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A facile electrochemical modification route in molten salt for Ti^{3+} self-doped spinel lithium titanate

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ABSTRACT

Ti^{3+} self-doped spinel $Li_4Ti_5O_{12}$ (LTO) particles were synthesized through a facile electrochemical modification route in NaCl-KCl molten salt electrolysis, and the formation mechanism is explored. Alternating Ti^{3+} self-doping significantly improves the electrochemical performance of the spinel $Li_4Ti_5O_{12}$ (LTO) particle, especially at high charge/discharge rates. According to the report, LTO, once introduced with oxygen vacancies or Ti^{3+}, will decrease the band gap about to 1.54 eV, which can dramatically improve the inherent electronic conductivity. Through the molten salt electrochemical modification technique, the Ti^{3+} species will be doped onto the surface of LTO, which was confirmed through transmission electron microscopy with EPR (namely electron spin resonance) spectra, X-ray photoelectron spectroscopy, X-ray analysis. As anodes in lithium-ion batteries (LIBs), the spinel $Li_4Ti_5O_{12}$ (LTO) particle electrode with self-doped Ti^{3+} can deliver stable discharge capacities of 168, 152, 131, 120, 102, 93 and 78 mAh g^{-1} at different rates of 0.5, 1, 5, 10, 15 and 20C, respectively. Meanwhile, like pure spinel LTO, they also carry strong cycling stability and demonstrate the capacity retention of 92.0%, though after 900 cycles under 5C. Our results indicate that pure-phase LTO is prepared by a molten salt method, and it is then electrochemically modified by a constant current to obtain conductive Ti^{3+}. Self-doped spinel $Li_4Ti_5O_{12}$ particles are a good alternative to facilitate the transfer of electrons, especially under high-rate conditions, because it shows good electronic and ionic conductivities. In addition, the molten salt synthesis and the electrochemical modification steps of this method are conducted in the same reactor with a simple process, strong operability and environmental friendly process.

1. Introduction

High energy-density storage has already become an urgent issue due to the rapid growth in new industries, especially in the areas of electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1]. Prevailing lithium-ion batteries (LIBs) have once been regarded as suitable candidates because of their long lifespan and safety [2–4]. Although there are various kinds of anode materials, considerable attention has been attached to spinel $Li_4Ti_5O_{12}$, which serves as a kind of potential anodic material for LIBs because of its compatibility with electrolytes and high voltage [5–7]. First, the two-phase lithium extraction/insertion mechanism result in the flat charge/discharge plateau [8,9]. The minimum chance of the formation of dendritic lithium and SEI greatly promote the potential of good safety and high rate capability. Additionally, during the lithium extraction and insertion processes, none volume change occurs. This is called as “zero strain”, which guarantees the long operation life and high cycling stability [10,11]. Nevertheless, the practical application of LTO as an anode in LIBs is severely hindered by its inferior rate capabilities resulting from both extremely poor electronic conductivity (10^{-13} S cm $^{-1}$) result from its wide band gap (3.0 eV for anatase and 3.2 eV for rutile) and its sluggish lithium-ion diffusion (10^{-10} ~ 10^{-17} cm^2 s^{-1}) [12–17]. In terms of the enhancement of the rate capability, many research endeavours have been devoted to overcoming these intrinsic drawbacks. The most commonly used strategies include reducing the size of the electroactive particles to the nanoscale [18–22], coating conductive layers on the $Li_4Ti_5O_{12}$ surface [23–25] and doping with appropriate ions or atoms. One typical approach focuses on altering the

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morphology by decreasing the particle size to the nanoscale or designing novel micro/nanostructures, such as nanotubes, nanocubes, and nanorods, in order to shorten the Li^+ diffusion length and enable faster Li^+ transport [26–28]. Another effective strategy is aimed at improving the electronic conductivity through cooperation with highly conductive agents, such as carbon materials, or doping foreign atoms, including N, B, Zn, and Sn, which is a highly attractive method because it not only benefits electron transfer but also offers more open channels in a specific direction for Li^+ diffusion owing to the slight modification in the LTO lattice [29–38]. However, notably, the doping of impurities causes heterogeneous impurity defects, causing a decrease in the thermal stability [39]. The electronic conductivity has been greatly increased, which is triggered by self-doping of oxygen vacancies and Ti^{3+}. For instance, Seung-Taek Myung et al. [40] conducted an experiment synthesizing Ti^{3+}-species-contained black-coloured anatase TiO_2, exhibiting strong cycling stability and superior rate capability. According to Shen et al. [41], Ti^{3+} sites are created through the control of the ambient atmosphere through hydrogenated $Li_4Ti_5O_{12}$. Nonetheless, to generate Ti^{3+} over the surface of LTO, according to most reports, it needs to prepare spinel-structured LTO. Afterward, it will be annealed in decreasing atmosphere, taking CO [42] and H_2 [43–46] under the vacuum conditions as examples [47], which are unsafe, tedious and harsh. The results and practical utilization in an uncontrolled Ti^{3+}titanium content will be limited consequently. Self-doping by a Ti^{3+} modification method can improve the electronic conductivity of material without introducing other impurities, but a more dangerous reducing gas is needed, and the production process is lengthy with high production costs, which is not conducive to industrial production. In this paper, a molten salt method is used to synthesize lithium titanate material, in which the molten salt phase is between the liquid and solid phase, possessing the advantages of both the liquid and solid phase methods. Meanwhile, since the lithium titanate material exhibits good electrochemical performance, a good grain morphology can result from the one-step method. The nanostructured LTO material with spinel morphology was synthesized by a molten salt method, and it was modified in situ at a constant current to reduce Ti^{4+} on the surface of LTO particles to Ti^{3+} to form self-doped Ti^{3+} on the surface of the LTO particles, thereby enhancing the conductivity of the LTO material. In addition, the electrochemical modification treatment can change and reduce the micromorphology of the LTO particles and further improve its electrochemical performance.

