

Li₄Ti₅O₁₂/Graphene composite as an anode for Li-ion battery

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Spinel structured Li₄Ti₅O₁₂ (LTO) is one of the most promising candidate anode material for Li-ion battery known as zero strain material, it has poor intrinsic electronic properties. In order to enhance it, graphene was used as additive. The LTO and graphene composites were synthesized by reduction process of graphene oxide via hydrothermal treatment. The powders were characterized by X-Ray diffraction (XRD), Infrared spectroscopy (FT-IR). For the galvanostatic discharge and charge measurements were performed at room temperature against Li/Li⁺ metal electrode.

INTRODUCTION

In the last decades, lithium ion batteries (LIBs) have been identified as one of the most sustainable system for energy storage because of its relatively high energy, power density, long shelf and cyclic life [1]. The few commercial electrodes are used as anode electrode, such as Li₄Ti₅O₁₂ (LTO), Si-based materials, and graphite which is widely used, also commercialized 20 years ago, because of being cheap, in abundance availability, low volume change (10%) during lithiation and delithiation processes compared with Si-based anodes. Among the Si-based anode materials, Li₂Si₅ has been paid more attention because of its nature, where exhibits high theoretical capacity (4008 mAh g⁻¹), which is about 10 times higher than graphite (330-430 mAh g⁻¹). However, it has the large volume changes about 300%, during the intercalation process, which cause disintegration and reduction of electrons contact between active materials, as a result the system runs poor electrochemical performance or even dies [2,3]. Therefore, the latest studies that meet stable performance and safety requirements, have been investigating for anode materials.

Owing to the requirements, the development of spinel LTO anode material studies have attracted immense attentions. LTO exhibits excellent performances, such as negligible volume change (less than 1%) during intercalation [4], high lithiation potential of 1.55 V (vs Li/Li⁺) [5], quick charge-discharge process, long cycle life, no formation of solid electrolyte interface and lithium dendrites. These features provide safety and could fit it in modern technologies. Nevertheless, the low specific capacity (theoretically 175 mAh g⁻¹),

natural poor electronic conductivity (<10⁻⁹ S cm⁻²) of LTO, retard its wide range applications [6,7]. To enhance the electrical performance of LTO many techniques are being used, such as doping aliovalent atoms (Sc³⁺, Ta⁵⁺, V⁵⁺, Nb⁵⁺, Al³⁺, Mg²⁺) [8-13], size reduction [14,15] surface coating or hybridizing with conductive materials (Ag, Cu, C and graphene). Even though, the developments of LTO capability have increasingly achievements, it still has a void to fill [16-19]. In this study, L₄Ti₅O₁₂ and graphene composites fabricated by reducing graphene oxide with 4, 6 and 8% by weight and half cells assembled for electrochemically enhanced anode material.

MATERIALS PREPARATION

The L₄Ti₅O₁₂ (LTO), which is mentioned in previous study [20], and graphene composites were synthesized by using hydrothermal method. First of all, 4, 6 and 8 % of Graphene oxide (GO, wt %), as a precursor, dissolved with hydrazine hydrate by weight ratio of 7:10 (Hydrazin:GO) in distilled water with the concentration of 0.5 mg/mL and dispersed well in ultrasonic bath. After, GO dispersed well, as-prepared LTO powder added and stirred for 10 minutes. The hydrothermal treatment was performed at 95 °C for 2 hours, stirred vigorously. During synthesis, pH set to be 10 by adding NH₄OH in order to synthesize graphene sheets with high charge density. Also, few drops of ethanol added to the mixture for avoid to agglomeration of reduced graphene sheets on the water surface, according to Zhang et al [19]. After the reduction process, the precipitations were

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washed well by methanol and distilled water and dried in a vacuum oven at 80 °C for 4 hours.

