Journal of Energy Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

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

http://www.journals.elsevier.com/journal-of-energy-chemistry/

In situ X-ray diffraction and thermal analysis of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ synthesized via co-precipitation method

Na Zhang[a], Xiaoyu Zhang[a], Erbo Shi[c], Shiyong Zhao[c], Kezhu Jiang[a], Di Wang[a], Pengfei Wang[a], Shaohua Guo[a], Ping He[a,*], Haoshen Zhou[a,b,**]

[a] *Center of Energy Storage Materials & Technology, College of Engineering and Applied Sciences, National Laboratory of Solid State Microstructures, and Collaborative Innovation Center of Advanced Microstructure, Nanjing University, Nanjing 210093, Jiangsu, China*
[b] *National Institute of Advanced Industrial Science and Technology (AIST), Umezono, 1-1-1, Tsukuba 305-8568, Japan*
[c] *Zhangjiagang Guotai Huarong New Chemical Material Co., Ltd, Suzhou 215634, Jiangsu, China*

ARTICLE INFO

Article history:
Received 16 April 2018
Revised 8 June 2018
Accepted 13 June 2018
Available online xxx

Keywords:
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Co-precipitation
Isothermal calorimetry
In situ X-ray diffraction

ABSTRACT

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) material is successfully synthesized with a modified co-precipitation method, in which $NH_3{\cdot}H_2O$ and EDTA are used as two chelating agents. The obtained $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ material has well-defined layered structure and uniform element distribution, which reveals an enhanced electrochemical performance with a capacity retention of 97.9% after 100 cycles at 0.2 C, and reduced thermal runaway from the isothermal calorimetry test. In situ X-ray diffraction (XRD) was employed to capture the structural changes during the charge–discharge process. The reversible evolutions of lattice parameters (*a*, *b*, *c*, and *V*) further verify the structural stability.

1. Introduction

Lithium-ion batteries (LIBs) have already captured worldwide attention in the past decades, due to their widely applications in electric vehicles (EVs) and various portable devices [1–4]. $LiCoO_2$, as the most commercial cathode material, has been studied in LIBs since adopted by Sony in 1991 [5]. However, $LiCoO_2$ cathode suffers from severe structural unstability and high cost, which hinders its application in high-energy electric vehicles [6]. As one of the alternative cathodes for $LiCoO_2$, $LiNiO_2$ has attracted much attention because of the low cost, high specific capacity and its similar layered structure to $LiCoO_2$. Nevertheless, the $LiNiO_2$ system encounters with some toughing problems, such as difficult synthesis, low thermal stability, and short cycling life [7–9].

One possible method to overcome the performance degradation of $LiNiO_2$ cathode is to replace metal ions (e.g. Mn, Al, Co, Fe, Mg) at Ni sites partially [10–15]. Among these substituting ions, a small amount of Co^{3+} and Al^{3+} co-doping is proved to enhance the structural stability of $LiNiO_2$ effectively. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) materials, which have large reversible capacity (~200 mAh g^{-1}) and modest cyclic stability, have been extensively studied and already used in Tesla for electric vehicle applications [16]. They are usually prepared by co-precipitation method with ammonia as the chelating agent. However, Al^{3+} is not easy to complex with ammonia, so it precipitates faster to form a lot of small particles. This will retard the particle growth and result in an inhomogeneous element distribution for NCA products [17]. Many researchers have tried to change the addition form of Al source to improve the homogeneity of the product. For instance, Meng and co-workers tried to use $AlO_2{}^-$as Al source to prepare $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ microspherical with uniform element distribution [18]. Zhang et al. obtained $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ material by the Al-compensation method [19], which shows significant effect. Other researchers also did some trials to adopt other chelating agent such as Ethylenediaminetetraacetic acid (EDTA) [20,21]. The reactivity of Al^{3+} is largely suppressed. However, as the most widely used chelating agent in co-precipitation, ammonia can well control the reaction speed of Ni^{2+}, Co^{2+} and make the pH fluctuate within a narrow range. Based on these previous work, our group has combined $NH_3{\cdot}H_2O$ with EDTA as two chelating agents to slow down the reaction rate of three metal cations simultaneously. $NH_3{\cdot}H_2O$ is pumped into the reactor as the common chelating agent while EDTA is previously mixed in the aqueous solution of $Al^{3+}$to control its reactivity. As a result, we obtained NCA materials with well-defined layered structure and uniform element distribution.

