Journal of Power Sources 261 (2014) 306–310

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure as superior cathode materials for Li-ion batteries

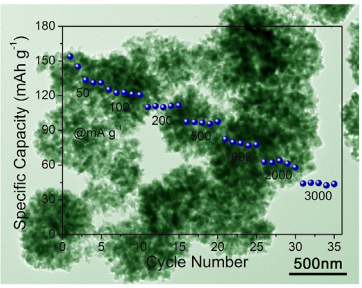
Yao Fu, Hao Jiang*, Yanjie Hu, Ling Zhang, Chunzhong Li*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

HIGHLIGHTS

- Hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure has been synthesized.
- The unique structure has the advantages of both nanostructure and microstructure.
- The $Li_4Mn_5O_{12}$ cathode exhibits excellent electrochemical performances for LIBs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 December 2013
Received in revised form
19 February 2014
Accepted 4 March 2014
Available online 13 March 2014

Keywords:
$Li_4Mn_5O_{12}$
Hierarchical porous nano/micro structure
Li-ion batteries
Cathode materials

ABSTRACT

To overcome the disproportionation reaction and Jahn-Teller distortion of Mn^{3+} in $LiMn_2O_4$ cathode materials, we demonstrate a facile route to synthesize hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure, which consists of numerous well-crystallized nanoparticles with diameters of 20–30 nm. The unique structure combines the advantages of both nanostructure and microstructure. When applied as cathode materials for Li-ion batteries, it exhibited a very high specific capacity of 161 mAh g^{-1} (theoretical value: 163 mAh g^{-1}) with intriguing rate performance and cycling stability.

1. Introduction

Lithium manganese oxides (LMO) have been widely studied as cathode materials for lithium ion batteries (LIBs) due to their intrinsic low-cost, environmental friendliness, abundant resources, and high safety [1–3]. Among this family, stoichiometric spinel $LiMn_2O_4$ has gained the most extensive investigations [4,5]. However, the $LiMn_2O_4$ suffers from large capacity fading during cycling due to the generation of soluble Mn^{2+} via a disproportionation reaction ($Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$) at a high electrode potential, as well as Jahn-Teller distortion of Mn^{3+} ions [5,6]. To overcome these limitations, one effective way is to diminish the Mn^{3+} content in LMO, such as form $Li_4Mn_5O_{12}$ where all the manganese ions are in the Mn^{4+} valence state. Actually, the spinel $Li_4Mn_5O_{12}$ is also a promising cathode material for LIBs in view of its three-dimensional interstitial space for Li^+ transport and high theoretical capacity of 163 mAh g^{-1} [7–9]. For example, Zhao et al. [8] reported $Li_4Mn_5O_{12}$ nanocrystallites prepared by spray-drying-assisted solid state reactions. Tian et al. [9] realized the synthesis of single crystalline $Li_4Mn_5O_{12}$ nanowires by a molten salt route. However, there are very limited reports on $Li_4Mn_5O_{12}$ in the

---

* Corresponding authors. Tel.: +86 21 64250949; fax: +86 21 64250624.
E-mail addresses: jianghao@ecust.edu.cn (H. Jiang), czli@ecust.edu.cn (C. Li).

http://dx.doi.org/10.1016/j.jpowsour.2014.03.005
0378-7753/

literature because of the difficulties in preparation resulting from the high covalent values of manganese atoms [8–10]. Besides, their electrochemical performances are still unsatisfactory.

Recently, much effort has been triggered to prepare nano/micro structured electrode materials for further improving the electrochemical performance [11–13]. In this regard, the nanosized primary particles can shorten the diffusion paths of Li^+, resulting in high rate performance. In addition, the microsized secondary structures can ensure a long-term cycle life and the endowment of a high volumetric energy density. For instance, Zhang et al. [14] reported a porous $Li_4Ti_5O_{12}$ microspheres aggregated by nanosized particles. Li et al. [15] realized the synthesis of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ hollow nano/micro hierarchical microspheres. Both the resulting materials exhibited enhanced electrochemical performance as electrodes for LIBs. Unfortunately, hierarchical $Li_4Mn_5O_{12}$ nano/micro structure still has not been realized until now.

Herein, we demonstrate a simple route to synthesize hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure by using MnO_2 ultrathin nanoflakes assembled microspheres as self-templates. The resulting unique structure consists of amounts of well-crystallized nanoparticles with diameters of ~20–30 nm. We believe it possesses three obvious advantages at least when applied as cathodes for LIBs. (a) The nanosized particles with high purity and crystallinity will greatly improve the utilization of active materials, and hence leading to a high specific capacity. (b) The porous feature can guarantee enough interaction between electrolyte and active materials, reducing Li^+ diffusion paths. Meanwhile, the numerous pores are also expected to digest the possible volume expansion during the repeated Li^+ insertion–extraction. (c) The microsized secondary structures will provide higher volumetric energy density than monodisperse nanoparticles. More importantly, we found that the as-synthesized $Li_4Mn_5O_{12}$ cathodes exhibited a very high specific capacity with intriguing rate and cycling performances for LIBs.