MATERIALS CHARACTERIZATIONS

Crystal structure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was characterized by X-Ray diffractometer (XRD: Shimadzu, Maxima-X-7000) with $\text{Cu K}\alpha$ (1.5406Å), scanning around 10° - 80° 2 theta degrees. For the Fourier-transformed infrared spectroscopy (FT-IR) analysis, the samples were mixed with KBr and infrared spectra were collected by using FT-IR (Shimadzu, IR Prestige-21) between wavenumber ranges of 4000-500 cm^{-1} .

ELECTROCHEMICAL MEASUREMENTS

Half cells were assembled as coin type cells (CR2032) with two-electrode cell electrochemical system that consists of $\text{Li} | \text{LiPF}_6 | \text{LTO/graphene}$. In order to prepare an anode electrode, homogeneous slurry which contains 84 wt.% LTO/graphene as active material, 7 wt.% carbon black as a conductive additive, and 7 wt.% of binder polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone was pasted on copper current collector foil and dried in a vacuum oven at 80 °C for 8 hours. The half cell assembly was performed in Argon-filled glove box using polypropylene (Celgard 2325) membrane separator. Lithium metal foil is used as both positive and counter electrode. 1M LiPF_6 solution in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) by 1:1 of volume as electrolyte. The discharge-charge performance was characterized on the CT2001A battery analyzer between 1-2.5 voltage range versus Li/Li^+ electrode at room temperature.

RESULTS AND DISCUSSION

The XRD patterns of as-prepared and synthesized samples are shown in Figure 1. All peaks of labelled as (111), (311), (222), (400), (331), (511), (440) and (531) planes observed at the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene. The samples fitted well with standardized pattern of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (JCPDS No. 49-0207) space group symmetry with $\text{Fd}\bar{3}m$ and lattice parameters found to be 8.347Å, 8.354Å, 8.356Å and 8.354Å for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene (4, 6 and 8 %) samples, respectively. The Rietveld analysis indicated the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cubic phase in synthesized LTO/graphene

composite. In other words, the cubic phase was not changed during reduction process presence of hydrazine which means no phase transition occurred. Moreover, no graphitic peak (JCPDS No. 75-1621) labelled as (002) defined around 2 theta of 26° which provides LTO/graphene composites have no stacking of graphene sheets, mentioned in Fim et al [21]. Also, no impurity peaks were determined.

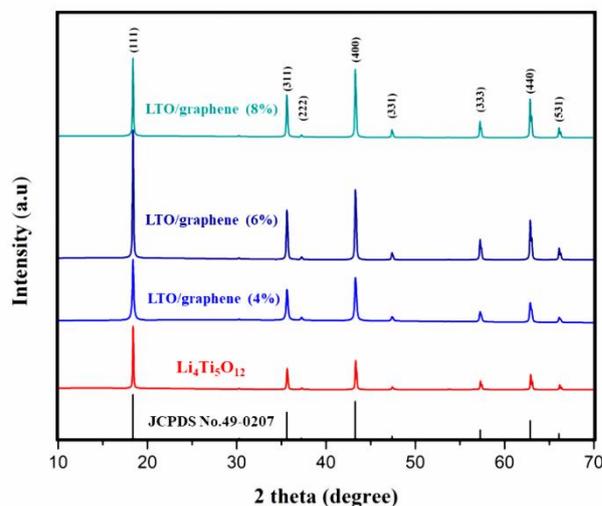


Figure 1: X-ray diffraction patterns of as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene composites different weight ratio of GO (4, 6 and 8 %).

FT-IR spectra data of all synthesized LTO/graphene (4, 6 and 8 %) composites and graphene oxide (GO) shown in Figure 2. In the spectrum of GO, the number of bands appeared at 1051, 1169, 1737 cm^{-1} , which indicate stretching of carboxyl (C-O), alkoxy (C-O), carbonyl, (C=O) surface groups of GO, respectively. Moreover, broad peak arose at wavenumber of 3340 cm^{-1} , indicates vibration of O-H group according to the Stankovich et al [22]. Whereas, in the synthesized LTO/graphene (4, 6 and 8 %) composites, two solid peaks observed at 471 and 657 cm^{-1} due to the asymmetric and symmetric band for $[\text{TiO}_6]$ octahedral of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively [23]. Also, in the spectrum of LTO/graphene composites, where no peaks observed that determine the surface groups with oxygen. It is a solid statement that indicates reduction of those groups with oxygen and shows conversion between GO and graphene by oxidation of hydrazine. For both GO and synthesized composite, peak appeared at 1623 cm^{-1} that suggests stretch which ascribed the sp^2 hybridized C=C bond that indicates to presence of aromatic rings in graphene sheets [24].

