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The effect of Si doping on the electrochemical characteristics of $LiNi_xMn_yCo_{(1-x-y)}O_2$

Seong-Hwan Na, Hyun-Soo Kim*, Seong-In Moon

Korea Electrotechnology Research Institute, Changwon 641-120, Korea

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Abstract

A new simple way of synthesizing $Li[NiMnCo]O_2$ was contrived and its electrochemical characteristics were enhanced by Si doping using solution-based synthetic route. The newly synthesized $Li[NiMnCo]O_2$ showed capacity of 175 mA h/g and good cycle life at a cut-off voltage of 4.5 V. Si-doping improved the rate capability, specific capacity, and cycle life of the material through increasing lattice parameters and lowering electrochemical impedance.

Keywords: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; Synthesis; Lithium; Battery; Cathode; Si

1. Introduction

The cathode material is detrimental to the performance and safety of Li-ion batteries. Nowadays, the prevalent cathode material is $LiCoO_2$ and many recent reports address the problem in synthesizing a cheaper, higher-capacity, and safer layered cathode material than this [1–4]. One of the promising candidates, $LiNiO_2$, has large capacity and good rate capabilities but shows so a high instability in its layered structure at high voltage above 4.5 V which may result in a battery hazard on overcharge or under other unexpected abuse conditions that it has failed to replace $LiCoO_2$ [5]. On the other hand, $LiMn_2O_4$, another candidate to replace $LiCoO_2$, shows good structural stability on overcharge but has low capacity and high reactivity with electrolyte at elevated temperature above 55 °C to replace $LiCoO_2$ [6].

Recently, Zhonghua Lu and D. D. MacNeil et al. [7,8] reported that pure phase of $Li[Ni_xCo_xMn_{1-x-y}]O_2$ could be synthesize by using 'Mixed Hydroxide Method' and the synthesized material showed high capacity about 175 mA h/g, good structural stability, and a good cycle life. Although it is a good material to substitute $LiCoO_2$, its rather complicated synthetic route such as water washing, filtering and repeated palletized sintering processes would be better to be abbreviated and some electrochemical properties like rate capability should be improved.

In this work, we invented a much more simple way to synthesize phase-pure $Li[Ni_xCo_xMn_{1-x-y}]O_2$ and improved its electrochemical properties by Si doping into the material.

2. Experimental

$LiNi_xMn_yCo_{(1-x-y)}O_2$ was synthesized by solution-base synthetic route. $Li(NO_3)\cdot H_2O$ (98%+, Aldrich), $Ni(NO_3)_2\cdot 6H_2O$(98%+, Aldrich), $Co(NO_3)_2\cdot 6H_2O$(98%+, Aldrich), $Mn(NO_3)_2\cdot 4H_2O$ (98%+, Aldrich) and poly (methyl phenyl siloxane) (Aldrich) were used as the starting materials. A stoichiometric amount of Li, Ni, Mn, and Co nitrates was dissolved in high purity ethanol (99.9% Duksan). Into this, desired amount of poly(methyl phenyl siloxane) (2–10 mol% of total transition metal ions) was added and stirred for about 30 min. The resultant solution was evaporated at open air at 70–80 °C to obtain pink-colored precipitate. The precipitate was pulverized and

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* Corresponding author. Battery Research Group, Korea Electrotechnology Research Institute, 28-1 Seongju-dong, 641-120, Changwon, Republic of Korea. Tel.: +82 55 280 1663; fax: +82 55 280 1590.

E-mail address: hskim@keri.re.kr (H.-S. Kim).

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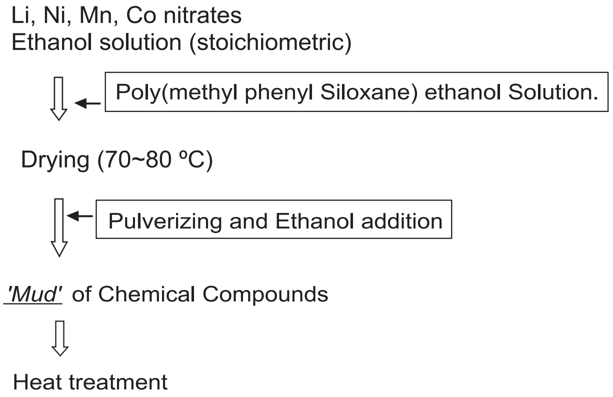

Fig. 1. Synthetic route of $Li[Ni_xMn_yCo_{(1-x-y)}]_pSi_{(1-p)}O_2$ powder.

added with pure ethanol to turn the powder into mud-like state. This mud-like precursor was heat-treated at 450–500 °C for about 5 h to obtain crude powder depleted of organic ingredients. The crude powder was ground to fine powder and heat-treated at 600–650 °C for about 3 h and 900–950 °C for about 5 h successively. The first step of heat treatment was intended for melting of Li-containing chemicals and the second step was for oxide structure formation. All the procedures were summarized in Fig. 1.

