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Microsized single-crystal spinel LAMO for high-power lithium ion batteries synthesized via polyvinylpyrrolidone combustion method

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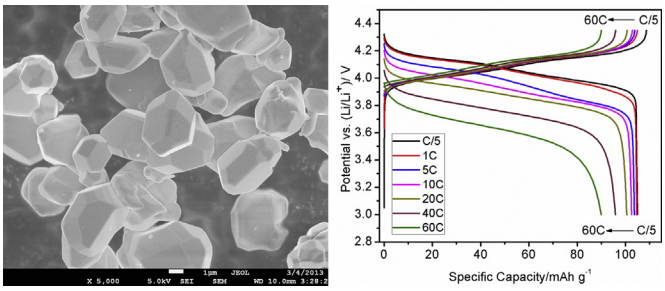
HIGHLIGHTS

- Microsized single-crystal $Li_{1.08}Mn_{1.89}Al_{0.03}O_4$ (LAMO) was synthesized via polyvinylpyrrolidone (PVP) combustion method.
- The microsized single-crystal LAMO shows excellent cycle performance.
- The microsized single-crystal LAMO exhibits excellent rate and low temperature performance.
- The microsized single-crystal LAMO has high lithium chemical diffusion coefficient.

GRAPHICAL ABSTRACT



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ABSTRACT

Microsized single-crystal $Li_{1.08}Mn_{1.89}Al_{0.03}O_4$ (LAMO) was synthesized via polyvinylpyrrolidone (PVP) combustion method. X-ray diffraction (XRD), scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM) characterization results indicate that the as-prepared LAMO has good crystallinity, uniform and smooth-surfaced morphology, and very low specific surface area. Galvanostatic charge-discharge tests demonstrate its excellent electrochemical performance. The capacity retentions at 30 °C and 55 °C are 98.8% and 93.3% respectively after 200 cycles at 1 C charge/discharge rate. Moreover, the LAMO exhibits excellent rate and low temperature performance. Even at high rates of 40 C and 60 C, the as-prepared LAMO are still able to deliver 91.2% and 85.6% capacity relative to the discharge capacity at C/5. The specific discharge capacity at −20 °C is 97.9 mAh g^{-1} which is 93.7% of the capacity discharging at 25 °C. To study the reason of the excellent rate performance, the potential intermittent titration technique (PITT) tests and cyclic voltammetry (CV) measurements were conducted and the lithium chemical diffusion coefficient (D_{Li^+}) was calculated.

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1. Introduction

The rapid development of electric vehicles requires advanced lithium ion batteries with higher power density and longer cycle life. Spinel $LiMn_2O_4$ is at present a very prospective candidate for the cathode (positive electrode) material due to its low cost, good safety, environmental friendliness, and relatively high voltage [1–3]. However, this material shows capacity fading along with cycling due to Jahn–Teller effect [4], oxygen deficiency [5,6], and Mn dissolution [4,7,8]. Li [4,9,10] and Al [11–18] doped $LiMn_2O_4$, abbr. LAMO, has improved cycle performance by lattice modification. Besides doping, to minimize spinel/electrolyte interface is also an important strategy to reduce Mn dissolution and other side

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reactions in order to further improve the cycle and storage performance [19,20].

To reduce the spinel/electrolyte interface, the specific surface area must be decreased. Then the particle size should be bigger and the surface should be smoother. Big secondary particles formed by small primary particles are not enough for lower specific surface area [21]. Single-crystal spinel $LiMn_2O_4$ has attracted attention [22–25] in the last decade because this morphology can further reduce the specific surface area. Previous studies show good cycle or storage performance but the rate performance is not good enough. Recently we synthesized microsized $LiNi_{0.5}Mn_{1.5}O_4$ [26] which showed better rate performance than nanosized or submicrosized materials. Thus, we hypothesize microsized single-crystal spinel LAMO should show excellent rate performance besides excellent cycle performance.

To synthesize microsized single-crystal spinel with excellent rate performance, proper method must be selected and condition should be carefully controlled. The simplest routine is calcined at high temperature (e.g., 1000 °C). However, if precursor is not well mixed, impurities will be easily introduced. In addition, without effective treatment after high temperature calcination, oxygen deficiency will be a serious obstacle for rate and cycle performance.

In this paper, we used a PVP (Polyvinylpyrrolidone)-assisted gel combustion method [26–29] developed by our group to synthesize the microsized single-crystal $Li_{1.08}Mn_{1.89}Al_{0.03}O_4$ (LAMO). PVP can fix metal ion on the macromolecular chain via chelation, so the precursor can be very uniform. The precursor was calcined at high temperature (1000 °C) to produce microsized single crystal. Then a low temperature (700 °C) annealing was performed after mixing a small quantity of lithium compound to lessen oxygen deficiency caused by high temperature [30,31]. The generated microsized single-crystal LAMO not only presented excellent cycle performance but also matched the rate performance of nano particles.

