Research Article

Structural Evolution and Electrochemical Performance of $\text{Li}_2\text{MnSiO}_4/\text{C}$ Nanocomposite as Cathode Material for Li-Ion Batteries

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High capacity $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite with good rate performance was prepared via a facile sol-gel method using ascorbic acid as carbon source. It had a uniform distribution on particle size of approximately 20 nm and a thin outlayer of carbon. The galvanostatic charge-discharge measurement showed that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode could deliver an initial discharge capacity of $257.1 \text{ mA h g}^{-1}$ (corresponding to 1.56 Li^+) at a current density of 10 mA g^{-1} at 30°C , while the $\text{Li}_2\text{MnSiO}_4$ electrode possessed a low capacity of 25.6 mA h g^{-1} . Structural amorphization resulting from excessive extraction of Li^+ during the first charge was the main reason for the drastic capacity fading. Controlling extraction of Li^+ could inhibit the amorphization of $\text{Li}_2\text{MnSiO}_4/\text{C}$ during the delithiation, contributing to a reversible structural change and good cycling performance.

1. Introduction

Environmental pollution and energy crisis promote people to search for renewable resources and energy storage device, such as batteries. Rechargeable Li-ion secondary batteries are attracting more and more attention due to their high energy density and environmental friendly features [1]. Recently, orthosilicate Li_2MSiO_4 ($\text{M} = \text{Fe}, \text{Co}, \text{Mn}$) materials were regarded as the candidate for cathodes [2–4] due to their high theoretical capacity (e.g., $\text{Li}_2\text{MnSiO}_4$: 330 mA h g^{-1}). Among this family, $\text{Li}_2\text{MnSiO}_4$ is much easier to achieve the transformation of $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ to carry out extraction of two Li^+ in comparison to other orthosilicates [5, 6]. Li et al. [7] prepared $\text{Li}_2\text{MnSiO}_4/\text{C}$ through a solution route. The composite electrode exhibited a discharge capacity of 209 mA h g^{-1} at the initial cycle and 140 mA h g^{-1} after ten cycles. Bhaskar et al. [8] fabricated $\text{Li}_2\text{MnSiO}_4/\text{C}$ by a facile nanocomposite gel precursor route. This composite electrode showed an initial discharge capacity of 330 mA h g^{-1} and a stable discharge capacity of 115 mA h g^{-1} for 30 cycles at room temperature. Devaraju et al. [9] adopted supercritical fluid

process to synthesize $\text{Li}_2\text{MnSiO}_4/\text{C}$ with a mean particle diameter of 4–5 nm. It showed a high capacity of about 320 mA h g^{-1} at the first cycle and $190\text{--}220 \text{ mA h g}^{-1}$ after 50 cycles. Carbon coating plays a critical role in the improvement of the electrical conductivity of the $\text{Li}_2\text{MnSiO}_4$ and consequently enhancement of discharge capacity. However, this material still has a large irreversible capacity loss and low capacity retention rate upon cycling. Structure change resulting from J-T effects and the dissolution of Mn caused by the disproportionate reaction ($\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$) were reported to be among other reasons for the drastic capacity fading of the $\text{Li}_2\text{MnSiO}_4$ material [6–8, 10, 11]. Recently, a new possible explanation regarding the amorphization transformation of the $\text{Li}_2\text{MnSiO}_4$ material during lithium ions extraction/insertion was also reported [7, 12, 13]. Although the theory has been put forward by Dominko et al. [13] in 2005, this explanation was not reinforced by substantial experimental results.

Herein, we prepared the $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite with a homogenous carbon distribution by a facile sol-gel method. The structure, morphology, and electrochemical

FIGURE 1: XRD patterns of as-prepared $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ powders.

performance of the $\text{Li}_2\text{MnSiO}_4$ materials were characterized by XRD, SEM, TEM, galvanostatic charge-discharge test, and CV. Possible capacity fading mechanism was presented.