X-ray diffraction (XRD) patterns were evaluated using a Philips PW1830 diffractometer and the scanning electron microscope (SEM) image of the particle was obtained using a Hitachi S-2700 machine.

The electrodes composition was 83:10:7 in mass% of active material: polyvinylidene difluoride (PVDF, Aldrich) as binder: Super-P carbon black (MMM Carbon) as current conductor. The PVDF was dissolved in *N*-methylpyrrolidinone (NMP, Kanto) and the active material and conductor mixture was added. After homogenization, the slurry was evacuated for 20 min to remove the residual air. The slurry was then coated on a thin aluminum foil (20 μm thick) and dried overnight in a 120 °C oven. The electrode was pressed with a pressure of 600–800 kg/cm^2 and finally punched to 15 mm diameter disks.

The electrochemical cells were prepared in standard 2016 coin cell hardware with single lithium metal foil used as both the counter and reference electrode. Cells were assembled in a dry room of which the dew point was below −55 °C. The electrolyte used for analysis was 1.15 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate/diethyl carbonate (EC/EMC/DEC, 3/5/2). The cells were taken out of dry room and placed on the battery testing system (Toscat 3000). The room temperature was controlled at 28 °C. The cells were aged for 5 h before the first charge to ensure full absorption of electrolyte into the electrode. Electrochemical impedance spectroscopy (EIS) was measured with IM6 (Zahner).

3. Results and discussioin

Fig. 2 shows the XRD pattern of Si-doped $LiNi_xMn_yCo_{(1-x-y)}O_2$ synthesized. There were no impurity phases and the R3-m layered structure was established well. The intensity ratio of the (104) peak to the (003) peak was about 0.5. The (018) peak and the (110) peak are separated well. In our experimental method, homogeneity of all the transition metal ions could be guaranteed because they are mixed in aqueous solution and it is more economical in material cost because there is no hydroxide-forming step using Li-hydroxide. Furthermore, it is more economical in process flow because there are no additional process steps

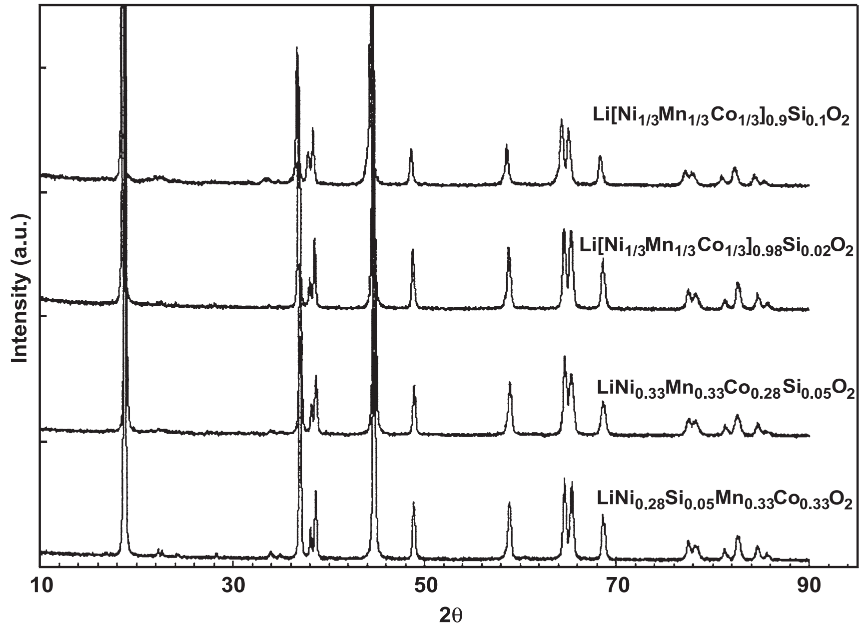

Fig. 2. XRD patterns of Si-doped $LiNi_xMn_yCo_{(1-x-y)}O_2$ powder.