



Full Length Article

New chemical approach to obtain dense layer phosphate-based ionic conductor coating on negative electrode material surface: Synthesis way, outgassing and improvement of C-rate capability



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ABSTRACT

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) based batteries have severe gassing behavior during charge/discharge and storage process, due to interfacial reactions between active material and electrolyte solution. In the same time, the electronic and ionic conductivity of pristine LTO is very poor and induces the use of nanoparticles which increase the outgassing phenomena. The coating of LTO particles could be a solution. For this the LTO spinel particles are modified with ionic conductor Li_3PO_4 coating using a spray-drying method. For the first time a homogeneous thin dense layer phosphate based conductor is obtained without nanoparticles, as a thin film material. It is so possible to study the influence of ionic conductor deposited on the negative electrode material on performances by the controlled layer thickness. This coating was characterized by XRD, SEM, XPS and TEM. The electrochemical performance of Li_3PO_4 coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is improved at high C-rate by the surface modification (improvement of 30 mAh g^{-1} at 5 C-rate compared to pristine LTO for 5 nm of coating), inducing by a modification of surface energy. An optimum coating thickness was studied. This type of coating allows a significant decrease of outgassing phenomena due the conformal coating and opens the way to a great number of studies and new technologies.

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1. Introduction

Nowadays, safety issues have to be overcome to implement Li-ion batteries in electric or hybrid electric vehicles (HEV) applications. Moreover, high rate charging and discharging are very important for these applications, because of the power needed for rapid acceleration and regenerative braking. Due to the dendritic lithium growth on the anode surface at high charging current with a conventional carbonaceous electrode, an electrochemical redox couple with higher equilibrium potentials must be used. Among all families of materials, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is a very promising anode material due to a flat and relatively high lithium insertion/extraction voltage at about 1.55 V vs Li^+/Li during charge and discharge with a theoretical capacity of 175 mAh g^{-1} within the voltage range of 2.5–1.0 V vs Li^+/Li . Thus the formation of Solid Electrolyte Interphase (SEI) is limited and lithium dendrite elec-

troplating avoided [1]. LTO is considered “zero strain” because the phase change caused by lithiation/delithiation only results in a slight (0.2%) change in volume. Despite these advantages, three major drawbacks frustrated the practical implementation of LTO: its low electrical conductivity ($\sim 10^{-13} \text{ S cm}^{-1}$), small lithium diffusion coefficients ($10^{-13} \text{ cm}^2 \text{ s}^{-1}$ to $10^{-9} \text{ cm}^2 \text{ s}^{-1}$) [2] and severe gassing during charge-discharge cycles, especially at elevated temperatures [3–6]. CO_2 and light alkanes were observed as gassing products [5,7–9], maybe produced from the interfacial reactions between LTO and organic electrolyte solution [4,10]. Although H_2 can be the most prominent gas component in the case of water presence.

Different methods were proposed to resolve separately each problem. One strategy to improve the rate performances is to nanosize LTO. Various nanomaterials have been studied including zero-dimensional LTO materials [11,12], one-dimensional materials as nanofibers [13,14], two-dimensional [15] and three-dimensional morphologies [16,17]. These nanosized LTO materials may show good rate performance with a capacity up to 135 mAh g^{-1} at 57C between 1.0 V and 2.5 V vs Li^+/Li [16], due to shorted distance for electron conduction and Li^+ ion transport within particles. However, nanosized LTO materials generally suf-

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fer from low initial coulombic efficiency and poor cycling stability due their low crystallinity. In addition, they are faced with the problem of low tap density, except for mesoporous LTO spheres. These nanoparticles, with a large surface area [15] up to $159 \text{ m}^2 \text{ g}^{-1}$, provide a large contact area between the electrode and the liquid electrolyte, increasing the different reactions between LTO surface and decomposition products leading to the outgassing phenomenon [3–6]. Another way to improve the rate performance, especially for microparticles, is to encapsulate LTO particles by a conductive second phase. These core-shell materials can be composed on surface by Zn layer [18], Ag [19], TiN [11] or ZnO [20] but the most common is the use of carbon-based materials (carbon [21–23], graphite [24,25] and nitrogen-doped carbon [26,27]). These carbon-based coating materials are electronic conductors, poor ionic conductors and so improve only the electronic conduction at the surface of and between particles. Their improvement of rate performance compared to the use of nanoparticles is therefore limited. To allow Li^+ ions transport along the surface, the carbon-based coating must be porous, leading to contact between LTO and liquid electrolyte, and so outgassing. Constructing a barrier layer at the LTO surface is an effective strategy to control the interfacial reactions between LTO and the surrounding electrolyte solution. Then, the appropriate coating must be characterized by a dense structuration to avoid direct contact between LTO and liquid electrolyte and at the same time present mixed ionic-electronic conductivity to improve the delivery of lithium ions and electrons to the surface of LTO and increase the high C-rate capability. Indeed, mixed electronic-ionic conductivity is necessary for the preservation of overall charges neutrality during lithium ions repeated intercalation/deintercalation. Recent results obtained on LiFePO_4 confirm that lithium ion transport along the surface may be as important as electrons transport [28,29].

