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FAST TRACK COMMUNICATION

Synthesis and improved electrochemical properties of $\text{Li}_2\text{MnSiO}_4$ cathodes

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Abstract

Superior performance $\text{Li}_2\text{MnSiO}_4$ cathodes with flower-like morphology are prepared by hydrothermal route for the first time. An x-ray diffraction pattern confirms the formation of the orthorhombic structure with $Pmn2_1$ space group. The prepared $\text{Li}_2\text{MnSiO}_4$ materials are subjected to heat treatment at 700°C to achieve complete crystallization in the presence of adipic acid. The $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cells delivered an initial discharge capacity 73 and 100 mAh g^{-1} for as-synthesized and heat-treated $\text{Li}_2\text{MnSiO}_4$, respectively. It is surprising to note that heat-treated $\text{Li}_2\text{MnSiO}_4$ exhibits more stable and superior cycling performance than reported values elsewhere, which is due to the unique morphology as well as carbon coating derived from the carbonization of adipic acid.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There is increasing interest in the development of cathode materials to replace commercially available toxic and expensive LiCoO_2 with high capacity. Regarding capacity, there is a severe imbalance between anode and cathode performance. Commercial carbonaceous anodes essentially serve as buffer Li-storage capacity which must be tuned to the inadequate capacity of selected cathode material. This clearly indicates that the route to any substantial advance in Li-ion battery performance must obviously lie in the direction of improving or searching for new cathodes [1]. Since the demonstration of electrochemical reversibility in polyanion framework materials, particularly in olivine phosphates (LiMPO_4 , $M = \text{Fe, Mn, Co and Ni}$), considerable attention has been focused towards the development of such framework materials [2, 3]. Olivine phosphates have severely suffered from poor rate performance due to their inherent conducting properties and limited capacities. Among the

olivine phase materials LiFePO_4 is noteworthy due to its appealing properties such as very stable electrochemical behaviour, excellent thermal stability, cost effectiveness, safety and eco-friendliness. To achieve such performance, the conductivity issue was circumvented by introducing surface modification such as carbon coating [3]. Similar to that of olivine phosphates, the orthosilicates (Li_2MSiO_4 , where $M = \text{Fe, Mn and Co}$) family of materials are also attracting candidates, particularly $\text{Li}_2\text{MnSiO}_4$ due to its overwhelming advantages such as cell safety, possibility of extraction of more than one Li^+ ion per unit formula, high theoretical capacity (333 mAh g^{-1}) V vs Li^+/Li , eco-friendliness, ease of preparation and cost effectiveness [4–9]. Moreover, the orthosilicate group materials render excellent thermal stability offered through strong Si–O bonding. Provided that the aforementioned advantages and structure of this compound are stable, a reversible exchange of up to two lithium ions per formula unit (possible exploration of $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couples) would be feasible. Although, $\text{Li}_2\text{MnSiO}_4$ materials also suffered similarly to olivine phosphates, with likely poor electronic conductivity and

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worse electrochemical behaviour [5–15]. The advantage of the hydrothermal approach is to prepare high surface area materials with desired morphology under relatively lower temperature conditions than with conventional solid state or sol–gel techniques. Taking this advantage into account, an attempt has been made to explore the possibility of using $\text{Li}_2\text{MnSiO}_4$ cathodes, prepared for the first time with the above approach. However, Dominko *et al* [5] failed in their attempt to prepare $\text{Li}_2\text{MnSiO}_4$ cathodes hydrothermally, whereas they succeeded for the case of $\text{Li}_2\text{FeSiO}_4$, when water was used as the solvent. Later, Lyness *et al* [16] successfully prepared the phase pure $\text{Li}_2\text{CoSiO}_4$ by introducing ethylene glycol (EG) into water (1 : 2 volume ratio). This is the same strategy we applied here for the successful preparation of $\text{Li}_2\text{MnSiO}_4$ using EG and water medium.

