



Preparation-microstructure-performance relationship of Li-rich transition metal oxides microspheres as cathode materials for lithium ion batteries



Wenfeng Ren^a, Yujuan Zhao^{a,b,c,*}, Xinsa Hu^a, Minghua Xia^a

^a College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

^b Guyue New Material Research Institute, Beijing University of Technology, Beijing 100124, China

^c Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing 100081, China

ARTICLE INFO

Article history:

Received 12 October 2015

Received in revised form 12 January 2016

Accepted 12 January 2016

Available online 15 January 2016

Keywords:

Lithium ion batteries

cathode materials

carbonate co-precipitation

inner structure

ABSTRACT

We report the preparation and characterization of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ ($=0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$) microspheres as cathode materials for lithium ion batteries. These microspheres were synthesized by carbonate co-precipitation and calcination with lithium salt. The samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, inductively coupled plasma-atomic emission spectrometer, and nitrogen adsorption. It is found that the synthesized samples, of spherical morphology with primary nanoparticles assembled in secondary microparticles, have a diameter of $\sim 5 \mu\text{m}$. When used as the cathode materials for lithium ion batteries, the sample prepared at aging time of 9 h with ammonia concentration of 0.6 mol L^{-1} shows excellent electrochemical performance. Their charge capacities are 274 mAh g^{-1} at the current density of 20 mA g^{-1} , much higher than those of the commercial LiCoO_2 and LiFePO_4 . More importantly, they exhibit excellent rate performances with a capacity of 165 and 144 mAh g^{-1} at the current densities of 600 and 1000 mA g^{-1} , respectively, superior to those of other reported Li-rich cathode materials. This work illustrates the relation among synthesis condition, inner structure and electrochemical performance, which has a positive effect on industry production.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, novel electrode materials with high energy density for lithium ion batteries have been of increasing interest for the new generation portable electronic devices and electric vehicles [1,2]. Among the existing cathode materials used in lithium ion batteries, the layered Li-rich transition metal oxides ($x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$, $\text{M}=\text{Co}$, Fe , and $\text{Ni}_{0.5}\text{Mn}_{0.5}$) are one of the most promising candidates mainly because of their high capacity ($>200 \text{ mAh g}^{-1}$) and high operating voltage [3–5], higher than that of commercial LiCoO_2 [6], LiMn_2O_4 [7], and LiFePO_4 [8]. However, their practical applications have been hindered by their high initial irreversible capacity and poor rate performance.

Currently, diverse approaches have been proposed to overcome these difficulties. For example, Kang et al. [9] and Kim et al. [10] reported that Li-rich cathode materials were pretreated with acidic solutions or fluoride to reduce initial irreversible capacity, which

could remove some Li_2O from the structure and generate a fluorinated layer which was chemically robust at high potentials. Voronov et al. [11] and Qiu et al. [12] observed that the initial coulombic efficiency of Li-rich cathode materials was increased by coating carbon and metal oxides, respectively, because the coated layer could keep the electrode materials from direct contact with the electrolyte, resulting in the formation of stable solid electrolyte interphase (SEI) film.

In addition, recent work demonstrated that the rate performance of Li-rich cathode materials could be enhanced by forming nanostructure materials, such as nanowires [13], nanorods [14], and nanoparticles [15], and also by introduction of porous structure [16–18]. Comparing with other Li-rich cathode materials, these nanostructure and porous structure could provide shorter diffusion length for Li ion and electron, resulting in higher rate performance. However, the electrodes prepared with nano-scaled materials turn out to be easily loosened and slough off [19]. As we know, the microsphere morphology in conventional electrode fabrication is preferred as it endows the electrodes with high packing density, high volumetric energy and power density, as well as good mobility to form a uniformly compact electrode layer [20].

* Corresponding author. Tel.: +86 10 67396474; fax: +86 10 67396158.

E-mail address: zhaoyujuan@bjut.edu.cn (Y. Zhao).

Therefore, designing an unique cathode material with micro spherical morphology composed of primary nanoparticles is imperative.

More importantly, inner structure of Li-rich cathode materials influences the electrochemical performance significantly [21,22]. Most researches are focused on exploring the optimum synthesis condition [23–25], investigating novel charge/discharge mechanism [26,27], coating protective layer [10–12,28] or doping metal and nonmetal elements [29] to improve the rate and cycling capability and reduce the initial irreversible capacities of Li-rich cathode materials. However, an important property for practical application, the inner structure of Li-rich cathode materials prepared using various methods, is ignored. The inner porous structure may provide the pathway for the electrolyte to diffuse from the surface to the center of the particle. Besides, it can shorten the diffusion pathway for Li ion and electron between the interior and the outer layer of the electrode materials during the charge-discharge processes, which may benefit to improve the electrochemical performance of Li-rich cathode materials.

