



High-rate and long-life performance of a truncated spinel cathode material with off-stoichiometric composition at elevated temperature



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ARTICLE INFO

Article history:

Received 6 October 2016

Received in revised form 28 November 2016

Accepted 15 December 2016

Available online 24 December 2016

Keywords:

LiMn₂O₄

Spinel

Cathode

Off-stoichiometric strategy

High capacity retention

ABSTRACT

A truncated octahedral structure spinel cathode material with a nominal composition of Li_{1.08}Al_{0.08}Mn_{1.85}Co_{0.05}O_{3.9}F_{0.1} (LAMCOF) and an Al-rich surface layer is successfully prepared by a sol-gel route combined with a temperature-controlled heat-treatment process. Concentration gradient of Mn⁴⁺ ions is found to decrease through the surface to the interior of the as-prepared sample. As the consequence, the LAMCOF sample delivers high rate capability and excellent cycling stability at elevated temperature, showing an initial discharge capacity of 111.1 mAh g⁻¹ and capacity retention of 70.5% over 850 cycles at 1C rate under 55 °C. Even at 5C rate under 55 °C, it also displays a high capacity of 102.5 mAh g⁻¹ with capacity retention of 80.0% over 850 cycles. These results reveal the importance of an off-stoichiometric strategy and a temperature-controlled heat-treatment process for the preparation of LiMn₂O₄-based spinel cathode material with unique crystal orientation and Mn⁴⁺-rich surface layer, which both decrease the Mn dissolution and provide interfacial stability while preserving fast Li⁺ diffusion, resulting in improvement of cycle performance and rate capability of the as-prepared material. This proposed synthesis method does not need a supplementary coating process and is likely suitable to prepare other high performance cathode materials.

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1. Introduction

Spinel LiMn₂O₄ (LMO) has received special attention as a very prospective cathode material for widespread large-scale applications because of the ever-increasing demand from plug-in hybrid electric vehicles (PHEVs), pure electric vehicles (EVs), and stationary energy storage systems in very recent years [1]. It has many intrinsic advantages including a high theoretical capacity of 148 mAh g⁻¹, low cost, abundant availability, nontoxicity, good thermal stability, and excellent rate performance resulting from its three-dimensional (3-D) channel structure [2]. Furthermore, it has a suitable Mn⁴⁺/Mn³⁺ redox potential (4.1 V versus Li⁺/Li) for the electrochemical stable window of most commercial electrolytes, which affords its high safety as a cathode material [3]. Despite these advantages, stoichiometric LMO has suffered from

continuous capacity fading upon extended cycles, especially at high temperature (≥55 °C), originated from Mn²⁺ dissolution into the electrolyte (2Mn³⁺_{solid} → Mn⁴⁺_{solid} + Mn²⁺_{solution}) [4] and then Mn deposition on the anode (Mn²⁺_{solution} → Mn⁰_{solid}) [5], and structural transformation that is induced by Jahn–Teller distortion of Mn³⁺ with high spin [6].

It is well known that the electrochemical properties of LMO are very sensitive to morphology, doping/substitution, crystal orientations, particle size distribution and surface structure. Many efforts have been devoted to improve the high-temperature cycle stability of LMO by various strategies and significant advancements have been achieved [7]. These strategies include optimization of electrolyte, doping/partial substitution by other elements, surface coating, morphology control, decrease of surface area and development of functional binder and separator. However, single

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strategy cannot effectively improve the high-temperature cyclability of LMO without sacrificing the specific capacity and rate performance. For example, Cho's group has prepared three cathode materials by coating of micro-sized LiMn_2O_4 using respective $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [8], $\text{Li}_{1.15}\text{Co}_{0.32}\text{Mn}_{1.53}\text{O}_4$ [9] and $\text{Li}_{1.15}\text{Al}_{0.32}\text{Mn}_{1.53}\text{O}_4$ [10] very recently. These three samples displayed a high initial capacity of $\sim 120 \text{ mAh g}^{-1}$ and good rate capability; however, with only capacity retention of 80 to 85% over 100 cycles at 1C rate under elevated temperature. Xiong *et al.* [11] enhanced the cycle performance of LMO by Li, F-codoped method. However, the specific capacity of the Li, F-codoped LMO is as low as 90 mAh g^{-1} at 0.5C under 55°C . Similarly, Yu *et al.* [12] improved the cycle performance of LMO effectively by multi-component cation substitution strategy, but they also achieved low capacity of $\sim 91 \text{ mAh g}^{-1}$ at 0.5C rate. Thus, a combination of two or multiple strategies to further enhance the electrochemical performance of LMO has also been developed and some very encouraging results have been achieved [7,10,13–20]. Especially, the cycle stability of LMO-based cathode materials at elevated temperature has been significantly improved by a synergistic role of dual-/multiple-elements doping and surface coating in very recent years [10,18–20]. This is due to the Mn^{2+} dissolution caused by Mn^{3+} disproportionation reaction can be alleviated and/or restrained by doping proper amount of ions into the host that stabilizes the local crystal structure and surface coating that produces a stable interface of active material and electrolyte. For instances, Hu *et al.* [19] reported a Li–Al–Si–O glassy solid electrolyte coated $\text{Li}_{1.05}\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_{3.95}\text{F}_{0.05}$ nanorods displayed superior rate performance and good high-temperature cycling performance (55°C), with an initial specific capacity of $\sim 94 \text{ mAh g}^{-1}$ and a capacity retention ratio of 96% after 200 cycles at 10C rate. Lee *et al.* [10] synthesized $\text{Li}_{1.15}\text{Mg}_{0.2}\text{Mn}_{1.65}\text{O}_4$ -coated $\text{Li}_{1.09}\text{Mn}_{1.83}\text{Al}_{0.08}\text{O}_4$ using a spray drying route. Investigation on the surface composition and structure of the surface-coated material shows that the metal ions in the coating material diffuse into the host material, and thus introduces a hierarchical atomic structure at the surface of the host material after heat-treatment. In addition, they illustrated that this coated sample exhibits a much lower activation barrier to lithium-ion diffusion than that of the uncoated sample, resulting in an outstanding high-temperature cyclability with an initial capacity of $\sim 106 \text{ mAh g}^{-1}$ and $\sim 90\%$ of capacity retention at 2C rate under 55°C .

