



Polyethylene glycol-assisted synthesis of hierarchically porous layered lithium-rich oxide as cathode of lithium ion battery



Min Chen ^{a, b, c}, Xingde Xiang ^{a, b, c}, Dongrui Chen ^{a, b, c}, Youhao Liao ^{a, b, c},
Qiming Huang ^{a, b, c, *}, Weishan Li ^{a, b, c, *}

^a School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China

^b Key Laboratory of Electrochemical Technology on Energy Storage and Power Generation of Guangdong Higher Education Institutes, South China Normal University, Guangzhou 510006, China

^c Engineering Research Center of Materials and Technology for Electrochemical Energy Storage (Ministry of Education), South China Normal University, Guangzhou 510006, China

HIGHLIGHTS

- Hierarchically porous layered lithium-rich oxide was synthesized with assistance of PEG2000.
- Using PEG2000 results in the microspheres and the porosity of the as-synthesized oxide.
- The unique morphology leads to excellent rate capability and cyclic stability of the oxide.

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ABSTRACT

A hierarchically porous layered lithium-rich oxide, $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, is synthesized by co-precipitation of metal oxalates with an assistance of a moderate polyethylene glycol (PEG2000). The morphology and crystal structure of the product are characterized by scanning electron microscope, transmission electron microscopy and X-ray diffraction, and its performance as cathode of lithium ion battery is evaluated with charge/discharge tests. It is found that the as-synthesized oxide exhibits excellent rate capability and cyclic stability: delivering an initial discharge capacity of 262 mAh g^{-1} at 0.1C ($1\text{C} = 250 \text{ mA g}^{-1}$) and 135 mAh g^{-1} at 4C , and possessing a capacity retention of 83% after 200 cycles at 4C . These performances can be attributed to the unique structure of the as-synthesized oxide: uniform secondary microspheres of about $10 \mu\text{m}$, which is composed of uniform primary microparticles of about $2 \mu\text{m}$, and hierarchically porous structure with pores distributed among primary and secondary particles. The hierarchically porous structure provides large reaction sites for lithium ion insertion/extraction and large space to buffer the volume change during cycling, leading to the excellent rate capability and cyclic stability of the as-synthesized oxide.

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1. Introduction

In the past decades, lithium-ion battery as an energy storage device has attracted global interest due to its long lifetime, high energy density and environmental friendliness, and has been successfully used in wireless electronic products including cell phones, laptop computers, digital cameras, etc. [1–5]. However, the energy

density of current lithium-ion battery cannot meet the requirement of large-scale applications such as in the area of electrical vehicles [6,7], which results mainly from the low specific capacity of currently available cathode materials including layered LiCoO_2 ($\sim 140 \text{ mAh g}^{-1}$) [8], spinel LiMn_2O_4 ($\sim 120 \text{ mAh g}^{-1}$) [9] and olivine LiFePO_4 ($\sim 170 \text{ mAh g}^{-1}$) [10]. Recently, much attention has been paid to layered lithium-rich oxide, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co, Fe, Cr, etc.}$), which could deliver a specific capacity of more than 250 mAh g^{-1} [11–14]. This layered lithium-rich oxide is composed of the intergrowth of LiMO_2 R-3m and Li_2MO_3 C2/m phases, which provides much better structure stability than the pure layered LiMnO_2 [3,11,15,16]. $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}$

* Corresponding authors. School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China.

E-mail addresses: huangqm@scnu.edu.cn (Q. Huang), liwsh@scnu.edu.cn (W. Li).

Li_2MnO_3 is a representative of many layered lithium-rich oxides that have been investigated. Unfortunately, the application of layered lithium-rich oxide in commercial cathode materials is limited by its poor cyclic stability and rate capability [17–19].

The morphology of battery materials is tightly related to their electrochemical performances. It has been known that the porous structure facilitates the improvement of rate capability of cathode materials in lithium ion battery due to the large specific surface area available for lithium insertion/extraction and the large space available to buffer the volume change during cycling [20–23]. To control the morphology, various polymers, including polyvinylpyrrolidone (PVP) [7,9,24], polyvinyl alcohol (PVA) [25], pluronic acid (P123) [26] and polyethylene glycol (PEG) [27], have been used as templates for material syntheses. Among these polymers, PEG has been most widely adopted because of its typical advantages including hydrophilicity, non-toxicity, and solubility in water and organic solvents [28–30].

Small particles are helpful for the rate capability improvement because of the short path for lithium diffusion inside the particles, but too small particles are detrimental to the cyclic stability due to the increased contact area between cathode materials and electrolyte, which might accelerate the decomposition of electrolyte and the dissolution of cathode materials [31]. In this work, we used PEG to control the morphology of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$. Two PEGs, PEG2000 and PEG4000, were considered. It was demonstrated that the sample synthesized with PEG2000 possesses a unique structure: uniform secondary microspheres of about 10 μm , which is composed of uniform primary microparticles of about 2 μm , and hierarchically porous structure with pores distributed among primary and secondary particles, and thus exhibits excellent rate capability and cyclic stability.

