Synthesis and Characterization of Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ as a Cathode Material for Lithium-Ion Batteries

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The synthesis, structure, and performance of carbon-containing Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ were studied in this work. A synthesis route has been developed for Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ materials, i.e., the carbon-containing Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ was synthesized by a solution route. The results of X-ray diffraction show that Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ solid solutions can be achieved in a wide compositional range. A capacity of 214 mA h/g and energy density of 593 Wh/kg has been achieved for the Li$_2$Mn$_{1-x}$SiO$_4$ (x = 0.5) sample.

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Rechargeable lithium-ion batteries are considered one of the most advanced energy storage systems. In recent years, polyanionic cathodes such as olivine-type LiMPO$_4$ have attracted much attention as next-generation cathodes with high voltage. 1-3 The polyanion-type route for Li$_2$Mn$_{1-x}$SiO$_4$ as a cathode material has been developed for Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ materials, i.e., the carbon-containing Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ was synthesized by a solution route. The results of X-ray diffraction show that Li$_2$Mn$_{1-x}$Fe$_x$SiO$_4$ solid solutions can be achieved in a wide compositional range. A capacity of 214 mA h/g and energy density of 593 Wh/kg has been achieved for the Li$_2$Mn$_{1-x}$SiO$_4$ (x = 0.5) sample.

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Manuscript submitted January 19, 2006; revised manuscript received June 19, 2006. Available electronically September 26, 2006.

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Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ solutions with a wide compositional range were formed. No noticeable change in lattice parameters was observed in all the compositional range ($x = 0$, 0.2, 0.5, 0.7, and 0.9). This demonstrates that Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ solid solutions with a wide compositional range were formed. The results of ICP-AES and chemical analysis for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ are shown in Table I. The results are in agreement with the calculated compositions during synthesis within a limited error.

The initial charge-discharge curves for carbon-containing Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ materials with a current rate of C/16 in a voltage range of 1.5-4.8 V are shown in Fig. 3. The charge-discharge profiles of carbon-containing Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ are similar, with the exception of Li$_2$FeSiO$_4$ ($x = 0$). Li$_2$FeSiO$_4$ ($x = 0$) showed a flat discharge profile at 2.8 V and then the development of a sloped profile. For samples with ($x = 0.2, 0.5, 0.7, 0.9$), the discharge curves showed a sloped profile over the entire compositional range. The discharge capacity increased with the increase in Mn content $x$ until $x = 0.5$, and then the capacity decreased with the Mn content. The discharge capacity increase with the increase in Mn content is due to Mn$^{4+}$/Mn$^{2+}$ operating predominantly on two-electron redox reaction, thereby improving the theoretical capacity of the Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ materials with the increase in Mn content. The capacity of the Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ sample decrease at higher Mn/Fe ratios might be caused by low conductivity of the Li$_2$MnSiO$_4$. All the Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ samples, with the exception of Li$_2$FeSiO$_4$ ($x = 0$), show poor cycling performance, as shown in Fig. 4. This was probably caused by the Jahn-Teller effect of Mn$^{3+}$ and the dissolution of the electrode materials by impure HF content in the electrolyte. The detailed fading mechanism of the materials is being investigated in the lab.

The variation of capacity and energy density with the Mn content $x$ of Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ can be seen in Fig. 5. A capacity of 214 mAh/g (86% of the theoretical capacity, 1.29 electrons per unit formula) was obtained for values of $x$ up to $x = 0.5$, the capacity then decreased for $x > 0.5$, and the highest energy density (593 Wh/kg) was achieved at $x = 0.5$ with an average discharge voltage of 2.76 V. Based on all of the results shown above, it is believed that Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ ($x = 0.5$) could be developed as a high capacity cathode material for Li-ion batteries.

**Conclusions**

We have demonstrated for the first time that a high capacity of 214 mAh/g can be achieved for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ at $x = 0.5$. Our experiments have shown that an optimized capacity and energy density for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ can be achieved at $x = 0.5$. Through adding sucrose to the synthetic precursors followed by a single sintering process, the Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ powder is readily prepared by a solution route. Compared with direct solid-state methods, our solu-

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**Figure 1.** (Color online) XRD patterns for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ ($x = 0$, 0.2, 0.5, 0.7, and 0.9).

**Figure 2.** (Color online) Lattice parameters as a function of the Mn content $x$ for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$.

**Figure 3.** (Color online) The first charge/discharge profiles of Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ ($x = 0$, 0.2, 0.5, 0.7, and 0.9).

**Figure 4.** (Color online) The cyclic performance of Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ ($x = 0$, 0.2, 0.5, 0.7, and 0.9).

**Table I.** Li, Fe, Mn, and Si contents in the as-prepared Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ obtained by ICP-AES and chemical analysis.

<table>
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<tr>
<th>Expected composition of the materials</th>
<th>Formula determined by ICP-AES and chemical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$FeSiO$_4$</td>
<td>Li$<em>{1.0}$Fe$</em>{1.0}$SiO$_4$</td>
</tr>
<tr>
<td>Li$_2$Mn$<em>x$Fe$</em>{1-x}$SiO$_4$</td>
<td>Li$<em>{1.0}$Mn$</em>{1.0-x}$Fe$_{2-x}$SiO$_4$</td>
</tr>
<tr>
<td>Li$_2$Mn$<em>x$Fe$</em>{1-x}$SiO$_4$</td>
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<tr>
<td>Li$_2$Mn$<em>x$Fe$</em>{1-x}$SiO$_4$</td>
<td>Li$<em>{1.0}$Mn$</em>{1.0-x}$Fe$_{2-x}$SiO$_4$</td>
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A sintering route can produce Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ materials at lower sintering temperatures and shorter sintering times. For Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$ ($x = 0.5$) samples, a high capacity of 214 mAh/g and energy density of 593 Wh/kg has been achieved.

Figure 5. (Color online) Variation of discharge capacity and energy density as a function of the Mn content $x$ for Li$_2$Mn$_x$Fe$_{1-x}$SiO$_4$.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China grants (no. 29925310, no. 20473060, and no. 20021002), and the Ministry of Science and Technology of China (grant no. 2001CB610506).

References