Electrochimica Acta 193 (2016) 16–23

Contents lists available at ScienceDirect

Electrochimica Acta

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

In-situ growth of $LiMnPO_4$ on porous $LiAlO_2$ nanoplates substrates from AAO synthesized by hydrothermal reaction with improved electrochemical performance

Jun Zhang[a,c], Shaohua Luo[a,b,c,*], Longjiao Chang[e], Shuo Bao[a,c], Jianan Liu[a], Aimin Hao[a,b,c], Zhiyuan Wang[b,c], Yanguo Liu[b,c], Qian Xu[d], Yuchun Zhai[a]

[a] School of Materials Science and Metallurgy, Northeastern University, Shenyang 110004, People's Republic of China
[b] School of Resources and Materials, Northeastern University at Qinhuangdao, Qinhuangdao 066004, People's Republic of China
[c] Key Laboratory of Dielectric and Electrolyte Functional Material Hebei Province, Qinhuangdao 066004, People's Republic of China
[d] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, People's Republic of China
[e] School of New Energy, Bohai University, Jinzhou 121013, People's Republic of China

ARTICLE INFO

Article history:
Received 20 December 2015
Received in revised form 28 January 2016
Accepted 4 February 2016
Available online 6 February 2016

Keywords:
$LiMnPO_4$
$LiAlO_2$ nanoplates
In-situ growth
Hydrothermal method
Electrochemical performance

ABSTRACT

$LiAlO_2$ composited $LiMnPO_4/C$ cathode material has been synthesized by in-situ growth hydrothermal method. The coexistence of minor $LiAlO_2$ in $LiMnPO_4$ plays an important role in electrochemical properties. The composite is characterized by XRD, SEM, HRTEM, Raman microprobe spectroscopy and their electrochemical properties are also studied. It shows that the $LiAlO_2$ is composed of pure α-$LiAlO_2$ phase with flaky-shaped nanoplates. $LiAlO_2$ nanoplates porous structure is inherited from anodic aluminum oxide (AAO) structure and serves as substrates to grow $LiMnPO_4$ nanocrystals, which provide a high surface area with a porous structure. The structure of $LiMnPO_4$ is not affected by $LiAlO_2$ nanoplates compositing. Among the investigated samples, the one with 6 wt.% $LiAlO_2$ exhibits a higher specific discharge capacity of 142.8 mAh/g at 0.05C rate with a high capacity retention of 94.8% after 50 cycles. Electrochemical impedance spectroscopy (EIS) results show that the lithium diffusion constant (D_{Li^+}) for 6 wt.% content $LiAlO_2$-$LiMnPO_4/C$ electrode is 2.07×10^{-14} cm^2/s which is higher than the values for other contents $LiAlO_2$-$LiMnPO_4/C$ electrode. The $LiAlO_2$ is effective in suppressing the increase of the interfacial resistance between the electrode/electrolyte interface during charge-discharge cycling.

1. Introduction

Being used as potential electrodes for Li-ion batteries, $LiMnPO_4$ has recently attracted attention due to its high energy capacity (20% higher than $LiFePO_4$), nontoxicity, lower cost and better chemical and thermal stability [1–5]. So, $LiMnPO_4$ becomes a promising material for the application of electric vehicles (EVs) and hybrid electric vehicles (HEVs) [6–8]. However, low intrinsic electronic conductivity ($<10^{-10}$ S/cm) and ionic conductivity [9,10] makes its practical capacity much lower than the theoretical capacity and inhabits its further use in commercial applications. Consequently, many research efforts have been focused on overcoming these problems and improving the electrochemical performance of $LiMnPO_4$.

