

Effect of Heat-treatment Temperature on the Electrochemical Performances of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ Composite Prepared through Polyol Process

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Abstract: The $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite was synthesized through a polyol process following by heat-treatment at intermediate temperatures. The precursors were precipitated from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{LiAc} \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in ethylene glycol by refluxing at 196°C for 16h, the dried powders were milled, pressed and heat-treated at 500°C, 600°C and 700°C for 10h. The obtained samples were characterized by X-ray diffraction, automatic elemental analyzer, field emission scanning electron microscope (FESEM), energy dispersive spectroscopy (EDS), and high resolution transmission electron microscope (HRTEM). As a result of the Rietveld refinement, two possible $\text{Li}_2\text{MnSiO}_4$ forms crystallizing in $\text{Pmn}2_1$ and $\text{P12}_1/\text{n1}$ space groups, respectively, are considered as the major phases, and Li_2SiO_3 is identified as the impurity phase. According to the FESEM observation, the mean particle size increases from 5–20nm to 20–40nm as the heat-treatment temperature increasing from 500°C to 700°C. Carbon is homogeneously distributed on the prepared $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites. The HRTEM examination confirms that the $\text{Li}_2\text{MnSiO}_4$ particles are surrounded by a very thin amorphous carbon layer. The electrochemical experiments reveal that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite heat-treated at 600°C for 10h has the higher electrochemical performance with an initial discharge capacity of 132.4mAh/g and a capacity retention ratio of 80% at the tenth cycle.

Key words: lithium manganese silicate; cathode material; polyol process; electrochemical performance

Increased demand for high energy density rechargeable batteries is a challenge for the development of lithium ion batteries. An olivine-structured LiFePO_4 is considered as a potential cathode material for lithium ion batteries because of its low cost, environmental compatibility, and long lifetime^[1-3]. However, it is difficult to reach the full theoretical capacity owing to the extremely low intrinsic electronic conductivity and low lithium diffusivity of LiFePO_4 . To overcome the limitation in the capacity, researchers have focused on the silicate family Li_2MSiO_4 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) because there are two lithium ions per unit formula that can be extracted in one cycle, and the theoretical capacity of this cathode material is about 330mAh/g. As an excellent candidate for cathode materials, the synthesis and electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ were first reported by Nyttén *et al.*^[4]. Later, various research groups attempted to fabricate $\text{Li}_2\text{MnSiO}_4$ by different approaches. For instance, Dominko and co-workers^[5-7] synthesized $\text{Li}_2\text{MnSiO}_4$ via a modified Pechini sol-gel process. It was experimentally shown that small particles in an intimate contact with a conducting phase (*i. e.* carbon) were needed due to the low conductivity of $\text{Li}_2\text{MnSiO}_4$ (about $5 \times 10^{-16} \text{ S/cm}$)^[7]. A chemical solution route was employed by Yang

et al.^[8-10] to prepare $\text{Li}_2\text{Mn}_{1-x}\text{Fe}_x\text{SiO}_4$, and the excellent electrochemical property was obtained with $x = 0.5$. Most recently, synthesis of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite by conventional solid state reaction has been reported by our research group^[11].

So far, polyol has been used to fabricate micro- and nano-sized inorganic powders, because it plays an important role in the crystal growth medium as a reducing agent^[12-14]. Kim *et al.*^[15-16] reported that olivine-structured LiFePO_4 and LiMnPO_4 synthesized by a polyol process possessed good capacity retention. It is well known that the properties of cathode materials vary with heat-treatment temperatures, and it is fascinating to study the effects of heat-treatment temperature on the properties of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite. In present work, $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode material was therefore synthesized through the polyol method followed by thermal treatment at temperatures ranging from 500°C to 700°C, and the morphologies and the electrochemical performances of the as-prepared samples were investigated.

