Electronic supplementary information

The controlling synthesis and improved electrochemical cycleability of Mn-doped $\alpha$-Fe$_2$O$_3$ hollow porous quadrangular prisms as lithium-ion battery anodes

Xinru Liu, Chenhao Zhao, Fan Feng, Faqi Yu, Wenpei Kang$^1$ and Qiang Shen*

Key Laboratory for Colloid and Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.

*Corresponding authors: tel.: +86-531-88361387; fax: +86-531-88364464; e-mail: qshen@sdu.edu.cn.

$^1$Present address: Department of Physics and Materials Science and Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong (P. R. China); also for correspondence (kwpsdu@163.com).

**Fig. S1** XRD patterns of Fe$_{1.7}$Mn$_{0.3}$O$_3$ samples obtained at various calcination temperatures.

Comparing the crystallinity of each sample shown above, the calcination temperature of oxalate precursors should be selected at 600 °C or higher.
Fig. S2 SEM images of Fe$_{1.7}$Mn$_{0.3}$O$_3$ samples obtained at a calcination temperature of (a) 400, (b) 500, (c) 600 and (d) 700 °C.

The solid-state transformation of MC$_2$O$_4$ to M$_2$O$_3$ (M = Fe-Mn) mainly replicates the skeletons of precursor, however, the release of gaseous CO$_2$ and CO could hardly endow the oxides with a porous feature when operated at a low calcination temperature of 400 or 500 °C (Fig. S2-a, b). Furthermore, when calcined at 700 °C, parts of resulting quadrangular prisms become cracked and their porous skeletons became vague in appearance owing to crystal fusion probably (Fig. S2-d). Therefore, the optimal calcination temperature of Mn-doped FeC$_2$O$_4$·2H$_2$O precursor was selected at 600 °C.
When used as the active substances of a Li-ion battery anode, the initial specific discharge capacities of these oxides obtained at 400, 500, 600 and 700 °C are 1231.2, 1262.6, 1189.9 and 1260.6 mAh g⁻¹. By comparison, the sample sintered at 400 or 700 °C shows rapid capacity decay and gives the 80th reversible value of 139.9 or 202.1 mAh g⁻¹; the discharge capacity of the powdered oxide obtained at 500 °C is nearly stable from the 2nd to 20th cycles and then gradually reduces to 470.1 mAh g⁻¹ at the 80th cycle; while the M₂O₃ (M = Fe-Mn) product collected at 600 °C exhibits a high cycling durability and retains a high reversible capacity of 1000.0 mAh g⁻¹ over 80 discharge-charge cycles.

In a word, the comparative cycling performances of Fe₁.⁷Mn₀.₃O₃ samples furthermore confirm that the optimal calcination temperature of Mn-doped FeC₂O₄·2H₂O precursor is 600 °C.