



## Superior Lithium Storage Properties of Carbon Coated $\text{Li}_2\text{MnSiO}_4$ Cathodes

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$\text{Li}_2\text{MnSiO}_4$  is synthesized by solid state reaction method under the optimized conditions of 900°C in Ar atmosphere. Here, adipic acid is used as the source material for carbon. Powder X-ray diffraction measurements confirm the  $\text{Li}_2\text{MnSiO}_4$  phase formation. The  $\text{Li}/\text{Li}_2\text{MnSiO}_4$  cell delivers initial discharge capacity of 160 mAh g<sup>-1</sup> at C/20 rate. After a few initial cycles, the cell exhibits a stable discharge behavior ~140 mAh g<sup>-1</sup> with coulombic efficiency over 90%. For the first time, we observed such stable discharge behavior for  $\text{Li}_2\text{MnSiO}_4$  electrodes. Thus, improved stability is due to proper optimization of the compound as well as the source material for carbon.

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Since the demonstration of reversible lithium extraction/insertion in polyanion frameworks with  $(\text{XO}_4)^{n-}$  (X = P, S, As and Mo) materials, such structures have been attractive to researchers for further development of advanced positive electrodes for rechargeable Li-ion batteries.<sup>1-5</sup> These include  $\text{LiMPO}_4$  (M = Fe, Mn, Co, and Ni) scaffold olivine structure compounds, in particular,  $\text{LiFePO}_4$ , which has been extensively investigated as one of the possible solutions for commercially available  $\text{LiCoO}_2$ . However, it has been limited to ~3.5 V.<sup>2,3</sup> Similarly, lithium-rich orthosilicates ( $\text{Li}_2\text{M}(\text{SiO}_4)^{4-}$ , where M is the divalent transition metal ion, likely Fe, Mn, and Co), are also very promising candidates to explore in place of  $\text{LiCoO}_2$  cathodes in lithium batteries. Among the orthosilicates,  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4$  are promising due to their appealing properties, such as a reversible exchange of up to two lithium ions per formula unit, structural stability, high thermal stability provided through strong Si-O bonding, high theoretical capacity (>300 mAh g<sup>-1</sup>), eco-friendly, natural abundance, and wide operating voltage.<sup>6-10</sup> Nevertheless, as with olivine phosphates, orthosilicates also suffered from its inherent electronic conductivity. In the case of olivine phosphate materials, especially  $\text{LiFePO}_4$ , the conductivity problem was circumvented by surface modification, for example, carbon coating.<sup>3</sup> In order to improve the conductivity, the same procedure is adopted for orthosilicate groups. The  $\text{Li}_2\text{MnSiO}_4$  provides more advantages than  $\text{Li}_2\text{FeSiO}_4$ , the exploration of  $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couples is possible rather than  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , which provides higher cell voltage.<sup>8</sup> Taking into account this advantage of  $\text{Li}_2\text{MnSiO}_4$ , the solid state reaction method has been utilized to prepare the material. Until now, no proper optimization of  $\text{Li}_2\text{MnSiO}_4$  has been reported and this leads to the poor electrochemical performance of the cell.<sup>8,10</sup> In this respect, we herein report the synthesis of  $\text{Li}_2\text{MnSiO}_4$  by a solid state method with the carbon source material from the carboxylic acid group, for example, adipic acid.

