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Ionic liquid-assisted solvothermal synthesis of hollow Mn_2O_3 anode and $LiMn_2O_4$ cathode materials for Li-ion batteries

Xin He, Jun Wang, Haiping Jia, Richard Kloepsch, Haidong Liu, Kolja Beltrop, Jie Li*

MEET Battery Research Center/Institute of Physical Chemistry, University of Muenster, Corrensstrasse 46, 48149 Muenster, Germany

HIGHLIGHTS

- Ionic liquid $BMIMBF_4$ is used as the directing agent in the synthesis.
- The specific morphology can be maintained from precursor to the target materials.
- The Mn_2O_3 anode and $LiMn_2O_4$ cathode can be achieved via a similar procedure.
- The materials show good electrochemical performance due to the special morphology.
- Use of molten salt in the synthesis positively affects the material performance.

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ABSTRACT

Mn-based Mn_2O_3 anode and $LiMn_2O_4$ cathode materials are prepared by a solvothermal method combined with post annealing process. Environmentally friendly ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate as both structure-directing agent and fluorine source is used to prepare hollow polyhedron MnF_2 precursor. Both target materials Mn_2O_3 anode and $LiMn_2O_4$ cathode have the morphology of the MnF_2 precursor. The Mn_2O_3 anode using carboxymethyl cellulose as binder could deliver slight better electrochemical performance than the one using poly (vinyldifluoride) as binder. The former has an initial charge capacity of 800 mAh g^{-1} at a current density of 101.8 mA g^{-1}, and exhibits no obvious capacity decay for 150 cycles at 101.8 mA g^{-1}. The $LiMn_2O_4$ cathode material prepared with molten salt assistant could display much better electrochemical performance than the one prepared without molten salt assistance. In particular, it has an initial discharge capacity of 117.5 mAh g^{-1} at a current density of 0.5C and good rate capability. In the field of lithium ion batteries, both the Mn_2O_3 anode and $LiMn_2O_4$ cathode materials could exhibit enhanced electrochemical performance due to the well formed morphology based on the ionic liquid-assisted solvothermal method.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have become widely used as power source for portable electronic devices [1–3]. However, further areas of application will be more difficult as they mostly demand higher power capabilities with lower costs, and enhanced safety in large systems. Thus, the development of high-energy, low-cost and long-life batteries has attracted more and more research interest recently. Due to this, new challenge of achieving high specific energy and stable cycling performance exists in the field for both anode and cathode materials.

On one side, nanostructured metal oxides have gained much attention because of their high theoretical capacities and are considered as promising candidates for next generation anode materials for Li-ion batteries. As one of the most interesting materials in this family, manganese based metal oxide, Mn_2O_3 shows its advantages of earth abundant and environmental benefit, in addition to its high theoretical capacity of 1018 mAh g^{-1} [4–9]. These advantages have aroused increasing attention on this material, especially on the electrochemical performance. However, Mn_2O_3 still faces an obstacle of limited life due to the volume expansion and particle agglomeration during cycling. Many approaches have been pursued to accommodate the volume changes of Mn_2O_3, such as fabrication of specific morphology and microstructure of Mn_2O_3. For example, the hollow spaces, straw-sheaf-shaped and porous microsphere Mn_2O_3 are synthesized and

* Corresponding author.
E-mail address: jie.li@uni-muenster.de (J. Li).

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reported, which can effectively facilitate the improvement of the electrochemical performance of the material [10–12].

On the other side, manganese based spinel $LiMn_2O_4$, with the advantages of high operating voltage, abundance, enhanced safety and environmental compatibility, has already showed its promising potential to be used as cathode material for lithium ion battery, especially in the application of high power system [13]. Early work demonstrated that $LiMn_2O_4$ cathode material shows poor cycling stability which associated with dissolution of manganese in the electrolyte and phase transition from cubic to tetragonal phase [14–16], and poor rate capability due to long distance for lithium ions to diffuse from bulk to surface [17]. To improve the capacity fading upon cycling, various doped spinel with partly replaced by Al, Co or Ru have been studied [18–21]. However, the specific discharge capacity or rate capability is relatively reduced as well, and these drawbacks still limit the large-scale application of cation doped $LiMn_2O_4$ materials. Recently, spinel $LiMn_2O_4$ materials with specific structures have been extensively prepared to improve the electrochemical performance. It is interesting that the different structures, such as nanoparticles [22–25], porous [26,27], mesoporous [28], and especially spheres [16,29–34] can exhibit good electrochemical performance. Thus, it is considered that taking Mn_2O_3 with specific morphology as the precursor, $LiMn_2O_4$ or other Mn-based cathode material with preserved morphology can be obtained by simply annealing the Mn_2O_3 with stoichiometric Li source [29]. In this point of view, both cathode and anode materials with controlled morphology can be prepared with almost one process.

The synthesis strategy for the fabrication of specific structure in the literatures mainly employs template as structure-directing agent [35,36]. Polymer template, which can be finally removed as organic composite by post calcination has been successfully applied in the synthesis approach of metal oxides [36]. In this work, Ionic liquid (IL) is proposed as the template due to its “tailoring” effect, and is expected to guide the synthesis pathway towards desirable nanostructure and morphology; meanwhile, it advances characteristic of environmental friend itself. Herein, for the first time we report the synthesis of hollow polyhedron MnF_2 by an ionic liquid-assisted solvothermal method. Based on the obtained polyhedron MnF_2 precursor, hollow polyhedron Mn_2O_3 anode material and hollow $LiMn_2O_4$ microsphere cathode material could be prepared by a simple post heat treatment. The electrochemical properties of the two materials used as anode material and cathode material, respectively for rechargeable Li-ion batteries are studied.

