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Synthesis of flower-like $LiMnPO_4$/C with precipitated $NH_4MnPO_4 \cdot H_2O$ as precursor

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ABSTRACT

Ammonium magnesium phosphate monohydrate ($NH_4MnPO_4 \cdot H_2O$) precursor was prepared by a novel precipitating process with manganese citrate complexes as intermediate. The morphology of the precursor observed by Scanning Electron Microscope (SEM) was flower-like which was self-assembled by plate-like particles. Further analysis by X-ray diffraction (XRD) revealed that the lattice of the plate crystal was orientated along (0 1 0) plane. By solid-state reaction of the precursor, with lithium acetate and glucose as carbon source, pure olivine structured $LiMnPO_4$/C composite was obtained and meanwhile, the original flower-like morphology could be retained.

1. Introduction

As a promising cathode material for lithium ion batteries, olivine structured lithium transition metal phosphate $LiMPO_4$ (M = Fe, Co, Mn) has attracted lots of attentions [1–5]. It has three-dimensional framework which stabilizes the structure during the lithium insertion and desertion [6]. Hence, this family of compounds delivers better reversible capacities and higher stability than any other ones [7,8]. In addition, its considerable advantages like low cost and environmental friendly make it have great potential to be applicated in large-scale, such as EV and HEV [9–12].

Lithium manganese phosphate ($LiMnPO_4$) has a flat 4.1 V plateau versus Li^+/Li which is regarded as a good alternative for $LiCoO_2$ [1,13–16]. And higher redox voltage for Mn^{2+}/Mn^{3+} also indicates its higher energy density than $LiFePO_4$ [17]. Up to now, tremendous studies have been conducted on $LiFePO_4$, focusing on the synthetic routes to improve the electrochemical performance or control the morphology [18–23]. Nevertheless, there have been few previous studies on the novel morphology for $LiMnPO_4$ compared to $LiFePO_4$. Fang et al. prepared rod and plate like $LiMnPO_4$ which range from 1 μm to 100 nm by hydrothermal method, and it was found that the morphology related to the reaction condition during hydrothermal process [24]. Choi et al. synthesized nanoplate $LiMnPO_4$ controlled by molten hydrocarbon assisted solid-state reaction [16]. Tarascon produced various types of $LiMnPO_4$ using ionic liquid as reacting media which should be conducted at temperature range of 220–250 °C [25].

$NH_4MPO_4 \cdot H_2O$ precursor based method for preparing $LiMPO_4$ (M = Fe, Mn, Co) has been reported in previous literatures. Tirado synthesized NH_4CoPO_4 by precipitating method, and then $LiCoPO_4$ was obtained through solid-state procedure [26,27]. Bramnik precipitated plate-like $NH_4MnPO_4 \cdot H_2O$ from aqueous solution and revealed that the pH value for the precipitating process would not influence the basic morphology of $NH_4MnPO_4 \cdot H_2O$ [28]. Here, we suggested a novel method to synthesize flower-like $NH_4MnPO_4 \cdot H_2O$ and $LiMnPO_4$, and that the electrochemical behavior were also reported.

2. Experimental

2.1. Synthesis of materials

0.002 mol manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, Sinopharm Chemical Reagent Co. Ltd., Shanghai, AR) and 0.002 mol citric acid monohydrate (Sinopharm Chemical Reagent Co. Ltd., Shanghai, AR) were dissolved in 10 ml deionized water, respectively. Then under magnetic stirring, the latter solution was poured into the former one, white precipitation appeared immediately in the mixed solution. After stirring for 6 h, 10 ml deionized water containing 0.002 mol ammonium dihydrogen phosphate ($NH_4H_2PO_4$, Sinopharm Chemical Reagent Co. Ltd., Shanghai, AR) was added into it and was stirred intensely for another 30 min. The pH value of the resulting solution was then adjusted to the range of 10.2–10.7 by adding ammonia ($NH_3 \cdot H_2O$, Zhitang Chemmicals Co. Ltd., Taicang) to precipitate $NH_4MnPO_4 \cdot H_2O$. After stirring for a short while, the obtained precipitate was