2. Experimental

2.1. Synthesis. $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite was prepared by a facile sol-gel method using $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Si}(\text{OC}_2\text{H}_5)_4$ as raw materials. Ascorbic acid served as chelating agent and carbon source. A solution containing Li and Mn in the molar ratio of 2:1 was stirred for half an hour, followed by the addition of ascorbic acid in aqueous solution, and thereafter, $\text{Si}(\text{OC}_2\text{H}_5)_4$ dissolved in ethanol was added. The mixed solution was continuously stirred at 80°C for 24 h and then heated in oven at 80°C overnight. Thereafter, the obtained xerogel was calcined at 650°C for 10 h in a furnace with a constant flow of argon and then left to cool down to room temperature. In order to make comparison, pure $\text{Li}_2\text{MnSiO}_4$ was prepared by similar process without the addition of ascorbic acid.

2.2. Measurements. X-ray powder diffraction (XRD) was collected by diffractometer (SmartLab, Japan) with $\text{Cu K}\alpha$ radiation. The scanning angle 2θ was ranging from 10 to 80° at a step of 0.02° . The morphology and particle distribution were observed by field emission scanning electron microscopy (FE-SEM, HITACHIS-4800, Japan) and transmission scanning electron microscopy (TEM, JEM-2100F, Japan). Carbon content in the composite was measured by elemental analyzer (Vario EL III, Germany).

The electrochemical performance of the material was characterized in a CR2032 coin cell. The working electrode was prepared by mixing 80 wt.% active materials and 10 wt.% carbon black with 10 wt.% polyvinylidene fluoride (PVDF) via using N-methyl-2-pyrrolidone as a solvent and thenceforward pasted the slurry on Al foil and subsequently dried in vacuum at 100°C overnight. The coin cell was assembled in a glove box filled with high pure argon using Li metal

as the counter and reference electrode, Celgard 2400 film as the separator, and 1M LiPF_6 dissolved in EC and DMC (1:1 w/w) as the electrolyte. Galvanostatic charge-discharge measurements (Land, China) were performed in the voltage range of 1.5–4.8 V or 1.5–4.15 V at the current density of 10 mA g^{-1} at 30°C . Cyclic voltammogram (CV) was carried out by CHI660D between 1.5 and 4.8 V at a scanning rate of 0.1 mV s^{-1} .

In order to investigate the structural change during charge-discharge process, the tested batteries were disassembled, and then the cathodes were washed by dimethyl carbonate (DMC) and alcohol and then dried in vacuum at 50°C . Ex situ X-ray diffraction analysis was performed on electrodes which were charged or discharged to different states using $\text{Cu K}\alpha$ radiation with 2θ from 10 to 60° at a step of 0.02° .

3. Results and Discussion

3.1. Structure and Morphology. Figure 1 shows the XRD patterns of as-prepared $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite. The observed diffraction peaks of both samples are in good well agreement with orthorhombic structure with a space group of $\text{Pmn}2_1$, which are the same as the previous reports [14–16]. Compared to the XRD pattern of $\text{Li}_2\text{MnSiO}_4$, the diffraction peaks of $\text{Li}_2\text{MnSiO}_4/\text{C}$ seem to be somewhat weaker, indicating that the presence of carbon could prevent growth of $\text{Li}_2\text{MnSiO}_4$ grains, thus decreasing the particle size. There are no obvious peaks of carbon observed maybe due to the low proportion or amorphization.

SEM image in Figure 2(a) presents the typical morphology of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite, which is composed of nanoparticles with an aggregation. TEM picture (Figure 2(b)) shows that it possesses the irregular shape and a uniform size distribution with a mean size of approximately 20 nm. Carbon wraps the $\text{Li}_2\text{MnSiO}_4$ particle to form a uniform coating with a thickness of 5 nm, as shown in Figure 2(c). This carbon film could suppress the particle growth during heat treatment and therefore shorten the pathway of lithium ion migration and effectively improve the electrical conductivity [17, 18]. The carbon content of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite is determined to 17.08 wt.% by the elemental analyzer.

