



Synthesis of Li-excess layered cathode material with enhanced reversible capacity for Lithium ion batteries through the optimization of precursor synthesis method



Wenwen Zhao^a, Shinji Yamamoto^b, Akinobu Tanaka^a, Hideyuki Noguchi^{a,*}

^a Department of Advanced Technology Fusion, Graduate School of Science and Engineering, Saga University, Honjo-1, Saga 840-8520, Japan

^b Nissan Research Center, Nissan Motor Co., Ltd., Natsushima-cho, Yokosuka, Kanagawa 237-8523, Japan

ARTICLE INFO

Article history:

Received 30 May 2014

Received in revised form 4 August 2014

Accepted 4 August 2014

Available online 13 August 2014

Keywords:

Lithium ion battery

Li excess cathode

Synthesis method

Improved cycleability

Rate performance

ABSTRACT

$\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cathode materials have been synthesized through a facile reduction-ion exchange of $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursors prepared by solid state (SS), spray dry (SD) and co-precipitation (CP) methods. The influence of precursor synthesis method on the structure, morphology and electrochemical performances of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ has been investigated. X-ray diffraction (XRD) results of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ demonstrate that all the samples exhibit similar XRD patterns as those of Lithium-excess layered cathode materials. Scanning Electron Microscope (SEM) images and Brunauer-Emment-Teller (BET) results present that the particle size, particle aggregation and surface area changed greatly with the precursor synthesis method. Galvanostatic charge-discharge results show that $\text{Li}_{1.41}\text{Ni}_{0.32}\text{Mn}_{0.66}\text{O}_{2+\delta}$ cathode prepared from co-precipitation precursor exhibited high first discharge capacity of ca. 270 mAhg^{-1} with an initial cycle efficiency as high as 98%. The discharge capacity of $\text{Li}_{1.41}\text{Ni}_{0.32}\text{Mn}_{0.66}\text{O}_{2+\delta}$ cathode after 30 cycles is over 250 mAhg^{-1} and it can deliver a discharge capacity roughly 210 mAhg^{-1} at a current density of 500 mA g^{-1} (2 C rate). Also, it was found that $\text{Li}_{1.41}\text{Ni}_{0.32}\text{Mn}_{0.66}\text{O}_{2+\delta}$ cathode shows enhanced electrochemical performance over the $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cathode with respect to reversible capacity and rate capability.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The success of lithium ion batteries (LIBs) has been proved by the conquer share in portable devices during the past several decades. It is definite that the increasing demand for LIBs greatly stimulates the development of novel electrode materials for LIBs. In order to further boost the energy density of LIBs to extend the application in plug-in hybrid electric vehicles (PHEV) and electric vehicles (EV), researchers are focusing on the searching for electrode materials with high energy density [1–4].

Lithium cobalt oxide LiCoO_2 has dominated the share of cathode materials market for LIBs for a quite long period due to its promising electrochemical properties such as high electric conductivity and good reversible during lithium insertion and de-insertion process [5,6]. However, the relatively low specific capacity and high cost of LiCoO_2 hinders its further application. Manganese based oxides with layer structure have been studied

intensively as attractive candidate cathode material for LIBs. Unfortunately, the LiMnO_2 has been found to suffer from phase transformation on cycling, which causes capacity fading during cycling [7,8]. Some strategies such as partially substitution of Mn with foreign metal ions have been involved to suppress the phase transformation [8]. The discovery of polyanion based cathode materials, such as LiFePO_4 and LiMnPO_4 , with olivine structure has drawn great attention owing to the advantages of being abundant, high thermal stability, environmentally benign, and inexpensive [9–12]. However, poly-anion materials show critical disadvantages of poor electronic and ionic conductivities, which is believed to be the main reason for the high polarization at high charge-discharge rate. Therefore, carbon coating and nanostructure approaches are required to overcome the above demerits [12].

Lithium-excess layered cathode materials, denoted as $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co, Fe}$), with layered structure have been a focus of studies and considered to be as next generation cathode materials for lithium ion batteries because of the high working voltage and high specific capacity over 230 mAh/g , which is significantly higher than the capacity of the above mentioned cathode materials [13–18]. Moreover, lithium and manganese rich

* Corresponding author. Tel.: +81952 28 8674; fax: +81 952 28 8591.

E-mail address: noguchih@cc.saga-u.ac.jp (H. Noguchi).

metal oxide have the advantages of low cost due to the high content of inexpensive manganese. Despite the excellent properties, this kind material shows large irreversible capacity at the initial cycle thus leads to a low first cycle efficiency and poor cycleability upon cycling. Therefore, it is necessary to improve the first cycle efficiency of this cathode material so as to meet the practical application requirements. A great variety of approaches have been applied to improve the first cycle efficiency and cycleability of Lithium-excess layered cathode materials [19–23]. Among them, the pre-cycling treatment demonstrated by Ito et al. is proved to be an effective way to resolve the above issues [19,20]. Other researchers have proposed surface modification of the electrode materials for reaching this goal [21–23].

