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Letter

Synthesis, characterization and electrochemical performance of Li_2MnSiO_4/C cathode material by solid-state reaction

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ABSTRACT

Li_2MnSiO_4/C cathode material was synthesized by a traditional solid-state reaction method with Li_2SiO_3 and $Mn(CH_3COO)_2{\cdot}4H_2O$ as starting materials and sucrose as the carbon source. These materials were mixed and ground using a planetary miller and treated thermally at 800 °C for 12 h in an argon atmosphere. The heat treating procedure was estimated utilizing the thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis. The prepared powder was consisted of majority of Li_2MnSiO_4 and minor impurities which were examined by X-ray diffraction (XRD). Field emission scanning electron microscopy (FESEM) morphology shown that the product of Li_2MnSiO_4/C has smaller particle size (about 30–80 nm), which is beneficial for Li-extraction/insertion kinetics. The initial charge capacity of the Li_2MnSiO_4/C electrode material obtained via solid-state reaction is 256 mAh/g (about 1.5 Li^+ per unit formula extracted) and about 0.77 Li^+ per unit formula is reversibly exchanged in the first cycle at a rate of C/16.

1. Introduction

$LiFePO_4$ has been extensively studied as a potential cathode material for lithium ion batteries because of its low cost, environment compatibility, and long cycle life. However, the theoretical capacity of $LiFePO_4$ is limited to 170 mAh/g. In this context, the silicate family Li_2MSiO_4 was focused on, as, at least in the principle, in Li_2MSiO_4 (M = Fe, Mn, Co, Ni) there are two lithium ions per unit formula which can be extracted in one cycle and the theoretical capacities are more than 320 mAh/g. In this class of materials, the synthesis and cathode performance of Li_2FeSiO_4 were first reported as an excellent candidate of cathode material by Nyten et al. in 2005 [1]. Subsequently, the electrochemical behavior of Li_2MnSiO_4 prepared via a modified Pechini sol–gel process was published by Dominko [2–4]. A solution route was adopted by Yang and co-workers to synthesize the $Li_2Mn_xFe_{1-x}SiO_4$ solid solution material, and the best electrochemical property was obtained in case of $x = 0.5$ [5–7].

In the present work, Li_2MnSiO_4/C cathode material was synthesized via the traditional solid-state reaction method, and the morphology and the electrochemical performance of this material were investigated.

2. Experimental

Li_2MnSiO_4/C powder was prepared by solid-state reaction using sucrose as the carbon source. Stoichiometric amounts of Li_2SiO_3 and $Mn(CH_3COO)_2{\cdot}4H_2O$ were firstly ball-milled for 24 h in a planetary miller with a ball-to-powder weight ratio of 10:1 and a rotation speed of 200 rpm. After ball-milling, the powder was dried at 60 °C in a vacuum box for 24 h, and then pressed into pellets. The pellets were then sealed in a quartz tube and fired at 800 °C for 12 h within an inertia atmosphere and cooled to room temperature. The same process of Li_2MnSiO_4/C preparation was applied for Li_2MnSiO_4 with out using sucrose.

Thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis were performed for 26.3 mg of the mixture of Li_2SiO_3 and $Mn(CH_3COO)_2{\cdot}4H_2O$ with a SDT Q600 instrument to investigate the material's thermal behavior from room temperature to 1000 °C at a heating rate of 20 °C/min within a nitrogen atmosphere. X-ray diffraction (XRD) pattern was recorded at ambient temperature using Rigaku-D/MAX-2400 diffractometer with Cu Kα radiation from $2\theta = 3^\circ$ to 90° at a step of 0.02°. The morphology of materials were investigated by JSM-6700F Field Emission Scanning Electron Microscopy (FESEM) with EDS.

Electrochemical experiment was performed using a coin-cell. The positive electrode was prepared using a mixture of active material (85 wt.%), conductive carbon black (5 wt.%) and poly-vinylidenefluoride (PVDF, 10 wt.%) dissolved in N-methylpyrrolidone (NMP). The slurry mixture was pasted on an Al foil, followed by drying at 120 °C for 12 h. The model test cells were assembled using lithium foil as an anode, 1 M $LiPF_6$ in 1:1 (volume ratio) ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte and Celgard 2400 membrane as separator in an argon-filled glove box. The charge–discharge cycles were carried out at room temperature and a constant current density of C/16 with cut-off voltage of 1.5–4.8 V.

