μAh·cm$^{-2}$·μm$^{-1}$, 321.4 μAh·cm$^{-2}$·μm$^{-1}$, 425.2 and 242.9 μAh·cm$^{-2}$·μm$^{-1}$, corresponding to a capacity retention of 64.43%, 72.20%, 92.01% and 56.65%. These results demonstrate that the SiO$_{0.7}$ of a specified thickness of 450 nm shows the excellent cycle performance with the high capacity. The good cyclability of SiO$_{0.7}$ anode with a thickness of 450 nm is also observed from the overlapped voltage profiles (Fig. S1).

To understand such a relationship between thickness and electrochemical performance, the EIS after cycling for 200 cycles were collected (Fig. 4(b)–(c)). After the 1st cycle, the charge-transfer resistance ($R_{ct}$) of SiO$_{0.7}$ anodes with the specified thickness of 90 nm, 270 nm, 450 nm and 630 nm are fitted to be 173 Ω·cm$^2$, 110 Ω·cm$^2$, 86 Ω·cm$^2$ and 141 Ω·cm$^2$, respectively. These impedances increase to 322 Ω·cm$^2$, 149 Ω·cm$^2$, 94 Ω·cm$^2$ and 345 Ω·cm$^2$ after the 200th cycle. The SiO$_{0.7}$ anode with a thickness of 450 nm demonstrates the minimum $R_{ct}$ as well as the variation during cycling. Such a low resistance should be a synergy effect between the rough Cu substrate, the moderate thickness of SEI layer and the suitable amounts of the inactive lithium compounds formed during discharge. The surface morphologies of SiO$_x$ anodes after the 200th cycle are shown in Fig. 4(d)–(g). First of all, all the dense SiO$_x$ films change into porous aggregates consisting of interconnected particles in the size of hundred nanometers. The porosity decreases with increasing film thickness. If more porous, the contact area between the electrodes and the electrolytes increases, enhancing formation of the SEI layers. Between the porosity and the SEI layer formed on porous electrode surfaces, the SiO$_{0.7}$ anode with a thickness of 450 nm should be the balance that enables the decreased charge transfer resistance. Second, many cracks appear in all the SiO$_x$ films. The SiO$_{0.7}$ anode in thickness of 450 nm would suffer less than the other three samples, endowing the interconnected paths for lithium transport inside the electrodes.

3 Conclusions

By means of thin-film type electrodes, the role of film thickness playing in the performance of SiO$_x$ anodes was investigated. It is found that changing the film thickness (90 nm–450 nm) of SiO$_{0.7}$ dramatically influences the cycle stability, initial coulombic efficiency and reversibility capacity. The SiO$_{0.7}$ anode with a thickness of 450 nm exhibits the superior performance in terms of cyclability, capacity and ICE. The highest initial coulombic efficiency (ICE) is 71.68% and the highest capacity retention is 92.01%. This benefits from the low charge transfer resistance, reduced formation of SEI layer and improved electrode integrity upon cycling, as evidenced by SEM images and EIS. All these benefits should stem from the moderate thickness of SiO$_{0.7}$ film anode, which induces the synergistic effect on formation of such insulators like lithium oxide/silicates during discharge. Functions such configuration as physical buffers, which relieve the large volume change of in situ formed Si particles from the reduction of SiO$_x$, and shield the electrolytes from further decomposition by suppressing electron leakage on the electrode surfaces. These results suggest that the control of the film thickness of SiO$_x$ is the key factor to improve the electrochemical performance.