2. Experimental

In the typical hydrothermal synthesis, 0.05 mol $\text{LiOH}\cdot\text{H}_2\text{O}$ was added to 0.0125 mol SiO_2 in 20 ml of distilled water and stirred. Separately, 0.0125 mol $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ was added to 10 ml of ethylene glycol and stirred until dissolution occurred. The two solutions were then mixed by stirring and kept for 1 h. Then, the slurry was transferred to a 40 ml Teflon-lined stainless-steel autoclave. The remaining volume was topped up with distilled water. The sealed autoclave was heated at 150 °C for 48 h and the resultant product was filtered off and dried at 60 °C overnight. Then the product was mixed with adipic acid and heat treated at 700 °C in Ar atmosphere for complete crystallization as well as for carbon coating. The detailed description of the characterization and cell assembly was described in our previous works [14–16] or elsewhere [17]. Briefly, x-ray diffraction (XRD, Rint 1000, Rigaku, Japan) measurements were carried out for structural analysis using $\text{CuK}\alpha$ radiation. Morphological studies were made using scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Electrochemical impedance spectroscopy (EIS) analysis was conducted using a Bio-Logic, France, electrochemical work station. All the electrochemical measurements were carried out in the CR2032 coin-type cell configuration. The composite cathode was fabricated under the optimized conditions of 12 mg accurately weighed active material, 11 mg of ketjen black and 3 mg of conductive binder (Teflonized acetylene black, TAB). The mixture was pressed on a 200 mm² stainless-steel mesh which served as the current collector and the prepared electrodes were dried at 130 °C for 5 h in a vacuum oven. The coin cell was made up of a cathode and metallic lithium as anode, which was separated by a porous polypropylene film (Celgard 3401). The 1M LiPF_6 in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1 v/v, Techno Semichem Co., Ltd, Korea) was used as electrolyte. The cycling studies were carried out between 1.5 and 4.8 V at ambient temperature with constant current density of C/20.

3. Results and discussion

Figure 1 represents the powder XRD pattern of $\text{Li}_2\text{MnSiO}_4$ electrodes. Both, as-prepared (hereafter denoted as bare

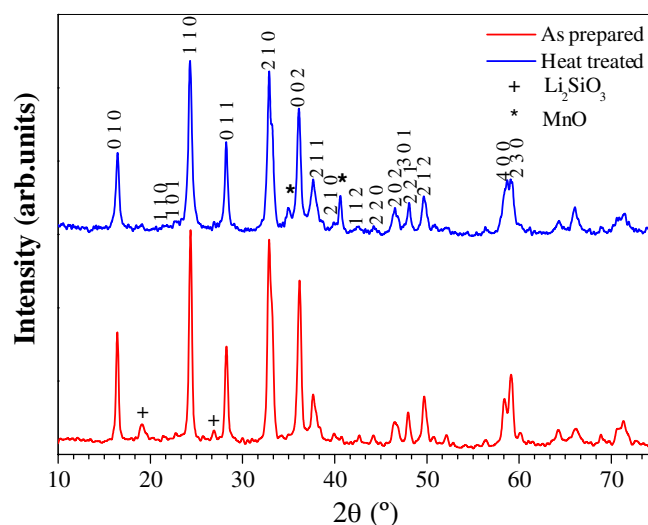


Figure 1. XRD patterns of hydrothermally synthesized $\text{Li}_2\text{MnSiO}_4$.

$\text{Li}_2\text{MnSiO}_4$) and heat-treated electrode (hereafter denoted as $\text{Li}_2\text{MnSiO}_4/\text{C}$) exhibited reflections with some small variation in the intensities. The appearances of satellite crystalline peaks are indexed with the orthorhombic structure with a $Pnm2_1$ space group [5–9]. There are no reflections corresponding to the starting materials used for this synthesis. Till now, the structural properties of $\text{Li}_2\text{MnSiO}_4$ are unclear and it depends on the synthesis conditions and starting materials used. Several authors claimed the existence of three kinds of polymorphs for $\text{Li}_2\text{MnSiO}_4$ which comprises $Pnm2_1$, $Pmnb$ and $P2_1/n$ space groups, respectively, [10]. For example, Dominko *et al* [11] reported $\text{Li}_2\text{MnSiO}_4$ having $Pmnb$ space group at 900 °C (all the synthesis routes, solid-state, sol–gel, hydrothermal, etc), Politaev *et al* [12] reported the existence of the $P2_1/n$ space group by solid-state reactions at 750–1150 °C, and Belharouak *et al* [8] also claimed the existence of the $Pnm2_1$ space group at 800 °C by the sol–gel route. In the present case, the crystalline peaks are indicative of the orthorhombic structure, which is analogous to the Li_3PO_4 pattern and exhibiting the $Pnm2_1$ space group [10]. The $\text{Li}_2\text{MnSiO}_4$ can be isostructural to certain forms of Li_3PO_4 : Mn^{2+} ions are present within a $[\text{SiO}_4]$ anionic silicate network that replaces $[\text{PO}_4]$ anionic phosphate network, and two Li ions are available in 3D channels. Further, we believe that the strong Si–O bond translates very stable electrochemical and thermal properties, i.e. safety issues. However, the impurity phases such as MnO and less amount of Li_2SiO_3 are also unavoidably present in all the phases prepared. A similar kind of impurity phase was also noticed by the researchers during synthesis of $\text{Li}_2\text{MnSiO}_4$ powders by various approaches or atmospheric conditions [5–14]. Based on the previous reports and this study it is confirmed that the preparation of phase-pure $\text{Li}_2\text{MnSiO}_4$ is a complicated one.

