Stability of Li₄MnSiO₄ cathodes for Li-ion batteries in different electrolyte systems.

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Introduction

Orthosilicate Li₄MnSiO₄ is a promising cathode material for Lithium-ion batteries due to the possibility of exchanging two Li⁺ per formula unit, corresponding to a theoretical capacity of 333 mAh g⁻¹. Li₄MnSiO₄ should also exhibit higher thermal stability than layered and spinel-like oxide cathode materials due to strong Si-O bonds [1]. The standard Fluorine-based electrolytes (i.e. LiPF₆) easily decomposes, especially at elevated temperatures, and form highly reactive HF in presence of traces of water [2]. This acid is known to cause degradation of orthosilicates [3]. Therefore an electrolyte system containing Fluorine-free salt is used in this study and his compatibility with orthosilicate cathodes is investigated.

Structural and morphological characterization of the synthetized Li₄MnSiO₄

<table>
<thead>
<tr>
<th>Phase identification and impurities</th>
<th>Li₄MnSiO₄ + MnO (4.36%)</th>
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</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pnm2₁</td>
</tr>
<tr>
<td>Lattice parameter (XRD)</td>
<td>a: 8.306(14) ; b: 5.384(14) ; c: 4.971(11) ; α°: 90° ; β°: 90° ; γ°: 90°</td>
</tr>
<tr>
<td>Surface area (BET)</td>
<td>55.75 m²g⁻¹</td>
</tr>
<tr>
<td>Crystal size (XRD)</td>
<td>15.55 nm</td>
</tr>
<tr>
<td>Particle size (TEM)</td>
<td>50-100 nm</td>
</tr>
<tr>
<td>Atomic ratio (Mn/Si)</td>
<td>1.05</td>
</tr>
<tr>
<td>Carbon coating (Elemental analysis)</td>
<td>5.3 %</td>
</tr>
</tbody>
</table>

Electrochemical performances in LiPF₆ EC:DMC (1:1)

Potential window: 4.8 – 2.0 V

Potential window: 4.8 – 1.5 V

• Very high initial capacity
• Rapid capacity fading

Electrochemical performances in Li(BC₄O₆)₂ EC:DMC (1:1)

Potential window: 4.8 – 2.0 V

Potential window: 4.8 – 1.5 V

• Very high initial capacity
• Plateau at 1.7 V

Electrochemical Impedance Spectroscopy of the system in LiPF₆ EC:DMC (1:1) at OCV

In the Nyquist plot we observe a semicircle at high frequencies overlapped with the semicircle ascribed to the charge-transfer resistance. It can be related to a film formation on the surface of the electrode. Electrochemical Impedance Spectroscopy experiments are also in progress to study the interface between Li₄MnSiO₄ electrode and the Fluorine-free electrolyte.

Conclusion

A nanosized Li₄MnSiO₄ sample has been synthesized and characterized. It shows different electrochemical behavior when cycled in standard and in Fluorine-free electrolyte systems in the potential range 1.5 - 4.8 V. Preliminary results by EIS suggest a film formation on the electrode surface in contact with LiPF₆ based electrolyte. Further studies are in progress to confirm this hypothesis.

References