

FACILE SYNTHESIS OF N-DOPED CARBON COATED LITHIUM ZINC TITANATE PARTICLES TOWARDS ENHANCED PERFORMANCE IN LITHIUM-ION BATTERY APPLICATIONS

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Abstract

Nitrogen-doped carbon coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (NC-LZTO) particles as an anode material for lithium-ion batteries (LIBs) are synthesized successfully using acetyl glucosamine as carbon source via a conventional solid state reaction, in which acetyl glucosamine transformed *in situ* into N-doped carbon layers and coated LZTO particles uniformly without templates or rigorous reaction conditions. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the samples. The results show that NC-LZTO sample exhibit obvious improvements in electrochemical properties compared with carbon coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (C-LZTO) sample and the pristine LZTO sample. The NC-LZTO sample with a continuous and high electronically conducting network demonstrated superior discharge capacity (201.9 mAh g^{-1} at 2C) and excellent cycle performance (219.4 mAh g^{-1} after 100cycles at 1C), indicating their promising application in LIBs.

Keywords

Lithium-ion batteries, N-doped carbon, lithium zinc titanate, electrochemical properties.

Introduction

The conventional graphite anode can not meet the requirements of the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to its safety problems^[1]. Titanium-based oxides, including spinel lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) are regarded as promising candidate material. It features a flat operating voltage plateau. And it is a zero-strain insertion material, which has excellent reversibility for lithium-ion migration^[2]. However, the low theoretic capacity of LTO (175 mAh g^{-1}) may prevent it from being widely used in large scale energy storage devices.

Recently, cubic spinel structure lithium zinc titanate ($\text{Li}_2\text{ZnTi}_3\text{O}_8$, LZTO) as a new kind of anode material have attracted more attention. It exhibits larger lithium storage capacity, lower discharge voltage plateau and favorable cycling stability. Unfortunately, LZTO suffers from its relatively poor electronic conductivity and high rate performance is subsequently disappointing^[3]. The most effective strategy is surface modification by coating conductive agents such as Ag, SnO_2 , carbon materials^[4]. Among the above mentioned agents, carbon is a common choice. Recently, nitrogen-doped carbon (NC) coating has been reported to further improve the interfacial stability and interfacial electric conductivity than pure carbon (C) due to more active defects in coating layer, which has also been proven in theory^[5]. As far as we know, there is no report on nitrogen-doped carbon coated $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (NC-LZTO) particles as anode material in LIBs. Herein, we

exploited a facile route to prepare LZTO particles coated with NC. The acetyl glucosamine was used as a carbon precursor, which contains elements of C, O, N, and H. The effects of NC and C coatings on the electrochemical performance of LZTO are investigated. The homogeneous distribution of the NC afford a higher capacity.

Experimental

The NC-LZTO composites were prepared using Li_2CO_3 , $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, TiO_2 (anatase, 5~10nm) and acetyl glucosamine as reagents. All reagents were dispersed in anhydrous ethanol without further purification ahead and ball-milled for 4 h in planetary ball mill, then transferred to a beaker and dried at 80 °C for 12 h. The obtained precursors were ground and heated at 750 °C for 4 h in N_2 atmosphere. Finally, the NC-LZTO composites were obtained. For comparison, the C-LZTO (using glucose instead of acetyl glucosamine) and the pure LZTO samples were prepared using the same process.

Results

Fig. 1 are the TEM images of NC-LZTO and C-LZTO particles. The TEM images shown in Fig. 1(a) and (c) reveal that both samples present good dispersion. Fig. 1(b) and (d) shows the magnified photos of the samples. It clearly shows that thin amorphous carbon layers are coated on the outer surface of LZTO grains and the thickness are

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estimated to be ca. 2~3nm, which could offer a good electronic conductive network for LZTO active materials.

The presence of N element in NC layers of NC-LZTO sample has been proven by X-ray photoelectron (XPS) and the Raman measurements.