3. Result and discuss

3.1. Thermal analysis—TG–DSC

Fig. 1 exhibits the results of simultaneous thermogravimetric and differential scanning calorimeter of a mixture containing the

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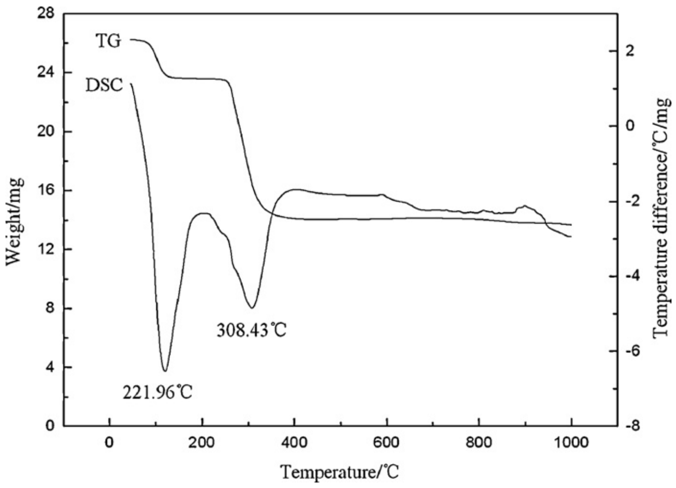

Fig. 1. TG–DSC curves of starting materials recorded from ambient to 1000 °C with a heating rate of 20 °C/min under nitrogen.

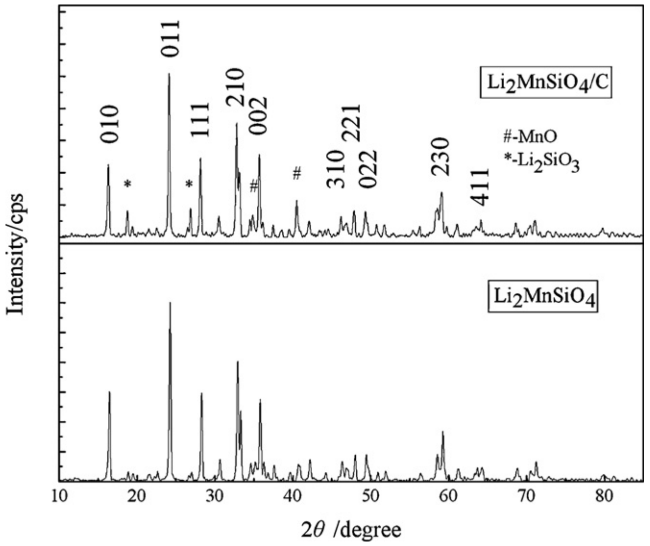

Fig. 2. XRD profile of Li_2MnSiO_4/C and Li_2MnSiO_4.

starting materials of Li_2SiO_3 and $Mn(CH_3COO)_2{\cdot}4H_2O$ in dynamic N_2 atmosphere. N_2 atmosphere is a protective gas frequently used for solid-state reaction. It will not react with the raw materials or the obtained Li_2MnSiO_4, even at high temperature, because in TG curve the weight of precursor sample was not changed anymore after 400 °C. This viewpoint can also be confirmed by the work of Khomane et al. [8] and Bellini et al. [9]. In the TG curve, it presents three steps of weight loss. The initial weight loss observed in the range of 45–130 °C is ascribed to the process of dehydration that results from the Mn source, which obviously corresponds to the endothermic peak at around 120 °C in the DSC curve. Subsequently, the second weight loss in the temperature range of 250–400 °C and a endothermic peak of 308 °C are shown, and it can be assigned to the decomposition of $Mn(CH_3COO)_2$. Finally, a slow and continuous decrease in weight of the mixture in the temperature range of 700–1000 °C may be attributed to the process of solid-state reaction, and at the same time there is an inconspicuous endothermic peak around 800 °C. In view of all, 800 °C was chosen as the final synthesis temperature.

3.2. XRD phase analysis

The XRD pattern of the as-synthesized Li_2MnSiO_4 and Li_2MnSiO_4/C powder are shown in Fig. 2. A majority of reflectance peaks can be assigned to Li_2MnSiO_4 phase, which have an orthorhombic unit cell in space group $Pmn2_1$. The lattice constants are $a = 6.3109(9)$ Å, $b = 5.3800(9)$ Å and $c = 4.9662(8)$ Å [2]. Five intense diffraction peaks are corresponding to the (0 1 0), (0 1 1), (1 1 1), (2 1 0) and (0 0 2) planes, respectively. However, a small amount of impurities at least MnO and Li_2SiO_3 are detected in both cases, whereas the impurities of Li_2MnSiO_4/C sample are more than that of Li_2MnSiO_4. The obvious large peak widths indicate that the crystallite size is small. According to following Scherrer's equation:

$$\delta = 0.9\frac{\lambda}{B\cos\theta} \qquad (1)$$

where δ is the crystallite size, λ is the X-ray wavelength ($\lambda = 1.5406$ Å) and B is the full width at half maximum (FWHM) of the XRD peak in radians. The mean size of the Li_2MnSiO_4 crystals are calculated to be about 45.2 nm and 36.5 nm correspond to the cases of Li_2MnSiO_4 and Li_2MnSiO_4/C, respectively. The details of structural studies of Li_2MnSiO_4 are being processed.

