



Titanium dioxide and carbon co-modified lithium manganese silicate cathode materials with improved electrochemical performance for lithium ion batteries



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ABSTRACT

A new composite of TiO₂ and carbon co-coated Li₂MnSiO₄ has been successfully prepared for the first time. The influence of TiO₂ on the structure and electrochemical performance is investigated by means of XRD, SEM, TEM, EDS, EIS and galvanostatic charge–discharge tests. The results indicate that TiO₂ and carbon have been successfully coated on the surface of Li₂MnSiO₄ without altering its orthorhombic structure. When assembled as cathode, the electrochemical performance is significantly improved after coating TiO₂. Specially, 3 wt.% TiO₂ coated Li₂MnSiO₄/C can display a discharge capacity of 186 mAh g^{−1} at 0.1 C, and 78 mAh g^{−1} is remained after 25 cycles at 0.5 C. This excellent electrochemical performance is due to the reason that TiO₂ and carbon hybrid layer are coated on the surface of Li₂MnSiO₄, which can alleviate the structural collapse and Mn dissolution in the electrolyte during charge–discharge process. In addition, the smaller charge transfer resistance and the larger lithium ion diffusion coefficient also contribute to the superior electrochemical performance.

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1. Introduction

Rechargeable Li-ion batteries have occupied the main market in portable energy storage due to the high energy density, long cycle life, no memory effect and environmental benign [1,2]. With the continuous progress in the development of electric and hybrid electric vehicles, the expanding demand for next-generation batteries with high energy density and safety is to satisfy the production. As we know, the performance of lithium ion batteries is mainly determined by the property of cathode materials. However, conventional cathode materials (LiCoO₂ and LiMn₂O₄) with the limited capacities can only allow one Li⁺ or less than one Li⁺ ion in per unit formular to insert into cathodic host lattice [3–5], which can't meet the demand of EV and HEV. Thus, seeking new cathode materials with high capacity and safety to replace the traditional materials becomes an urgent task for researchers.

Recently, polyanion compounds with (XO₄)^{n−} group (X = P, Si, Mo, etc.) have been extensively investigated as potential cathode materials for lithium ion batteries [6]. Of these materials, lithium metal orthosilicates (Li₂MSiO₄, M = Fe, Mn, Co, etc.) have attracted extensive attention owing to their overwhelming advantages such as their potential

ability to realize a two-electron transfer reaction of the M²⁺/M⁴⁺, given more expectations of the high theoretical capacity of ~330 mAh g^{−1} [7,8]. Moreover, the orthosilicate group materials can render high thermal stability through strong Si–O bond [9]. Among the lithium orthosilicate, cathodic Li₂MnSiO₄ is highlighted due to the potential insertion/extraction of two Li⁺ ions with the oxidation of Mn⁴⁺/Mn³⁺ couple in the potential range [10,11].

Similar to the olivine phosphates, Li₂MnSiO₄ suffers from the same drawbacks such as slow lithium ion diffusion and poor electronic conductivity [12], which inhibits its specific capacity under high rate conditions. Up to date, many methods have been employed to overcome these drawbacks, including carbon coating, synthesis of nano-sized particles, and doping with metal ion [13–16]. Wherein, carbon coating is a feasible and effective way to enhance the electron conductivity between the particles [8,15,17]. Another drawback is the poor cycle performance with quick capacity fading due to the structural instability and manganese dissolution. Aravindan [18] reported Li₂MnSiO₄/C composite electrode with 42% carbon could exhibit a stable discharge behavior of ~140 mAh g^{−1} for 40 cycles at 0.05 C, but such large amount of carbon certainly dilutes the volumetric capacity of the cathode. And oxides coating (ZrO₂ [19], ZnO [20], Al₂O₃ [21], SiO₂ [22], CuO [23], TiO₂ [24]), which has been widely used on other materials, can effectively suppress side reactions on the interface between electrode and electrolyte, decrease the charge transfer resistance and improve the structural stability.