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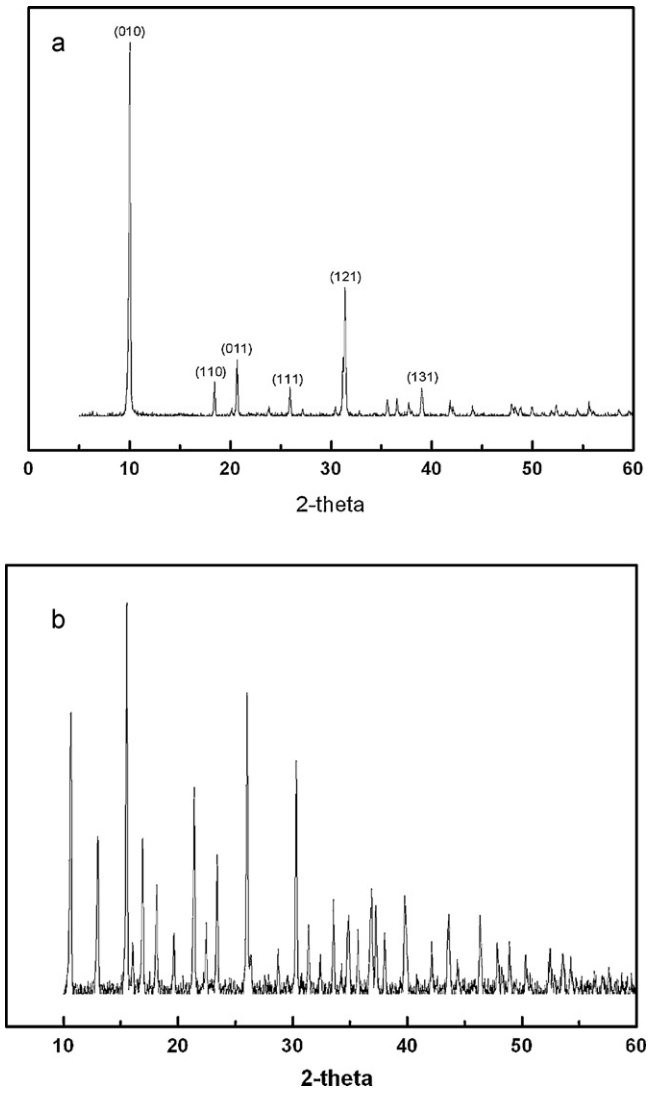

Fig. 1. (a) The XRD data of as-prepared $NH_4MnPO_4{\cdot}H_2O$. (b) The obtained white precipitate obtained by adding citric acid.

filtered and washed for several times with distilled water and acetone, and dried at 80 °C overnight.

With respect to the as-prepared $NH_4MnPO_4{\cdot}H_2O$, the stoichiometric amounts of lithium acetate dehydrate ($LiAC{\cdot}2H_2O$, Sinopharm Chemical Reagent Co. Ltd., Shanghai, AR) and glucose (Sinopharm Chemical Reagent Co. Ltd., Shanghai) (1:9 weight ratio to that of $LiMnPO_4$ to be yielded) were mixed. After milling for 1 h, the precursors were heated at 310 °C for 1 h in the atmosphere of Ar containing 5% H_2. After being cooled down to room temperature, the products were milled again for another 30 min, and then calcined at 550 °C for 10 h in the same atmosphere.

2.2. Characterization

The X-ray diffraction (XRD) measurement was carried out on a Bruker D8 Advance X-ray diffraction using Cu Kα radiation source (λ = 1.5406 Å) with a step size of 4° min^{-1} from 10° to 80°. The powder morphology was observed by scanning electron microscope (SEM) on JEOL JSM-6390.

