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Study on Surface Fluorination Constructed Pre-lithiated Silicon Oxide Fluorine-rich Interface and Its Electrochemical Performance

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Abstract: This study focuses on the hot topics in SEI research, increasing the content of the inorganic compound LiF to construct an artificial fluorine-rich interface. A strategy for surface fluorination of pre-lithiated carbon-coated SiOx (Li-SiOx/C) materials is proposed, in which lithium carbonate and lithium hydroxide on the surface of Li-SiOx/C are in situ converted into LiF, thereby constructing an artificial fluorine-rich LiF SEI on the Li-SiOx/C surface and endowing Li-SiOx/C with excellent cycling performance.

Keywords: Fluorine-rich SEI; LiF; Li-SiOx/C;Surface fluorination

1. INTRODUCTION

Lithium-ion batteries (LIBs) are widely used in various energy consumption fields due to their high gravimetric energy, high power density, long cycle life, and low self-discharge, and can greatly alleviate the energy crisis and the environmental hazards caused by fossil fuel combustion. Currently, commercial LIBs use graphite as the anode and lithium metal oxides as the cathode,with theoretical specific capacities of approximately $372mAhg^{-1}$~$200mAhg^{-1}$, respectively. Among next-generation anode materials, silicon (Si) has a theoretical specific capacity as high as $4200mAhg^{-1}$, is abundant and inexpensive, and has a suitable lithiation/delithiation potential; however, it suffers from a huge volume change during cycling, low Coulombic efficiency, and low capacity retention. Silicon monoxide (SiOx), as another derivative of silicon-based anode materials, has a lower volume expansion than pure Si and is simple to prepare, making it a promising main material for next-generation anodes. The oxygen in SiOx can react with lithium ions during charge/discharge to form lithium silicate and lithium oxide phases, effectively mitigating volume expansion. However, during lithiation/delithiation, lithium ions react with lattice oxygen to form irreversible phases, consuming active lithium from the cathode and lowering the initial Coulombic efficiency (ICE); its poor conductivity hinders electron transport; and the still-high volume expansion leads to particle pulverization and performance degradation during cycling.

To address these issues, researchers have carried out extensive work on structural design (nanostructuring, core-shell structures, yolk-shell structures), silicon-carbon composites (carbon layers, graphene layers, carbon nanotube layers), element doping (transition metals, active metals, etc.), and surface coatings, which have to some extent improved the poor conductivity, volume expansion, and low ICE of SiO_x. Among these, lithium doping enables pre-lithiation outside the battery system, pre-forming irreversible lithium silicate and lithium oxide phases inside the material, reducing lithium-ion consumption and improving ICE. However, unavoidable air exposure during material preparation converts part of the surface active lithium into lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH); moreover, the pre-lithiation-generated orthosilicate phase (Li_4SiO_4) also converts into Li_2CO_3 and LiOH during air storage and slurry preparation with aqueous binders, which is detrimental to the anode material.

To solve these problems, constructing an artificial solid electrolyte interphase (SEI) has become key. The SEI formed by decomposition of conventional ester-based electrolytes on the anode surface is compositionally non-uniform and rich in loose, porous organic components, resulting in poor mechanical strength and ionic conductivity; the volume expansion of SiOx during lithiation/delithiation continuously destroys the SEI layer, and the exposed fresh Si reacts with the electrolyte, consuming more active lithium ions and electrolyte and leading to reduced efficiency and deteriorated cycling performance. The SEI is dominated by organic components and jointly composed of inorganic components such as LiF, Li_2CO_3, and organic lithium species. Among them, LiF has strong advantages in improving the rigidity and mechanical strength of the SEI: it possesses relatively excellent ionic conductivity and low electronic conductivity, and rigid LiF (ELiF=64.97GPa) helps enhance the overall mechanical strength of the SEI.

2. RESULTS

2 g of carbon-coated silicon monoxide (SiOx/C) particles with a particle size of 5–6μm and 0.2g of a lithium-containing compound were uniformly mixed and placed in a tube furnace. Argon was introduced for air displacement for 30 min, followed by programmed heating to 700 °C and heat treatment for 5 h. After natural cooling, prelithiated SiOx/C (Li-SiOx/C) was obtained. 1 g of the as-prepared Li-SiOx/C was placed in the downstream zone of a tube furnace, and 1 g of polyvinylidene fluoride (PVDF) powder was placed in the upstream zone at a PVDF-to-Li-SiOx/C mass ratio of 1:1, and the reaction was conducted under an argon atmosphere. The upstream zone was heated to 800 °C at 10 °C min^{-1} and pyrolyzed for 2.5 h, while the downstream zone was heated to 500 °C at 5 °C min^{-1} and pyrolyzed for 2 h, ensuring that both ends reached the reaction temperature simultaneously. After complete reaction, the furnace was naturally cooled to room temperature to obtain LiF-coated Li-SiOx/C (Li-SiOx/C-F).

2.1 Characterization of pre-lithiated silicon

The modified matrix material used was prelithiated silicon monoxide (Li-SiOx/C), as shown in Fig.1a. After

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prelithiation, the initial charge/discharge capacity of SiO_x decreased to some extent, compared with the SiOx/C anode, the initial charge specific capacity dropped from 1517.6mAhg^{-1} to 1301.7mAhg^{-1}. However, the initial Coulombic efficiency (ICE) of the Li-SiO_x/C anode was greatly improved, increasing from 76.48% for SiO_x/C to 89.72%, as shown in Fig. 1b. The improvement in ICE is crucial for the application of Si-based anode materials in full-cell systems, as it can greatly reduce lithium-ion consumption from the cathode and enhance the long-term cycling performance of lithium-ion batteries.