2. Experimental

2.1. Materials synthesis

$0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ was synthesized by oxalate co-precipitation. Typically, 5.14 g lithium acetate ($\text{LiCH}_2\text{COO} \cdot 2\text{H}_2\text{O}$), 5.29 g manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), 1.29 g nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), and 1.29 g cobaltous acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were dissolved in 70.0 mL distilled water under constant magnetic stirring and then the solution was heated to 55 $^\circ\text{C}$. Stoichiometrically, 5 wt. % excess Li source was added to compensate the loss during high temperature calcination treatment. Subsequently, 10.00 g PEG2000 or PEG4000 was added to the solution and then 7.20 g oxalate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in aqueous solution was added dropwise for the co-precipitation of metal ions. The resulting suspension was evaporated at 90 $^\circ\text{C}$ to get viscous precursor. To obtain the final product, the precursor was dried at 120 $^\circ\text{C}$ under vacuum to get rid of residual water, presintered at 450 $^\circ\text{C}$ for 5 h and calcined at 800 $^\circ\text{C}$ under air atmosphere for 12 h. The obtained samples were denoted as PEG2000-LMNCO and PEG4000-LMNCO. For comparison, the sample synthesized without assistance of PEG was also obtained and denoted as LMNCO. The compositions of the as-synthesized samples were confirmed with inductively coupled plasma atom emission spectrometry (ICP-AES, IRIS HR, America). The obtained compositions of PEG2000-LMNCO and LMNCO were $\text{Li}_{1.17}\text{Mn}_{0.56}\text{Ni}_{0.14}\text{Co}_{0.13}\text{O}_2$ and $\text{Li}_{1.18}\text{Mn}_{0.56}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, respectively, which are close to the desired value ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$, or $\text{Li}_{1.20}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$). Both samples have the same composition, suggesting that any difference in performance between two samples is caused by other factors than composition.

2.2. Physical characterizations

The morphologies of the as-synthesized samples were characterized by emission scanning electron microscopy (SEM, JSM-6380, Japan) and transmission electron microscopy (TEM, JEOL JEM-2100HR). Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA 7 with an air flow of 10 mL min^{-1} and a heating rate of 10 $^\circ\text{C min}^{-1}$. The structural analysis of as-synthesized samples was carried out on a powder diffractometer (Bruker D8 Advanced Diffractometer System, Germany) with Cu-K α radiation. The diffraction patterns were recorded in the 2 θ degree range from 10 $^\circ$ to 80 $^\circ$ with a scanning step of 5 $^\circ \text{min}^{-1}$. The specific surface area and pore size distribution were determined with Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2020 M) at the temperature of liquid nitrogen (77 K). Tap density measurement was carried out in a small cylindrical centrifuge tube by tapping the tube till the volume of the samples does not change.

2.3. Electrochemical measurements

Electrochemical measurements were conducted by using a half coin-type cell (CR2025) assembled in a glove box (MBraun, Germany) under an argon atmosphere at room temperature (25 $^\circ\text{C}$). A slurry was prepared by mixing of 80 wt. % active material, 10 wt. % acetylene black, and 10 wt. % polyvinylene difluoride (PVDF) in N-methyl pyrrolidone (NMP). The resulting slurry was cast on aluminum foil and dried in a vacuum oven at 120 $^\circ\text{C}$ for 24 h to obtain the working electrode. Metallic lithium foil was used as the counter electrode, 1 M LiPF_6 in the mixed solvents of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) (EC:DEC:EMC = 3:2:5 in weight) as the electrolyte and a polypropylene microporous film (Cellgard 2300) as the separator. The charge/discharge tests were performed on LAND CT 2001A battery test system (China) in the range of 2.0–4.8 V (vs. Li^+/Li) at various current rates. Electrochemical impedance spectroscopy (EIS) was performed on Auto lab (PGSTAT-30, Eco Chemie B.V. Company) in the frequency range from 100 kHz to 0.01 Hz.

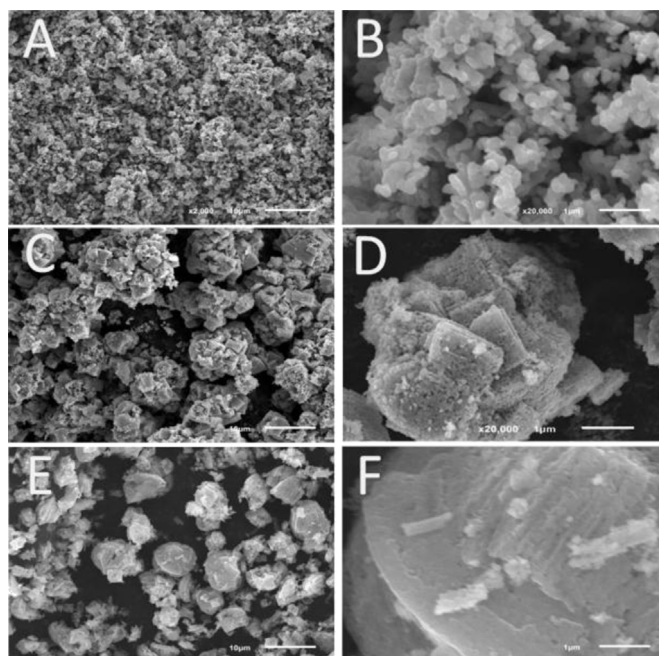


Fig. 1. SEMs of LMNCO (A, B), PEG2000-LMNCO (C, D) and PEG4000-LMNCO (E, F).

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