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Improved electrochemical performance of zinc oxide coated lithium manganese silicate electrode for lithium-ion batteries

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ABSTRACT

ZnO-coated Li_2MnSiO_4/C composites have been successfully prepared by a preliminary formation of Li_2MnSiO_4/C by facile sol–gel method and a following coating process with ZnO via a wet chemical process. Phase compositions and morphology of the products have been investigated by XRD, SEM, TEM and EDX. The physical characterizations manifest that nano-layer ZnO has been successfully coated on the Li_2MnSiO_4 particle surface. Among the samples, 1 wt% ZnO coated Li_2MnSiO_4/C shows the best performance with an initial discharge capacity of 183 mAh g^{-1} at 0.1C rate and the specific capacities of 142 and 134 mAh g^{-1} at the high rate of 0.5C and 1C, respectively, which is much better than Li_2MnSiO_4/C without coating ZnO. The better electrochemical performance can be attributed to the significantly decrease of the charge transfer resistance and improvement of lithium ion diffusion coefficient after coating ZnO, which is beneficial for the rapid insertion/extraction of lithium ions.

1. Introduction

Lithium ion batteries have drawn a lot of attention as one of the most promising power sources for electric vehicles (EV) or hybrid electric vehicles (HEV), and residential energy storage applications [1–3]. Electrode materials, especially the cathode materials, play an important role in achieving the energy demands. However, the available energy density of conventional cathode materials, such as $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$, is difficult to be enhanced owing to the limited lithium intercalation stoichiometry, which can only allow one Li^+ or even less than one Li^+ in per unit formular to insert into cathodic host lattice [4–6]. Therefore, it is necessary to develop new cathode materials with high energy density, low cost and high safety to meet these requirements.

Among the types of cathode materials, polyanion-type materials lithium orthosilicate, Li_2MSiO_4 (M = Mn, Fe and Co), have attracted considerable attention recently as cathode materials due to the overwhelming advantages, such as low cost, high theoretical capacity (330 mAh g^{-1}) owing to the possibility of extraction of more than one Li^+ ion in per unit formular, and high thermal stability provided through strong Si–O bonding. Among the lithium orthosilicate, Li_2MnSiO_4 is much more promising than Li_2FeSiO_4 and Li_2CoSiO_4, due to possible oxidation of Mn^{4+}/Mn^{3+} couple within the potential range of present electrolyte systems, resulting in high energy density [7,8].

Nevertheless, Li_2MnSiO_4 suffers from poorer electronic conductivity ($\sim10^{-16}$ S cm^{-1}), when compared with other cathode materials such as $LiCoO_2$ ($\sim10^{-4}$ S cm^{-1}), $LiMn_2O_4$ ($\sim10^{-6}$ S cm^{-1}) and $LiFePO_4$ ($\sim10^{-9}$ S cm^{-1}). This property has been considered as one of the major causes of limiting its high-rate performance [9]. Carbon coating has been claimed as an effective method to address the shortcoming. Lee et al. reported that in-situ carbon-coated Li_2MnSiO_4 nanoparticles were prepared by employing an adipic acid-assisted sol–gel process, resulting in superior electrochemical performance [10]. Aravindan prepared Li_2MnSiO_4/C composite electrode with 42% carbon, which exhibited a very stable discharge behavior ~140 mAh g^{-1} for 40 cycles at 0.05C, but such large amount of carbon certainly dilutes the volumetric capacity of the cathode [11]. Another feasible way to enhance the battery performance is to incorporate ions to the as-prepared Li_2MnSiO_4. For example, Li_2MnSiO_4 cathodes substituted by Mg^{2+} could deliver better electrochemical performance [12].

