Solid State Ionics 320 (2018) 113–117

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Fabrication of N-doped carbon-coated $Li_4Ti_{5-x}Co_xO_{12}$ anode for lithium-ion batteries

Huaixin Liu*, Caina Su, Xuemei Li, Yong Guo

College of Chemistry and Environmental Engineering, Shanxi Datong University, Datong 037009, PR China

ARTICLE INFO

Keywords:
$Li_4Ti_5O_{12}$ anode
Co^{2+}-ion doping
N-doped carbon
Li-storage performance

ABSTRACT

In this work, the Co^{2+}-ion doping and N-doped carbon coating are adopted to improve the intrinsic and apparent electronic conductivities of $Li_4Ti_5O_{12}$. This co-modified composite is fabricated through a ball-milling process followed by one-step solid-state reaction. XRD results demonstrate that the doped Co^{2+} does not destroy the spinel-type structure and it has successfully doped into the crystal structure of $Li_4Ti_5O_{12}$. TEM images reveal that the surface of $Li_4Ti_{5-x}Co_xO_{12}$ particle is coated by a thin N-doped carbon layer with a thickness of 3–4 nm. Benefiting from the improved conductivity, the obtained composite displays an excellent rate capability and a stable cyclic property. Thus, the Co^{2+}-ion doped and N-doped carbon-coated $Li_4Ti_5O_{12}$ anode has great potential for the application of lithium-ion batteries.

1. Introduction

In the last decades, lithium-ion batteries with good safety, high-power density and long cycle-life, have attracted great attention and been used in the electric vehicles and many energy storage devices [1,2]. It is well known that the anode material plays an important role in determining the electrochemical properties of lithium-ion batteries. Therefore, various efforts have been devoted to explore the high-performance anodes for electrochemical energy storage. Recently, the spinel-type $Li_4Ti_5O_{12}$ material has been regarded as a potential electrode for the application of lithium-ion batteries due to its zero-strain feature, high potential plateau and good environmental characteristic [3–5]. Nevertheless, the poor electronic conductivity (ca. 10^{-13} S cm^{-1}) and low Li^+-ion diffusion coefficient for the pristine $Li_4Ti_5O_{12}$ material significantly limit its high-rate capacity and long cycle-life for lithium-ion batteries [6,7].

Up to now, many approaches have been made to overcome these obstacles, including fabricating the nanosized $Li_4Ti_5O_{12}$ particles [8,9], doping with metal ions (Sb^{5+} [10], Co^{2+} [11], Ce^{3+} [12], Mg^{2+} [13], Fe^{3+} [14]) and coating with conductive materials [15–19]. The nanostructure of $Li_4Ti_5O_{12}$ can shorten the diffusion pathway and facilitate the transport of electrons/Li^+-ions, while the metal doping and surface coating can improve the intrinsic and apparent electronic conductivities respectively. For instance, Zeng et al. [10] reported that the Sb^{5+}-doped $Li_4Ti_5O_{12}$ hollow sphere was prepared using a hydrothermal route and the obtained product exhibited a higher Li^+-ion diffusion coefficient (1.28×10^{-12} cm^2 s^{-1}) than the pristine $Li_4Ti_5O_{12}$ sample (3.27×10^{-13} cm^2 s^{-1}). Jung's group synthesized the N-doped carbon coated $Li_4Ti_5O_{12}$ by a refluxing process [15], and the results revealed that the composite showed excellent Li-storage performances. Despite these researches, there are few literatures reported on the metal doped and carbon coated $Li_4Ti_5O_{12}$ composite. It can be speculated that this co-modification strategy can greatly enhance the electrochemical properties of $Li_4Ti_5O_{12}$ anode for lithium-ion batteries.

In our present work, the N-doped carbon-coated $Li_4Ti_{5-x}Co_xO_{12}$ composite used as anode for lithium-ion batteries has been firstly fabricated by using a one-step solid-state reaction. The doped Co^{2+}-ion can improve the intrinsic conductivity of $Li_4Ti_5O_{12}$, while the N-doped carbon coating can further enhance the apparent conductivity. The electrochemical measurements reveal that the prepared composite exhibits outstanding Li-storage performance. As a consequence, this anode presented here has great potential for the application of energy storage.