1 Experimental

$\text{Li}_2\text{MnSiO}_4$ powders were prepared in a round-bottom

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flask equipped with both a refrigerating unit and a stirring unit to ensure constant reflux and mechanical agitation, respectively. The precursors were precipitated from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{LiAc} \cdot 2\text{H}_2\text{O}$, and $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in ethylene glycol by refluxing at 196°C for 16h. The obtained precipitate was filtered, dried at 150°C for 24h, and milled with sucrose as the carbon source for 24h in a planetary ball mill with a ball/powder ratio of 10:1 at a rotation speed of 200r/min. Afterwards, the powders were pressed in the form of a pellet, transferred to a quartz tube, and sealed in vacuum. The pellets were heat-treated at 500°C , 600°C and 700°C for 10h in an inert atmosphere at rate of $5^\circ\text{C}/\text{min}$, and cooled naturally to room temperature.

The crystalline phases of the samples were identified by X-ray diffraction (Rigaku-D/MAX-2400) with $\text{CuK}\alpha$ radiation. The data were collected in the range between 5° and 90° in step of 0.02° . The structure and lattice parameters were confirmed by the Rietveld Refinement Method using Topas. The carbon content was analyzed using the automatic elemental analyzer Vario EL III. The surfaces and morphologies of the samples were observed using a field emission scanning electron microscope (JSM-6700F), scanning electron microscope (Quanta 200) equipped with energy dispersive spectroscopy (EDS), and high resolution transmission electron microscope (JEM-3010), respectively. The electrochemical characteristics were measured in a vacuum-sealed coin-cell. The positive electrode was prepared using a mixture of active material (80wt%), conductive carbon black (10wt%), and polyvinylidene fluoride (10wt%) dissolved in N-methyl-2-pyrrolidone. The slurry was pasted on an Al foil, then dried at 120°C for 12h. The model test cells were assembled using a lithium foil as an anode, 1mol/L LiPF_6 in 1:1 (volume ratio) ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte, and Celgard 2400 membrane as a separator in an argon-filled glove box. The charge-discharge cycles were carried out at room temperature and a constant current density of $C/30$ with cut-off voltage of 1.5–4.8V.

2 Results and discussion

XRD patterns of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite heat-treated at different temperatures are shown in Fig. 1. Figure 1 (a) is an unclear XRD pattern of the

$\text{Li}_2\text{MnSiO}_4/\text{C}$ heat-treated at 500°C for 10h. With increasing heat-treatment temperature up to 700°C , the crystalline phases become clearer and intense; however, peaks relating to the impurity phase and different space groups of $\text{Li}_2\text{MnSiO}_4$ appear in comparison with that heat-treated at 600°C . The Rietveld structural refinement technique is used to identify main and impurity phases and to describe the structure of the obtained sample. The XRD pattern of the sample heat-treated at 700°C with its Rietveld refinement is represented in Fig. 2. The impurity phase can be referred to Li_2SiO_3 (ICSD-100402). This is indexed on an orthorhombic system with space group of $\text{Ccm}2_1$ with refined cell parameters: $a = 0.93324\text{nm}$, $b = 0.54145\text{nm}$, and $c = 0.46461\text{nm}$. The pattern can be explained as a coexistence of $\text{Pmn}2_1$ (ICSD-155274) and $\text{P}12_1/n1$ (ICSD-245536) $\text{Li}_2\text{MnSiO}_4$ polymorphs in a ratio of 1:0.82. Refined lattice parameters for $\text{Li}_2\text{MnSiO}_4$ crystallized in the space group of $\text{Pmn}2_1$: $a = 0.63038\text{nm}$, $b = 0.53793\text{nm}$, and $c = 0.50110\text{nm}$, and $\text{Li}_2\text{MnSiO}_4$ crystallized in the space group of $\text{P}12_1/n1$: $a = 0.62810\text{nm}$, $b = 1.0861\text{nm}$,