To date, many efforts such as conductive surface coating [11–13], particle size reduction [14,15] and cations/metal oxides doping have been applied to improve the electronic conductivity and lithium ion mobility of $LiMnPO_4$. On increasing the electronic conductivity, it is a common practice to prepare carbon coated materials. A thin carbon layer can provide a path for electrons without blocking the access of Li^+ ions. The effectiveness of surface carbon depends on the type and amount of the carbon source being used. Additionally, other surface modification with metallic particles can increase the electronic conductivity of $LiMnPO_4$, but little for ionic conductivity. Recently, coating of Li-contained oxides such as $Li_4Ti_5O_{12}$, $LiNbO_3$, Li_2TiO_3, Li_2ZrO_3, Li_2SiO_3 and $LiAlO_2$ on $LiCoO_2$ particles and $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$ cathode materials have been reported as an effective modification technique [16–23]. For example, Wu et al. [24,25] reported $LiMnPO_4/C$ with an average size of 75 nm synthesized by sol-gel combined ball milling and quenching method showing a reversible capacity of 131 mAh/g at 0.05C. Recently, Wu and coworkers synthesized $xLiMn_{0.9}Fe_{0.1}PO_4 \cdot yLi_3V_2(PO_4)_3/C$ composite cathode

---

* Corresponding author at: School of Resources and Materials, Northeastern University at Qinhuangdao, Qinhuangdao 066004, People's Republic of China
E-mail addresses: luosh00@126.com, luoshaohua@tsinghua.org.cn (S. Luo).

http://dx.doi.org/10.1016/j.electacta.2016.02.018

materials by a ball-milling and post-calcination method. Among them, $5LiMn_{0.9}Fe_{0.1}PO_4 \cdot Li_3V_2(PO_4)_3/C$ exhibited the highest reversible capacity of 158.1 mAh/g at 0.05C. The sample also shows good cycling performance at various C-rates. Two modification methods have been employed simultaneously to improve the electrochemical properties of $LiMnPO_4$. And moreover, it can effectively enhance the electrochemical performance due to their good conductivity and internal tunnels for Li^+ transportation during charge/discharge processes [26,27].

Furthermore, $LiAlO_2$ particles have a wide application on lithium secondary battery [28]. The compound $LiAlO_2$ is known to exist in three possible allotropes, namely, α-$LiAlO_2$, β-$LiAlO_2$, γ-$LiAlO_2$. Compared with β and γ phase, the Li atom in α-$LiAlO_2$ is generally the most reactive and solely extractable, which is due to the good Li electrophilicity, a significantly smaller energy for Li binding to its neighboring atoms and a dramatic difference in energetic behavior upon dislocating a Li atom from its equilibrium position in different phases [29]. In the structure of α-$LiAlO_2$ there are only octahedral aluminum ions with the same lamellar hexagonal system. The α-$LiAlO_2$ phase has the hexagonal lattice structure (R3m, a = 2.799Å,c = 14.18 Å) [30] of layered Li-O-Al-O, because the Al-O bonds are very stable. For all of these applications, fine lithium aluminate powders as a superionic conductor material with high surface area and considerable lithium-ion conductivity are desirable for improving the rate capability and cycling stability of $LiMnPO_4$. To the best of our knowledge, however, there have been no reports on $LiAlO_2$ modified $LiMnPO_4$ composite materials as yet. Inspired by these findings, we try to form $LiAlO_2$-$LiMnPO_4/C$ composite particles, and investigate the effects of $LiAlO_2$ on electrochemical performances of olivine structure $LiMnPO_4$ materials.

2. Experimental

All of the chemicals were used as received without any pretreatment or further purification.

2.1. Synthesis of AAO and $LiAlO_2$

Nanoporous AAO templates were fabricated by a two-step anodization process. A high-purity aluminum plate (99.999%, 8 cm × 3 cm × 0.3 mm) was annealed at 600 °C for 5 h in N_2 atmosphere and degreased in acetone. After electropolishing to a mirror finish in a 1:4 (v/v) perchloric acid/ethanol solution at room temperature for 2∼3 min at a current of 15 A, the anodization was carried out in a 0.3 mol/L phosphoric acid solution at 80 V and 25 °C for 3 h. Then the alumina layer was removed in a mixture aqueous solution of phosphoric acid and chromic acid. Subsequently, the anode was anodized for 10 h in the same condition again and became AAO template with high ordered nanoporous arrays (∼100 nm in diameter). The $LiAlO_2$ preparation was on the AAO template substrate. The AAO and Li_2CO_3 (at a 1:3 molar ratio) was mixed in the deionized water, the mixture then moved into Teflon-lined autoclave reacted a few hours. The resulting precursors were dried at 80 °C under vacuum and then calcined at 550 °C in air. Two-dimensional nanosturcture porous $LiAlO_2$ nanoplates were synthesized.

