Current Applied Physics 13 (2013) 1350–1353

Contents lists available at SciVerse ScienceDirect

Current Applied Physics

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

Preparation and characteristics of $Li_4Ti_5O_{12}$ with various dopants as anode electrode for hybrid supercapacitor

Byunggwan Lee, J.R. Yoon*

R&D Center, Samwha Capacitor, 124 Buk-ri, Namsa-myeon, Cheoin-go, Yongin-si, Kyunggi-do 449-884, Republic of Korea

ARTICLE INFO

Article history:
Received 31 August 2012
Received in revised form
5 April 2013
Accepted 5 April 2013
Available online 17 April 2013

Keywords:
LTO
Lithium titanate
Lithium titanium oxide
Hybrid supercapacitor
Hybrid capacitor

ABSTRACT

Spinel-$Li_4Ti_5O_{12}$ is successfully synthesized by a solid phase synthesis. The $Li_4Ti_5O_{12}$ powders with various dopants (Al^{3+}, Cr^{3+}, Mg^{2+}) synthesized at 800 °C are in accordance with the $Li_4Ti_5O_{12}$ cubic spinel phase structure. The dopants are inserted into the lattice structure of $Li_4Ti_5O_{12}$ without causing any changes in structural characteristics. In order to study the effect on various dopants, the hybrid supercapacitor is prepared by using un-doped $Li_4Ti_5O_{12}$ and doped $Li_4Ti_5O_{12}$ in this work. The electrochemical performance of the hybrid supercapacitor is characterized by impedance spectroscopy and cycle performance. The results show Cr^{3+} and Mg^{2+} dopants enhance the conductivity of $Li_4Ti_5O_{12}$. Also, Al^{3+} substitution improves the reversible capacity and cycling stability of $Li_4Ti_5O_{12}$. It is found that effect of dopant on the electrochemical performance of $Li_4Ti_5O_{12}$ as electrode material for hybrid supercapacitor where the EDLC and the Li ion secondary battery coexist in one cell system.

1. Introduction

An electric double-layer capacitor (EDLC), also known as supercapacitor is energy storage device that demonstrate excellent characteristics such as long cycle life and rapid charge and discharge [1]. While batteries have the limitation of short operational life [2]. These properties already have made them suitable for a lot of application in electric vehicle and renewable energy plants. Several types of supercapacitors can be categorized, depending on the charge storage mechanism as well as the active materials used as negative and positive electrodes. EDLC is based on the electric double layer capacitance of electrode materials with high surface area such as activated carbon (AC). While pseudo capacitance arises from reversible faradaic reactions occurring at the electrode. Hybrid supercapacitors include various combinations of positive and negative materials such as activated carbon/$LiMn_2O_4$, activated carbon/$Li_4Ti_5O_{12}$ [3,4]. The spinel-$Li_4Ti_5O_{12}$ has been attracted as a promising electrode material of energy storage device, because of near zero strain in the unit cell volume during the charging and discharging. It can accommodate lithium ions during the charging, resulting in a structural transition from spinel-$Li_4Ti_5O_{12}$ to rock-salt phase $Li_7Ti_5O_{12}$ without noticeable changes in the lattice parameter. The $Li_4Ti_5O_{12}$ inserts three lithium ions per formula unit with a theoretical capacity of 175 mAh g^{-1}, and shows a voltage flat at 1.55 V versus Li/Li+, which prevents the electrolyte decomposition and the growth of lithium dendrites [4]. However, conventional $Li_4Ti_5O_{12}$ has a low Li^+ diffusion coefficient and poor electron conductivity, and accordingly has a serious problem of poor output power characteristics. To improve the low conductivity, many methods have been developed, such as cation doping [5], carbon coating and synthesis of nano-sized particle, and deposition of metallic grain on $Li_4Ti_5O_{12}$ particle surface [7]. Synthesizing the nano-sized particles via various methods can be proposed. Because small particle size will obviously shorten Li^+ diffusion path and broaden the electrode/electrolyte contact surface [5]. There are various synthesis methods for fabrication of the $Li_4Ti_5O_{12}$ such as solid-state reaction [6–8], sol–gel method [9–11], hydrothermal method [12], spray pyrolysis method [13], molten salt method [14] and microwave irradiation [15]. Generally, the spinel-$Li_4Ti_5O_{12}$ has been synthesized by a conventional solid-state reaction using TiO_2 and Li_2CO_3 (or LiOH) as starting materials at the high temperatures. Because solid-state reaction with Li and Ti source as raw materials is easy and economical. Recently, to enhance the electrical conductivity of the $Li_4Ti_5O_{12}$, many researchers reported the effect on the crystal and electro-chemical performance of $Li_4Ti_5O_{12}$, by doping various transition metal cation into Li or Ti site such as $Li_{4/3-y/3}M_yTi_{5/3-2y/3}O_4$ (e.g., Fe^{3+}, Ni^{3+} and Cr^{3+}) [16–19], $Li_4M_yTi_{5-y}O_{12}$ (Al^{3+}, Mn^{4+}, V^{4+}, and Fe^{3+}) [20,21]. Chen et al. [22] reported that the substitution of Mg^{2+} ions for Li^+ ions in the structure, i.e., $Li_{4-x}Mg_xTi_5O_{12}$ with mixed Ti^{3+}/Ti^{4+} valence. It can lead to