### Materials and Methods

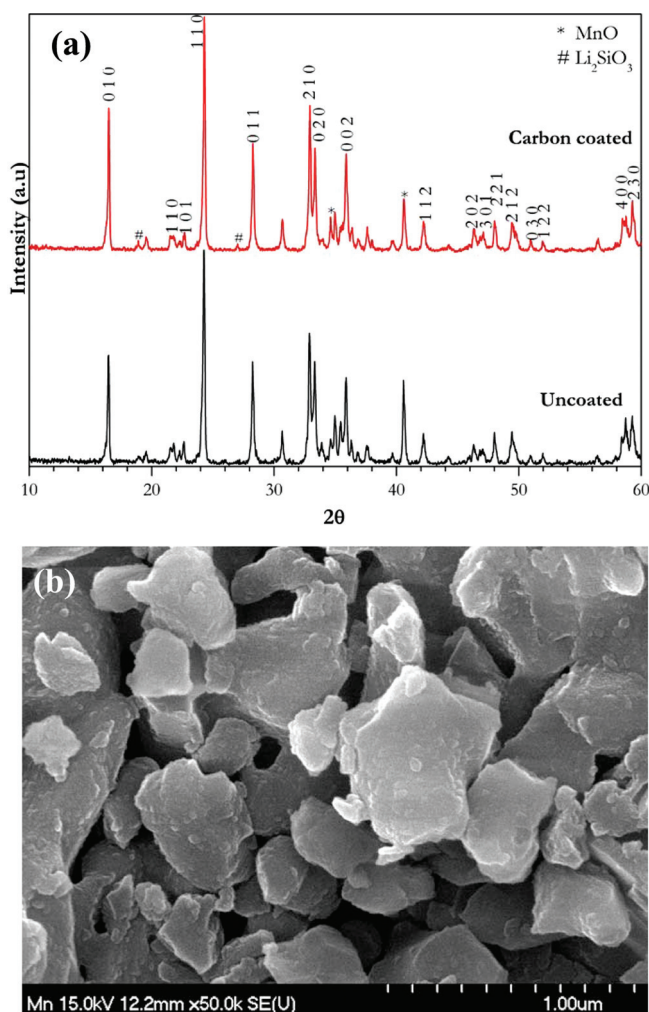
The solid state reaction was employed to prepare the  $\text{Li}_2\text{MnSiO}_4$  powders. Analytical grade  $\text{LiOH}\cdot\text{H}_2\text{O}$  (Junsei 95%),  $\text{MnCO}_3$  (Aldrich, USA, 99.9%), and  $\text{SiO}_2$  (Aldrich, USA, 99.9%) were used as the starting materials. Adipic acid (Aldrich, USA, 99%) was used as the carbon source during the synthesis in order to improve the electronic conductivity of  $\text{Li}_2\text{MnSiO}_4$  particles, and its concentration was fixed at 0.2 mol. (based on the optimization). First, the stoichiometric amounts of starting materials were fine ground with adipic acid and fired at 400°C for 4 h in air. Then, this intermediate product was again fine ground using a mortar and placed into a tubular furnace at 900°C for 12 h under an Ar atmosphere to get the resultant product.

The structural properties of  $\text{Li}_2\text{MnSiO}_4$  were carried out using an X-ray diffractometer (XRD, Rint 1000, Rigaku, Japan) with a Cu-K $\alpha$  radiation source. The morphological feature was investigated using a scanning electron microscope (SEM, S-4700, Hitachi, Japan). CR 2032 coin cells were assembled to evaluate the electrochemical properties of synthesized  $\text{Li}_2\text{MnSiO}_4$ . The metallic lithium serves as anode and synthesized  $\text{Li}_2\text{MnSiO}_4$  acts as cathode. The 1.0 M  $\text{LiPF}_6$  in an EC/DMC (1:1 v/v, Techno Semichem Co., Ltd, Korea) mixture was used as the electrolyte solution with porous polypropylene film (Celgard 3401) serving as a separator. The electrodes were comprised of 12 mg active material, 11 mg of ketjen black, and 3 mg of Teflonized acetylene black binder in the stainless steel mesh. A detailed description of the electrode preparation and fabrication of cells were given in our previous papers<sup>11,12</sup> and are available elsewhere.<sup>3</sup>

### Results and Discussion

Figure 1a represents the powder x-ray diffraction pattern of synthesized  $\text{Li}_2\text{MnSiO}_4$  with and without carbon coating. The XRD patterns showed the well-defined sharp intense reflections, which reflect the crystalline nature of the synthesized  $\text{Li}_2\text{MnSiO}_4$  and without any reflections related to the starting materials. Further, no obvious difference has been observed between the carbon coated and uncoated materials. It is well known that  $\text{Li}_2\text{MnSiO}_4$  exists in three kinds of polymorphs with  $Pnm2_1$ ,  $Pmnb$ , and  $P2_1/n$  space groups. For example, Dominco et al.<sup>13</sup> reported the  $\text{Li}_2\text{MnSiO}_4$  having  $Pmnb$  space group at 900°C (by solid state, sol-gel, and hydrothermal), Politaev et al.<sup>14</sup> reported the existence of  $P2_1/n$  space group through solid state reactions and Belharouak et al.<sup>15</sup> also claimed the existence of  $Pnm2_1$  space group by the sol-gel route. In the present case, the crystalline peaks are indicative of orthorhombic structure, which is analogous to  $\text{Li}_3\text{PO}_4$  pattern. The  $\text{Li}_2\text{MnSiO}_4$  can be isostructural to certain forms of  $\text{Li}_3\text{PO}_4$ :  $\text{Mn}^{2+}$  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 a smaller amount of  $\text{Li}_2\text{SiO}_3$  are also unavoidably present in all the prepared phases.<sup>6,10,16</sup> de Dompablo et al.<sup>17</sup> have succeeded in preparing the  $\text{Li}_2\text{MnSiO}_4$  material in the absence of MnO under various pressure conditions. However, the formation of  $\text{Mn}_2\text{SiO}_3$  could be unavoidable under such abnormal pressure conditions.<sup>7,8,10</sup> Morphological features of the synthesized  $\text{Li}_2\text{MnSiO}_4$  powder are presented in Fig. 1b. It is obvious to notice that the uneven size particles around 1  $\mu\text{m}$  are distributed throughout the volume subjected to investigation. In addition, the appearance of some small sized, i.e., submicrometer, particles is also seen along with the