2. Experimental

2.1. Synthesis procedure

The single-crystal spinel LAMO was prepared by the PVP-assisted gel combustion method developed by our group. In detail, $LiOAc{\cdot}2H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ (Li:Mn:Al = 1.08:1.89:0.03), and PVP (the molar ratio of PVP monomer to total metal ions was 2.0) were dissolved in deionized water and pH = 3 was achieved by adding 1:1 HNO_3. The mixture was stirred and dried at 120 °C in air to obtain dried gel. The dried gel was ignited on a hot plate for several minutes to induce a combustion process. The resulting precursor was preheated at 400 °C for 2 h and then calcined at 1000 °C for 6 h in air. The heating rate was 5 °C min^{-1}. After heat treatment, the oven was switched off and the sample was cooled down naturally. 1 wt% Li_2CO_3 was added into the calcined sample and mixed evenly. At last, the mixture was heated at 700 °C for 6 h in air followed by natural cooling.

2.2. Physical characterization

The analysis of the phase purity and the structural characterization were made by X-ray powder diffraction (XRD) using a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation that was operated over a 2θ range of 15–70° in a continuous scan mode with a step size of 0.01°. The lattice parameters were refined by TOPAS software. The particle size and morphology of the samples were examined using a JEOL 7500F scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) analysis was carried out via a Philips CM200FEG at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory and the acceleration voltage was 200 kV. The specific surface area was measured by a Brunauer–Emment–Teller (BET) N_2 adsorption method with a Micromeritics Tristar II 3020 surface area and porosity analyzer. Before the measurement, the sample was heated at 300 °C for 4 h to remove adsorbed water thoroughly.

2.3. Electrochemical tests

All electrochemical performances were evaluated using CR2325 coin cells except for low temperature test in which CR2025 coin cell was used. The coin cells were fabricated with the LAMO cathode, lithium foil anode, 1 mol L^{-1} $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate, and a Celgard 2400 polypropylene separator.

The cathodes were prepared by mixing 88 wt.% active material, 6 wt.% acetylene black (AB) and 6 wt.% polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) to form a slurry. The slurry was stirred for 4 h and then cast onto aluminum foil using a MSK-AFA-III Film Coater (MTI Corporation), dried at 120 °C in air for 2 h and then heated at 130 °C under vacuum for 12 h to prepare the cathode film. The film was punched into discs (diameter = 13 mm) and then pressed at a static pressure of 4–6 MPa. The electrode discs typically had an active material loading of about 5 mg.

The coin cells were assembled in an argon-filled glove box and galvanostatic charge–discharge tests were performed using Maccor 4000 except low temperature test in which LAND CT2001A was used. The potential intermittent titration technique (PITT) test and cyclic voltammetry (CV) measurements were conducted using Bio-Logic VMP-3 multichannel electrochemical Analyzer.

3. Results and discussion

The XRD patterns of the single-crystal spinel LAMO is displayed in Fig. 1. All diffraction peaks can be indexed as a cubic spinel structure and $Fd\bar{3}m$ space group, and no obvious impurity phases are observed in the sample. All of the peaks are narrow and sharp, indicating good crystallinity. The lattice parameter a is 8.2137(8), which is close to other reported values [16,17].

Fig. 2a shows the SEM image of the single-crystal spinel LAMO. The morphology is almost monodispersed truncated-octahedron and the surface of particles is very smooth. The specific surface area is 0.241 ± 0.025 m^2 g^{-1}, which is very low. The sizes of 150

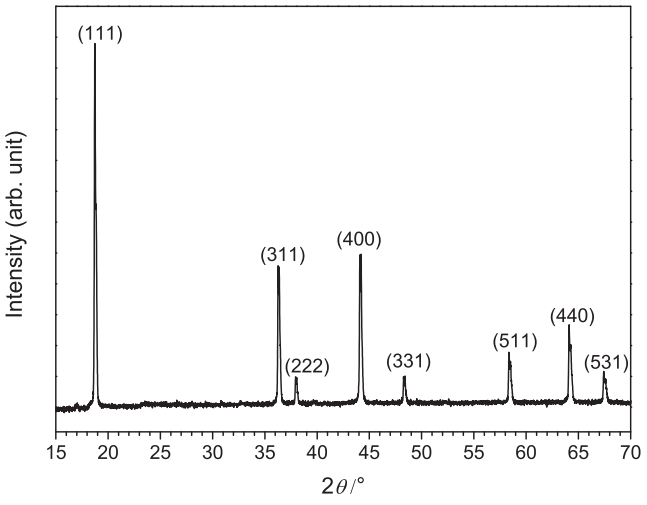

Fig. 1. XRD patterns of the single-crystal spinel LAMO.