



Binder-free hybrid $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode for high performance lithium-ion batteries



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ABSTRACT

We have developed a new binder-free hybrid anode material for lithium-ion batteries, by directly coating spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles using in-situ polymerization of styrenesulfonate (SS) to form a core-shell structure. The resulting hybrid anode has significantly improved electrochemical performance, with higher reversible capacity, rate-capability, and capacity value compared with pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Of the initial discharge capacity of 239.2 mAh g^{-1} , 95.6% was retained after 100 cycles at 0.1 C-rate. The high cycle performance with increased discharge capacity is attributed to the coated poly(styrenesulfonate) (PSS) shell, which takes part in lithium ion storage and prevents the growth of a solid electrolyte interface (SEI) layer. The fast electron transfer in PSS also allows high rate-capability. Moreover, we clarify the contribution of carbon conductor in the range of 0.01 V–1.0 V.

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1. Introduction

Rechargeable batteries have become indispensable in everyday life. Most portable electronic devices, electric vehicles, and medical devices use rechargeable batteries for energy storage. Among various rechargeable batteries, lithium-ion batteries are especially prominent because of their high working voltage, high energy density, and portability [1–6]. Current Li-ion batteries use graphite, Sn, or Si as anode materials. However, graphite has poor performance with a highly irreversible reaction and forms lithium dendrite when cycled at high C-rate [7,8]. Meanwhile, Sn and Si undergo structural reorganization with huge volume changes during the charge/discharge process [9–11].

To solve these problems, many researchers have explored alternative anode materials. Recently, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been considered among the most promising anode materials. Although it has a relatively low capacity, there is active research to apply it to hybrid electric vehicle (HEV) batteries because of the possibility of realizing high power. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows a very flat voltage plateau in charge–discharge curves, due to the two-phase equilibrium junction. The LTO anode can intercalate up to three

lithium ions per formula unit, which allows a theoretical capacity of 175 mA h g^{-1} with low volume change during electrochemical reaction. Furthermore, the operating voltage is high and the surface of the negative electrode is not formed by the electrolyte decomposition reaction. Therefore, the efficiency of the initial charge and discharge cycle is almost 100%. The LTO anode could exhibit stable charging and discharging characteristics, making it an attractive candidate for stable rechargeable lithium-ion batteries.

However, due to the slow diffusion rate of lithium ions and low electronic conductivity in its structure, LTO suffers from capacity loss and poor rate capability [12–15]. To solve these problems, the synthesized LTO particles should be small (nanometers in size) and highly porous, in order to shorten the ion movement distance with carbon coating. These approaches have resulted in improved electrochemical properties during charge and discharge [16–19].

Nevertheless, highly porous nanoparticles require a large amount of solvent to prepare the slurry when manufacturing the electrode plate, resulting in lower productivity. Porous and nano-sized particles are also sensitive to moisture. Upon exposure to air, excess moisture is adsorbed on the surface of the particles. Residual moisture in the electrode can decompose the material electrochemically into hydrogen in the cell and release a large amount of gas, thereby deteriorating the cell performance [20]. Coating the hydrogenated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with carbon also presents a

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safety problem [21–23]. In addition, the usage of porous nanoparticles and carbon coating lowers the energy density of lithium-ion batteries. Therefore, we need a novel strategy to achieve both high energy density and high rate-capability for the LTO-based anodes.

In this study, poly(styrenesulfonate) (PSS) was composited with LTO without binder because poly(styrenesulfonate) can store the lithium ion and rapidly exchange the ions to improve rate-capability and energy density. PSS was coated on LTO surfaces by in-situ polymerization to facilitate the lithium ion migration. PSS contains sulfonyloxy radicals in the repeat unit structure, and it can quickly interact with the lithium cations and transfer them inside the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle. Moreover, replacing the carbon with PSS and Li-doped poly(3,4-ethylenedioxythiophene) (PEDOT) in the electrode as conductor enables the fabrication of binder-free electrodes. The conducting polymer can help bind the particles, and improves the energy density compared to when using non-conductive binders. As a result, excellent electrochemical performance was confirmed, together with increased capacity and high rate-capability.

2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) powder was prepared by a solid-state reaction. Li_2CO_3 and TiO_2 powders were mixed in a ball mill for 1 h at 3000 rpm. The mixed powders were sintered at 850°C for 10 h. Then, the PSS-coated LTO anode material was obtained by in-situ polymerization of styrenesulfonate (SS). LTO was mixed with SS (Aldrich) with LiCl in water. After removal of the liquid phase by filtration, the product was dried at room temperature under high

vacuum. To obtain the LTO–PSS composite by polymerization, the LTO–SS, 2,20-azobis(2-methylpropionitrile) (AIBN, Alfa), and dimethylformamide (DMF, Alfa) were added into a flask, sealed with a septum, deoxygenated by flushing with argon, and stirred at 90°C for 12 h. The LTO particles were coated with 10 wt.% PSS. Through X-ray diffraction (XRD, Ulvac-PHI PHI Quantera-II) and Fourier transform infrared spectroscopy (FT-IR, BRUKER OPTIK GMBH IFS 66/S), the structure and chemical composition of the prepared samples were characterized. XPS spectra of LTO–PSS were obtained with a PHI 5500 spectrometer, and Al $K\alpha$ irradiation (1485.6 eV) was used as the X-ray source at an anode voltage of 13.8 kV. The morphology and elemental mapping were observed with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy, using a Nanonova 230 scanning electron microscope (FEI, USA).