3.2. Electrochemical Performance. Figure 3 shows the CV curves of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode. Two cathodic peaks located at 2.6 V and 4.4 V during first charge may be attributed to the side reaction and Mn oxidation, respectively. But during first discharge, it shows two broad reduction peaks located at 2.9 and 3.7 V maybe due to $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{3+}$, respectively. In subsequent cycles, the CV profile displays no obvious discrepancy, demonstrating that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode has a good electrochemical reversibility.

Figure 4 shows the charge and discharge curves of $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes for the initial cycles. The discharge capacity at the first, second, and fifth cycles of $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite is 257.1, 250.2, and 225.4 mAh g^{-1} , respectively, while the corresponding values are only 25.6,

FIGURE 2: Images of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite (a) FE-SEM; (b) and (c) TEM.

FIGURE 3: Cyclic voltammetry (CV) curve of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode at a scanning rate of 0.1 mV s^{-1} .

FIGURE 4: Charge and discharge curves of $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes during the first, second, and fifth cycles.

FIGURE 5: Charge-discharge plots of $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes at various rates.

FIGURE 6: Cycling performance of $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes between 1.5 and 4.8 V.

23.8, and 25.9 mAh g^{-1} for $\text{Li}_2\text{MnSiO}_4$. The rate performance of the electrodes after the first cycle is presented in Figure 5. The discharge capacities of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode are 250.1, 180.4, 168.5, and 32.9 mAh g^{-1} at 0.03 C, 0.1 C, 0.5 C, and 1 C ($1\text{ C} = 330\text{ mA g}^{-1}$), respectively. While the $\text{Li}_2\text{MnSiO}_4$ electrode almost could not discharge when increasing the current density, the superior discharge capacity and rate performance of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode are attributed to the enhancement of the electrical conductivity and the short pathway for Li-ion migration.

The carbon coating effectively improved the charge and discharge performance of the $\text{Li}_2\text{MnSiO}_4$ material. However, the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode exhibited poor cycling stability as shown in Figure 6. The capacity retention rate after 50 cycles was only 30.6% (78.6 mAh g^{-1}), while the $\text{Li}_2\text{MnSiO}_4$

FIGURE 7: XRD patterns of $\text{Li}_2\text{MnSiO}_4/\text{C}$ at each stage during first charge and discharge cycle (x is the amount of extraction/insertion of Li^+).

electrode has good cycling performance without capacity loss, although its capacity is low. The reason for serious capacity fading of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode is probably related to excessive Li^+ extraction from host lattice, leading to structural collapse and/or irreversible structural change during the charge process. This speculation will be discussed later in this work.

We employ the ex situ XRD analysis to confirm whether the drastic capacity fading was caused by structural change during cycling. Figure 7 shows the XRD patterns of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode with different charge and discharge states at the first cycle (x is the amount of extraction/insertion of Li^+). The more Li^+ gets out, the weaker diffraction peak intensity becomes. When more than 1.66 Li^+ was delithiated, the diffraction peaks corresponding to the $\text{Li}_2\text{MnSiO}_4$ phase vanished. Note that the crystalline structure was not

FIGURE 8: XRD patterns of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes charged and discharged to different states in the first cycle (the voltage range of 1.5 to 4.15 V).

FIGURE 9: XRD patterns of $\text{Li}_2\text{MnSiO}_4/\text{C}$ charged and discharged between 1.5 and 4.15 V after 21 cycles.

recovered after the subsequent discharge. This demonstrates that the crystalline $\text{Li}_2\text{MnSiO}_4$ transforms to amorphous state by the excessive delithiation. This result is consistent with that of Dominko's [13] and may be the main reason which causes the capacity fading. In order to confirm whether there is reversible structure change when the extraction of Li^+ is less than 1.66 Li^+ , we control charge cut-off voltage at 4.15 V. Figure 8 shows the XRD pattern of $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite charged and discharged to different states at the first cycle (the voltage range of 1.5 to 4.15 V). The crystal structure of $\text{Li}_2\text{MnSiO}_4$ can be recovered after the first discharge, indicating that the $\text{Li}_2\text{MnSiO}_4$ structure did not change under this charge and discharge term. From the partial enlarged figure in Figure 8, the diffraction peak shifts to the right with Li^+ extraction during charge and moves back by lithiation during discharge. This means that the structure change is reversible during charge and discharge if the exchanged amount of

FIGURE 10: Charge-discharge curves of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode during the first, second, and fifth cycles between 1.5 and 4.15 V.

