

Supplementary data

Three-dimensional architectures of spinel-type LiMn_2O_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 ($0.5 \text{ cm} \times 0.5 \text{ cm}$) 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 productsTable S1. Specific surface area of MnCO₃, Mn₂O₃ and LiMn₂O₄.

C_{ag} (wt%)	S_{BET} (m ² /g)		
	MnCO ₃	Mn ₂ O ₃	LiMn ₂ O ₄
0	0.34	17.7	1.98
0.5	0.43	13.9	1.34
4.0	1.40	36.1	2.71

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

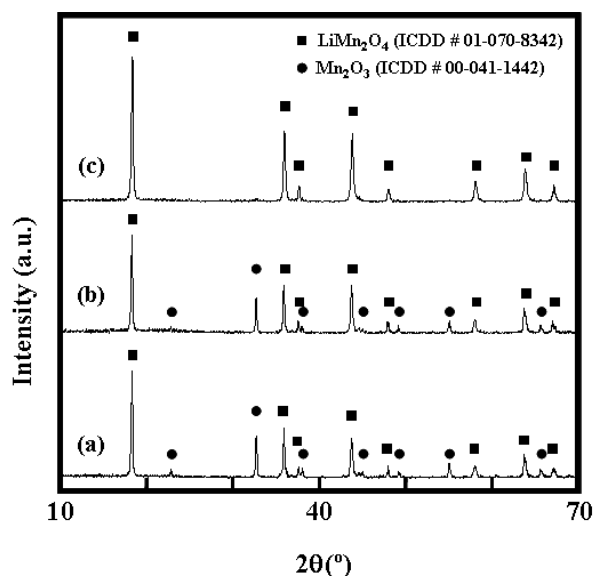
SI-3. Discussion on Li : Mn molar ratios

Figure S1. XRD patterns of products reacted with Li₂CO₃ at Li :Mn = 0.95 : 2 (a), 1 : 2 (b) and 1.05 : 2 (c) ($C_{ag} = 4.0$ 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.^{*}). 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.

* X. M. He, J. J. Li, Y. Cai, Y. W. Wang, J. R. Ying, C. Y. Jiang, C. R. Wan, *J. Solid State Electrochem.* 2005, **9**, 438.