---

* Corresponding author. Tel.: +82 10 68058134; fax: +82 31 3327661.
E-mail address: yoonjungrag@yahoo.co.kr (J.R. Yoon).

1567-1739/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cap.2013.04.002

excellent electrochemical properties of hybrid supercapacitor with outstandingly high power density and high energy density.

However, research on $Li_4Ti_5O_{12}$ with dopants has almost focused on only anode material of rechargeable lithium ion battery.

In this work, the nano-sized spinel-$Li_4Ti_5O_{12}$ with various dopants (Al, Cr, Mg) was prepared by solid-state reaction and then studied the effect on electrochemical properties as anode material of hybrid supercapacitor.

2. Experimental

2.1. Sample synthesis and characterization

Samples with Pristine spinel-$Li_4Ti_5O_{12}$ and spinel-$Li_4Ti_5O_{12}$ with various dopants (Al, Cr, Mg) were synthesized using a conventional solid-state reaction. Raw materials were prepared by mixing appropriate amounts of starting materials of TiO_2 (Showa denko), Li_2CO_3 (Japan Pulp and Paper), Al_2O_3 (Kojundo Chemical Laboratory, Toyo Japan), Cr_2O_3 (Kojundo Chemical Laboratory, Toyo Japan), MgO (Kojundo Chemical Laboratory, Toyo Japan). They were mixed according to a stoichiometric ratio with $Li_4Al_{0.15}Ti_{4.85}O_{12}$, $Li_{3.95}Cr_{0.15}Ti_{4.9}O_{12}$, and $Li_{3.85}Mg_{0.15}Ti_5O_{12}$ following ball mill for 24 h in ethanol (99.9%). The resulting powders were dried at 80 °C. To obtain the final pristine $Li_4Ti_5O_{12}$ and doped $Li_4Ti_5O_{12}$, the mixed precursors were heat-treated at 800 °C for 12 h under air atmosphere. The crystal structures of synthesized powers were characterized by X-ray diffraction (Rigaku, D/Max-2500, Tokyo, Japan). XRD spectra were recorded with Cu Kα ($\lambda = 1.5406$ Å) radiation in the diffraction angle of 2θ from 10 to 80° at a scan rate of 5° min^{-1}. And the morphology and micro structure were observed using a scanning electron microscopy (Jeol).

2.2. Preparation of electrode films and electrochemical measurements

The charge and discharge measurements were performed on a pouch cell. The negative electrode of the hybrid supercapacitor was prepared by mixing of pristine $Li_4Ti_5O_{12}$ and Al^{3+}, Cr^{3+}, Mg^{2+} doped $Li_4Ti_5O_{12}$, conductive carbon black (Super P) and poly-vinylidene fluoride (PVdF) as a binder in the weight ratios 80:10:10. N-Methyl pyrrolidinone (NMP) was used as a solvent. The positive electrode of the hybrid supercapacitor was prepared by mixing of activated carbon (MSP-20), conductive carbon black, and polytetrafluoroethylene (PTFE) as a binder in the weight ratios 75:15:10. The slurry obtained after mixing was coated on an aluminum current collector (20 μm) and dried at 150 °C in order to remove the NMP solvent. The electrode density of negative (30 μm) and positive electrode (100 μm) was 1.1 g/cm^3 and 0.5 g/cm^3, respectively. The electrolyte was a 1 M solution of $LiPF_6$ in ethylene carbonate and dimethyl carbonate (EC-DMC 3:7 in volume). Pouch-type cells were assembled with positive electrode/separator/negative electrode in a glove box filled with high purity argon gas. And then the electrochemical performance was evaluated in the potential range of 0–3.0 V at room temperature by using a programmable multi-channel battery tester (Arbin Instruments) and the impedance measurements were carried out on IviumSoft impedance analyzer in the frequency range of 10^{-1} to 10^{-6} Hz. The capacitances of cells were calculated by the formula (1) from the time–voltage curve.

$$C = \frac{I\Delta t}{\Delta V}$$

where V is the voltage, I is a constant discharge current, and t is the time period.