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Combined with the advantages of carbon and oxide coating, we prepared TiO₂-coated Li₂MnSiO₄/C by a preliminary formation of Li₂MnSiO₄/C via a facile sol–gel method and the following coating process with TiO₂ nano layer via a wet chemical process in this paper, with the expectation of superior electrochemical performance. And the effect of contents of TiO₂ on the structure and electrochemical performance has been investigated. The results indicate that the electrochemical performance has been improved, especially of high rate performance. To the best of our knowledge, it is the first time to enhance the charge–discharge capacity of Li₂MnSiO₄ by coating TiO₂ and carbon on its surface, and we have proved that this is an effective way.

2. Experimental

2.1. Synthesis of Li₂MnSiO₄/C

The stoichiometric amount of LiCH₃COO·2H₂O, Mn(CH₃COO)₂·4H₂O and Si(OC₂H₅)₄ (TEOS) (the molar ratio of Li:Mn:Si is 2:1:1) were firstly dissolved in ethanol and distilled water mixed solution (V_e/V_w = 2:1), and the solution was vigorously stirred at room temperature. A certain amount of acetic acid as catalyst and glucose as carbon source were added to the above solution, respectively. After adequately magnetic stirring, the transparent solution was evaporated at 80 °C in oil bath to form wet gel, and dried at 120 °C for 24 h under a vacuum atmosphere. Then the obtained precursor was pre-sintered at 400 °C for 4 h, and calcined at 650 °C for 6 h in a reductive atmosphere (5% H₂ + 95% N₂). After cooling to room temperature, Li₂MnSiO₄/C cathode materials were obtained.

2.2. Synthesis of TiO₂-coated Li₂MnSiO₄/C

The as-prepared Li₂MnSiO₄/C was coated with TiO₂ by wet chemical process. Firstly, Ti(C₃H₇O)₄ was dissolved in anhydrous ethanol, and then Li₂MnSiO₄/C were added into the above solution under magnetic stirring. Followed by sonication for 1 h and continuously stirring for another 2 h, the solution was transferred to oil bath and evaporated at 80 °C. The resulting powder was annealed at 650 °C for 1 h under N₂ atmosphere. For coating various contents of TiO₂ (0, 1, 3, 5 wt.%), we only needed to adjust the amount of Ti(C₃H₇O)₄.

2.3. Structure and morphology characterization

The crystal structures of the synthesized materials were characterized by a powder diffractometer equipped with a Cu Kα source at a scan rate of 6° min⁻¹ ranging from 15° to 80°. For ex situ structural analysis of the cycled materials, the cells were disassembled and the electrode was rinsed with DMC several times to remove the LiPF₆ electrolyte and then dried at room temperature. The surface morphology and crystal structure were observed with a field-emitting scanning electron microscope (SEM, SU8000 Series) and a transmission electron microscope (TEM, JEM-2100F), respectively. The concentrate of Mn in electrolyte after certain cycles was investigated by ICP analyzer (ICPE-9000, SHIMADZU). The carbon content was determined from thermogravimetric analysis (TGA, NETZSOH STA 449C).

2.4. Electrochemical performance characterization

The electrochemical performances of as prepared samples were investigated using 2032 type coin cells. The working electrode was constructed by mixing the active material, super P, and polyvinylidene fluoride (PVDF) at a weight ratio of 80:10:10 in an appropriate amount of N-methyl-2-pyrrolidone with the assistance of ultrasound. The slurry of uniform mixture was pasted on aluminum foil current collector and dried at 120 °C for 12 h in vacuum. The active materials load on the current collector were around 2–3 mg. The coin-type cells were assembled in an argon-filled glove box, employing lithium foil as anode electrode, Celgard 2320 membrane as separator and 1 M LiPF₆ dissolved

in ethylene carbonate (EC)/diethyl carbonate (DEC) (2:3, v/v) as electrolyte. The galvanostatic charge–discharge cycles were carried out at different rates within a voltage range of 1.5–4.8 V (vs. Li/Li⁺) at room temperature. The electrochemical impedance spectroscopy (EIS) was performed by GAMRY PC14-750 electrochemical workstation in the frequency range from 10 mHz to 100 kHz with an amplitude of 5 mV.

