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Improving the electrochemical performance of $LiMnPO_4$/C by liquid nitrogen quenching

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ABSTRACT

$LiMnPO_4$/C cathode material is prepared by a sol–gel combined ball milling and liquid nitrogen quenching method. XRD results reveal that quenching does not destroy the structure of $LiMnPO_4$. The quenched sample, which is well crystallized with a single olivine type $LiMnPO_4$ phase, shows a slightly contracted lattice parameters of *a*, *b* and *c* compared with the un-quenched sample. SEM and particle size analysis results reveal that quenching can inhibit the growth and agglomeration of $LiMnPO_4$/C particles. TEM results show that quenching can result in the formation of a number of defects in $LiMnPO_4$ crystals. Electrochemical tests indicate that liquid nitrogen quenching can greatly improve the electrochemical performances of $LiMnPO_4$/C. The quenched sample shows the initial discharge capacities of 131.6, 125.8, 103.3 and 56.4 mAh g^{-1} at 0.05, 0.1, 0.5 and 1 C rates, respectively, which are much higher than those of un-quenched one.

1. Introduction

Nowadays, $LiCoO_2$ is the most widely used cathode material in Li-ion batteries. However, it is expensive, unsafe and toxic, which largely limits its applications in power supplies, electric (EV) and hybrid electric (HEV) vehicles, and so on. Therefore, developing low-cost, safe and environmentally friendly cathode materials to substitute $LiCoO_2$ is highly desired. Among various researched cathode materials, the cheap and environment-friendly $LiMnPO_4$ appears to be quite attractive due to its high potential plateau of 4.1 V [1,2], which is compatible with that of $LiCoO_2$. However, $LiMnPO_4$ exhibits very low electronic conductivity and slow Li-ion diffusion, which lead to its very poor electrochemical performance [3]. Currently, several methods such as carbon coating [4,5], metal cation doping [6–12], particle size reducing and morphology controlling [13–18] have been reported to improve the electrochemical performance of $LiMnPO_4$.

Quenching technology is widely used in the preparation of powder materials, such as semiconductors, crystals, nanomaterials and alloys. Recently, quenching technology has been used to improve the electrochemical performance of $LiFePO_4$ [19,20], $Li_3V_2(PO_4)_3$ [21] and $Li_4Ti_5O_{12}$ [22]. As those reports, rapid quenching can decrease the grain size of powder materials and produce some crystal defects, which are beneficial to their performances. In this study, we introduce a liquid nitrogen quenching technology to modify the $LiMnPO_4$/C cathode material. As a result, its electrochemical performances are remarkably improved.

2. Experimental

$LiMnPO_4$/C was prepared by a sol–gel combined ball milling and liquid nitrogen quenching method, using manganese acetate, lithium dihydrogen phosphate and citric acid as raw materials. The molar ratio of Mn:P was 1:1, while the molar ratio of citric acid was adjustable. The raw materials were dissolved in deionized

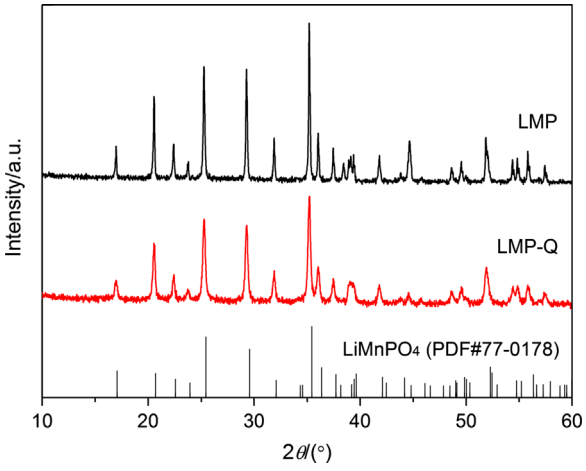

Fig. 1. XRD patterns of LMP and LMP-Q.

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water to obtain a solution, the solution was kept at 70 °C for 10 h during magnetic stirring to obtain a gel, and then the gel was placed in vacuum at 80 °C for 12 h to form a dried gel. The dried gel was pretreated at 350 °C for 3 h in argon atmosphere. Then the obtained powders were ground with oxalic acid by high energy ball milling for 5 h, where the mass ratio of the powders and oxalic acid is 10:1. Finally, the mixture was calcinated in a tube furnace at 650 °C in argon atmosphere. After calcined for 10 h, the red-hot powders were immediately quenched in liquid nitrogen, and the cooled powders were collected and ground. For comparison, a sample prepared by natural cooling (cooled with furnace) was also obtained. The samples prepared by liquid nitrogen quenching and natural cooling are labeled as LMP-Q and LMP, respectively.