Surface coating or modifying with metal oxide is also an effective way in enhancing the electrochemical performance, which has been widely used on other cathode materials. Coating of Al_2O_3 [13], and SiO_2 [14] on the surface of $LiMn_{1.5}Ni_{0.5}O_4$ particles could suppress the formation of HF and the dissolution of transition metal ions. TiO_2 [15], ZrO_2 [15,16], CeO_2 [17], and Cr_2O_3 [18] have been

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used to construct the surface-coated $LiMn_2O_4$ phase. And the electrochemical performance of $LiFePO_4$/C composites have been improved after coating or modifying with SiO_2 [19], CuO [20], and V_2O_3 [21]. In a word, the surface modification can effectively suppress the side reaction at the electrode surface and decrease the charge transfer resistance, which could significantly improve the electrochemical performance of the materials. However, coating metal oxide on the surface of Li_2MnSiO_4 has not been reported up to now.

Currently, ZnO is widely used as surface coating material, due to its low cost, environmental friendliness, thermal and structural stability in the air. ZnO has been applied to the surface modification of various cathode, including $LiMn_{1.5}Ni_{0.5}O_4$ [22], $LiMn_2O_4$ [23], $LiCoO_2$ [24], $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ [25] and $LiFePO_4$ [26].

Therefore, ZnO is chosen as a coating layer on the surface of Li_2MnSiO_4/C to improve its electrochemical performance in this paper. Li_2MnSiO_4/C materials coated with different content of ZnO have been successfully prepared by acetic acid assisted fast sol–gel method. To the best of our knowledge, this is the first attempt to employ a metal oxide to improve the electrochemical properties of Li_2MnSiO_4 cathode materials. The effect of coating with different mass percents of ZnO is examined. The phase compositions and morphology of the samples have been characterized by XRD, SEM and TEM. The electrochemical performance is investigated by galvanostatic charge–discharge measurement and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Synthesis of Li_2MnSiO_4/C

Firstly, a stoichiometric amount (the molar ratio of Li:Mn:Si is 2:1:1) of $LiCH_3COO{\cdot}2H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$ and $Si(OC_2H_5)_4$ (TEOS) were dissolved in ethanol and distilled water mixed solution ($V_e/V_w = 2:1$), and the solution was vigorously stirred at room temperature followed by the addition of acetic acid as catalyst. Then glucose was added to the resultant solution as carbon source. After adequately magnetic stirring for 2 h, the transparent solution was evaporated at 80 °C in oil bath to form the wet gel, and dried at 120 °C for 24 h under a vacuum atmosphere. The resulting precursor after grinding finely was pre-sintered at 400 °C for 4 h, then pressed into pellets and calcined at 650 °C for 6 h in a reductive atmosphere (5% H_2 + 95% N_2). Then cooled to room temperature, Li_2MnSiO_4/C cathode material was obtained.

2.2. Synthesis of ZnO-coated Li_2MnSiO_4/C

For coating of ZnO on Li_2MnSiO_4/C cathode material, different stoichiometric amounts of zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] and Li_2MnSiO_4/C were dissolved in anhydrous ethanol and continuously stirred for about 2 h. Afterwards the solution was evaporated at 80 °C. The resulting powder was then annealed at 400 °C for 4 h under N_2 atmosphere. At last, Li_2MnSiO_4/C coated with different amounts of ZnO (1, 3, 5 wt%) were prepared.

2.3. Structure and morphology characterization

The crystal structures of the synthesized materials were characterized by a power diffractometer equipped with a Cu Kα source at a scan rate of 6° min^{-1} ranging from 15° to 80°. The surface morphology was observed with a field-emitting scanning electron microscope (SEM, JEM-2100F) and a transmission electron microscope (TEM, S-4800).

