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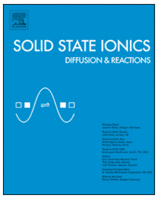

Conductive PEDOT-decorated $Li_4Ti_5O_{12}$ as next-generation anode material for electrochemical lithium storage

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ABSTRACT

Spinel $Li_4Ti_5O_{12}$ material has been regarded as the next-generation anode for lithium-ion batteries owing to its excellent safety and good structural stability. Nevertheless, the low electrical conductivity and bad Li^+-ion diffusion efficiency of pristine $Li_4Ti_5O_{12}$ greatly limit its wide applications in electrochemical energy storage. Herein, the nanosized $Li_4Ti_5O_{12}$ crystals are prepared via a simple sol-gel method to shorten the diffusion pathway of Li^+-ion. Meanwhile, the conductive PEDOT layer is adopted to modify the electrical conductivity of $Li_4Ti_5O_{12}$. The PEDOT-coated $Li_4Ti_5O_{12}$ composite is successfully prepared by using the in-situ polymerization method. Benefit from the advantages of nanosized $Li_4Ti_5O_{12}$ particles and conductive PEDOT coating, the obtained electrode exhibits enhanced electrochemical performances. It can deliver the initial discharge capacities of 169.6 and 125.2 mAh g^{-1} at 0.1 and 20 C. These results demonstrate that the designed composite is a potential electrode for high-rate electrochemical lithium storage.

1. Introduction

Nowadays, the development of lithium-ion batteries with high-power density, excellent cycle-life and good safety is still a big challenge for the practical applications [1–3]. In this context, extensive efforts have been made to find advanced electrodes to enhance the lithium-storage property of lithium-ion batteries. Spinel-type $Li_4Ti_5O_{12}$ are being widely explored for high-property energy storage because of its excellent safety, low cost and good structural stability [4,5]. It possesses a zero-strain structure with small volume change during Li^+-ion insertion and extraction procedure. Moreover, it has a stable voltage of around 1.55 V which can prevent the formation of SEI film [6]. Unfortunately, the low electrical conductivity and bad Li^+-ion diffusion efficiency of $Li_4Ti_5O_{12}$ [7,8] significantly inhibit its applications for high-rate energy storage. Up to the present, various strategies have been devoted to solve the problems.

Nanostructured $Li_4Ti_5O_{12}$ has shown enhanced rate properties because of the shortened Li^+-ion diffusion pathway [9,10]. Doping with other metal ions [8,11,12] is a simple strategy to enhance the intrinsic conductivity of $Li_4Ti_5O_{12}$. Besides, designing and preparing carbon materials [5,13–16] decorated $Li_4Ti_5O_{12}$ is the most facile and effective approach to improve the apparent conductivity. In recent years, conductive polymers such as PPy [17], PANI [18], PTh [19] and PEDOT [20,21], have been studied as the coating materials to modify the electrodes for energy storage due to their high electrical conductivity. For instance, it was found that the 1D $Li_4Ti_5O_{12}$ nanorods coated with PEDOT exhibited better electrochemical performances than the carbon-decorated $Li_4Ti_5O_{12}$ composite [22]. However, the effects of PEDOT on the battery property of 0D $Li_4Ti_5O_{12}$ nanoparticles are still unknown.

In this work, the conductive PEDOT-decorated 0D $Li_4Ti_5O_{12}$ (denoted as LTO@PEDOT) has been designed and fabricated for the first time using a facile sol-gel approach combined with the in-situ polymerization route. The results demonstrate that the surface of LTO is successfully coated by the conductive PEDOT with a thickness of about 5 nm and this PEDOT layer has no influence on the phase of LTO material. Compared with the pristine LTO electrode, the LTO@PEDOT shows superior lithium-storage performances. Therefore, the LTO@PEDOT composite is a potential electrode for high-property electrochemical lithium storage.