In our recent study we have developed a facile synthetic route for the synthesis of Li_2MnO_3 related cathode materials through the simultaneously reduction-ion exchange reaction of $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursor in LiNO_3 - LiI molten salt [24]. It was found the obtained $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ show enhanced first cycle efficiency and cycleability as cathode material for lithium ion batteries. The reversible capacity of the as-prepared $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ was around 230 mAh/g after 30 cycles. In order to further improve the specific capacity and rate capability of this kind of cathode material, we turned to the optimization of the precursor synthesis method. Besides solid state combustion (SS) method in previous study, spray dry (SD) and carbonate co-precipitation (CP) method were employed for the synthesis of $\text{P3-Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursors in this study. The influence of precursor synthesis method on the structure and electrochemical properties of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cathode were investigated. Moreover, further investigation for the difference between the conventional ion exchange sample and reduction-ion exchange sample were also carried out in this study.

2. Experimental

2.1. Synthesis of $\text{P3 Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursors through various methods

$\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ was prepared through a simple combustion method as described in previous study [24]. Typically, stoichiometric amounts of nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) and sodium nitrate (NaNO_3) were mixed in triethylglycol. The mixture was fired at around 400°C and ash like powder can be obtained after the vigorous decomposition of organic materials. The decomposed powder was ball-milled for 1 h and was subsequently calcinated at 700°C in air for 10 h to form P3 type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursor. The sample is hereafter referred as $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ -SS.

Spray dry method was carried out with a spray drying instrument (pulvis mini-spray GB22, Yamato, Japan). The precursor solution was prepared by dissolving stoichiometric NaNO_3 , $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in water. The solution was then pumped into the spray dry instrument for reaction. The obtained power was heated at 350°C and ground. The ground power was ball-milled for 1 h and was subsequently calcinated at 700°C in air for 10 h to synthesize P3 type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursor.

Carbonate co-precipitation method was employed to synthesis precursors with uniform particle size distribution. Stoichiometric solutions of MnSO_4 , NiSO_4 and mixed with the Na_2CO_3 solution under magnetic stirring at 55°C . The precipitated powders were filtered and washed with large amount of water and then followed by drying at 80°C for 12 h. The obtained powder was sintered at 500°C for 6 h and was subsequently ground. The ground power was then mixed with stoichiometric

amount of NaNO_3 and the mixture was subsequently calcinated at 700°C in air for 10 h to form P3 type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ precursor.

2.2. Synthesis of $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ and $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$

The as prepared P3 $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ was used to synthesize $\text{Li}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ through normal ion exchange method as reported before [24]. Typically, $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ was mixed with LiNO_3 and LiCl and grounded for ion exchange. The mole ration of Li ion to Na ion was approximately 5:1. After soaking in the melt for 6 h, the mixture was left to cool to room temperature. After the product was washed with hot water, filtered and dried, black power can be obtained.

Reduction-ion exchange of the obtained precursors was done by using the molten salt of mixture of LiNO_3 and LiI at 280°C in air for 6 h. After the melt was allowed to cool to room temperature, the mixture was washed with hot water to remove the residual lithium salt. Then, it was filtered and the recovered powder was dried at 80°C for 12 h.

2.3. Instrumentation

The structure of the compounds was characterized by powder X-ray diffraction measurement (XRD) for two theta value from 10° to 80° ($\text{CuK}\alpha$ radiation, XRD-7000, SHIMADZU). Induced coupled plasma (ICP) was used to determine the chemical composition of the obtained compounds. The morphology of the compounds was observed by Scanning Electron Microscope (SEM, HITACHI, S-3000N) and Transmission Electron Microscope (TEM, JEOL, JEM-1210). Dynamic light scattering (DLS) measurements were carried out with an electrophoretic light scattering spectrophotometer at a fixed 165° scattering angle (Otsuka ELS-Z). Nitrogen adsorption-desorption isotherm were carried out after the samples were out-gassed and dehydrated at 200°C for 24 h (Micromeritics Gemini 2360, SHIMADZU). The specific surface area of each sample was calculated from the Brunauer-Emment-Teller (BET) method. The tap density is achieved by mechanically tapping a measuring cylinder containing a power sample. After observing the initial volume, the cylinder is mechanically tapped, and volume readings are taken until little further volume change is observed. Generally, replicate measurements were carried out for the determination of tap density.

2.4. Electrochemical characterization

CR2032 type coin cells were assembled to evaluate the electrochemical properties of the obtained compounds. Lithium foil was used as the anode and polypropylene as separator. For the fabrication of working electrodes, 20 mg active material together with 10 mg conducting binder (Teflon:Acetylene black = 1:2) was mixed and pressed on the stainless steel mesh. Then, the electrodes were dehydrated by a vacuum dry at 180°C for 6 h. The electrolyte used was 1 M lithium phosphorus hexafluoride (LiPF_6) in a mixture of ethylene carbonate (EC) and dimethyl carbonate with (DMC) volume ration of 1:2. The cells were assembled in a glove box filled with pure argon gas. The assembled cells were cycled at a current rate of 20 mA g^{-1} between 2.5 V and 4.7 V at 50°C . Cyclic voltammetry (CV) measurement at 50°C was performed at a scan rate of 0.1 mV s^{-1} between 2.0 V and 4.7 V with Li as counter and reference electrode.

Download English Version:

<https://daneshyari.com/en/article/185172>

Download Persian Version:

<https://daneshyari.com/article/185172>

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