

Ultrathin atomic layer deposited ZrO₂ coating to enhance the electrochemical performance of Li₄Ti₅O₁₂ as an anode material

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1. Introduction

Spinel Li₄Ti₅O₁₂ (LTO) has attracted increasing attention as an alternative to graphite due to its high working potential of the redox couple Ti⁴⁺/Ti³⁺ (ca. 1.55 V vs. Li/Li⁺) and negligible volume change during charge and discharge process.^[1] In most previous studies, the electrochemical performance of LTO was evaluated in a voltage window of higher than 1 V. Recently, there is increasing awareness that it is necessary to study the LIB performance of LTO at a lower voltage than 1 V, in order to study the over-charge behaviors of LTO for safety concern and pursue higher energy density.^{2,3} In this case, solid electrolyte interphase (SEI) will form at the surface of LTO, and the SEI formation need be suppressed properly in order to enhance the cycling performance and coulombic efficiency of LTO in an extended voltage window.

Atomic layer deposition (ALD) is a thin film technique which can realize excellent coverage and conformal film deposition with precisely controlled thickness at nanoscale level.⁴ Recently, ALD has been applied in LIBs for deposition of surface-modification materials on electrodes, thereby improving their LIB performance.^{5,6} ALD is advantageous to control the thickness and uniformity of the coating materials. We have done systematic works to develop this kind of coating materials (Al₂O₃, ZrO₂, TiO₂) by ALD,⁷⁻⁹ and apply them in both anode and cathode of LIBs.^{10,11} In the present work, we will show the result of applying ALD-coated ZrO₂ to modify the LTO electrode, aiming at alleviating the SEI formation and improving its LIB performance.

2. Experimental

The LTO was prepared by a microwave-assisted hydrothermal method, and showed nanoflower-like structure.¹² The coating of ZrO₂ was directly conducted on the LTO electrode at 150 °C by ALD using Zr(NMe₂)₄ and H₂O as precursors (Fig.1, left). The thickness of ZrO₂ coating was controlled by varying ALD cycles from 1, to 2, 5, 10 and 50, and the prepared sample is named as LTO-1, LTO-2, LTO-5, LTO-10 and LTO-50 respectively.

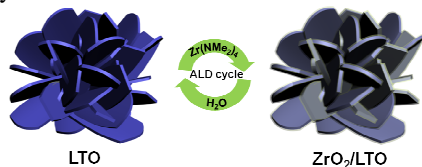


Fig.1 Schematic diagram of LTO and LTO coated with ZrO₂ by ALD.

3. Results and discussion

The coating of ZrO₂ was confirmed by SEM, EDS and HRTEM characterizations. The LIB performance of LTO with and without ZrO₂ coatings were evaluated by cyclic voltammetry (CV) and galvanostatic charge-discharge measurements.

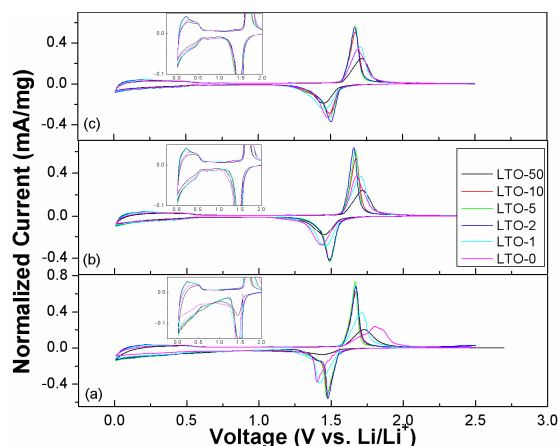


Fig.2 CV curves of LTO-0, LTO-1, LTO-2, LTO-5, LTO-10 and LTO-50 during the (a) first, (b) second and (c) third cycle at a scanning rate of 0.1 mV s⁻¹ between 0.1-2.5 V (insets show the enlarged parts below 1 V).

The CV result indicated that ZrO₂ coating with 2, 5 and 10 ALD cycles could effectively reduce the electrochemical polarization of the LTO electrode (Fig.2). Charge-discharge test revealed that the LTO electrodes with 1-, 2- and 5-cycle ZrO₂ coating exhibited higher specific capacity, better cycling performance and rate capability than the pristine LTO in a voltage range of 0.1-2.5 V. However, ZrO₂ coating with more than 5 ALD cycles could lead to degraded performance of LTO. Mechanism for the enhanced electrochemical performance of LTO was explored by electrochemical impedance spectroscopy, and the reason was attributed to the suppressed formation of solid electrolyte interphase and the improved electron transport by ultrathin ZrO₂ coating.

This work provides a novel and effective approach to improve the electrochemical performance of anode materials via surface-modification by atomic layer deposition. It is believed that this work will be inspirational for other researchers and beneficial for the development of lithium ion batteries used in PHEVs and EVs.

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