2. Experimental

In a typical synthesis of MnF_2, 0.5 g $Mn(AC)_2$ and 7 ml 1-Butyl-3-methylimidazolium tetrafluoroborate (Solvionic 99.5%, as structure-directing agent) were first dissolved in 54 ml deionized water under stirring for half hour. Then the solution was transferred into a Teflon-lined autoclave. The autoclave was sealed and heated at 160 °C for 3 h. Afterwards, the autoclave was cooled to room temperature naturally. The brown precipitate was collected by filtration, washed thoroughly with deionized water and dried at 80 °C for 12 h to obtain the MnF_2 precursor.

Mn_2O_3 anode material was synthesized by a direct post heat treatment of the MnF_2 precursor at 600 °C for 5 h in muffle furnace. As for the synthesis of $LiMn_2O_4$ cathode material, a molten salt method was adopted to help to maintain the formed specific morphology and to obtain better dispersed secondary particle [37–43]. $LiOH{\cdot}H_2O$, the obtained Mn_2O_3 and NaCl were mixed thoroughly. Note that the molar ratio between Li and Mn is 1.02: 2, and the NaCl (Sigma Aldrich) is three times of total raw materials (Mn_2O_3 and $LiOH{\cdot}H_2O$) in weight. Then the mixture was calcined at 800 °C in air for 10 h, and cooled to room temperature naturally. The as prepared powder was well washed with deionized water to remove the residual NaCl, and the $LiMn_2O_4$ cathode material (named as MS − $LiMn_2O_4$) was achieved after being dried in vacuum at 120 °C for 12 h. For comparison, $LiMn_2O_4$ was also prepared in a similar process without adding NaCl (named as NMS − $LiMn_2O_4$).

The crystal structure of the prepared materials was characterized by X-ray diffraction (XRD) in the 2θ range of 10–90° at a scan rate of 0.0196°/step, which was performed on the Bruker D8 Advance (Germany) with Cu K_α radiation at room temperature. Particle morphology was evaluated by using field-emission scanning electron microscopy (FE - SEM, Zeiss Auriga). The focused-ion beam (FIB - SEM) study was carried out to investigate the interior of the obtained hollow polyhedron.

Anode electrodes were prepared by casting slurry with the composition of Mn_2O_3 active material, Super C65 conductive agent and poly (vinyldifluoride) (PVdF) or Carboxymethyl cellulose (CMC) binders at a weight ratio of 70:20:10, onto copper foil (1.13 cm^2) and dried overnight in a vacuum at 80 °C. Cathode electrodes were prepared in a similar procedure, with the weight ratio of $LiMn_2O_4$ material, Super C65 and PVdF binder at 80:10:10, the aluminium foil (1.13 cm^2) was used as the current collector. Both slurries were prepared by magnetic stirring for 12 h to maintain hollow-morphology. The mass loading values of the active materials were about 1.5 mg cm^{-2} for Mn_2O_3 anode electrode and 2.0 mg cm^{-2} for $LiMn_2O_4$ cathode electrode, respectively. The electrodes were assembled into CR2032 coin cells with lithium metal as counter electrode and 1 M $LiPF_6$ in 3:7 (in weight) ethylene carbonate (EC): dimethyl carbonate (DEC) as electrolyte. Galvanostatic cycling measurements were carried out on Maccor series 4000 battery testers in a voltage range of 0.01–3.0 V (nominal current, 1C = 1018 mA g^{-1}) for Mn_2O_3 anode, and 3.0–4.5 V (nominal current, 1C = 120 mA g^{-1}) for $LiMn_2O_4$ cathode, respectively.

3. Results and discussion

Fig. 1 shows the corresponding XRD patterns of the MnF_2 precursor and the Mn_2O_3, NMS − $LiMn_2O_4$ and MS-$LiMn_2O_4$ materials. In Fig. 1a, all diffraction peaks could be signed to tetragonal MnF_2 (JCPDS standard card no. 24-727) with space group of $P4_2/mnm$, which indicates that in addition to its function of directing the structure IL also took part in the reaction. It reacted with Mn^{2+} under high pressure and formed MnF_2. The Mn cations are situated in the grey MnF_6-octahedral. Through thermal treatment, the tetragonal MnF_2 was transformed into orthorhombic Mn_2O_3 (JCPDS Card No. 24-0508) with space group of $Ia-3$ (Fig. 1b). Mn atoms are located in the octahedral 24d sites with the oxygen ions occupying the 48e sites. The Mn cations process Mn–O bonds between edge-sharing MnO_6-octahedral. After being annealed together with LiOH, the orthorhombic Mn_2O_3 was then transformed into spinel $LiMn_2O_4$ with space group of $Fd-3m$, as proved by Fig. 1c and d. The Li cations locate in the tetrahedral sites while Mn cations are still in the octahedral sites. The new formed Mn_2O_4 structure provides edge-sharing octahedra, which supply the framework with a three-dimensional network of tunnels for Li diffusion. For both the NMS - $LiMn_2O_4$ and MS-$LiMn_2O_4$ materials, no impurities could be found for all these obtained materials, and the strong and sharp reflection peaks suggest that the prepared materials are well crystallized. In addition, the relative ratio of (111) to (400) for the MS-$LiMn_2O_4$ (~2.80) is much larger than that for the NMS-$LiMn_2O_4$ (~1.96), indicating that the MS - $LiMn_2O_4$ has the structure with dominant plane of (111) [44].

The morphologies of the obtained materials were then characterized by SEM. Fig. 2a shows the SEM image of the MnF_2 composite