2. Experimental

The N-doped carbon-coated $Li_4Ti_{5-x}Co_xO_{12}$ (LTCO@NC) composite was fabricated using a ball-milling process followed by one-step solid-state reaction. The Li_2CO_3, TiO_2 and $Co(NO_3)_2{\cdot}6H_2O$ with a mole ratio of 2:4.85:0.15 were used as the starting materials. First, the agents and glucose were added into the alcohol under continuous ball-milling for 6 h to obtain the homogeneous slurry. Second, the mixed slurry was dried at 80 °C overnight to remove the excess alcohol. Third, the resulting precursor was heated at 850 °C for 10 h under Ar/NH_3 atmosphere to get the LTCO@NC product. In addition, the Co^{2+}-doped

* Corresponding author.
E-mail address: liuhuaixinji@163.com (H. Liu).

https://doi.org/10.1016/j.ssi.2018.02.035
Received 12 December 2017; Received in revised form 19 February 2018; Accepted 22 February 2018

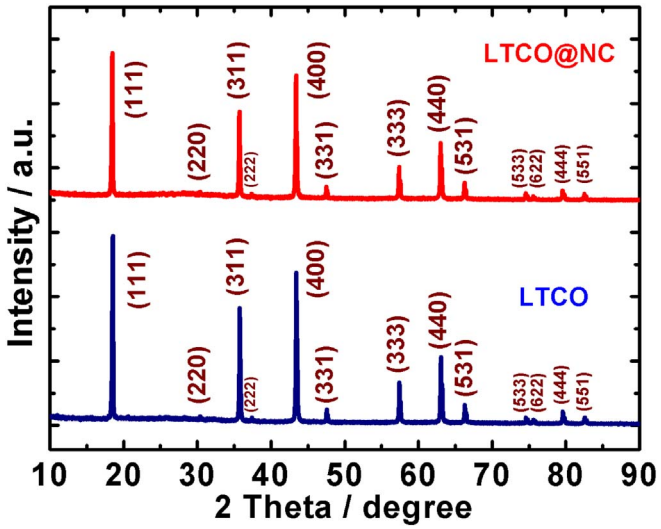

Fig. 1. XRD profiles of LTCO and LTCO@NC powders.

$Li_4Ti_5O_{12}$ (LTCO) sample was also fabricated through the similar process under Ar atmosphere without adding the glucose.

The crystal structures of LTCO and LTCO@NC powders were tested by XRD (DX 2700). The morphologies for the fabricated samples were conducted by SEM (HITACHI S-4800) equipped with the EDS. TEM and HRTEM (JEM-200CX) were performed to study the microstructures of LTCO and LTCO@NC particles. Raman spectra were recorded on an RM-2000 spectrometer. The content of N-doped carbon for the LTCO@NC composite was measured by TG under air atmosphere.

The Li-storage performances of LTCO and LTCO@NC materials were studied using the coin-cells. The working anode was synthesized by mixing the active material, super P and PVDF (85:8:7) in NMP solution. Then, the slurry was coated uniformly on a Cu foil and dried at 100 °C overnight. Afterwards, the cells were assembled in a glovebox with the Li metal as the reference electrode, Celgard 2400 as the separator and 1 M $LiPF_6$ (EC:DMC = 1:1) as the electrolyte. All the discharge and charge tests for LTCO and LTCO@NC were measured in a voltage range of 1.0–2.4 V at 25 °C. The EIS measurement was performed on a CHI760C electrochemical station.

3. Results and discussion

The XRD profiles for the LTCO and LTCO@NC samples are shown in Fig. 1. It can be found that all the main peaks of both samples are indexed to the spinel-type $Li_4Ti_5O_{12}$ (PDF No. 26-1198) with a space group of Fd-3m [5,7]. Obviously, the intensity of the peaks for LTCO@NC is lower than that of LTCO because of the coated N-doped carbon layer. The doped Co^{2+}-ion has no influence on the crystal structure of $Li_4Ti_5O_{12}$ and it has successfully doped into the lattice of $Li_4Ti_5O_{12}$, which are consistent with the reported results [11]. Moreover, no diffraction patterns of N-doped carbon can be detected in the XRD profile for the LTCO@NC composite, due to its low content or amorphous form.