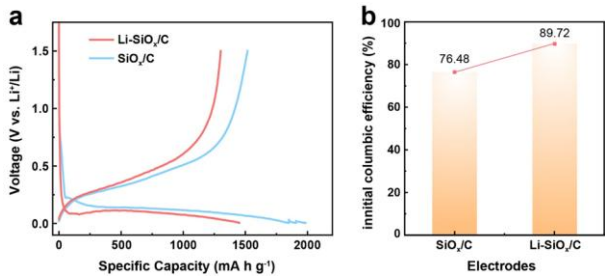


Figure1 (a) Initial charge and discharge profiles of SiOx/C and Li-SiOx/C, (b) initial coulombic efficiency comparison between SiOx/C and Li-SiOx/C.

The SEM images of SiOx/C before and after prelithiation are shown in Fig.2. The pristine SiOx/C material exhibits a relatively smooth surface (Fig.2.2a,b), and the small particles on the surface originate from the jet milling process. In contrast, after prelithiation, the particle surface becomes rough, as shown in Fig.2.2c,d. This is because during prelithiation, part of the active lithium on the material surface inevitably contacts air, forming abundant Li_2CO_3 and LiOH; moreover, during high-temperature prelithiation, part of the carbon layer on the SiOx/C surface is destroyed, which also contributes to the roughened particle surface.

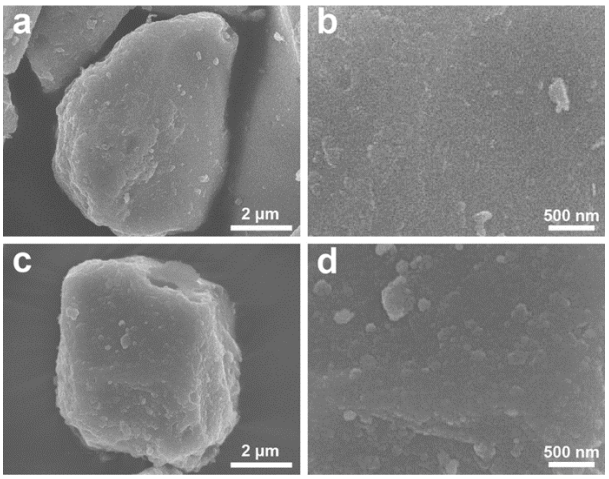


Figure2 SEM images of (a-b) SiOx/C and (c-d) Li-SiOx/C.

2.2 Structure and morphology characterization of Li-SiOx/C-F

As shown in Fig.3a and Fig3d, the coating layer on the Li-SiO_x/C-F particle surface is dense and uniform. As shown in Fig.3b and3e, unlike the fine particulate structures present on the surface of Li-SiO_x/C, the alkaline species on the Li-SiO_x/C-F particle surface were successfully converted into a uniform lamellar structure. High-resolution TEM results show that the LiF layer on the Li-SiO_x/C-F particle surface is approximately 2nm thick, as shown in Fig.3f. The measured lattice spacing is 0.23nm, Elemental analysis characterization confirms that F is uniformly dispersed on the particle surface, and EDS mapping indicates the presence and uniform dispersion of Si, O, C, and F elements. These results demonstrate that LiF-coated Li-SiOx/C-F can be obtained through a simple fluorination process, and the reaction can be confined to the alkaline species (Li_2CO_3, LiOH) on the particle surface without damaging the original structure.

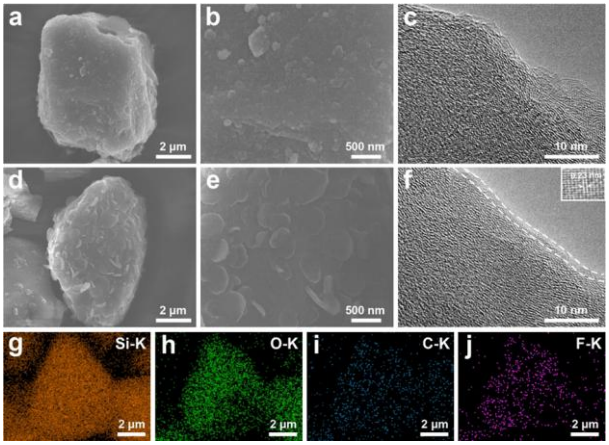


Figure3 SEM images of (a-b) Li-SiOx/C and (d-e) Li-SiOx/C-F, (c) HRTEM image of Li-SiOx/C, (f) HRTEM image of Li-SiOx/C-F with inset showing the lattice fringe. (g-j) SEM-EDS elemental mapping images of Si, O, C and F of Li-SiOx/C-F.

3. CONCLUTION

This work proposes a modification strategy based on in situ surface fluorination, in which Li2CO3 and LiOH on the surface of prelithiated SiOx/C anode are converted in situ into an artificial LiF SEI via high-temperature reaction with a fluorine-containing gas. This eliminates the harmful side reactions of the alkaline species on the material surface during anode cycling, and the coated LiF layer endows the SEI with higher mechanical strength and density, thereby improving the cycling stability of the Li-SiOx/C-F anode. Experiments demonstrate that this artificial SEI construction method is simple to prepare, low in cost, and has broad application prospects, providing a simple and effective solution for the practical application of Si-based anodes in lithium-ion batteries.

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