2. Experimental section

2.1. Preparation of Ti^{3+} self-doped LTO and pristine LTO powders in NaCl-KCl

In this study, LTO powders were prepared via a one-step of molten salt synthesis method. The precursors of the LTO powder samples were synthesized using Li_2CO_3 (analytically pure 99.9%), TiO_2 (anatase, average particle size: 800 nm, purity >99%, Panzhihua Tianlun Chemical Corporation, Panzhihua, China) (denoted as LTO-ME). The precursors were mixed and ground in a mortar and pestle. The molar ratio of TiO_2 and Li_2CO_3 was 5:2. The molar ratio of the eutectic mixture of NaCl-KCl was fixed at 1:1, and it was used as the solvent. The mixed salts were mixed thoroughly, ground in a mortar and pestle and then dried under vacuum at 120 °C for 24 h to minimize the water content in the molten salt (NaCl-KCl). Then, the precursor and solvent were respective mixed in two graphite crucibles and immediately transferred to a muffle furnace. In one graphite crucible, the mixed precursor powders were calcined at 850 °C for 3.5 h, and then, the whole graphite crucible was taken as the cathode, and a graphite rod (diameter 5 mm) was inserted into the outer corundum of the crucible as the anode; a 1 A current was applied for 0.5 h for constant current electrolysis, and then molten salt modification technique was used to reduce Ti^{4+} to Ti^{3+} on the surface of the LTO particles.

At last, the whole device was cooled to room temperature. 10 °C min^{-1} was kept as the heating rate for all the temperature settings. Through the processes of cooling and solidification, deionized water was used to immerse the solid mixture. Then, the salt elements also dissolved. Metal oxide particles served as the precipitated powders. They are water-insoluble, which can keep the precipitates separated. The particles obtained then were collected. Afterward, they would be treated for 24 h with vacuum under 80 °C so that the residual water can be eliminated from the surface of the particle. Then, the dried powders are subjected to electrochemical measurements and structural characterization.

For comparison, in another graphite crucible, the mixed precursor powders were calcined at 850 °C for 4 h and were synthesized under the same conditions without the introduction of a current for electrochemical modification (denoted as LTO-M).

2.2. Composition and structural determination

The phase composition was studied by X-ray diffraction (XRD Holland) using Co Kα radiation in the range of 10°–80° (2θ) and operated at 40 kV and 30 mA with a scanning rate of 0.06°/s. The morphology of the powders was observed by scanning electron microscope (SEM, Japan) and an FEI Titan 80–300 transmission electron microscope (TEM, Japan). The chemical states of various elements at the surface were analysed on a PerkinElmer PHI-5000C multifunctional X-ray photoelectron spectrophotometer (XPS, America). Electron spin resonance (EPR, Germany) spectra were obtained using a Bruker EMX-10/12 EPR spectrometer.

2.3. Electrode preparation, coin cell assembly and electrochemical measurements

The working electrode consisting of paste mixture of LTO has been used for the electrochemical testing, serving as a kind of active material. During this process, the polyvinylidene fluoride (PVDF) was used as the binder which is mixed with *N*-methyl-2-pyrrolidone. Acetylene black was used as the conducting additive. The weight ratio was kept at 80:10:10.

Afterward, a cooper foil was coated with the paste. Then, it was dried at vacuum for 12 h under 100 °C. The electrode preparation process was quite similar. The electrochemical test was set at about 3 mg cm^{-2}. An argon-filled glove box was used to assemble the experimental cells (*M*-Braun Unilab) with 1 M $LiPF_6$/EC-DMC (1:1, v/v) as the electrolyte and a Celgard 2400 membrane as the separator and metal lithium foil as the counter. The cells were cycled galvonostatically from 1 V to 2.5 V (vs. Li^+/Li) over the CT2001A battery-testing instrument. VersaSTAT4 electrochemical workstation has been used to measure the CV (cyclic voltammetry) from 1 to 2.5 V (vs. Li^+/Li). The scan rate has been kept at 0.1 mVs^{-1}. EIS, namely electrochemical impedance spectroscopy measurements were implemented under the range of 0.01 ~ 10^5 Hz through a VersSTAT4 electrochemical workstation.

3. Result and discussion

3.1. Material synthesis and characterization

The molten salt electrochemical modification process of the Ti^{3+} self-doped spinel $Li_4Ti_5O_{12}$ particles is schematically illustrated in