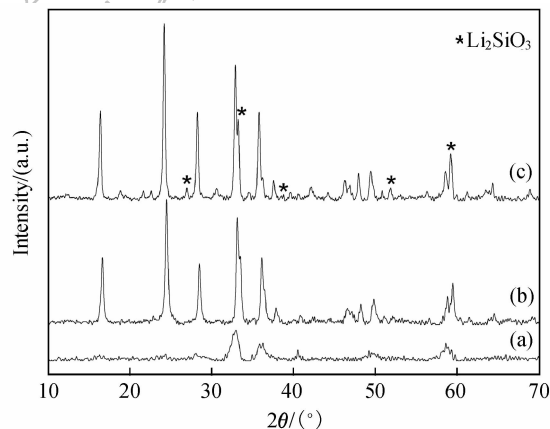


Fig. 1 XRD patterns of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites heat-treated at different temperatures

(a) 500°C ; (b) 600°C ; (c) 700°C

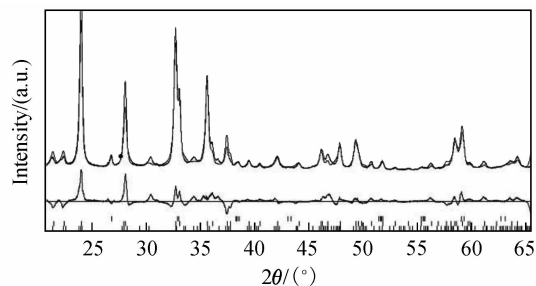


Fig. 2 XRD patterns of the sample heat-treated at 700°C with its Rietveld refinement

Vertical bars mark reflection positions of the three phases included in the refinement (from top to bottom): $\text{Li}_2\text{MnSiO}_4$ ($\text{Pmn}2_1$), $\text{Li}_2\text{MnSiO}_4$ ($\text{P}12_1/n1$), and Li_2SiO_3 ($\text{Cmc}2_1$)

and $c = 0.50042 \text{ nm}$. The “R-factors” of structure $R_p = 13.92\%$, $R_{wp} = 19.56$, $R_{exp} = 2.44\%$. However, $P2_1/n$, $Pmnb$, and $Pmn2_1-I$ polymorphs of $\text{Li}_2\text{MnSiO}_4$ are not found in our experimental samples. The reason is directly related to the different synthesizing conditions. According to previous reports, high heat-treatment temperature and quenching were needed to obtain $P2_1/n$ ^[17], slow cooling rate caused the formation of the $Pmn2_1$ and $Pmnb$ polymorphs^[5], $P2_1/n$ and $Pmnb$ (most stable form) were obtained at an intermediate heat-treatment temperature (900°C) and slow cooling rate^[18]. In the present work, synthesis of $\text{Li}_2\text{MnSiO}_4$ through polyol method followed by heat-treatment at 700°C for 10h resulted the formation of the $Pmn2_1$ and $P12_1/n1$ polymorphs of $\text{Li}_2\text{MnSiO}_4$ as the main phases and Li_2SiO_3 as the impurity phase. The quantitative analysis data from the Rietveld refinement are 52.65% for $\text{Li}_2\text{MnSiO}_4$ in $Pmn2_1$, 42.94% for $\text{Li}_2\text{MnSiO}_4$ in $P12_1/n1$, and 4.41% for Li_2SiO_3 in $Ccm2_1$.

Using the Scherrer's equation, the calculated mean size of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ crystals heat-treated at 600°C and 700°C are 21nm and 24nm, respectively. As the heat-treatment temperature rises, crystal size of $\text{Li}_2\text{MnSiO}_4/\text{C}$ slightly increases.

Elemental analysis for the obtained samples indicate that the carbon content of $\text{Li}_2\text{MnSiO}_4/\text{C}$ powders heat-treated at 500°C , 600°C and 700°C are 12.5%, 12.3% and 12.6%, respectively. This confirms that the carbon content of $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites heat-treated at different temperatures is consistent within the error range. Figure 3 represents a typical EDS map analysis on carbon content of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite as a function of heat-treatment temperature. From that, we can roughly determine the distribution of carbon in the three samples within the submicron range. The amount of carbon through the entire scanned map does not change significantly for all the samples, so the distribution of car-

bon in the obtained materials is uniform.