Previous experimental results [21] and first-principles calculations [22] both demonstrated that the electrochemical activity and the Mn dissolution of LMO-based materials are largely dependent on the lattice orientation of the surface interfacing with electrolytes. The {100} and {110} crystal surfaces of LMO are beneficial for Li^+ diffusion, but also most vulnerable to Mn dissolution [21,22]. As an attempt to address these two contradictory issues, three successful examples [23–25] to enhance the high-temperature cycling and rate performance of LMO have been achieved by developing a truncated octahedral structure of LMO by a templating synthesis. In these samples, most surfaces {111} are aligned to the crystal orientations with minimal Mn dissolution, while only a small part of the structure is truncated along the orientations to facilitate Li^+ diffusion and thus provide high rate performance.

It is worth noting that a significant progress on the improvement of the high-temperature cyclability and rate performance of LMO has been achieved by previously reported literatures [7,10–20,23–25]. However, it is still a great challenge to simultaneously achieve LMO with high rate performance and long cycle stability at elevated temperature in a simple synthesis route. That is because the mixing of an active material with coating material by wet chemistry method combined with annealing is too complicated and is not always guaranteed to obtain uniform

nanoscale surface coatings, especially in large-scale production. Moreover, the design concept of crystal orientations with a special morphology often needs a particular precursor, which cannot be easily synthesized in large scale by a simple route. Consequently, substantial trials and simple routes for the preparation of LMO-based materials with excellent cycle performance and good rate performance at elevated temperature without sacrificing their specific capacity are still in imminent demand. In this paper, the authors present a simple and efficient synthesis method by controlling the off-stoichiometry and calcination temperature to prepare the spinel $\text{Li}_{1.08}\text{Al}_{0.08}\text{Mn}_{1.85}\text{Co}_{0.05}\text{O}_{3.9}\text{F}_{0.1}$ cathode materials with desired surface Mn oxidation state, a truncated octahedral structure and Al-rich surface layer. The prepared LMO-based cathode material demonstrated enhanced cycle performance and rate capability at elevated temperature, as discussed consequently.

2. Experimental section

An off-stoichiometric sample (lithium and aluminum-excess sample) with a nominal composition of $\text{Li}_{1.08}\text{Al}_{0.08}\text{Mn}_{1.85}\text{Co}_{0.05}\text{O}_{3.9}\text{F}_{0.1}$ (LAMCOF) was synthesized by a sol-gel method using citric acid as a chelating agent. Firstly, $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.8225 g), LiF (0.0519 g) and citric acid monohydrate (4.4129 g) were dissolved in 30 ml of deionized water. Then, 60 ml of another mixed solution containing $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.6002 g), $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (9.0682 g) and $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (0.2491 g) was added successively into the above solution with vigorous stirring at 50°C . After stirring for 30 min, the pH value of the mixed solution was adjusted to 8.0 by adding ammonia. Subsequently, the solution was kept at 90°C till the sol formed. After drying the sol at 110°C for 12 h under vacuum, the as-prepared gel was milled and then calcined at different temperatures (750, 800 and 850°C , respectively) with a heating rate of $3^\circ\text{C}/\text{min}$ for 12 h under air to achieve the products, which were named as S1, S2 and S3, respectively. It is worth pointing out that the purpose of applying different calcination temperatures here are to study the morphology of the obtained products. For comparison, a stoichiometric sample with a nominal composition of $\text{Li}_{1.05}\text{Al}_{0.05}\text{Mn}_{1.85}\text{Co}_{0.05}\text{O}_{3.9}\text{F}_{0.1}$ (S4) was prepared by similar procedures as those of S2 except no excess lithium and aluminum sources were used.

The crystalline structure, morphology and surface composition were characterized by X-ray powder diffraction (XRD, Bruker D8 Advance, Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ nm}$), scanning electron microscopy (SEM, Merlin, Zeiss Germany), transmission electron microscopy (TEM, JEM-2100, Japan) and X-ray photoelectron spectroscopy (XPS, Escalab 210, Germany), respectively. The lattice parameters were obtained from the fitted data using Jade 5.0 software. The binding energies of different elements were calibrated with reference to the C_{1s} level of carbon (284.8 eV). The manganese dissolution content of the samples was determined quantitatively by Atomic Absorption Spectroscopy (AAS) using a HITACHI Z-2300 instrument. The detail test processes as following: firstly, the half cells made by the S2 and S4 electrodes were cycled at 5C rate under 55°C for different cycles (100, 200, 400 and 1000 cycles). Then they were dismantled in a glovebox and the Li anodes were dissolved completely in 50 mL of HNO_3 (0.01 mol L^{-1}). Finally, the obtained aqueous solutions were measured utilizing AAS to determine the Mn content.

For the fabrication of cathodes, the as-prepared active materials were mixed with carbon black and polyvinylidene fluoride (PVDF) (in mass ratio of 8:1:1) in N-methylpyrrolidinone. The slurry obtained was coated onto aluminum foil and then dried at 110°C overnight under vacuum. The mass loading of the active material was $\sim 2.0 \text{ mg cm}^{-2}$. The coin cells were assembled with a lithium metal anode isolated from the cathode by a porous separator

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