Table 1
Lattice parameters of LMP and LMP-Q.

Sample	a/Å	b/Å	c/Å	V/Å^3
LMP	10.4452	6.0994	4.7465	302.3969
LMP-Q	10.4386	6.0971	4.7401	301.6846

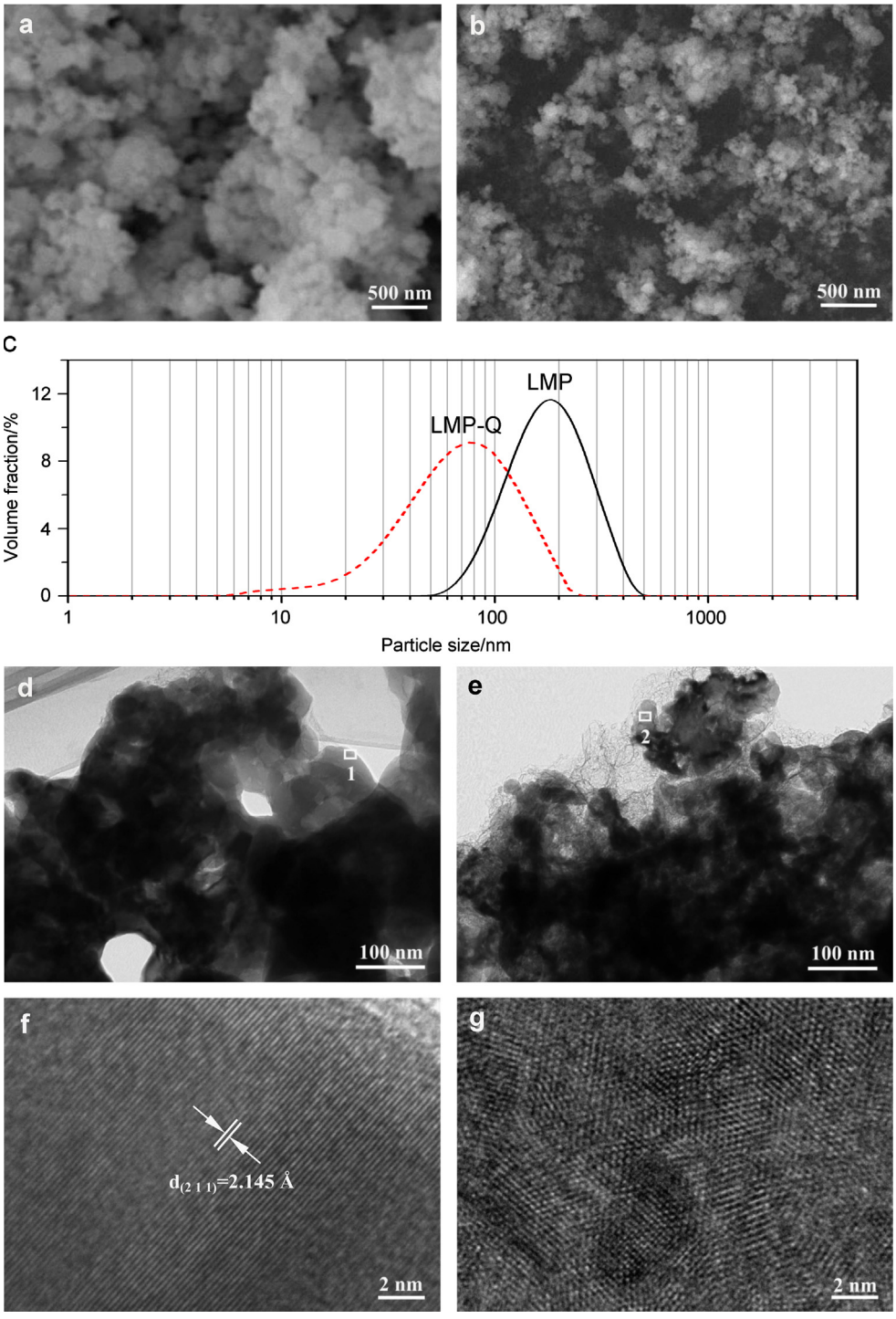

Fig. 2. SEM images of LMP (a) and LMP-Q (b), particle size distributions of LMP and LMP-Q (c), TEM images of LMP (d) and LMP-Q (e), HRTEM images of the selected areas 1 (f) and 2 (g).