The morphologies of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ powders were observed by FESEM, as shown in Fig. 4. The obtained $\text{Li}_2\text{MnSiO}_4$ powders possess spherical shapes and uniform particle size distribution. The mean particle size is in the range of 5 – 20nm, 10 – 30nm, and 20 – 40nm for the samples heat-treated at 500°C , 600°C , and 700°C , respectively. The FESEM images also prove that as the heat-treatment temperature increases from 500°C to 700°C , the mean particle size increases, indicating the growth of the primary particles at higher temperature.

Figure 5 displays HRTEM images of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite. It can be seen that the $\text{Li}_2\text{MnSiO}_4$ nanoparticles are surrounded by a very thin layer of amorphous carbon in all samples, and the crystallinity of the samples is improved by heat-treatment temperature up to 700°C for 10h.

The charge-discharge profiles of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites at $C/30$ current rate at room temperature are plotted in Fig. 6. As can be seen, the initial charge capacity of the obtained samples prepared at 500°C , 600°C , and 700°C are 221.8, 218.7 and 260.8mAh/g, respectively. So, there are more than 1 Li^+ per unit formula that can be extracted from all of the cathode material samples prepared by polyol method, and the largest charge capacity of 260.8mAh/g is related to the cathode material heat-treated at 700°C , whereas the reversible capacity of the cathode materials heat-treated at 500°C , 600°C , and 700°C are 117, 132.4 and 124 mAh/g, respectively. The higher value of the reversible capacity was noted in the sample heat-treated at 600°C for 10h.

The cycle ability of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode composite at $C/30$ current rate between 1.5V and 4.8V is shown in Fig. 7. The discharge capacities of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites heat-treated at 500°C , 600°C , and 700°C are 64, 106 and 96 mAh/g after 10 cycles,

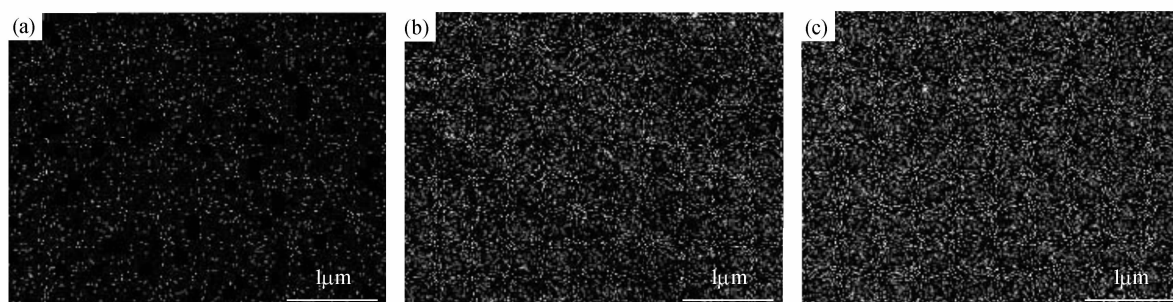


Fig. 3 EDS map analysis of carbon on the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite heat-treated at different temperatures

(a) 500°C ; (b) 600°C ; (c) 700°C

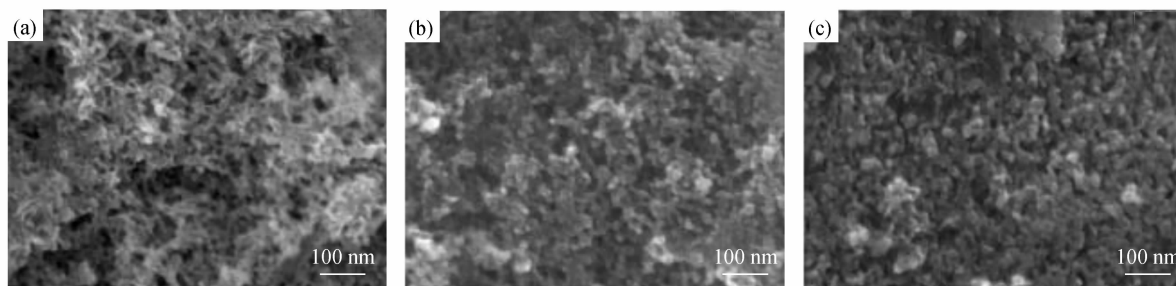


Fig. 4 FESEM micrographs of $\text{Li}_2\text{MnSiO}_4/\text{C}$ samples heat-treated at different temperatures
(a) 500°C; (b) 600°C; (c) 700°C