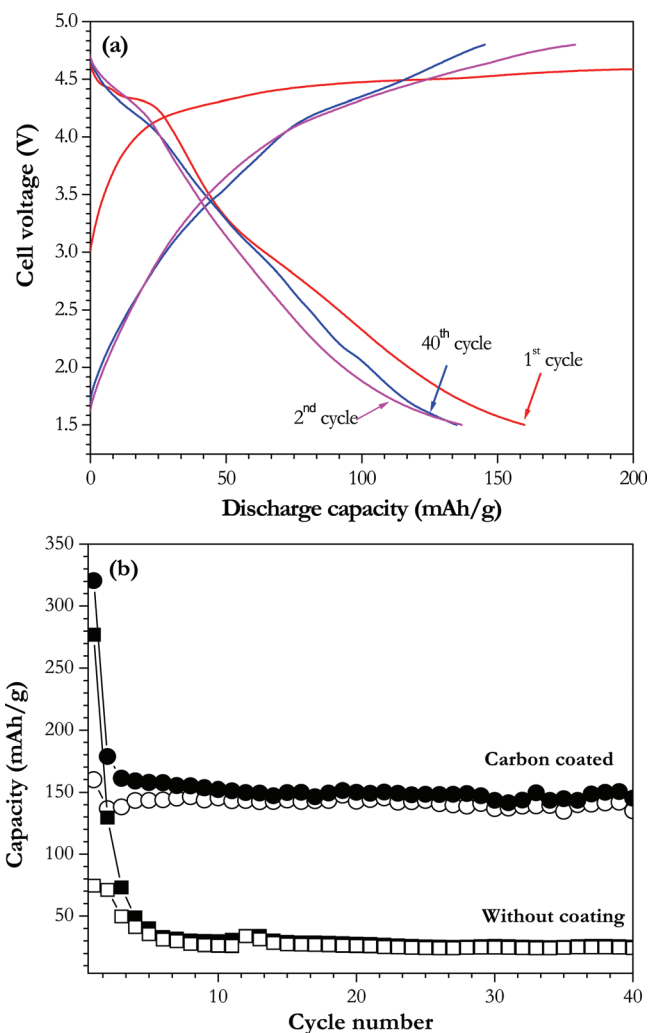
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**Figure 1.** (Color online) (a) X-ray diffraction pattern of  $\text{Li}_2\text{MnSiO}_4$  synthesized at  $900^\circ\text{C}$  under Ar flow and (b) scanning electron microscopic images of the carbon coated  $\text{Li}_2\text{MnSiO}_4$  particles.

larger size particles. It is well known that, in the solid state method, controlling the particulate morphology is too complicated.

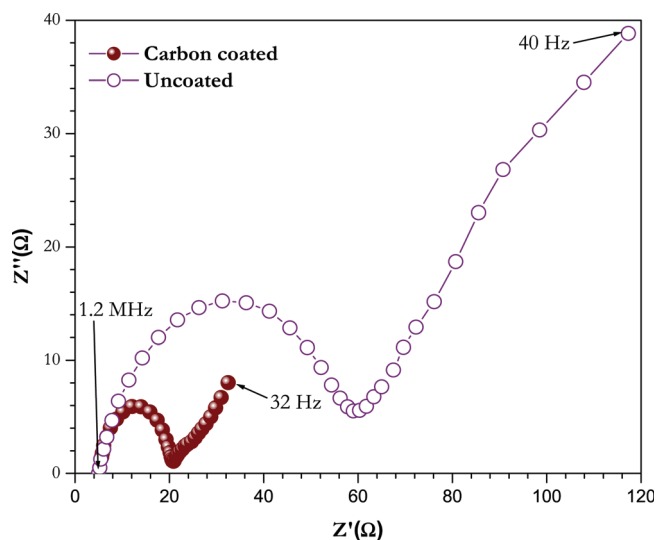
Figure 2a displays the charge-discharge traces of a synthesized  $\text{Li}/\text{Li}_2\text{MnSiO}_4$  cell at ambient temperature. The  $\text{Li}/\text{carbon coated } \text{Li}_2\text{MnSiO}_4$  cell was fabricated and cycled between the potential windows of 1.5–4.8 V at C/20 rate. The synthesized material has a theoretical capacity of  $333 \text{ mAh g}^{-1}$  while extracting 2 moles of  $\text{Li}^+$  per formula unit. During the first charge,  $1.92 \text{ Li}^+$  ions per formula unit have been extracted from the  $\text{Li}_2\text{MnSiO}_4$  host. However, in the discharge process,  $0.96 \text{ Li}^+$  ions per formula only were reinserted instead of  $1.92 \text{ Li}^+$  and a similar kind of variation is also noticed by other researchers.<sup>8,10</sup> After the first cycle, there is no such kind of drastic variation observed and a meager capacity fading will continue for few initial cycles. Thereafter the cell showed a very stable discharge behavior up to 40 cycles measured. Figure 2b represents the cycling profiles of  $\text{Li}/\text{carbon coated}$  and  $\text{uncoated } \text{Li}_2\text{MnSiO}_4$  system at room temperature. The cell delivered almost stable discharge capacity of  $\sim 140 \text{ mAh g}^{-1}$ , which is equal to  $0.85 \text{ Li}^+$  ion per formula unit. However, the uncoated  $\text{Li}_2\text{MnSiO}_4$  material showed poor cycling performance, exhibiting a discharge capacity of 75 and  $24 \text{ mAh g}^{-1}$  for the first and fortieth cycle, respectively. Uncoated  $\text{Li}_2\text{MnSiO}_4$  material also presents a stable capacity  $\sim 24 \text{ mAh g}^{-1}$ , which indicates that there is no active participation of silicates in the electrochemical process and the observed capacity may be due to the presence of conductive additive.<sup>18</sup> To the best of our knowledge, no work has been reported for such stability and this is



