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Preparation of $Li_4Ti_5O_{12}$ nanosheets/carbon nanotubes composites and application of anode materials for lithium-ion batteries

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ABSTRACT

$Li_4Ti_5O_{12}$ nanosheets (LTO NSs)/carbon nanotubes (CNTs) composites are synthesized using a facile, reproducible, and scalable strategy. In the hydrothermal process, the introduction of CNTs significantly improves the rate performance of LTO NSs. The incorporation of CNTs into the LTO NSs forms a delicate conductive network for rapid electron and lithium ions transport, resulting in excellent rate performance and superior cycling performance. LTO NSs/7.5%-CNTs composites show the highest reversible capacity and high-rate capability (a reversible capability of 157, 145, 132, 118, and 105 mA h g^{-1} at 1, 2, 3, 4, 5 A g^{-1}, respectively) with good cycling performance (approximate 6.9% capacity loss after 1000 cycles at 2 A g^{-1} with a capacity retention of 135 mA h g^{-1}), which is apparently larger than pristine LTO NSs. The significantly improved rate capability and cycling performance of the LTO NSs/CNTs composites are mainly attributed to their the lower polarization of potential difference, the larger diffusion coefficient of lithium ion and smaller charge-transfer resistance than pure LTO NSs.

1. Introduction

High power performance and long cycle life are essential to the lithium ion batteries (LIBs) technology, which is one of the key issues for solving the energy crisis such as for powering automotive vehicles, etc [1–3]. However, current LIBs using graphite as the anode material exhibit poor rate performance induced by their low Li diffusion coefficient, low capacity and serious safety issues caused by the solid electrolyte interphase (SEI) film [4–10]. Developing high-performance electrodes materials has been an essential component of the current endeavor for the next generation of LIBs.

Among the potential anode materials for LIBs, a variety of Ti-based materials have been intensively investigated due to their high safety and excellent cycling stability [11–15]. Especially, spinel LTO has attracted considerable attention because of its intrinsic characteristics. LTO exhibits an extremely flat charge-discharge plateau at about 1.55 V vs Li/Li^+, which makes it safe by avoiding the SEI film formation [16–20]. In addition, spinel LTO is a zero-strain insertion material, which has excellent reversibility toward lithium insertion/extraction reaction [21–25]. These two features make it a promising anode material for lithium ion batteries used in the fields of hybrid electric vehicles and large-scale energy storage, in which long cycle, high safety, and high power density are highly desired. However, the main disadvantage that restricts the application of LTO is the low electronic conductivity and lithium diffusion coefficient, resulting in poor rate capability of the lithium ion batteries [26,27]. Many methods have been applied to solve these issues, which include doping with other ions [28–30] and using nanostructures [24,28,31–35] and electronically conductive coatings [36–45]. Moreover, the assembly half cell with metal lithium might affect cycle performance of cell. In the process of dissolution and precipitation of metal lithium (especially, charge/discharge process at large current), lithium dendrites will grow on the surface of metal lithium plate, which lead to loss of active lithium and capacity fading. However, $LiFePO_4$ (LFP)/LTO and $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)/LTO full cells can form stable solid electrolyte interface (SEI) layer, which reduce initial capacity loss and improve the reversibility of full cells [46–48]. Nevertheless, it remains a great challenge to synthesize nanostructured LTO anodes with desirable architectures and design reasonable assembly model for fulfilling the requirements of high rate and long life.

Carbon nanotubes (CNTs) have attracted much attention due to their one-dimensional structure with high length-to-diameter

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ration, combined with high porosity and high surface area. CNTs display the outstanding physical properties, such as high electrical conductivity, mechanical strength and chemical stability [49–51]. The introduction of CNTs as a conducting substrate into LTO will provide large contact area between LTO and electrolyte during electrochemical processes and shorten the transport distance for both lithium ions and electrons. Hence, it is highly satisfactory to improve the capacity and rate performance of LTO. In this work, we have successfully synthesized LTO NSs/CNTs composites. The CNTs are incorporated into the LTO NSs and dispersed fully on the surface of LTO NSs. LTO NSs/CNTs composites exhibit much improved rate capability and cycling performance compared with pristine LTO NSs.

2. Experimental section

2.1. Materials

Ethyl alcohol absolute, tetrabutyl titanate (TBT), $LiOH{\cdot}H_2O$ and polyvinylidene difluoride (PVDF) were of analytical grade and purchased from Shanghai Chemical Corp. Multi-wall CNTs purchased from Beijing DK Nano Technology Co. Ltd. French Arkema The electrolyte solution with 1 M $LiPF_6$/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume) were purchased from Guangzhou Tinci Materials Technology Co. Ltd. Other chemicals and solvents are reagent grade and commercially available. Deionized water was used for all experiments.