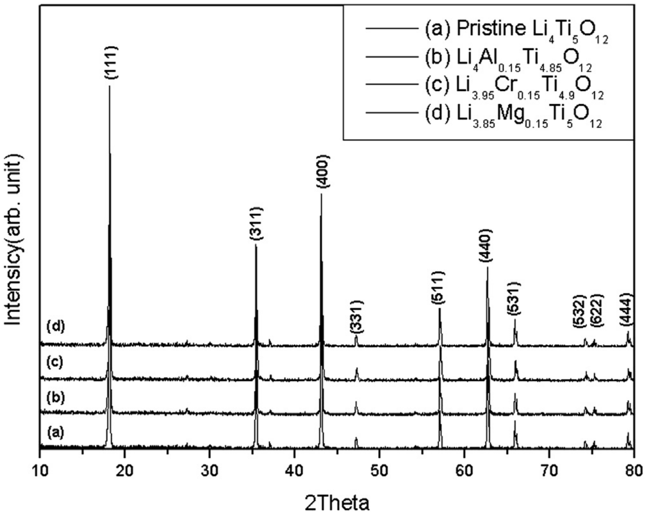

Fig. 1. XRD patterns of the (a) pristine $Li_4Ti_5O_{12}$, (b) $Li_4Al_{0.15}Ti_{4.85}O_{12}$, (c) $Li_{3.95}Cr_{0.15}Ti_{4.9}O_{12}$, and (d) $Li_{3.85}Mg_{0.15}Ti_5O_{12}$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of all the synthesized powders. It was found that the diffraction patterns of all the specimens were similar, with an Fd3m space group $Li_4Ti_5O_{12}$ cubic spinel phase structure. It exhibited the diffraction peaks at 2θ (deg.) values around 18°, 37°, 43°, 49°, 58°, 63°, 66°, 75°, 76° and 79° corresponding to (111), (311), (400), (331), (511), (440), (531), (533), (622) and (444) planes, respectively. There is no visible evidence for the formation of secondary phase. This finding indicates that the dopants have entered the lattice structure of $Li_4Ti_5O_{12}$ without causing any changes in structural characteristics. The XRD fitting results are shown in Table 1. The evolution of the 'α' was consistent with the modification of the ionic radii induced by the respective substitution. Since ion radii of Al^{3+} (0.051 nm), Cr^{3+} (0.063 nm) and Mg^{2+} (0.066 nm) were smaller than Ti^{4+}, Li^{+} (0.068 nm), the lattice parameter 'α' of all substitutions were smaller than the pristine $Li_4Ti_5O_{12}$.

Fig. 2 shows the SEM images of the pristine $Li_4Ti_5O_{12}$ and doped $Li_4Ti_5O_{12}$ powders. As shown in Fig. 2, the samples have a compact morphology consisting of small grains. The micrographs reveal that the morphology and particle size were not affected by the dopants. It is apparent that the morphology of the powders is regular nanoparticles with good dispersivity, and the SEM shows homogeneous appearance with an average particle size of 400–500 nm in diameter. At room temperature, the impedance measurements of the hybrid supercapacitor are shown in Fig. 3. All cells fabricated by pristine $Li_4Ti_5O_{12}$ and doped $Li_4Ti_5O_{12}$ were charged to 3 V. Several important points are observed. The impedance curves show semicircle in the high frequency region, which could be assigned to charge-transfer resistance, inclined line in the low frequency region, which could be assigned to Warburg impedance. As shown in

Table 1
Lattice parameter 'α' of pristine $Li_4Ti_5O_{12}$ and $Li_4Ti_5O_{12}$ doped with Al, Cr, and Mg.

Sample	Lattice parameter 'α' (Å)
$Li_4Ti_5O_{12}$	8.358
$Li_4Al_{0.15}Ti_{4.85}O_{12}$	8.354
$Li_{3.95}Cr_{0.15}Ti_{4.9}O_{12}$	8.857
$Li_{3.85}Mg_{0.15}Ti_5O_{12}$	8.359