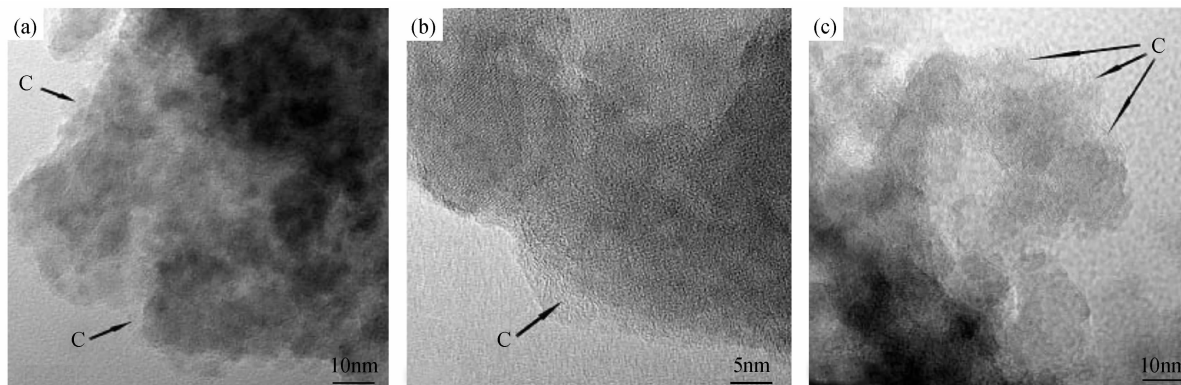


Fig. 5 HRTEM images of $\text{Li}_2\text{MnSiO}_4/\text{C}$ particles heat-treated at different temperatures
(a) 500°C; (b) 600°C; (c) 700°C

and the cell retains 55%, 80%, and 77% of its initial discharge capacity after 10 cycles, respectively. The experimental results show that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode material heat-treated at 600°C has the higher electrochemical performances than those heat-treated at 500°C and 700°C for 10h. A better crystallinity, pure phase, decreased particle size and its uniform distribution promotes the diffusion of lithium ions in the solid.

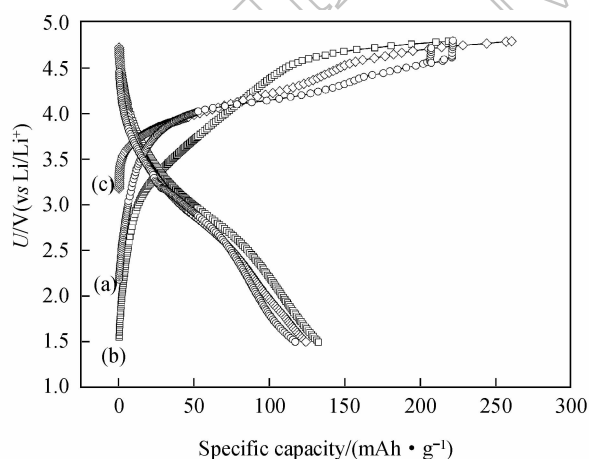


Fig. 6 Charge-discharge curves of $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode materials heat-treated at different temperatures
(a) 500°C (circle); (b) 600°C (rectangle); (c) 700°C (diamond)