2.2. Synthesis of $LiMnPO_4/C$

The Li_3PO_4 precursor was precipitated by dropping 1.7 mol/L H_3PO_4 (85%) into a 2.0 mol/L LiOH (99%) aqueous solution using the peristaltic pump (the flow rate was 3.3 ml/min). The resulting white precipitates were washed with distilled water and dried in air at 120 °C. For all syntheses, the reactants such as $MnSO_4 \cdot H_2O$ (99%) and the above Li_3PO_4 (in a 3:1 molar ratio) dissolved in 1:2 volume ratio PEG400-H_2O mixed solvents and stirred for 0.5 h. Then, the slurry was transferred into a Teflon-lined autoclave, and heated at 160 °C for 9 h. Finally, the products were filtered off and washed several times with deionized water and anhydrous alcohol thoroughly and dried at 80 °C for 3 h to get $LiMnPO_4$ precursor. The as-prepared $LiMnPO_4$ precursor was mixed with ascorbic acid at 1:0.25 weight ratio within alcohol solution, mixed homogeneously and dried for 12 h. Then the dried composite powder was calcined at 550 °C for 3 h under N_2 atmosphere to get $LiMnPO_4/C$ material.

2.3. Synthesis of $LiAlO_2$-$LiMnPO_4/C$ composite

The procedures for different contents of $LiAlO_2$-$LiMnPO_4/C$ composite materials were prepared by in-situ growth hydrothermal method. Li_3PO_4 and $MnSO_4 \cdot H_2O$ (99%) (in a 1:3 molar ratio) and a certain contents $LiAlO_2$ substrates were dissolved in 1:2 volume ratio PEG400-H_2O mixed solvents and stirred for 0.5 h. Then we put it under vacuum treatment to ensure the subsequent immersion. The subsequent procedures were the same with the preparation of $LiMnPO_4/C$ mentioned above. Finally, the $LiAlO_2$-$LiMnPO_4/C$ composite material was obtained.

2.4. Characterization

The samples were studied by X-ray diffraction (XRD, DX-2500) using Cu Kα radiation (λ = 1.5406 Å) from 2θ = 10–90° at a scan

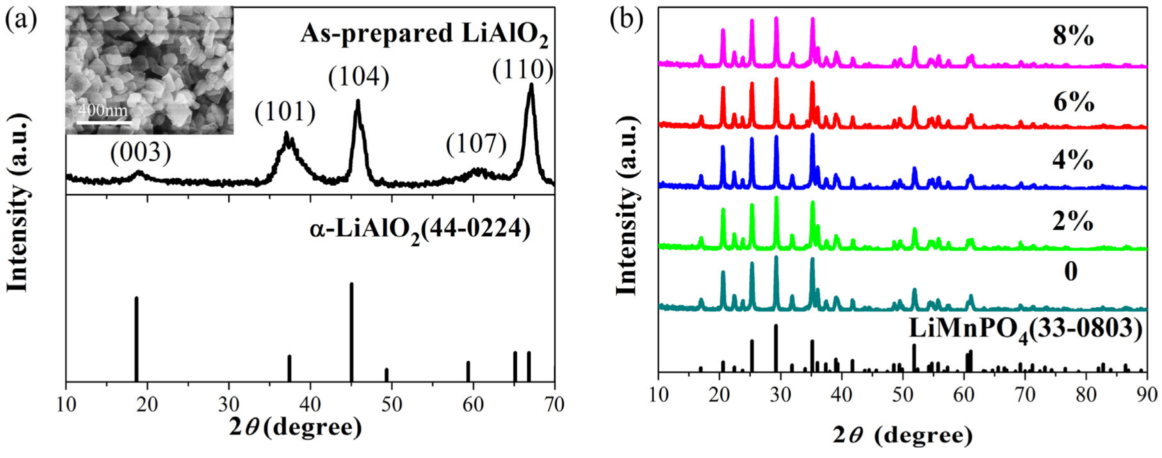

Fig 1. X-ray diffraction patterns of (a) $LiAlO_2$ nanoplates after heat treatment at 550 °C, inset: SEM of $LiAlO_2$, and (b) prepared with different amounts of $LiAlO_2$.