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[*] Corresponding author.
[**] Corresponding author at: Center of Energy Storage Materials & Technology, College of Engineering and Applied Sciences, National Laboratory of Solid State Microstructures, and Collaborative Innovation Center of Advanced Microstructure, Nanjing University, Nanjing 210093, Jiangsu, China.

E-mail addresses: pinghe@nju.edu.cn (P. He), hszhou@nju.edu.cn (H. Zhou).

https://doi.org/10.1016/j.jechem.2018.06.007
2095-4956/

On the other hand, Ni-rich cathode materials suffer from poor thermal stability, which is the biggest problem that hinders its practical application in EVs [22]. Extensive thermal analysis methods, particularly differential scanning calorimetry (DSC), have been applied to investigate the thermal behavior of Ni-rich cathode materials [23]. However, these tests usually demand high temperatures because of the sensitivity limitations. The commercial availability of high sensitivity isothermal calorimeters makes it possible to study thermal behavior at room temperature [24], which motivates us to use it in lithium ion batteries. In this work, our group demonstrates a practical employment of Thermal Activity Monitor (TAM) technique in understanding the exothermic behavior for NCA coin-type cells for the first time.

Additionally, understanding the intrinsic reaction mechanisms, especially the relationship between electrochemical performance and structure stability of electrode materials is scientifically interesting for the development of both LIBs and SIBs [25–27]. In situ spectroscopic techniques such as nuclear magnetic resonance (NMR), X-ray diffraction (XRD), Raman spectroscopies are powerful methods to probe reaction mechanisms in LIBs [28]. In this work, in situ X-ray diffraction analysis was conducted to measure the structural evolution of NCA materials during electrochemical cycling and to get insight into the lithium storage mechanism.

2. Experimental

2.1. Preparation of materials

$Ni_{0.8}Co_{0.15}Al_{0.05}(OH)_2$ precursor was prepared via a co-precipitation method by using a 5 L continuous stirred tank reactor (CSTR). $NiSO_4{\cdot}6H_2O$ and $CoSO_4{\cdot}7H_2O$ were dissolved in 500 mL deionized water to obtain a 1.5 M solution, while $Al_2(SO_4)_3{\cdot}18H_2O$ solution was obtained by dissolving a certain amount of EDTA (molar ratio of EDTA to transition metal = 1.0). 200 mL of 1 M $NH_3{\cdot}H_2O$ was added into the reactor as base solution and heated to 60 °C. Subsequently, the metal solutions were pumped into the reactor with the same flow rate simultaneously. A 3.0 M NaOH solution was used as the precipitation agent to maintain the pH of the mixed solution at 11.0 ± 0.1, and a 4 M $NH_3{\cdot}H_2O$ compensated the loss of ammonium, along with N_2 as a protective gas. After the 8 h reaction time, the as-prepared precursor was filtered, washed and vacuum dried in a vacuum oven at 120 °C for 12 h. To obtain the final $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ product, the precursor was thoroughly mixed with 5 wt % excess $LiOH{\cdot}H_2O$. Then the mixture was sintered at 550 °C for 5 h and 750 °C for 15 h sequentially under a flowing oxygen atmosphere. Schematic diagram of the synthesis process is illustrated in Scheme 1.