3 Conclusions

$\text{Li}_2\text{MnSiO}_4/\text{C}$ composite was prepared through a polyol process following by heat-treatment at intermediate temperatures. The precursors were precipitated from $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{LiAc} \cdot 2\text{H}_2\text{O}$ and $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ in ethylene glycol by refluxing at 196°C for 16h, then dried powders were milled, pressed, and heat-treated at 500°C, 600°C, and 700°C for 10h. According to the Rietveld refinement, two possible $\text{Li}_2\text{MnSiO}_4$ forms crystallizing in $\text{Pmn}2_1$ and $\text{P}12_1/\text{n}1$ space groups were considered as the major phases, and Li_2SiO_3 was identified as the impurity phase. As observed by FESEM, the mean particle size of the samples increases from 5–20nm to 20–40nm as the heat-treatment temperature increases from 500°C to 700°C. Carbon is homogeneously distributed on the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites. The HRTEM examination confirms that the $\text{Li}_2\text{MnSiO}_4$ particles are surrounded by a very thin amorphous carbon layer. The electrochemical experiment performed as a function of heating temperature revealed that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite synthesized at 600°C for 10h possessed the higher

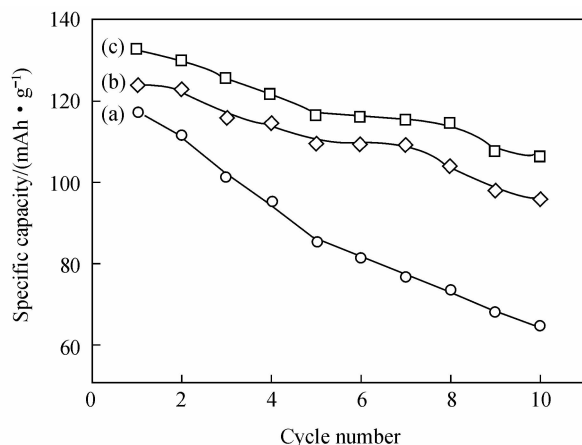


Fig. 7 Electrochemical cycling performances of $\text{Li}_2\text{MnSiO}_4/\text{C}$ cathode materials heat-treated at different temperatures (a) 500°C (circle); (b) 600°C (rectangle); (c) 700°C (diamond)

electrochemical performance with an initial discharge capacity of 132.4 mAh/g and a capacity retention ratio of 80% at the tenth cycle.

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热处理温度对多元醇合成 $\text{Li}_2\text{MnSiO}_4/\text{C}$ 电化学性能的影响

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摘要: 采用多元醇法合成 $\text{Li}_2\text{MnSiO}_4/\text{C}$ 复合材料: 将 $\text{Si}(\text{OC}_2\text{H}_5)_4$ 、 $\text{LiAc} \cdot 2\text{H}_2\text{O}$ 、 $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ 在乙二醇中 196°C 回流 16h, 沉淀物过滤、干燥以后与蔗糖混合并在 500、600 和 700°C 分别加热 10h, 自然冷却到室温。利用 X 射线衍射、元素分析、场发射扫描电镜、高分辨透射电镜等手段对合成样品进行表征。Rietveld 精修表明, 合成样品中存在两种 $\text{Li}_2\text{MnSiO}_4$ 相, 空间群分别为 $\text{Pmn}2_1$ 和 $\text{P}12_1/\text{n}1$, 还有 Li_2SiO_3 杂相。FESEM 观察显示当热处理温度从 500°C 升高至 700°C 时, 样品的颗粒粒径从 5 ~ 20nm 提高到 20 ~ 40nm。 $\text{Li}_2\text{MnSiO}_4/\text{C}$ 复合材料中的碳分布是均匀的。HRTEM 分析表明在 $\text{Li}_2\text{MnSiO}_4$ 颗粒上包覆有一层无定型的碳薄膜。电化学性能测试表明, 在 600°C 保温 10h 得到的样品具有最佳的电化学性能, 首次放电容量达到 132.4 mAh/g, 10 次循环后容量保持率为 80%。

关键词: 硅酸锰锂; 正极材料; 多元醇法; 热处理温度; 电化学性能

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