2. Experimental

The pristine LTO sample was prepared through the simple sol-gel approach as described previously. In a typical process, the stoichiometric CH_3COOLi and $Ti(OC_4H_9)_4$ were added to the ethanol under continuous stirring for 30 min. Afterwards, the solution was heated at

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90 °C to evaporate the ethanol solution. Finally, the obtained precursor was annealed at 500 °C for 2 h and heated at 800 °C for 5 h under air condition. The LTO@PEDOT composite was prepared using the in-situ polymerization method. During the synthesis procedure, the PEDOT coating was synthesized through the oxidative polymerization of EDOT using the $(NH_4)_2S_2O_8$ as oxidation agent. The EDOT was firstly put into the 0.1 M HCl under stirring for 30 min. Afterwards, the synthesized LTO powder and $(NH_4)_2S_2O_8$ were added to the above solution and stirred for 10 h. At last, the obtained powder was washed 3 times with deionized water and heated at 70 °C to get the LTO@PEDOT.

The phases of LTO and LTO@PEDOT materials were analyzed through XRD equipped with Cu Kα radiation. The morphology was investigated by SEM and TEM. The surface composition of LTO@PEDOT composite was studied by XPS. TG test was performed under air atmosphere to evaluate the content of PEDOT in the LTO@PEDOT sample. The battery properties of LTO and LTO@PEDOT anodes were investigated by the CR2025 cells. The working electrode was prepared by mixing LTO or LTO@PEDOT (87 wt%), carbon black (8 wt%) and PVDF (5%) dissolved in NMP. Afterwards, the mixture was casted onto the aluminium film and heated at 110 °C overnight. Finally, the cells were assembled using lithium as counter electrode, Celgard 2300 as separator and 1 M $LiPF_6$ in EC/DMC (1:1, v:v) as electrolyte. The coin-cells were measured at various densities between 1.0 and 2.5 V using a CT2001 tester. EIS was tested using a CHI 600D electrochemical workstation to analyze the electrochemical kinetics of the electrodes.

3. Results and discussion

Fig. 1a illustrates the XRD patterns of the synthesized LTO and LTO@PEDOT powders. All the diffraction peaks for the two powders are assigned to the cubic spinel-type phase (JCPDS no. 49-0207). No other impurities can be observed in the XRD curves. These results are in good agreement with the reported literatures [9,15,22]. Furthermore, the XRD results also reveal that the coated PEDOT layer has no influence on the phase structure of LTO. To evaluate the content of PEDOT in the LTO@PEDOT composite, TG test was performed under air atmosphere as shown in Fig. 1b. Obviously, no weight loss is observed for the pristine LTO material. For the LTO@PEDOT sample, the content of PEDOT can be estimated to be 9.6 wt%. The XPS survey spectrum of LTO@PEDOT is illustrated in Fig. 1c, which indicates that the Li, Ti, O, C and S elements are existed in the LTO@PEDOT material. The Ti2p spectrum (Fig. 1d) shows the strong bands at about 458.8 and 464.7 eV, presenting the binding energy of Ti2p3/2 and Ti2p1/2 [23,24]. Besides, as given in Fig. 1e,f, the C1s (284.8 eV) and S2p (164.0 and 165.2 eV) peaks in the XPS profile demonstrate the existence of PEDOT in the LTO@PEDOT sample.

Fig. 2 illustrates the SEM images of LTO and LTO@PEDOT samples. For the pristine LTO material (Fig. 2a,b), the particles are well-crystallized with a particle size of 140 nm. After coating with PEDOT (Fig. 2c,d), the morphology and particle size of LTO@PEDOT are almost unchanged compared to that of LTO. The related EDX images of Ti, O, C and S are presented in Fig. 2e, which show that these elements are homogeneously distributed in the LTO@PEDOT particles. The microstructures of LTO and LTO@PEDOT are also analyzed by TEM. As shown in Fig. 3a,b, the surface of LTO sample is smooth without any coating layers. On the contrary, a thin amorphous coating with a thickness of several nanometers is coated on the surface of LTO particle (Fig. 3c,d). The apparent electrical conductivity for the pristine LTO material can be greatly improved due to this conductive PEDOT layer [22]. Moreover, the insets in Fig. 3b,d show the HRTEM images of LTO and LTO@PEDOT, revealing the good crystallinity of the two samples.

