Supplementary data

Three-dimensional architectures of spinel-type LiMn$_2$O$_4$ prepared from biomimetic porous carbonates and their application to a cathode for lithium-ion batteries

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SI-1. Additional information about the experimental conditions of electrochemical measurements

The area of working electrodes was ca. 0.25 cm$^2$ (0.5 cm × 0.5 cm) and the mass of the electrodes was ca. 2.5 mg, which corresponded approximately to 10 mg/cm$^2$. The current density was 0.1, 0.2 and 0.5 A/g (1.0, 2.0 and 5.0 mA/cm$^2$, respectively). C-rate was ca. 0.68, 1.4 and 3.4 C, respectively (these values were calculated using 148 mAh/g as a theoretical capacity).
SI-2. Specific surface area of the products

Table S1. Specific surface area of MnCO₃, Mn₂O₃ and LiMn₂O₄.

<table>
<thead>
<tr>
<th>C_{ag} (wt%)</th>
<th>S_{BET} (m²/g)</th>
<th>MnCO₃</th>
<th>Mn₂O₃</th>
<th>LiMn₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.34</td>
<td>17.7</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.43</td>
<td>13.9</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1.40</td>
<td>36.1</td>
<td>2.71</td>
<td></td>
</tr>
</tbody>
</table>

A highly porous framework of the products prepared at C_{ag} = 4.0 provided relatively large surface area in all compounds (MnCO₃, Mn₂O₃ and LiMn₂O₄). On the other hand, S_{BET} of Mn₂O₃ and LiMn₂O₄ prepared at C_{ag} = 0.5 was smaller than that at C_{ag} = 0 in spite of the presence of an agar gel. The low S_{BET} value of the product at C_{ag} = 0.5 could be caused by the size of the secondary particle larger than that of the spherical particles prepared without agar.
SI-3. Discussion on Li : Mn molar ratios

Figure S1. XRD patterns of products reacted with Li₂CO₃ at Li : Mn = 0.95 : 2 (a), 1 : 2 (b) and 1.05 : 2 (c) (Ca₉g = 4.0 wt%).

Spinel-type LiMn₂O₄ were prepared by calcination of Mn₂O₃ as an intermediate phase with Li₂CO₃. The intermediates were mixed and then reacted with Li₂CO₃ at 560°C for 4 h and at 750°C for 20 h. The molar ratio of Li₂CO₃ : Mn₂O₃ (Li : Mn) varied in a range between 0.95 : 2 and 1.05 : 2 (The heat treatment process was suggested by Xiang et al.²). Figure S1 shows the XRD patterns of the products. Although Mn₂O₃ was heated with a stoichiometric amount of Li₂CO₃ (Li : Mn = 1.00 : 2), a diffraction peak of Mn₂O₃ was detected. This result could be attributed to a deficiency of lithium due to the partial formation of a nonstoichiometric spinel. The diffraction peak of Mn₂O₃ in the XRD pattern disappeared and single-phase spinel-type LiMn₂O₄ were obtained at Li : Mn = 1.05 : 2. In this work, synthesis of spinel-type LiMn₂O₄ was carried out at Li : Mn = 1.05 : 2 to avoid a residual of Mn₂O₃.