FIGURE 11: Cycling performance of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes at a voltage range of 1.5 ~ 4.15 V.

Li^+ is low. Therefore, controlling exchanged amount of Li^+ can restrain $\text{Li}_2\text{MnSiO}_4$ transforming into amorphous state. This is also confirmed by the XRD pattern of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode after 21 cycles, as shown in Figure 9.

Figure 10 shows the charge and discharge curves of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode at the first, second, and fifth cycles, where the electrode shows similar discharge capacity, indicating that the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode exhibits good reversible reactions between the potential of 1.5 and 4.15 V. The cycling performance of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode between 1.5 and 4.15 V is shown in Figure 11. Note that the capacity retention rate of the $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode after 21 cycles is significantly enhanced to 81.8%, which is much higher than 55.3% when the electrode is charged to 4.8 V. This good cycling performance is ascribed to the high structural stability achieved

by controlling the Li content in the electrode. Based on ex situ XRD experiments and electrochemical measurements, the structural amorphization caused by excessive Li^+ extraction from host lattice is the main reason for drastic capacity fading. Controlling extraction of Li^+ can inhibit this amorphization and achieve reversible structural change and good cycling performance.

4. Conclusions

An in situ carbon coated $\text{Li}_2\text{MnSiO}_4/\text{C}$ has been prepared by a facile sol-gel method using ascorbic acid as carbon source. XRD, SEM, and TEM studies confirm the formation of the $\text{Li}_2\text{MnSiO}_4$ with orthorhombic crystal and its particle size is approximately 20 nm, surrounded by a uniform carbon coating. High electrical conductivity and small particle size obtained by in situ carbon formation contribute to the enhancement of the rate performance. The $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite exhibits good electrochemical performance with a discharge capacity $257.1 \text{ mA h g}^{-1}$ at the first cycle, while the pure $\text{Li}_2\text{MnSiO}_4$ only shows a low discharge capacity of 25.6 mA h g^{-1} . However, capacity retention of $\text{Li}_2\text{MnSiO}_4/\text{C}$ is only 30.6% after 50 cycles. The ex situ XRD analysis reveals that the structural amorphization caused by excessive Li^+ extraction from host lattice is the main reason for this drastic capacity fading. Controlling extraction of Li^+ can inhibit this amorphization and contributes to the reversible structural change and good cycling performance. Hence, it is suggested that the effective way to achieve a high capacity of the $\text{Li}_2\text{MnSiO}_4$ material is to find useful methods, such as doping or substitution, to stabilize its structure, rather than only modifying the surface state.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries," *Journal of the Electrochemical Society*, vol. 144, no. 4, pp. 1188–1194, 1997.
- [2] A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson, and J. O. Thomas, "Electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ as a new Li-battery cathode material," *Electrochemistry Communications*, vol. 7, no. 2, pp. 156–160, 2005.
- [3] M. K. Devaraju, T. Tomai, A. Unemoto, and I. Honma, "Super-critical hydrothermal synthesis of rod like $\text{Li}_2\text{FeSiO}_4$ particles for cathode application in lithium ion batteries," *Electrochimica Acta*, vol. 109, pp. 75–81, 2013.