2.2. Characterization of materials

The actual ratios of Li:Ni:Co:Al were verified by inductively coupled plasma test (ICP, Optima5300DV). The X-ray photoelectron spectroscopy (XPS) results were obtained on a PHI 5000 VersaProbe. The morphology and elemental distribution were investigated by a scanning electron microscope (FESEM, Hitachi SU8010). The fine crystal structure was analyzed by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010). Powder X-ray diffraction (XRD) experiments were carried out on a Bruker D8-Advanced X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) in the 2θ range of 10°–70°. The crystal structure was refined using the Rietveld method using GSAS software. In situ XRD observation was conducted on the same instrument based on a special in situ cell with an aluminum window for X-ray penetration. For the isothermal calorimetry test, a Thermal Activity Monitor (TAM, AIR) is introduced. R2032 half-cell containing our cathode was loaded into a closed ampoule bottle (20 mL) and lowered to a thermal equilibrium position in the calorimeter. The temperature was constant at 30 °C.

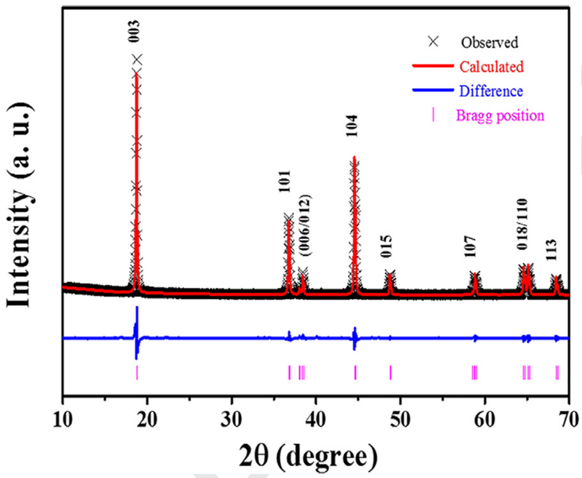

Fig. 1. Experimental and calculated XRD patterns for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ sample: (black) observed; (red) calculated; (blue) difference plot; (purple bars) Bragg reflections.

2.3. Coin-type cells assembly and electrochemical tests

The electrochemical performances were obtained using a R2032 coin-type cell at 25 °C. NCA cathode was prepared as follows. 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride binder were intimately mixed in an N-methyl-2-pyrrolidone (NMP) solution. Then the slurry was coated on aluminum foil and dried at 120 °C in a vacuum oven for 12 h. Each working electrode was cut into a disk with a diameter of 12 mm and the mass loading was controlled about 1.5–2.0 mg. The testing coin-type cells were assembled in an argon-filled glove-box using lithium foil as the counter electrode and Celgard 2300 polypropylene as the separator. The electrolyte solutions were 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 in volume). Galvanostatic charge–discharge tests were carried out on a battery testing system (LAND 2001A Wuhan Jinnuo Corp., China). Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI 760E, Chenhua Corp., Shanghai, China).

3. Results and discussion

The stoichiometry of the final product was first verified by an inductively coupled plasma (ICP) analysis (Table S1 in Supporting information). The obtained molar ratio of Li:Ni:Co:Al is 1.0315:0.7939:0.1620:0.0476, which is very closed to the designed ratio of NCA material (1:0.8:0.15:0.05). To confirm the structure of the as-prepared NCA material, we conducted powder X-ray diffraction (XRD) test and the result is shown in Fig. 1. Rietveld refinements of the XRD pattern are also shown. All the diffraction peaks are well index to a hexagonal $LiNiO_2$ phase with a layered structure (JSPDS no. 09-0063), revealing high phase purity. The calculated value of $I_{(003)}/I_{(104)}$ is 1.55 (> 1.2), c/a is 4.95 (> 4.9), which imply no obvious cation mixing in the lattice [29]. In addition, the strong splitting of (006)/(012) and (018)/(110) peaks indicates a well-developed layer structure [14]. Schematic illustration of the layered structure is given in Fig. S1. Detailed structural parameters of the as-prepared sample are obtained from Rietveld refinements using the GSAS package, which are summarized in Table 1. The small value of R_{wp} and R_p (< 10%) indicates the reliability of the refinement results.

Please cite this article as: N. Zhang et al., In situ X-ray diffraction and thermal analysis of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ synthesized via co-precipitation method, Journal of Energy Chemistry (2018), https://doi.org/10.1016/j.jechem.2018.06.007