2.4. Electrochemical performance characterization

To examine the electrochemical performances of as prepared samples, galvanostatic charge–discharge cycles were carried out at different rates over a voltage range of 1.5–4.8 V (vs. Li/Li^+) by using 2032 type coin cells at room temperature. 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-pyrrolidine with the assistance of ultrasound. The slurry was pasted on aluminum foil current collector and dried at 120 °C for 12 h in vacuum. A solution of 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (2:3, v/v) was used as electrolyte and lithium foil as anode electrode. The active material load on the current collector was around 2–3 mg. The coin-type cells were assembled in an argon-filled glove box, in which the content of water and oxygen was controlled below 5 ppm. The assembled electrochemical cells were tested between 1.5 and 4.8 V (vs. Li^+/Li) at a desired current with a Neware battery testing system at room temperature. The electrochemical impedance spectroscopy (EIS) was performed by applying an AC signal from 10 mHz to 100 kHz with an amplitude of 5 mV using a GAMRY PC14-750 electrochemical workstation.

3. Results and discussion

3.1. Structure and morphology of morphology of ZnO-coated Li_2MnSiO_4/C

Fig. 1 shows the XRD patterns of pristine and ZnO-coated Li_2MnSiO_4/C cathode materials. It can be seen that the diffraction of all the samples can be indexed to the orthorhombic crystal structure with *Pmn2₁* space group, which is in good agreement with the previous reports [27–29]. The peaks of MnO marked by "$*$" can be observed in all the samples, except the 1 wt% ZnO-coated sample. This indicates that proper amount of ZnO coating can restrain the formation of MnO impurity, which can contribute to a better electrochemical performance. The XRD patterns of all the samples are similar and there is no evidence of diffraction peaks for ZnO, which is due to its low content or amorphous structure. In addition, no obvious site change of characteristic peaks can be observed after coating ZnO, indicating ZnO is coated on the surface of Li_2MnSiO_4/C particles rather than diffuses into the lattice.

SEM is performed to provide the evidence for the change of surface before and after ZnO coating. The SEM images of Li_2MnSiO_4/C are shown in Fig. 2(a) and (c). As can be seen, the morphology of the Li_2MnSiO_4/C is not homogeneous with the particle sizes varying from tens of nanometers up to several micrometers, which is due to the nanocrystal agglomeration during the calcining process. In addition, the surface of pure sample is smooth before coating. As for the sample coated with 1 wt% ZnO (Fig. 2(b) and (d)), the particle size is more uniform compared with Li_2MnSiO_4/C. Moreover, the surface becomes rough after coating ZnO, which could increase the effective surface area and provide more active sites for electrochemical reactions, favoring the abundant contact with the electrolyte. And this is beneficial for improving its electrochemical performance. From the TEM in Fig. 2(e), it can be observed clearly that micrometer particles consist of primary particles ranging from 15 to 30 nm. As is shown in Fig. 2(f), nonuniform nanolayer ZnO is coated on the surface of the Li_2MnSiO_4 and lattice strips can still be clearly seen, indicating the coating layer does not alter its crystal structure, which is consistent with the result of XRD. The thickness of the coating layer is about 2–4 nm.

Fig. 3 presents the SEM image with the corresponding elemental mappings and Energy Dispersive Spectroscopy (EDS) of 1 wt%

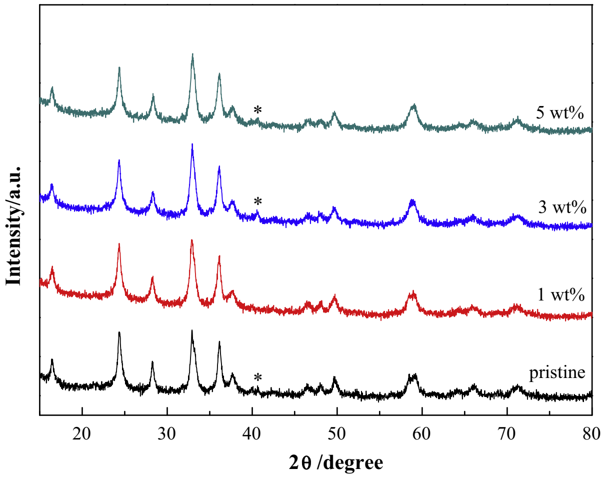

Fig. 1. XRD patterns of pristine Li_2MnSiO_4/C and ZnO coated $LiMnSiO_4$/C.