- [4] V. Aravindan, K. Karthikeyan, K. S. Kang, W. S. Yoon, W. S. Kim, and Y. S. Lee, "Influence of carbon towards improved lithium storage properties of $\text{Li}_2\text{MnSiO}_4$ cathodes," *Journal of Materials Chemistry*, vol. 21, no. 8, pp. 2470–2475, 2011.
- [5] A. Kokalj, R. Dominko, G. Mali, A. Meden, M. Gaberscek, and J. Jamnik, "Beyond one-electron reaction in Li cathode materials: designing $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$," *Chemistry of Materials*, vol. 19, no. 15, pp. 3633–3640, 2007.
- [6] S. K. Liu, J. Xu, D. Z. Li, Y. Hu, X. Liu, and K. Xie, "High capacity $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite prepared by sol-gel method for lithium-ion batteries," *Journal of Power Sources*, vol. 232, pp. 258–263, 2013.
- [7] Y.-X. Li, Z.-L. Gong, and Y. Yang, "Synthesis and characterization of $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite cathode material for lithium ion batteries," *Journal of Power Sources*, vol. 174, no. 2, pp. 528–532, 2007.
- [8] A. Bhaskar, M. Deepa, T. N. Rao, and U. V. Varadaraju, "In situ carbon coated $\text{Li}_2\text{MnSiO}_4/\text{C}$ composites as cathodes for enhanced performance li-ion batteries," *Journal of the Electrochemical Society*, vol. 159, no. 12, pp. A1954–A1960, 2012.
- [9] M. K. Devaraju, T. Tomai, A. Unemoto, and I. Honma, "Novel processing of lithium manganese silicate nanomaterials for Li-ion battery applications," *RSC Advance*, vol. 3, pp. 608–615, 2013.
- [10] T. Muraliganth, K. R. Stroukoff, and A. Manthiram, "Microwave-solvothermal synthesis of nanostructured $\text{Li}_2\text{MSiO}_4/\text{C}$ ($\text{M} = \text{Mn}$ and Fe) cathodes for lithium-ion batteries," *Chemistry of Materials*, vol. 22, no. 20, pp. 5754–5761, 2010.
- [11] Y. Zhao, C. X. Wu, J. X. Li, and L. H. Guan, "Long cycling life of $\text{Li}_2\text{MnSiO}_4$ lithium battery cathodes under double protection from carbon coating and grapheme network," *Journal of Materials Chemistry A*, vol. 1, no. 12, pp. 3856–3859, 2013.
- [12] D. Sun, H. Y. Wang, P. Ding et al., "In-situ synthesis of carbon coated $\text{Li}_2\text{MnSiO}_4$ nanoparticles with high rate performance," *Journal of Power Sources*, vol. 242, pp. 865–871, 2013.
- [13] R. Dominko, M. Bele, A. Kokalj, M. Gaberscek, and J. Jamnik, " $\text{Li}_2\text{MnSiO}_4$ as a potential Li-battery cathode material," *Journal of Power Sources*, vol. 174, no. 2, pp. 457–461, 2007.
- [14] K. Karthikeyan, V. Aravindan, S. B. Lee et al., "Electrochemical performance of carbon-coated lithium manganese silicate for asymmetric hybrid supercapacitors," *Journal of Power Sources*, vol. 195, no. 11, pp. 3761–3764, 2010.
- [15] A. Kojima, T. Kojima, M. Tabuchi, and T. Sakai, "Synthesis of $\text{Li}_2\text{MnSiO}_4$ cathode material using molten carbonate flux method with high capacity and initial efficiency," *Journal of the Electrochemical Society*, vol. 159, no. 5, pp. A532–A537, 2012.
- [16] F. Wang, J. Chen, C. Wang, and B. L. Yi, "Fast sol-gel synthesis of mesoporous $\text{Li}_2\text{MnSiO}_4/\text{C}$ nanocomposite with improved electrochemical performance for lithium-ion batteries," *Journal of Electroanalytical Chemistry*, vol. 688, pp. 123–129, 2013.
- [17] D. Rangappa, K. D. Murukanahally, T. Tomai, A. Unemoto, and I. Honma, "Ultrathin nanosheets of Li_2MSiO_4 ($\text{M} = \text{Fe}$, Mn) as high-capacity Li-ion battery electrode," *Nano Letters*, vol. 12, no. 3, pp. 1146–1151, 2012.
- [18] D. M. Kempaiah, D. Rangappa, and I. Honma, "Controlled synthesis of nanocrystalline $\text{Li}_2\text{MnSiO}_4$ particles for high capacity cathode application in lithium-ion batteries," *Chemical Communications*, vol. 48, no. 21, pp. 2698–2700, 2012.