Figure 2 represents the morphological features of bare $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$. The flower-like morphology is formed during the nucleation growth in the presence of ethylene glycol and water under hydrothermal treatment. It is apparent that the bare $\text{Li}_2\text{MnSiO}_4$ flower showed smoother morphology than the heat-treated one. In the

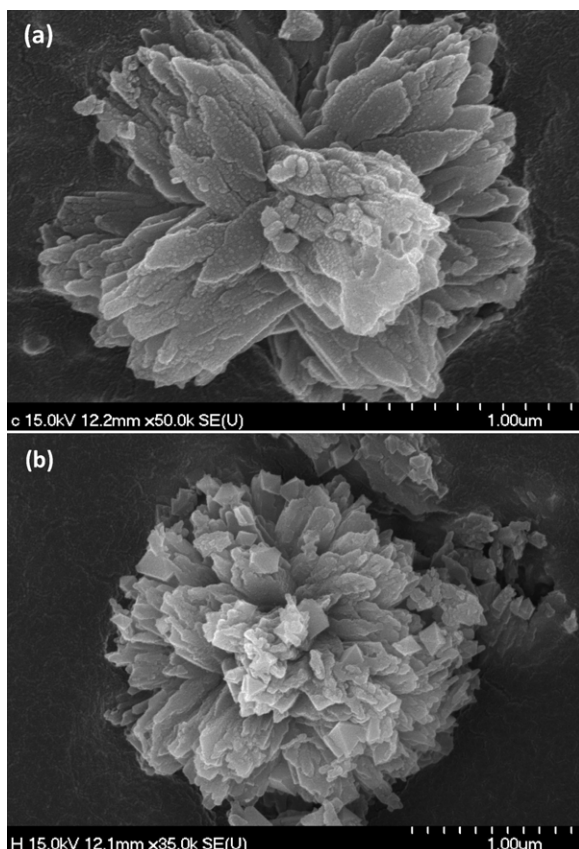


Figure 2. Scanning electron microscopic pictures of (a) as-synthesized and (b) heat-treated $\text{Li}_2\text{MnSiO}_4$.

case of $\text{Li}_2\text{MnSiO}_4/\text{C}$, it appeared as highly crystallized along with some tiny crystals bounded between the flower petals. As expected, such morphology may translate into good electrochemical properties due to its high surface area, unique morphology and high interconnection with nearest neighbouring particles rather than the conventional particles, for diffusion of Li^+ ions.

The cell performance of the bare $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ material is presented in figure 3. The cells delivered the initial discharge capacities 73 and 100 mAh g^{-1} , respectively, for bare $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes at C/20 rate against lithium. The cycling profiles of the $\text{Li}/\text{Li}_2\text{MnSiO}_4/\text{C}$ are very stable ($\sim 100 \text{ mAh g}^{-1}$) for the observed 40 cycles when compared with the bare $\text{Li}_2\text{MnSiO}_4$ material with columbic efficiency over 95%. At the same time, bare $\text{Li}_2\text{MnSiO}_4$ experiencing the continuous capacity fade for a few initial cycles presented a lower discharge capacity profile (30 mAh g^{-1}). Such improvement and excellent cycling performance may be ascribed to the carbonization of gelating agent, which forms a thin layer of carbon on the surface of the parent material. In addition, the crystallization of such particles cannot be excluded during high temperature sintering. Until now, no work has been reported for such stability even around for 100 mAh g^{-1} [5–14]. Further, these results are comparable to other eco-friendly cathode materials for the place of toxic LiCoO_2 [19]. As mentioned above, the $\text{Li}_2\text{MnSiO}_4$ materials ($3 \times 10^{-14} \text{ S cm}^{-1}$ [6]) have also suffered from their inherent conducting properties. The