The first charge/discharge profiles of the anode materials at 0.1 C between 1.0 and 2.5 V are given in Fig. 4a. Obviously, both electrode materials show flat plateaus at about 1.55 V, corresponding to the three Li^+-ions insertion and extraction reactions based on the Ti^{3+}/Ti^{4+} redox couple [25]. Differently, the LTO@PEDOT composite displays a higher capacity of 169.6 mAh g^{-1} than the pristine LTO material (164.7 mAh g^{-1}). As shown in Fig. 4b, the LTO@PEDOT also shows better cycling property than LTO. It can deliver the capacity of 168.2 mAh g^{-1} over 40 cycles at 0.1 C with the capacity retention ratio of 99.2%. However, the 40th discharge capacity for LTO electrode decreases to 160.7 mAh g^{-1} which is 97.6% of its first capacity.

To evaluate the electrochemical kinetics of LTO and LTO@PEDOT electrodes, EIS was carried out after 40 cycles as shown in Fig. 4c. The EIS of both anodes exhibit a semicircle and a line in the high and low frequency regions. Note that the semicircle is corresponded to the charge-transfer resistance (Rct) at the electrode/electrolyte interfaces [15,26]. The small intercept is related to the solution resistance (Rs)

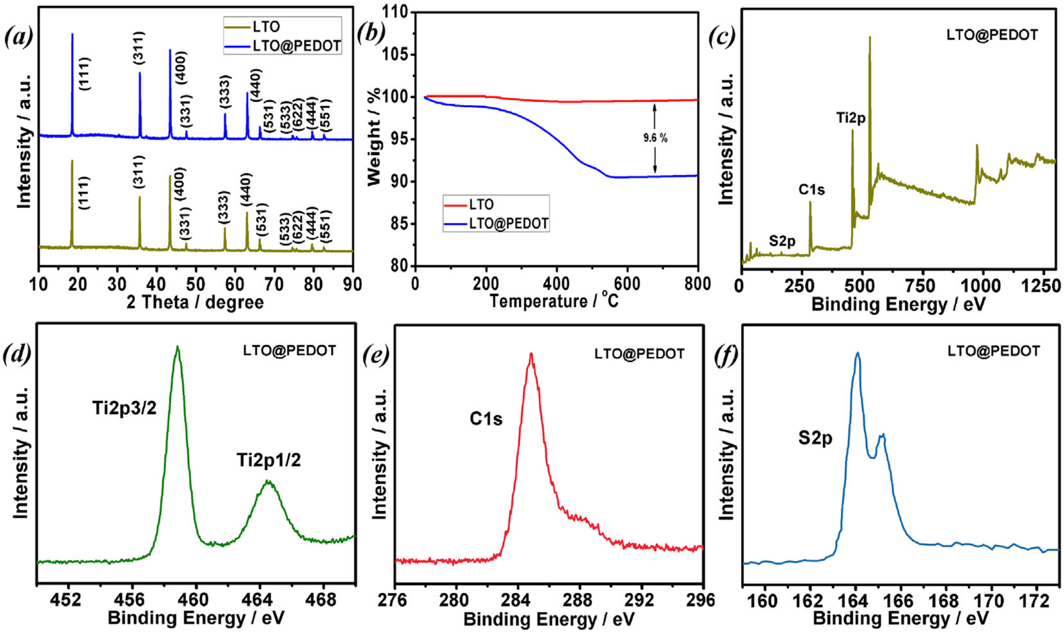

Fig. 1. (a) XRD patterns and (b) TG profiles of LTO and LTO@PEDOT; (c) XPS survey spectrum of LTO@PEDOT composite; (d–f) Ti2p, C1s and S2p spectra of LTO@PEDOT.