3. Results and discussion

3.1. Structure and morphology of TiO₂-coated Li₂MnSiO₄/C

The X-ray diffraction patterns of the as-prepared samples are illustrated in Fig. 1. All the reflections of the samples are in good agreement with the reported results and can be indexed as the orthorhombic structure with a space group of *Pmn*2₁ [25,26]. The small peak observed in all the prepared samples at the angle of around 41° (marked by “*”) corresponds to the impurity of MnO, and similar impurity phase has also appeared in other reports [27–29]. Carbon is generated from the carbonization of glucose, and no obvious diffraction peaks of carbon are observed in all the patterns, which could be attributed to the amorphous nature of carbon. Moreover, the diffraction peaks of TiO₂ are not detected in the coated samples, which is most likely due to its low content. Compared with the pristine Li₂MnSiO₄/C, no apparent shift of the peaks can be observed after coating TiO₂, which indicates that TiO₂ prefers to be coated on the surface of Li₂MnSiO₄ particles rather than diffusing into the lattice.

SEM measurement is carried out to investigate the morphologies of pristine and 3 wt.% TiO₂-coated sample, presented in Fig. 2(a, b). The morphology of the Li₂MnSiO₄/C is not homogeneous, with the particle size varying from tens of nanometers up to several micrometers. Compared to the pristine sample, the surface morphology has not been obviously changed after coating 3 wt.% TiO₂, except that the degree of the aggregation of primary particles has been alleviated, which shortens the pathway of lithium ion migration. TEM and HR-TEM images of 3 wt.% TiO₂ coated sample are presented in Fig. 2(c, d). The results show that the micrometer particles consist of primary particles with average size of less than 50 nm. Seen from HRTEM, TiO₂ goes through the carbon layer and is coated on the surface of Li₂MnSiO₄. In addition, the lattice fringe of TiO₂ and Li₂MnSiO₄ can be clearly observed. The large lattice fringes with a spacing *d* of about 0.532 nm represent (010) planes of Li₂MnSiO₄ (PDF 04-014-1657), while the smaller spacing *d* of about 0.435 nm corresponds to (110) planes of TiO₂ with the space group of *Pbnm* (PDF 49-1433). The results indicate

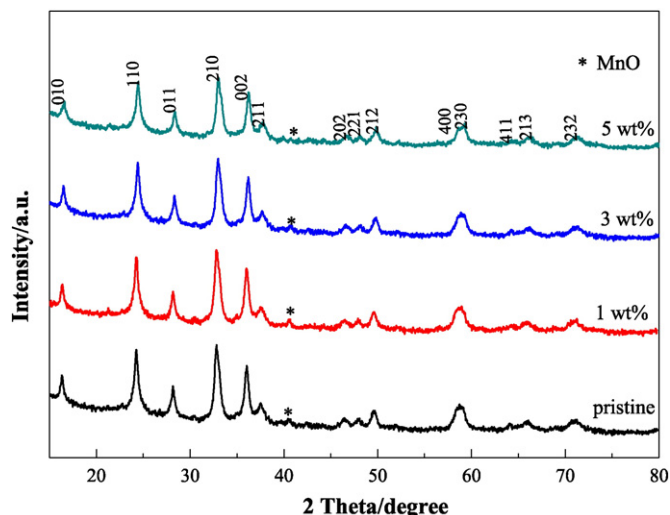


Fig. 1. XRD patterns of pristine Li₂MnSiO₄/C and TiO₂ coated Li₂MnSiO₄/C.

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