3.3. FESEM morphology analysis

Scanning electron micrographs of Li_2MnSiO_4 and Li_2MnSiO_4/C samples are shown in Fig. 3a and b. The particle size of Li_2MnSiO_4 ranges from 50 to 300 nm, and in the case of Li_2MnSiO_4/C that ranges from 30 to 80 nm. The smaller particle size and better size distribution of Li_2MnSiO_4/C are due to the presence of carbon, which hindered the growth of the Li_2MnSiO_4 particles and covered them. The uniformity distribution of carbon in the final composite material can be seen from EDS mapping analysis of the whole area of Fig. 3c shown in Fig. 3d.

3.4. Electrochemical properties of Li_2MnSiO_4 sample and Li_2MnSiO_4/C sample

The electrochemical properties of the pristine Li_2MnSiO_4 and the carbon coated cathode material were investigated. The initial charge/discharge cycles of Li_2MnSiO_4 and Li_2MnSiO_4/C powder are shown in Fig. 4a and b, respectively. A large irreversible capacity is found during the first cycle for both samples. For pristine Li_2MnSiO_4 sample, during the first charge about 1 Li^+ per unit formula can be extracted from the pristine sample (i.e. charge capacity of 168 mAh/g), whereas only 0.29 Li^+ per unit formula can be inserted back during the following discharge (i.e. discharge capacity of 47.6 mAh/g). The sample coated by carbon demonstrates the first charge capacity value of 256 mAh/g, however, the discharge capacity only achieve 129 mAh/g. This indicates that the efficiency of first cycle is also low and the reversible and irreversible capacities are almost equal. It means that the electrochemical performance of Li_2MnSiO_4 is partly increased by carbon coated and it can be farther improved according to the theoretical capacity of 333 mAh/g. The relative poor performance of both samples may be due to the impurities in sample and the unsuitability of carbon addition content. Thus, the optimum process parameters should be explored in the future through careful investigation.

The cycle life of Li_2MnSiO_4/C at the C/16 rate to a cut-off voltage between 1.5 and 4.8 V is shown in Fig. 5. The sample prepared by the solid-state reaction method yields a similar inferior cycle life, compared with the sample manufactured by means of the sol–gel method [2]. After 10 cycles, the discharge capacity of Li_2MnSiO_4/C sample is only about 3.2 mAh/g. Beyond all doubt, it is significant to reveal the mechanism of capacity fading and improve its cycle performance. XRD [3,7] and ATR-IR [7] have been used to study the