2. Experimental section

2.1. Synthesis

All the reagents used in the experiments were of analytical grade (purchased from Sigma–Aldrich) and used without further purification. Firstly, ultrathin MnO_2 nanoflakes aggregations were prepared by a simple strategy based on our previous report [15]. In a typical procedure, 0.396 g of $Mn(NO_3)_2 \cdot 6H_2O$ and 0.1 g of triblock copolymer PEO-PPO-PEO (P123) were dissolved in 20 mL of deionized water. Then, 20 mL of 0.1 M $KMnO_4$ as an aqueous solution was added dropwise into the above mixture at room temperature. After stirring for 10 min, the black precipitate was collected by filtration, washed with deionized water and absolute ethanol, and finally dried at 60 °C for 6 h. The resulting products (ultrathin MnO_2 nanoflakes assembled microsphere) were dissolved into hexane, and then mixed with $LiOH \cdot H_2O$ dispersed in ethanol with a stoichiometric ratio (Li/Mn = 1:1.25), following by stirring at 60 °C until dried. Finally, hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure was obtained after the above mixture was annealed at 600 °C for 6 h in air.

2.2. Characterization

The as-prepared products were characterized with X-ray powder diffractometer (XRD; Rigaku D/Max 2550, Cu Kα radiation) at a scan rate of 1° min^{-1}, scanning electron microscopy (FESEM; Hitachi, S-4800), and transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV.

2.3. Electrochemical measurements

Electrochemical measurements were performed using cointype 2016 cells. The working electrode were prepared by mixing the as-synthesized active materials, carbon black, and poly(vinyl difluoride) (PVDF) with a weight ratio of 70:20:10, and then pasted on pure Al foil. The electrode area was 1.13 cm^2. The active materials loading was about 0.4 mg cm^{-2} with a thickness of 50 μm. Pure lithium foil was used as counter electrode, and the separator was a polypropylene membrane (Celgard 2400). The electrolyte consists of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume). The cells were assembled in an argon-filled glove box. Cyclic voltammogram experiment was performed on an Autolab PGSTAT302N electrochemical workstation at scan rates of 0.1 mV s^{-1}. The charge and discharge measurements were carried out on a LAND-CT2001C test system at different current densities.

3. Results and discussion

Fig. 1 shows the XRD pattern of the hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure. All of the diffraction peaks can be readily indexed to $Li_4Mn_5O_{12}$ with spinel phase of face-centered cubic structure (JCPDS, No: 46-0810). No other characteristic peaks from impurities, such as $LiMn_2O_4$, MnO_2, are detected in the pattern, indicating a high purity. And the strong diffraction peaks in the pattern also suggest a highly crystalline nature of the as-synthesized $Li_4Mn_5O_{12}$.

The corresponding SEM image was shown in Fig. 2, which revealed that the spherical aggregations are made of many nanoparticles. Detailed structural information was further investigated by TEM observations. From a low magnification TEM image (Fig. 3a), amounts of pores are clearly observed in each spherical aggregation. Fig. 3b shows a representative hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure assembled from numerous nanoparticles with diameters of ~20–30 nm, which is in agreement with the SEM result. It is worth mentioning that such a hierarchical porous nano/micro structure is robust and it cannot be destroyed into fragments or primary nanoparticles even under severe ultrasonic treatment. The high resolution TEM images further reveal the stability of the spherical aggregations. In Fig. 3c, it can be observed that a crystal boundary (the area in the yellow box) exists between the adjacent $Li_4Mn_5O_{12}$ nanocrystallites. An interplanar spacing of 0.47 nm matches well with the distance of the (111) plane of $Li_4Mn_5O_{12}$. In another high resolution TEM image (Fig. 3d), the

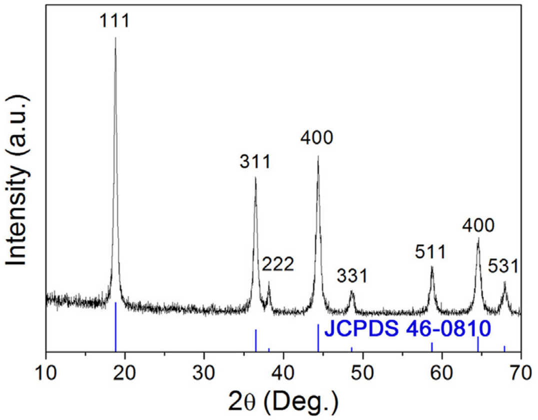


Fig. 1. XRD pattern of the as-prepared hierarchical porous $Li_4Mn_5O_{12}$ nano/micro structure.