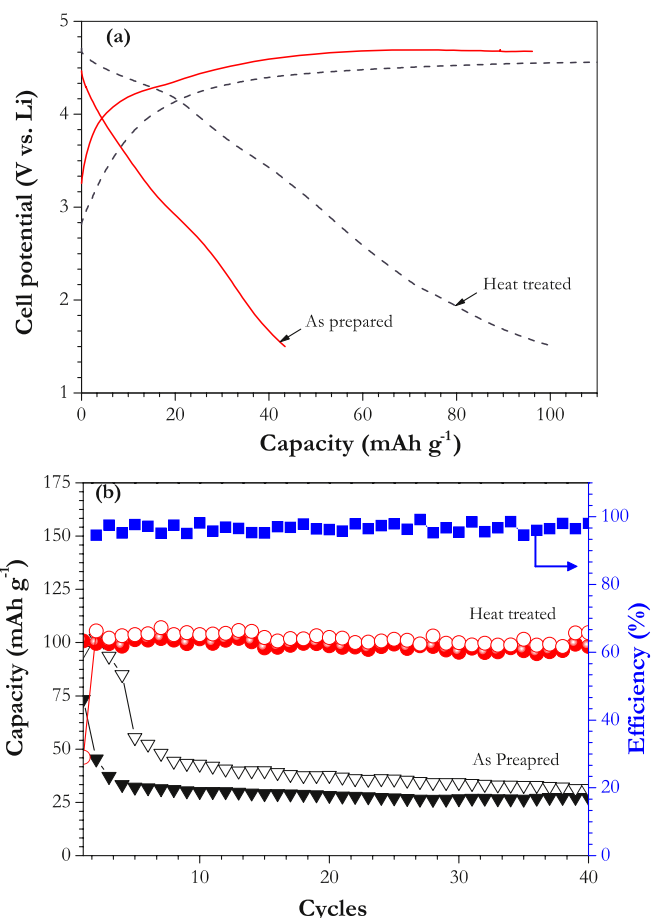


Figure 3. (a) Charge-discharge traces and (b) the cycling profile of $\text{Li}/\text{Li}_2\text{MnSiO}_4$ cell at ambient temperature with columbic efficiency (Open symbols—charge capacity and filled symbols—discharge capacity).

carbonization of gelating agent or, in other words, the carbon coating, provides the improved electronic conductivity for $\text{Li}_2\text{MnSiO}_4/\text{C}$ [14, 15, 17]. The presence of carbon provides excellent interconnectivity between nearest neighbouring particles, which allows faster diffusion of Li^+ ions into the host during the cycling process or in other words, the improvement in kinetic properties [17, 18]. However, in this study, we are not able to realize the extraction of more than one Li^+ ion in both cases. Generally, spherical size morphology is preferred for real time applications, which has a profound effect on the formulation of the high-speed process with sufficient contact with other cell components (binder and towards current collector). Flower-like morphology provides slower kinetics due to the wing-like shape. At the same time, stable electrochemical stability $\text{Li}_2\text{MnSiO}_4$ has been achieved by hydrothermal synthesis. A detailed investigation is underway to tune the morphology to spherical shape with an expectation of a similar kind of stability and marching beyond one Li^+ ion extraction.

In order to realize the effects of heat treatment/carbon coating on the electrical conductivity of $\text{Li}_2\text{MnSiO}_4$, ac impedance measurements were conducted and presented in figure 4. The high-frequency semicircle is ascribed to solid electrolyte interface and/or contact resistance, the semicircle

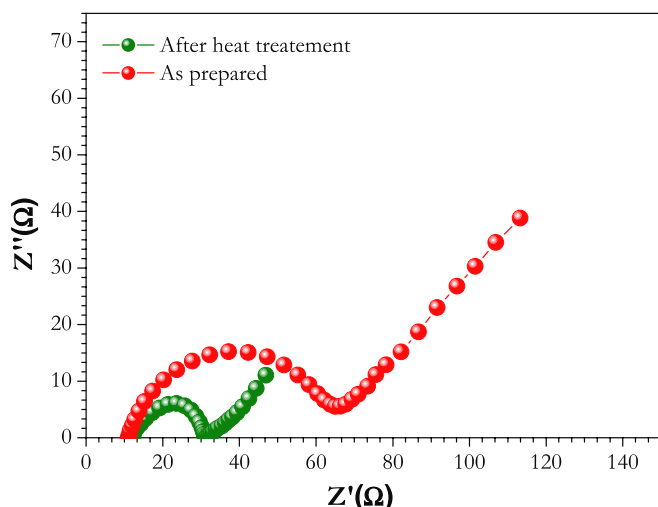


Figure 4. Electrochemical impedance spectroscopy (EIS) plots of $\text{Li}_2\text{MnSiO}_4$ electrodes.

in the medium-frequency region is assigned to the charge-transfer (CT) impedance on the electrode/electrolyte interface, and the inclined line at an approximate 45° angle to the real axis corresponds to the lithium diffusion kinetics towards the electrodes [20]. It could be seen that the diameter of the semicircle in the medium-frequency region for the heat-treated electrode is much smaller than the as-prepared one, revealing a lower CT impedance and indicating that the electronic conductivity of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ was dramatically improved after carbon coating and the presence of carbon, which significantly improved cycling performance of the cell.

4. Conclusion

To conclude, the hydrothermal route was employed for the successful preparation of $\text{Li}_2\text{MnSiO}_4$ materials with flower-like morphology. X-ray reflections confirmed the orthorhombic structure with the $Pmn2_1$ space group. The heat-treated $\text{Li}_2\text{MnSiO}_4$ exhibited superior performance in terms of its electrochemical stability of $\sim 100 \text{ mAh g}^{-1}$ and it was achieved by crystallization as well as carbon coating via gelating agent. The improvement in the electronic conductivity was validated through electrochemical impedance spectroscopy.

Acknowledgments

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