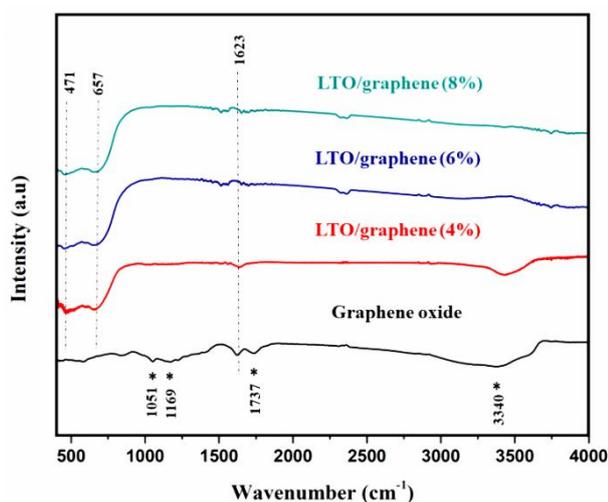


Figure 2: FT-IR spectra of LTO/Graphene and Graphene oxide.

The discharge curves of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LTO/graphene composites shown in Figure 3. The specific capacities of samples were measured at 2 C rate under constant current. Presented in the Figure 3, the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows narrow discharge curve at 1.5 V, which corresponds with the phase transition between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ [25]. Moreover, specific discharge capacity of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was 139 mAh g^{-1} . Hence, specific capacities for LTO/graphene (4, 6 and 8 %) composites were 145 mAh g^{-1} , 149 mAh g^{-1} and 154 mAh g^{-1} , respectively. In which, improvement was observed in increasing with graphene content.

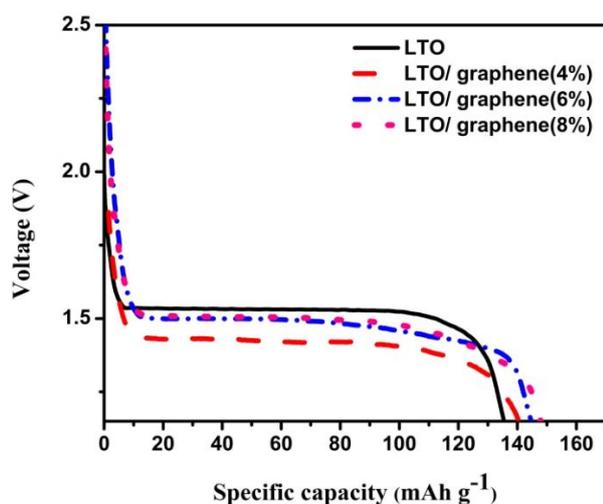


Figure 3: The discharge capacity curves of the LTO and LTO/graphene composites at 2 C rates.

CONCLUSIONS

We successfully fabricated LTO/graphene composites with by hydrothermal treatment of hydrazine hydrate with the various content of

graphene oxide (4, 6 and 8 %). FT-IR results suggest that peak arose at 1623 cm^{-1} indicated transformation between graphene oxide and graphene. Furthermore, composing graphene into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ enhance its lithium storage capability depends on graphene content. At the 2 C rate, initial discharge of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was 139 mAh g^{-1} and the specific capacity increased as 145, 149 and 154 mAh g^{-1} by increment of graphene content. In the present work we imply LTO/graphene composite material has better performance than pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, also graphene may supply LTO's poor electronic conductivity properties.

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