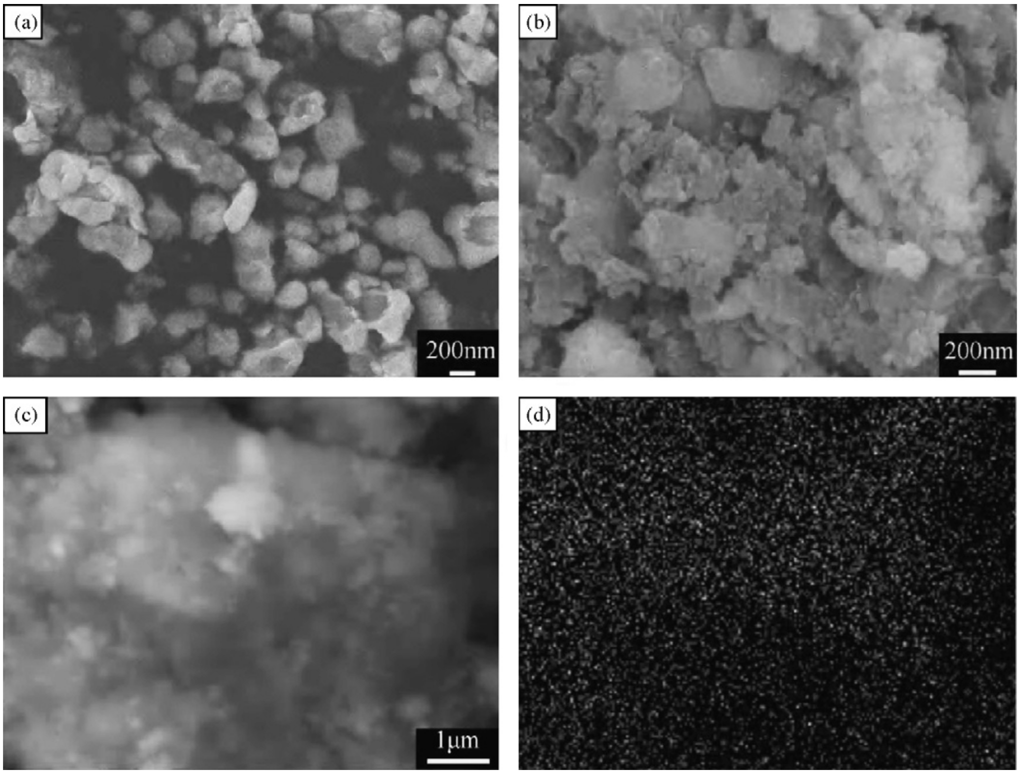

Fig. 3. FESEM micrographs of (a) Li_2MnSiO_4 and (b) Li_2MnSiO_4/C; (d) EDS analysis of Li_2MnSiO_4/C sample of whole area shown in (c).

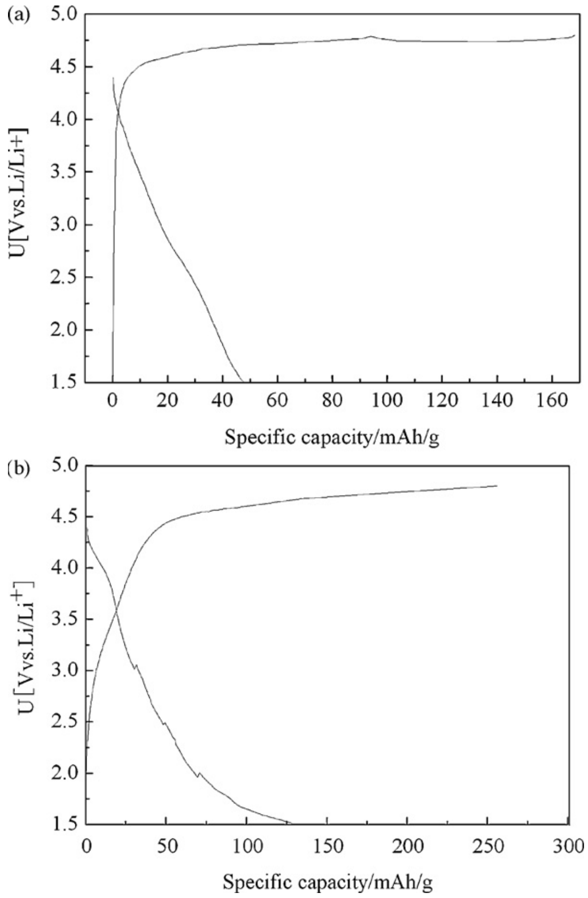

Fig. 4. The initial charge/discharge curves of (a) Li_2MnSiO_4 and (b) Li_2MnSiO_4/C samples at C/16.

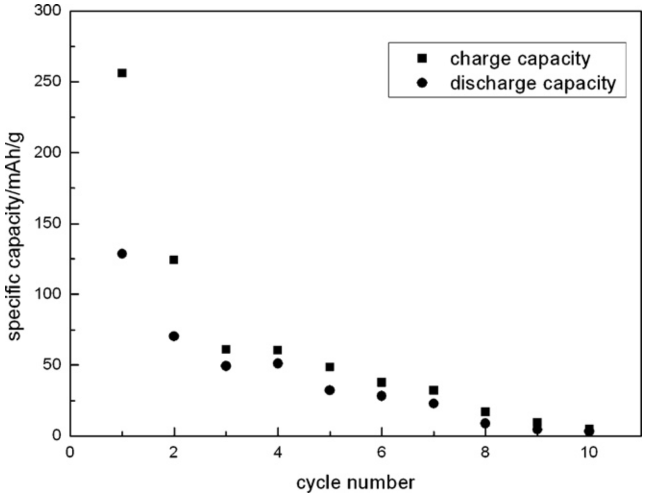

Fig. 5. Cycle life curve of Li_2MnSiO_4/C sample.

problem of material aging, and the results showed that the active material transfers from a crystalline state to an amorphous state after the first charge. However, the particular and causation of the collapse of the initial structure after first charge are not clear.

4. Conclusions

Li_2MnSiO_4/C was synthesized by the solid-state reaction method. The temperature range of 700–1000 °C corresponds to the solid-state reaction, which is obtained from the TG and DSC curve. Characterization by XRD and FESEM shows that it has a Li_2MnSiO_4 main phase and minority impurities and its particle size ranges from 30 to 80 nm. The Li_2MnSiO_4/C composite compound is found to exhibit electrode properties with a reversible capacity of

129 mAh/g at C/16 rate in the first cycle at room temperature. It is indicated that the specific capacity faded severely in 10 cycles.

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