So, if we can perform a dense coating type, with a mixed ionic and electronic conductivities, which encapsulates perfectly particles, it could be a real breakthrough combined with the appropriate shape and dimension of LTO particles. To perform this type of “hybrid-coating”, the combination of different coating materials well known in the literature for their specific properties could be envisaged. Carbon coating shows excellent electronic conductivity. On the other hand, even if lithium phosphates are well known as good lithium ion conductors, their synthesis as a homogeneous dense layer on the surface of particles remains quite difficult. Indeed, by sol-gel method [30] or ball milling [31], Li_3PO_4 (LPO) nanoparticles were obtained on the surface of coated materials and do not correspond to our desired morphology. Before processing the direct synthesis on appropriate morphology and structure of LTO particles with optimized mixed hybrid-coating, the homogeneous coating of LTO particles by Li_3PO_4 ionic conductor must be realized. To encapsulate the particles with specific dense layer, the Spray-drying method, which is an industrial method, could be used. In the domain of electrode materials, for 3 years, some papers have presented the synthesis of LTO nanoparticles by this method [32–34]. In this paper, for this, a pristine LTO particle size around 500 nm was used to discriminate the effect of ionic conductor coating from the effect of lithium diffusion path decrease with the use of nanometer particles (inferior to 100 nm). The effect of this ionic coating on properties and outgassing phenomena were studied.

2. Experimental

2.1. Synthesis of materials

Commercial LTO particles with a particle size around 500 nm were used as pristine material. They were broken by means of a Sonicator in a mixture solution of water and tetrahydrofuran (THF),

before being dried by spray-drying (Büchi Mini Spray-Dryer B-290) at 220°C . THF is just added in 1:1 ratio to decrease the solution evaporation temperature. A part of this material is conserved as pristine LTO material. To prepare the particles coated by lithium orthophosphate, ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) is dissolved in a mixed water and THF solution (1:1). The LTO particles after sonication were added to the above solution and shaken overnight at room temperature. The prepared suspension is transferred to the Spray-dryer equipment to dry particles with phosphate coating. As phosphate material around LTO particles is not dissolved in absolute ethanol, the surface modification with Li_3PO_4 was prepared through the dispersion of as-prepared phosphate-LTO powder in an absolute ethanol solution of lithium acetate. The lithium acetate solution is added drop by drop in phosphate-LTO particles suspension in absolute ethanol. After evaporation of ethanol at 80°C , the obtained powder was annealed at 450°C for 5 h and at 700°C for 4 h in air atmosphere. The amount of Li_3PO_4 corresponds to 5 wt% and 10 wt% of the LTO powder.

2.2. Materials characterization

The phase composition was characterized by X-ray diffraction on a Bruker D8 diffractometer using the $\text{Cu K}\alpha$ radiation in the 2θ range from 10° to 60° with a step of 0.01° . The morphology and chemical composition of samples were studied by field-emission gun scanning electron microscopy (FEI Quanta 200 F) fitted with Energy Dispersive X-ray Spectroscopy (EDS) (X-Max Silicon Drift Detector 80 mm^2 Oxford Instrument). Transmission Electron Microscopy (TEM) was performed using FEI Tecnai F20 S-TWIN operating at 200 kV with a scanning mode (STEM) and fitted with an EDS. Electron diffraction patterns were obtained through Selected Area Electron Diffraction (SAED). The X-Ray photoelectron spectroscopy (XPS) was conducted with a XPS KRATOS Axis Ultra^{DLD} instrument using X-ray from an aluminum anode (monochromatic $\text{K}\alpha$ X-rays) as a source at UCCS Regional Platform of Surface Analysis. The spectrometer was calibrated using the photoemission lines of Ag $3d_{5/2}$, Au $4f_{7/2}$ and Cu $2p_{3/2}$. The peaks were recorded with constant pass energy of 40 eV and a step of 0.1 eV for core-peak levels and valence band. The diameter of the irradiated area of the sample was $110 \mu\text{m}$. For each sample, different areas were analyzed. Charging effects were observed and compensated by an applied current of 1.4 A. To check if a sample is not damaged by X-rays during measurements, one scan per element was collected before and after XPS core peaks acquisition performed on a sample. The Casa software was used to fit photoelectron spectra using a least squares algorithm. The background in narrow range spectra was accommodated by a nonlinear Shirley function. The experimental curves were fitted using combinations of Gaussian (70%) and Lorentzian (30%) distributions. Quantification was performed on the basis of Scofield's relative sensitivity factors.

2.3. Electrochemical characterization

Electrochemical performances of the pristine LTO and Li_3PO_4 (LPO) modified LTO were examined based on galvanostatic testing of Swagelok[®] cells with the conventionally prepared electrode materials with and without coating, a lithium electrode as counter electrode and LP30 (EC:DMC 1:1 weight, LiPF_6 1 M, MERK) as liquid electrolyte. The electrodes were dried before use to avoid moisture. For each material, 5 Swagelok[®] cells were prepared from the same electrode batch to confirm the results and guarantee the reproducibility of characterization. The electrochemical impedance spectroscopy was performed from Swagelok cells with three electrodes: our conventionally prepared LTO and modified LTO electrodes, a lithium disc as counter electrode and a lithium micro-electrode as reference electrode. With this configuration, we

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