The electrodes were prepared by mixing the LTO–PSS and Li-doped PEDOT (supplied by 7 King, Co.) conducting polymer in a weight ratio of 90:10. The mixture was added into N-methyl-2-pyrrolidinone (NMP, Aldrich) solvent to form a viscous slurry, which was cast on aluminum foil and dried at 80°C under vacuum for 6 h. The film was cut into circular discs with areas of 0.95 cm^2 and masses of $\sim 4.0\text{ mg}$ for use as the electrodes. Two-electrode

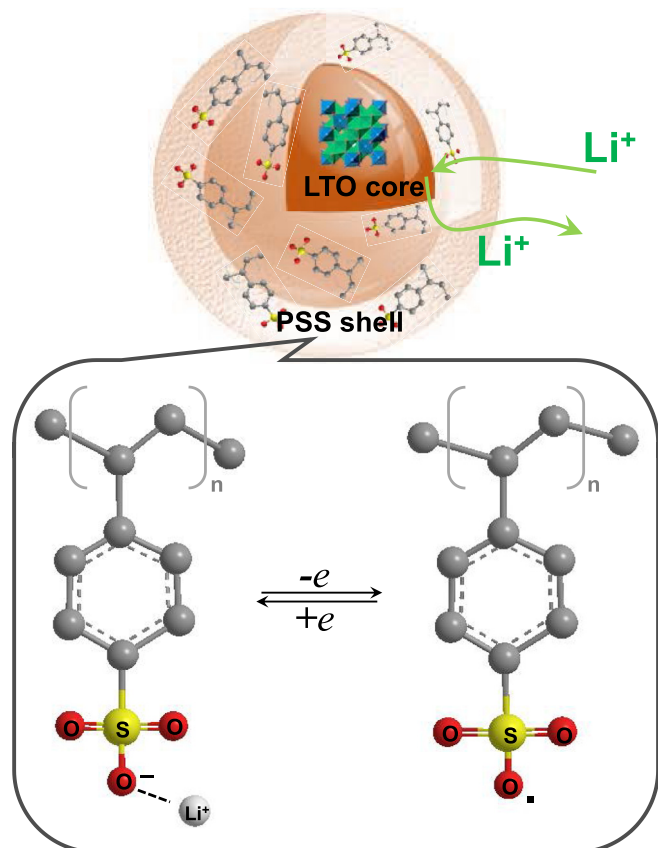


Fig. 1. Schematic diagram of the electrochemical mechanism of LTO–PSS core-shell and PSS.

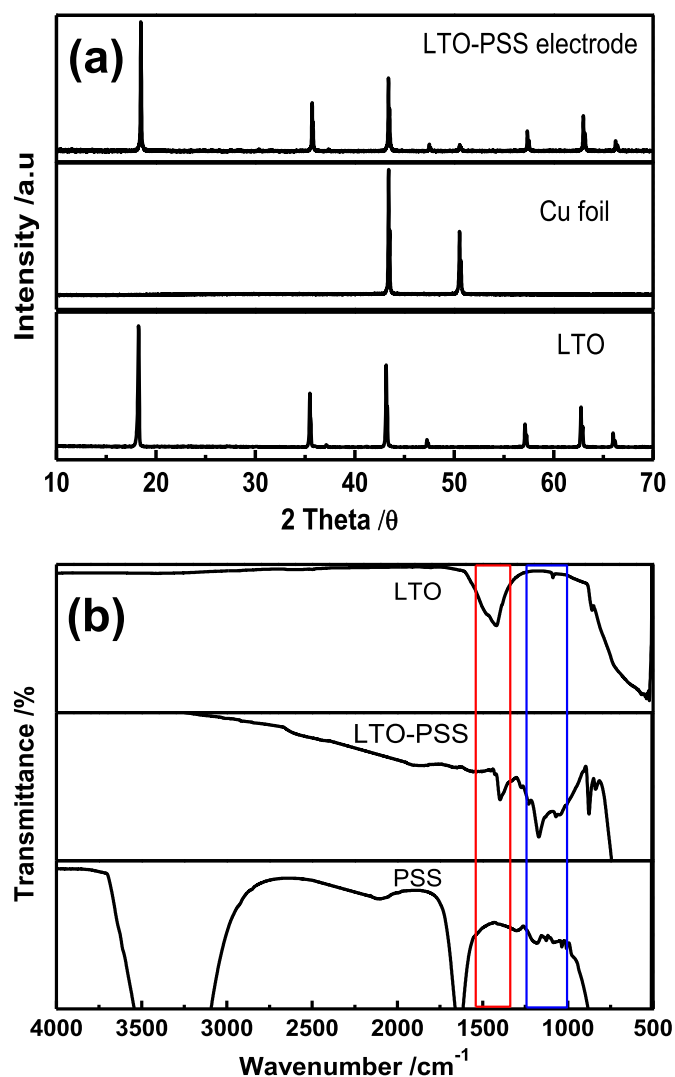


Fig. 2. (a) XRD patterns of LTO–PSS, Cu, and pure LTO. (b) FT-IR spectra of the pure LTO, LTO–PSS, and PSS.

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