



## Facile synthesis of porous $\text{LiMn}_2\text{O}_4$ spheres as positive electrode for high-power lithium ion batteries

Liu Jiang Xi<sup>a</sup>, Hong-En Wang<sup>a</sup>, Zhou Guang Lu<sup>a,b</sup>, Shi Liu Yang<sup>a</sup>, Ru Guang Ma<sup>a</sup>, Jian Qiu Deng<sup>a</sup>, C.Y. Chung<sup>a,\*</sup>

<sup>a</sup> Department of Physics and Materials Science, City University of Hong Kong, Hong Kong Special Administrative Region

<sup>b</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha, PR China

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### ABSTRACT

A  $\text{LiMn}_2\text{O}_4$  cathode material with novel porous spherical morphology exhibiting excellent electrochemical performance has been successfully prepared by using  $\alpha\text{-MnO}_2$  urchin-like structure as a self-sacrificial template. These cathode powders are characterized with X-ray powder diffractometry (XRD), field-emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET) method and inductively coupled plasma emission spectrometry (ICP–AES). Furthermore, electrochemical properties have been studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge/discharge cycling at various current rates. The results reveal that the porous  $\text{LiMn}_2\text{O}_4$  spheres possess outstanding high rate capability and extremely high cycle stability at room temperature as well as elevated temperature. When tested at 10 C and 20 C rates, the first discharge capacities are up to 93.7 and 76.0  $\text{mAh g}^{-1}$ . After 1000 cycles, the corresponding retention rates of capacities are more than 71% and 62% at room temperature. When cycled at 60 °C and 10 C rate, the first discharge capacity is 61.1  $\text{mAh g}^{-1}$  between 3 and 4.5 V. After tested for 250 cycles at 60 °C, the retention rate of capacity is over 76%. This makes the porous  $\text{LiMn}_2\text{O}_4$  cathode a promising candidate for high-power lithium ion batteries which may be used in demanding application such as electric vehicles.

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### 1. Introduction

Rechargeable lithium ion batteries (LIBs) are one of the most promising energy storage devices for electric vehicles (EV) and hybrid electric vehicles (HEV), which possess high energy density, high power density, low cost, superior safety, and stable cycling lifespan. The spinel  $\text{LiMn}_2\text{O}_4$  is generally considered as an excellent alternative to  $\text{LiCoO}_2$  in power LIBs because it is inexpensive, safe and environmentally friendly [1–3]. However, its wide application in EV or HEV has been largely hindered by its poor rate capability and particular failure due to the dissolution of Mn into the electrolytes at elevated temperature [4]. The improvements of electrochemical reversibility and stability of spinel  $\text{LiMn}_2\text{O}_4$  at high rate and elevated temperature for LIBs recently are becoming extremely challenging research topics for scientists and R&D engineers [5–9].

The capacity decay and poor cycling stability of  $\text{LiMn}_2\text{O}_4$  cathode materials are mainly the detrimental consequences due to the dissolution of manganese in the electrolyte [10], the phase transition from cubic to tetragonal phase [11], and the changes

of particle morphology or crystallinity [12,13]. Besides, the poor rate performance of bulk lithium ion electrode materials is primarily attributed to the very long distance for lithium ions to diffuse through the electrodes [14,15]. However, the transport distances of lithium ions in the solid can be considerably reduced due to the nanometer-sized powder electrode leading to much faster Li ion intercalation/deintercalation process [16,17]. Therefore, down-sizing of  $\text{LiMn}_2\text{O}_4$  particles is of great help to improve the high-rate performance. Recently, spinel  $\text{LiMn}_2\text{O}_4$  nanomaterials with various morphologies have been extensively prepared to improve their rate capabilities for LIBs, such as nanoparticles [18], nanotubes [19], nanowires [20], nanobelts [21], nanorods [22], and hollow nanospheres [23]. Single-crystalline nanotubes of spinel  $\text{LiMn}_2\text{O}_4$  exhibit superior high rate capabilities and good cycling stability, and about 70% of its initial capacity can be retained after 1500 cycles at 5 C rate [19]. The high-quality single crystalline spinel  $\text{LiMn}_2\text{O}_4$  nanowires showed high thermal stability and excellent cycle performance at high rate charge–discharge [20]. The  $\text{LiMn}_2\text{O}_4$  nanorods showed a high charge storage capacity at high power rates compared with commercially available powders, and more than 85% of the initial charge storage capacity was maintained after over 100 cycles [22]. Besides, mesoporous  $\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$  spinel showed higher rate capability relative to the corresponding bulk material (50% higher specific capacity