2.2. Materials Characterization

TEM (Transmission Electron Microscopy) observation was conducted on a Philips TECNAI-12 instrument. SEM (Scanning electron microscopy) was applied to investigate the morphology, which was carried out with Hitachi S-4800 (Japan). Diffraction (XRD) data were obtained with a graphite monochromator and Cu Kα radiation ($\lambda = 0.1541$ nm) on a D8 advance superspeed powder diffractometer (Bruker). Raman spectra were recorded by a Renishaw in Via Raman microscope. Cyclic voltammograms were carried out with a CHI660c electrochemical workstation (Chenghua, China).

2.3. Electrochemical Tests

Anode electrodes were prepared by mixing the LTO NSs/CNTs composites (80%) with 10% acetylene black as a conductive material, and 10% polyvinylidene difluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidinone (NMP). Then, the slurries of the mixture were evenly cast onto an aluminum foil current collector by coating machine. After coating, the electrodes were dried at 80 °C for 10 h to remove the solvent before pressing. The average thickness of film is about 13.0 μm. The electrodes were punched in the form of disks and then vacuum-dried at 120 °C for 12 h. And then the coin cells (CR 2032 coin-type cell) were assembled with metallic lithium as the counter/reference electrode, 1 M $LiPF_6$ in EC/DMC/EMC (1:1:1 by volume) as electrolyte, and Celgard 2400 polypropylene as separator in an high-purity argon-filled glovebox (Vacuum Atmospheres Co., Ltd).

Cyclic voltammetry (CV) measurements were performed using a electrochemical workstation (CHI660 E, Chenghua, China) at a scan rate of 0.1 mV s^{-1} between 0.5 and 2.5 V. Electrochemical impedance spectroscopic (EIS) experiments were performed with an Autolab Electrochemical Analyzer (Ecochemie, Netherlands). EIS measurement is carried out at 100% state of charge (SOC). Galvanostatic charge (lithium insertion) and discharge (lithium extraction) cycling of the cells were carried out using a battery test system (CT-3008W, Xinwei, China) at the different current densities between 0.5 and 2.5 V (*vs.* Li^+/Li) to observe ratio performance, and at the current density of 2 A g^{-1} to observe cycle stability.

2.4. Preparation of LTO NSs/CNTs composites

In the typical synthesis procedure, 1.7 g of TBT, 0.204 g $LiOH{\cdot}H_2O$ and different amounts of CNTs were thoroughly mixed in 20 mL of ethanol at room temperature. The solution was mixed completely using a mechanical stirrer in a closed flask with three necks container in dry environment for about 12 h and then, 25 mL of deionized water was add to the container. After strongly stirring for 30 min, the ivory solution was transferred to a 50 mL Teflon-lined stainless autoclave and was placed in an oven at 180 °C for 36 h. The white powder deposited at the bottom of the reactor were collected and separated by centrifugation, followed by washing with ethanol for 3 times, and then dried in an oven at 60 °C for 8 h. To form the LTO NSs/CNTs composites, the precursor was heated at 700 °C for 6 h in a horizontal tube furnace under Ar atmosphere. For comparison, we also prepared the sheet-like LTO using the same procedure without the CNTs.

3. Results and discussion

3.1. Characterization of LTO NSs/CNTs composites

Fig. 1A shows the XRD patterns of the LTO NSs and LTO NSs/CNTs composites. In Fig. 1A(a), all the identified diffraction peaks are unambiguously assigned to the phase pure LTO NSs. The character peaks appear at 18.3°, 35.6°, 43.2°, 47.4°, 57.2°, 62.8°, 66.1°, 74.3°, 75.4°, and 79.3°, corresponding well with the (111),

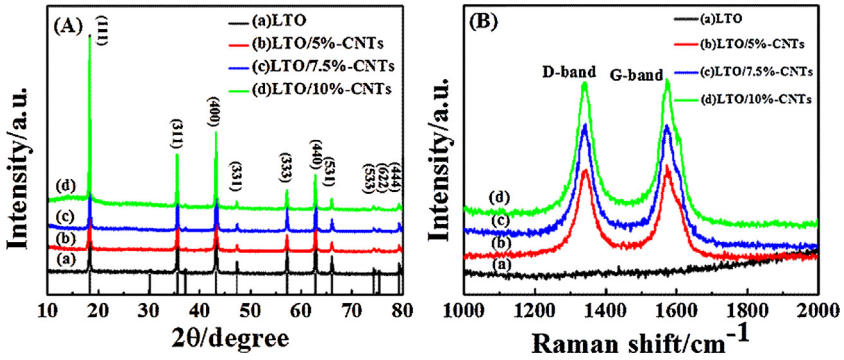

Fig. 1. (A) XRD pattern of the LTO NSs and LTO NSs/CNTs composites various weight ratios of CNTs (5%, 7.5%, 10%); (B) Raman spectra of the LTO NSs and LTO NSs/CNTs composites various weight ratios of CNTs (5%, 7.5%, 10%).