The SEM and EDS dot mapping images of LTCO and LTCO@NC particles are shown in Fig. 2. According to Fig. 2a, e, the morphologies of the prepared LTCO and LTCO@NC samples are similar. Differently, the particle size of LTCO@NC is smaller than that of LTCO, demonstrating that the N-doped carbon layer can prevent the growth of particles during the annealing procedure [17,20]. As illustrated in Fig. 2b–d, the Ti, O and Co elements are uniformly dispersed in the LTCO sample. Except for the Ti, O and Co elements, the C and N elements are also distributed in the LTCO@NC sample (Fig. 2f–j) which proves the existence of N-doped carbon layer in this composite.

The nanostructures for the LTCO and LTCO@NC particles have been also characterized using TEM as illustrated in Fig. 3. It can be noted from Fig. 3a, b that the LTCO has a large particle size of 200–600 nm in diameter and the surface of LTCO is very smooth without any coated materials. For the LTCO@NC composite (Fig. 3d), it shows a small particle size of about 200 nm on an average, which can reduce the Li^+-ion diffusion pathway and thus enhance the Li-storage performances [15]. Besides, the HRTEM image in Fig. 3e indicates that the N-doped

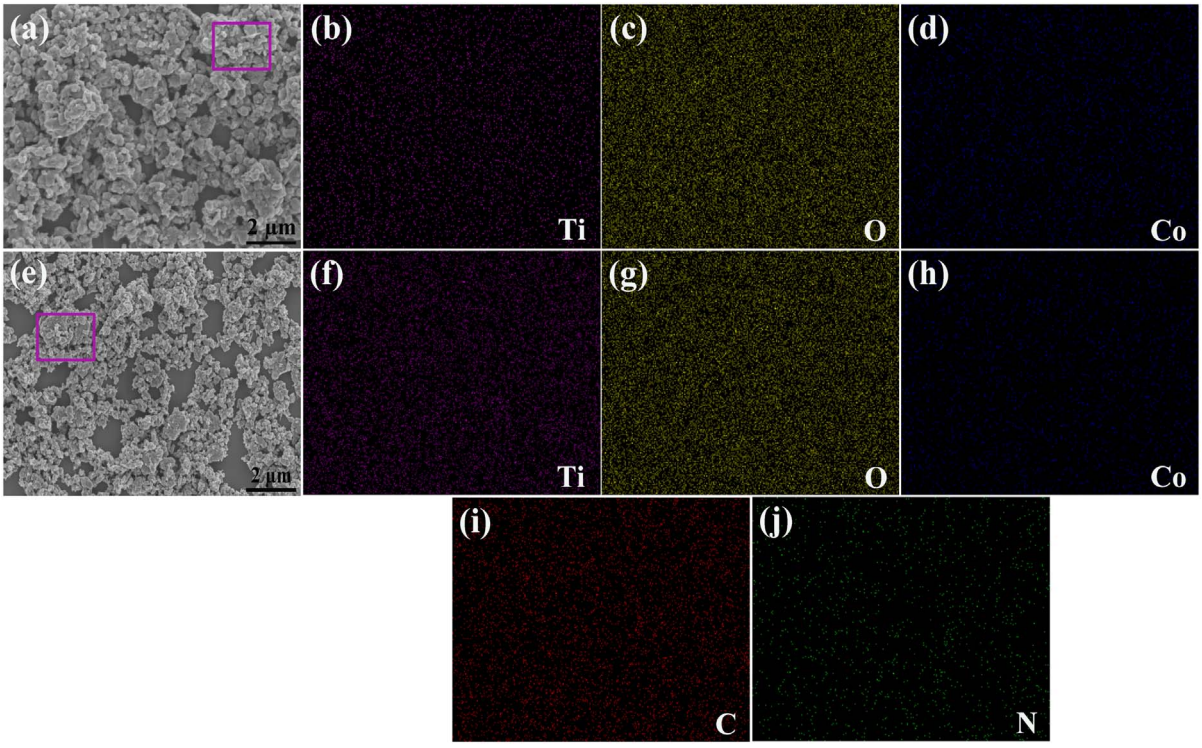

Fig. 2. SEM and EDS dot mapping images of (a–d) LTCO and (e–j) LTCO@NC particles.