The electrochemical performance of as-prepared $LiMnPO_4$ was investigated using coin cells assembled in an argon-filled glove box (SIMATIC OP7, MBRAUN). The cell was composed of a lithium anode and a cathode that was a mixture of prepared $LiMnPO_4$ (70%), Super P Carbon black (20%) and polytetrafluoroethylene (PTFE) (Dupont) (10%). The mixture was rolled into a thin sheet with uniform thickness, then it was cut into 10 × 10 mm section before being pressed to a aluminum mesh. Typical loading of the active material is about 10 mg cm^{-2}. The electrolyte was 1 M $LiPF_6$ dissolved in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight), and Celgard 2300 was used as separator. The electrochemical charge–discharge measurements were carried out in the voltage range from 2.5 to 4.6 V vs. Li^+/Li on LAND CT 2001 cell test instrument (Wuhan Kingnuo Electronic Co, China). All the tests were performed at room temperature.

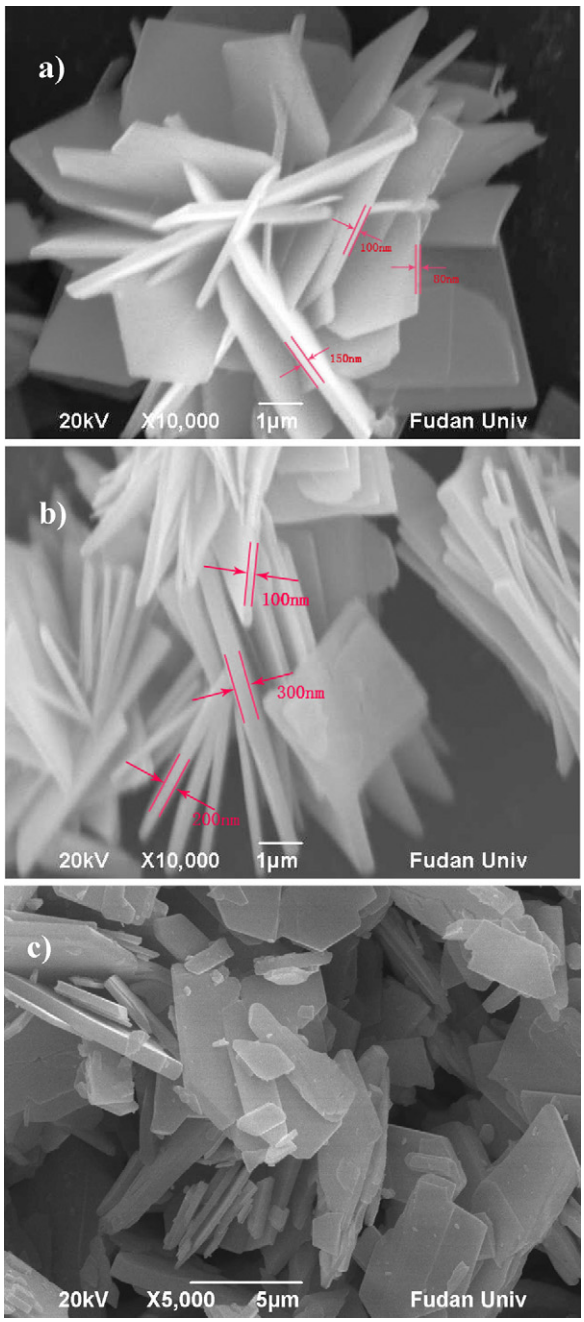

Fig. 2. The SEM photos of as-prepared $NH_4MnPO_4{\cdot}H_2O$, (b) with adding citric acid. (b) Without adding citric acid.

3. Results and discussion

3.1. Characterization of $NH_4MnPO_4{\cdot}H_2O$

The diffraction pattern of as-prepared $NH_4MnPO_4{\cdot}H_2O$ was displayed in Fig. 1(a). It could be concluded that all the diffraction peaks can be ascribed to Pmn2 structure without any impurities. And the sharp peak also indicated the high crystallization. The major lattice plane was emphasized in figure. It was worth mentioning that the peak intensity ratio of our sample showed some difference compared with the previous report [28]. It showed a strong orientation effect in (0 1 0) plane. To explore the forming