**Figure 2.** (Color online) (a) Charge-discharge curves of  $\text{Li}/\text{carbon coated } \text{Li}_2\text{MnSiO}_4$  cell at C/20 rate, (b) cycling profiles of  $\text{Li}/\text{Li}_2\text{MnSiO}_4$  cells cycles between 1.5 and 4.8 V at C/20 rate (open symbols are for discharge capacity, filled symbols for charge capacity).

one of the best results obtained for  $\text{Li}_2\text{MnSiO}_4$  electrodes in any synthesis routes concerned.<sup>7,8,10</sup> This kind of improvement in  $\text{Li}_2\text{MnSiO}_4$  cathodes may be ascribed to the proper optimization (for example, temperature condition and adipic acid concentration) as well as carbon coating from the source of adipic acid. The adipic acid is an excellent source material for carbon coating. This was convincingly proven by us for the case of  $\text{LiFePO}_4$  cathodes in either solid state<sup>19</sup> or sol-gel.<sup>20</sup> For this system, we have optimized 0.2 mol. adipic acid against the total metal ions present in  $\text{Li}_2\text{MnSiO}_4$ , because orthosilicates also suffered from inherent conducting properties ( $3 \times 10^{-14} \text{ S cm}^{-1}$  for  $\text{Li}_2\text{MnSiO}_4$ )<sup>8</sup> similar to that of olivine phosphates ( $\sim 10^{-9} \text{ S cm}^{-1}$ ). Thus, the introduction of carbon coating in situ is necessary to improve the electrochemical properties. Such carbon coating not only improves conducting properties of materials, which also ensures improved cyclability and prevents the aggregation of particles during synthesis process. From this study, we conclude that the introduction of carbon coating provides the improved electrochemical properties of the  $\text{Li}_2\text{MnSiO}_4$  material via enhanced electrical conductivity. A more detailed investigation about the structural properties during charge-discharge process is under way and will be communicated later.

In order to understand the effects of carbon coating on the electrical conductivity of  $\text{Li}_2\text{MnSiO}_4$ , ac impedance measurements were conducted and presented in Fig. 3. The high-frequency semicircle is



**Figure 3.** (Color online) Electrochemical impedance spectrum of  $\text{Li}_2\text{MnSiO}_4$  electrodes.

ascribed to solid electrolyte interface and/or contact resistance, the semicircle 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  $45^\circ$  angle to the real axis corresponds to the lithium diffusion kinetics toward the electrodes.<sup>21</sup> 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 carbon coated  $\text{Li}_2\text{MnSiO}_4$  was dramatically improved after carbon coating, which significantly improved cycling performance of the cell.

### Conclusion

To conclude, the  $\text{Li}_2\text{MnSiO}_4$  was successfully synthesized by solid state reaction method in the presence of adipic acid at  $900^\circ\text{C}$  under Ar flow. X-ray diffraction measurements confirm the crystal-line nature of the synthesized material with the  $Pmn2_1$  space group. Surface morphological images corroborate the micrometer size particulate nature of the synthesized  $\text{Li}_2\text{MnSiO}_4$ . The Li/carbon

coated  $\text{Li}_2\text{MnSiO}_4$  cell showed initial discharge capacity of  $160 \text{ mAh g}^{-1}$ . After a few initial cycles, the cell showed a discharge capacity of  $\sim 140 \text{ mAh g}^{-1}$  up to the fortieth cycle measured. This improved electrochemical stability and capacity might be due to the introduction of carbon in the form of adipic acid. The enhancement in electrical conductivity was confirmed by electrochemical impedance measurements.

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