References

[1] HATCHARD T D, DAHN J R. In situ XRD and electrochemical study of the reaction of lithium with amorphous silicon. Journal of the Electrochemical Society, 2004, 151(6): A838–A842.
[2] GAO T, QU Q, ZHU G, et al. A self-supported carbon nanofiber paper/sulfur anode with high-capacity and high-power for application in Li-ion batteries. Carbon, 2016, 110: 249–256.
[3] MA H, JIANG H, JIN Y, et al. Carbon nanocages@ultrathin carbon nanosheets: one-step facile synthesis and application as anode material for lithium-ion batteries. Carbon, 2016, 105: 586–592.
[4] CHAN C K, PENG H L, LIU G, et al. Crystalline-amorphous core-shell silicon nanowires for high capacity and high current battery electrodes. Nature Nanotechnology, 2008, 3: 31–35.
[5] YANG H, FAN F, LIANG W, et al. A chemo-mechanical model of lithiation in silicon. Journal of the Mechanics & Physics of Solids, 2014, 70(1): 349–361.
[6] KIM H, CHO J. Superior lithium electroactive mesoporous Si@carbon core-shell nanowires for lithium battery anode material. Nano Letters, 2008, 8(11): 3688–3691.
[7] PENG K, JIE J, ZHANG W, et al. Silicon nanowires for rechargeable lithium-ion battery anodes. Applied Physics Letters, 2008, 93(3): 033105–1–3.
[8] MIYAZAKI R, OHTA N, OHNISHI T, et al. Anode properties of silicon-rich amorphous silicon suboxide films in all-solid-state lithium batteries. Journal of Power Sources, 2016, 329: 41–49.
[9] TAKEZAWA H, IWAMOTO K, ITO S, et al. Electrochemical behaviors of nonstoichiometric silicon suboxides (SiO$_x$) film prepared by reactive evaporation for lithium rechargeable batteries. Journal of Power Sources, 2013, 244: 149–157.
[10] SONG S W. Roles of oxygen and interfacial stabilization in enhancing the cycling ability of silicon oxide anodes for rechargeable lithium batteries. Journal of the Electrochemical Society, 2013, 160(6): A906–A914.
薄膜厚度对α-SiOₓ薄膜负极电化学性能的影响

孟祥鲁¹²³，霍翰宇¹²，郭向欣¹⁴，董绍明¹

(1. 中国科学院上海硅酸盐研究所，高性能陶瓷和超微结构国家重点实验室，上海 200050；2. 中国科学院大学，北京 100049；3. 上海科技大学 物质科学与技术学院，上海 201210；4. 青岛大学 物理学院，青岛 266071)

摘 要：近年来，SiOₓ作为锂离子电池负极，由于其良好的循环稳定性、较大的容量以及对成分调控的可行性，引起了广泛的关注。以往的许多研究都集中在阐明氧含量对SiOₓ负极的影响，尺寸效应对性能的影响规律很少被研究。此工作研究了不同厚度的薄膜型SiOₓ负极材料的电化学性能。溅射制备SiOₓ电极的Si/O比值为0.7，膜厚为450 nm时，电极初始库仑效率(ICE)为71.68%，容量保持率为92.01%。以上的最优性能主要归功于电荷转移电阻低、SEI层形成减少和循环过程中电极的结构稳定性。研究表明，作为LIBs负极，控制SiOₓ负极的厚度可以有效改善电极材料的电化学性能。

关 键 词: SiOₓ;薄膜负极;薄膜厚度;循环稳定性;容量;锂离子电池

中图分类号: TQ174 文献标识码: A
Influence of Film Thickness on the Electrochemical Performance of $\alpha$-SiO$_x$ Thin-film Anodes

MENG Xiang-Lu$^{1,2,3}$, HUO Han-Yu$^{1,2}$, GUO Xiang-Xin$^{1,4}$, DONG Shao-Ming$^1$

(1. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; 2. University of Chinese Academy of Sciences, Beijing 100049, China; 3. College of Material Science and Technology, ShanghaiTech University, Shanghai 201210, China; 4. College of Physics, Qingdao University, Qingdao 266071, China)

Fig. S1  (a) The galvanostatic discharge-charge voltage profiles of the SiO$_{0.7}$ anodes with a thickness of 450 nm of 1st, 10th, 100th, 200th and 300th cycle and (b) the dQ/dV differential curve of the first cycle profile of the SiO$_{0.7}$ anodes with a thickness of 450 nm