\* Corresponding author. Tel.: +852 34427835; fax: +852 34420538.

E-mail address: [appchung@cityu.edu.hk](mailto:appchung@cityu.edu.hk) (C.Y. Chung).

at a rate of 30 C, 3000 mA g<sup>-1</sup>) at ambient temperature with good stability at elevated temperatures, and without the need for deliberate coating or doping with foreign ions [24]. Hollow microspheres of LiMn<sub>2</sub>O<sub>4</sub> have been synthesized and used as a cathode material in lithium ion batteries, which showed that hollow microspheres of LiMn<sub>2</sub>O<sub>4</sub> exhibited better rate capability than the solid microspheres [25]. Therefore, it can be concluded that the electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub> electrodes appreciably depends on the morphology, the crystalline phase, and the porosity of the structure.

Usually, electrodes made of sub-micron size spherical particles show higher volumetric energy density compared with irregular shaped nanoparticles. It is because microsized spherical particles can easily be packed attaining relatively higher tap density [26]. However, the micron solid spheres have longer ion and electron transportation distance as compared with nanoparticles because the electrolyte cannot penetrate into the internal volume of the solid spheres easily. Hence, an ideal structure for LiMn<sub>2</sub>O<sub>4</sub> with both high volumetric energy density and high rate capability should be a porous microsphere consisted of nanocrystallites tightly compacted to form three-dimensional channels for ion diffusion. On one hand the porous microsphere can increase the interfacial area between microsphere and electrolyte; on the other hand it might lead to possible increase in the dissolution of Mn<sup>3+</sup> into the electrolyte. However, lithium-rich compositions within the Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub> system (0 < x ≤ 0.33) could exhibit good cycling performance, which can be attributed to the high average oxidation state and the presence of less soluble Mn<sup>3+</sup>, but at the same time compromising the energy storage capacity [24,27–29]. But, high rate capability becomes even more important to ensure high utilization of the reduced theoretical capacity [24]. Porous LiMn<sub>2</sub>O<sub>4</sub> spheres have been synthesized by ultrasonic spray pyrolysis method [7,30–32]. In particular, Zhang et al. [30] reported that porous LiMn<sub>2</sub>O<sub>4</sub> spheres prepared by a single-step ultrasonic spray pyrolysis method could deliver excellent rate performance about 100 mAh g<sup>-1</sup> at 10 C and Ni substitution could contribute to improving electrochemical performances in the voltage range of 4.95–3.5 V.

In this paper, we reported the synthesis of spinel lithium-rich LiMn<sub>2</sub>O<sub>4</sub> porous spheres (LMO-PS) by a facile solid-state reaction method using urchin-like α-MnO<sub>2</sub> structure as a self-sacrificial template. Moreover, we compared the electrochemical performances of LMO-PS with those of lithium-rich LiMn<sub>2</sub>O<sub>4</sub> partly porous spheres (LMO-PP) and total lithium-rich LiMn<sub>2</sub>O<sub>4</sub> solid spheres (LMO-SS), which revealed that LMO-PS had the best rate performance and cycling stability.

## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. Synthesis of α-MnO<sub>2</sub> urchin-like structures

Analytical grade MnSO<sub>4</sub>·H<sub>2</sub>O, AgNO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and deionized water were used to prepare α-MnO<sub>2</sub> urchin-like structures via a homogeneous catalytic route as reported elsewhere [33] with some modifications. All chemicals were used without further purification. In a typical synthesis, 0.4 mmol MnSO<sub>4</sub>·H<sub>2</sub>O and 0.4 mmol Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were mixed in 100 mL distilled water at room temperature. Then 4 mL 0.059 mmol L<sup>-1</sup> of AgNO<sub>3</sub> solution was added. After the homogeneous solution was settled for 2 days at room temperature, the precipitate was collected and washed with absolute ethanol and distilled water for several times. Subsequently, the powders were dried in a vacuum.

#### 2.1.2. Synthesis of spherical MnCO<sub>3</sub> spheres

The synthesis method of spherical MnCO<sub>3</sub> spheres was similar to previous report [25]. 1 mmol MnSO<sub>4</sub>·H<sub>2</sub>O and 2 mmol of NaHCO<sub>3</sub> were separately dissolved in 70 mL distilled water. Then, 7 mL ethanol was added to the MnSO<sub>4</sub> solution under stirring, and the NaHCO<sub>3</sub> solution was then directly added. The resulting mixture was left at room temperature for 3 h to precipitate. The as-prepared MnCO<sub>3</sub> solid microspheres were collected, washed with distilled water and absolute alcohol several times, and then dried in a vacuum.

#### 2.1.3. Synthesis of α-MnO<sub>2</sub> burr-like microspheres

The synthesis of α-MnO<sub>2</sub> burr-like microspheres was reported elsewhere [34] and similar to the method described in Section 2.1.1. The difference is that H<sub>2</sub>SO<sub>4</sub> (98 wt.%, 4 mL) was added to the mixture of MnSO<sub>4</sub>·H<sub>2</sub>O and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.4 mmol) solution.

#### 2.1.4. Synthesis of LMO-PS, LMO-PP and LMO-SS

As-prepared α-MnO<sub>2</sub> urchin-like structures, MnCO<sub>3</sub> microspheres and α-MnO<sub>2</sub> burr-like microspheres were mixed with LiOH·H<sub>2</sub>O with the molar ratio of 1.2:2 independently. They were then dispersed into 2 mL ethanol, ground to form a fine mixture, dried at room temperature, and then calcined at 800 °C in atmospheric condition for 10 h. The LMO-PS, LMO-PP and LMO-SS were prepared, respectively.

### 2.2. Characterization of the as-prepared samples

The crystalline structures of the as-prepared products were characterized by X-ray diffraction (XRD) technique using a Siemens X-ray diffractometer with Cu Kα radiation. Specific surface area and average pore size were determined by nitrogen adsorption–desorption isotherms at 77 K using a NOVA 1200e Surface Area & Pore Size Analyzer (Quantachrome Instruments). The element composition of the as-prepared product was analyzed by inductively coupled plasma emission spectrometry (ICP-AES, ICPE 9000 Shimadzu). The morphologies of the as-prepared products were examined by a field-emission SEM (Hitachi S4800).

### 2.3. Electrochemical performance measurement

The electrochemical properties of the products were analyzed by making CR2025 coin-type cells with lithium metal as the negative electrode. The cathode slurry was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) in the weight ratio of 70:20:10. The blended slurry was then cast onto an aluminum foil current collector and dried at 120 °C for 10 h in a vacuum oven. Then, circular (1.6 cm<sup>2</sup>) cathode discs were punched from the aluminum foil. The punched cathodes were weighed to determine the amount of active materials (typically about 6 mg) before being loaded into coin-type cells. The cell was assembled in a glove box filled with high purity argon gas with low concentration of oxygen and low humidity. The electrolyte composed of 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume). Galvanostatic charge/discharge experiments were performed between 3.0 and 4.5 V at different current densities (1 C rate corresponds to the current density of 148 mA g<sup>-1</sup>). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) analyses were recorded on a Zahner IM6 electrochemical station. The amplitude of the AC signal was 5 mV over the frequency range between 100 kHz and 0.01 Hz. The sweep potential range of CV is between 3.5 and 4.5 V.

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