In this work, the granule shape, inner structure, physical and electrochemical properties of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LLNMO) microspheres were adjusted by controlling ammonia concentration and aging time during the process of carbonate co-precipitation. The obtained LLNMO have not only the preferred microspherical morphology, but also the well-developed inner porous structure, which are quite obvious structural characteristics conducive to the high performance of Li-rich cathode materials. It is found that the LLNMO microspheres exhibit good rate and cycling performance. The work demonstrates the relation among synthesis condition, inner structure and electrochemical performance for spherical cathode materials in lithium ion batteries.

2. Experimental

2.1. Material synthesis

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Na_2CO_3 , and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were used as the starting materials, all of which were chemically pure and used without further purification. Typical synthetic procedures were as follows: 200 mL of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ mixed aqueous solution (the concentration of total metal ions was 2.0 mol L^{-1} , and the molar ratio of Ni:Mn = 1:3) was pumped into a continuous stirred reactor. At the same time, Na_2CO_3 solution (aq.) of 2.0 mol L^{-1} and various concentrations of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (aq.) as a chelating agent were also fed into the reactor. The concentration of the solution, pH (~ 8.0), temperature (50°C), and stirring speed (1000 rpm) of the mixture in the reactor were carefully controlled. The resultant slurry was aged in a continuous stirred reactor at 50°C for different times. Then, the spherical $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ particles were filtered and washed, and then dried in a vacuum oven at 100°C for 10 h. Thereafter, the obtained $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$ powder was mixed with a desired amount of Li_2CO_3 (A 5 mol% excess was used to compensate any lithium evaporative losses), and calcined by two steps, which are firstly

pretreated at 500°C for 6 h and then calcined at 900°C for 15 h under air atmosphere. Note that the heating rate was maintained at 5°C min^{-1} . To optimize the synthesis conditions and investigate the product formation mechanism, the experimental parameters such as ammonia concentration and aging time were varied while keeping all other parameters constant and the samples thus obtained were listed in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the synthesized materials were carried out using D8 XRD with Cu $K\alpha$ radiation at room temperature. The microscopic features of the sample were observed by scanning electron microscopy (SEM) (JEOL, JSM6400) with energy dispersive X-ray (EDX) spectroscopy and field-emission transmission electron microscopy (TEM) (Philips Tecnai G2, F20, Holland). The chemical composition of the synthesized materials was determined by an Inductively Coupled Plasma-Atomic Emission spectrometer (ICP-AES) (Thermo Elemental, IRIS Intrepid ER/S). The porous property of the samples was investigated using physical adsorption of nitrogen at liquid-nitrogen temperature (-196°C) on an automatic volumetric sorption analyzer (Micromeritics ASAP 2020). Prior to the measurement, the sample was degassed at 200°C for 5 h under vacuum. The specific surface areas were determined according to the Brunauer-Emmett-Teller (BET) method in the relative pressure range of 0.05–0.2. The tap-density of samples was measured with a standard cylinder marked with a volume value. The cross-section features of microspheres were prepared with a cross section polisher (JEOL, IB-09010CP). Thermogravimetric (TG) analysis was carried out on an EXSTAR TG/DTA 6300 (Seiko Instruments, Japan) using a heating rate of $10^\circ\text{C min}^{-1}$ in air (200 mL min^{-1}). Surface chemistry was carried out using X-ray photoelectron spectroscopy (XPS) using an ESCALab250 electron spectrometer from Kratos Analytical Ltd. with monochromatic 150 W AlK α radiation. Pass energy for the narrow scan is 30 eV. The chamber pressure was about 6.5×10^{-10} bar. The binding energies were referenced to C 1s at 284.8 eV.

2.3. Electrochemical measurement

Electrochemical characterizations were performed using a CR2032 coin cell for electrochemical analysis with a lithium metal as the anode electrode separated by glass microfiber filters (Whatman). The electrolyte solution was 1 mol L^{-1} LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate with a 1:1 volume ratio. The cathode electrode was composed of 80 wt.% active material, 10 wt.% super P carbon black, and 10 wt.% polytetrafluoroethylene. CR2032 coin-type cells were assembled in an argon-filled glove box. The galvanostatic charge and discharge tests were carried out by the CT2001A LAND testing instrument (Wuhan LAND electronics Co., Ltd., China) in a voltage range between 2.0 and 4.8 V at a current rate of 0.1, 0.2, 1, 2, 3 and 5C ($1\text{C} = 200 \text{ mA g}^{-1}$) at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were carried out

Table 1
Synthesis conditions used for preparing $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ microspheres.

Sample ($\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$)	Precursor ($\text{Ni}_{0.25}\text{Mn}_{0.75}\text{CO}_3$)	ammonia concentration (mol L^{-1})	aging time (h)
S-0.2-9	P-0.2-9	0.2	9
S-0.4-9	P-0.4-9	0.4	9
S-0.6-9	P-0.6-9	0.6	9
S-0.8-9	P-0.8-9	0.8	9
S-0.6-3	P-0.6-3	0.6	3
S-0.6-6	P-0.6-6	0.6	6

Download English Version:

<https://daneshyari.com/en/article/6609162>

Download Persian Version:

<https://daneshyari.com/article/6609162>

[Daneshyari.com](https://daneshyari.com)