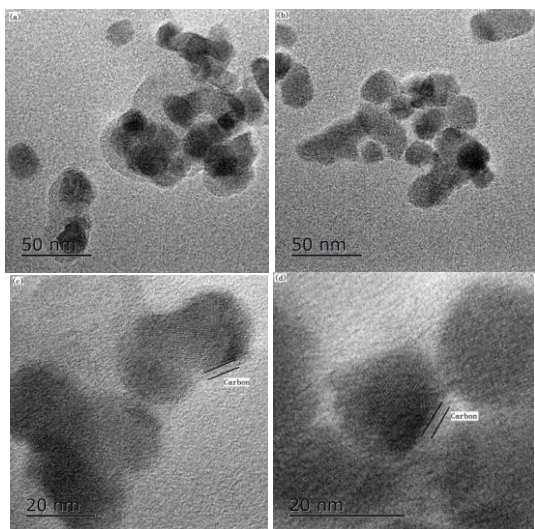


Figure 1. TEM images of C-LZTO sample (a and c) and NC-LZTO sample (b and d) at different amplifications.

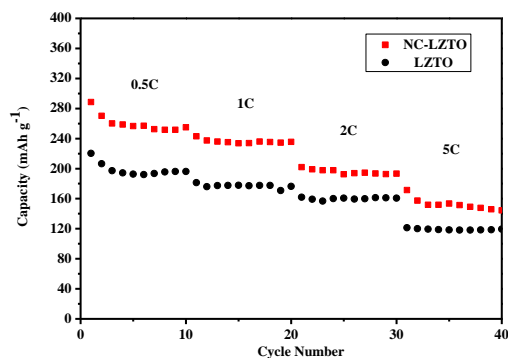


Figure 2. The rate performances of NC-LZTO sample and the pristine LZTO sample at different current rates.

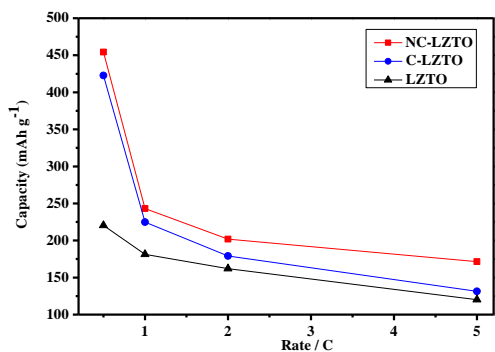


Figure 3. The rate capabilities of NC-LZTO sample and C-LZTO sample compared with the pristine LZTO sample.

As shown in Fig. 2, the rate capabilities of NC-LZTO and LZTO samples were compared by charging/discharging at various current densities from 0.5C to 5C (1C=220 mA g⁻¹). It is clearly that coated sample NC-

LZTO exhibit a higher discharge capacity than the pure LZTO. At 0.5C, the discharge capacity of NC-LZTO sample is still 255 mAh g⁻¹ after 10cycles, much higher than that of the pristine LZTO sample (196.1 mA g⁻¹). When the current densities increase to 1, 2 and 5C, the capacity of the pristine LZTO sample decreases from the original 220.3 mAh g⁻¹ to 181.3, 162 and 120.1 mAh g⁻¹. However, Improved rate performances are exhibited in NC-LZTO sample. a reversible capacity of 243.1, 201.9 and 171.5 mAh g⁻¹ can still be delivered.

As shown in Fig.3, the capability of sample NC-LZTO is better than sample C-LZTO. And the rate performances of sample C-LZTO could be enhanced to some extent compared with the pure LZTO.

Conclusions

In summary. The NC-LZTO sample with a uniform nitrogen-doped carbon (NC) layer exhibits improved electrochemical performances. At rate of 1C, NC-LZTO sample shows the discharge capability of 243.1 mAh g⁻¹, much higher than that of the pristine LZTO (181.3 mAh g⁻¹). Besides, after 100 cycles at 1C, the capacity retention of NC-LZTO sample was 219.4 mAh g⁻¹, indicating excellent cycle performance. While the pristine LZTO only delivered 170 mAh g⁻¹. Compared to the pristine LZTO, the enhanced capabilities of NC-LZTO sample and C-LZTO sample are ascribed to carbon layers coated on the surface of the LZTO particles. The carbon layers formed a continuous electronic conducting network and also hinder agglomeration of the LZTO particles. However, the superior electrochemical performance of NC-LZTO sample to C-LZTO sample are due to the nitrogen (N) element contained in NC layer, which could lead to the production of more C-vacancies in carbon layers, probably further improving the Li diffusion. Thus N-doping will further stabilize the coating layers, and then more beneficial to the electrochemical performances.

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