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# Electrochemical characteristics of layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and with different synthesis conditions

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## Abstract

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ had been successfully prepared from spherical composite carbonate via a simple uniform-phase precipitation method [P. He, H. Wang, L. Qi, T. Osaka, J. Power Sources, in press] at normal pressure, using nickel, cobalt and manganese sulfate and ammonia bicarbonate as reactants. The preparation of spherical composite carbonate was significantly dependant on synthetic condition, such as the reaction temperature, feed rate, molar ratio of these reactants, etc. The optimized condition resulted in spherical composite carbonate of which the particle size distribution was uniform, as observed by scanning electronic microscopy (SEM). Calcination of the uniform composite carbonate with lithium carbonate at high temperature led to a well-ordered layer structured $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as confirmed by X-ray diffraction (XRD), without obvious change in shape. Due to the homogeneity of the composite carbonate, the final product, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, was also significantly uniform, i.e., the average particle size was of about 10 μm in diameter and the distribution was relatively narrow. As a result, the corresponding tap density was also high, approximately 2.32 g cm$^{-3}$, of which the value is very near to that of commercialized $LiCoO_2$. In the voltage range of 2.8–4.2, 2.8–4.35 and 2.8–4.5 V, the discharge capacities of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode were 159, 168 and 179 mAh g$^{-1}$, respectively, with good cyclability.

*Keywords:* Spherical; Composite carbonate; Uniform-phase precipitation; Lithium-ion cell; Cathode material

## 1. Introduction

Currently, the most widely used cathode material in lithium-ion secondary battery is $LiCoO_2$, because of its simple producing process, high specific capacity and long circle life [1]. While concerning about the relatively high cost of cobalt, its safety when abused and the interesting higher specific capacity had led to the study of some new cathode materials, such as $LiNi_xCo_{1-x}O_2$, $LiFePO_4$ and $LiNi_xCo_yMn_{1-x-y}O_2$.

The optimum electrode material should combine lower cost as well as greater safety and performance compared to $LiCoO_2$. The sample had lower cost for the use of nickel and manganese, which were both abundant in the lithosphere. When it was charged to 4.6 V and then discharged to 2.5 V, it manifested the specific capacity of 200 mAh g$^{-1}$, which was higher than $LiCoO_2$ without sacrificing circle life. Having been charged to 4.4 V and analyzed by thermogravimetry/differential thermal analysis (TG/DTA), it had much less heat flow and higher onset temperature than $LiCoO_2$.

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was first proposed by Ohzuku and Makimura [2]. They initially prepared it by solid state reaction method and re-prepared by mixed hydroxide method [3]. Chowdari and co-workers [4] also prepared it at 1000 °C by mixed hydroxide method and reported that the predominant oxidation states of Ni, Co and Mn in the compound were $2^+$, $3^+$ and $4^+$, respectively. However, a closer inspection of their results reveals some contradictory information on the electrochemical behavior, such as the shape of initial charge curve, reversible capacity and cyclic performance. This strongly implied that the electrochemical characteristics of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ are prone to be affected by preparation condition. Li et al. studied [5] the influence of preparation method on the structural and electrochemical characteristics of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ in order to further improve its electrochemical performance, and found that

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the difference in preparation method resulted in the difference in the color and morphology (shape, particle size and specific surface area) and thereby the difference in the shape of the first charge curve, reversible capacity and the rate capability.

Mixed hydroxide method was a usual method to get the precursor of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$; Lee et al. [6] had done much work on the synthetic optimization of the synthesis of $Mn_{1/3}Ni_{1/3}Co_{1/3}(OH)_2$. But in hydroxide co-precipitation method, $Mn^{2+}$ ion is precipitated as $Mn(OH)_2$ but oxidized gradually to $Mn^{3+}$ (MnOOH) or $Mn^{4+}$ ($MnO_2$) in aqueous solution. Therefore, preparing the precursor reproductively is very difficult. However, in carbonate homogeneous precipitation method, the oxidation state of Mn is always $2^+$ and stable in aqueous solution, thereby very effective for industrial application owing to its high reproducibility. Cho et al. [7] studied the effect of calcination temperature on the character of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ with $Mn_{1/3}Ni_{1/3}Co_{1/3}CO_3$ as the precursor; we feel the effects of synthetic condition on the precursor should also be studied.

## 2. Experimental

For preparing transition metal carbonate powders $Mn_{1/3}Ni_{1/3}Co_{1/3}CO_3$, we used $MnSO_4{\cdot}4H_2O$, $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ and $NH_4HCO_3$ as the starting materials, all of which were of technical grade and used without further purification. An aqueous solution of $Co_{1/3}Ni_{1/3}Mn_{1/3}SO_4$ with a concentration of 0.5 mol m$^{-3}$ was pumped into a continuously stirred tank reactor (CSTR, volume 1 l). At the same time, $NH_4HCO_3$ solution of 2.0 mol dm$^{-3}$ was also fed into the reactor. The reaction temperature and feed rate of the reactants to the reactor were controlled carefully. After vigorous stirring at 75–90 °C for 12 h, the homogenously precipitated carbonate powder $Mn_{1/3}Ni_{1/3}Co_{1/3}CO_3$, hereafter referred as a precursor, was filtered off and dried without washing at 110 °C for 10 h. Then, EDTA titration was applied to decide exact amount of transition metal ions which were mixed with lithium salt in the pre-heated powder. To synthesize $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material, a more than stoichiometric amount of lithium hydroxide was mixed with the pre-heated powders and calcined at 500 and 1000 °C, respectively, in air.

Powder X-ray diffraction (XRD) employing Cu Kα radiation was used to identify the crystalline phase of the prepared powders by means of an X-ray diffractometer (MultFlex, Rigacu, Japan). The shape and size of the as-prepared samples were observed by scanning electronic microscope (SEM, JSM-5600LV, JEOL, Japan). The concentrations of lithium and cobalt, nickel, manganese, etc., in the resulting materials were analyzed using an inductively coupled plasma spectrometer (ICP, Optima 4300DV, PE Ltd.). Charge–discharge tests were performed with coin type cell (CR2032) with applying a current density of 20 mA g$^{-1}$ at 25 °C. Composite positive electrodes were prepared by thoroughly mixing the active material (80 wt%) with carbon black (5 wt%), acetylene black (5 wt%) and polyvinylidene fluoride (10 wt%) in *N*-methyl-pyrrolidinone and extruding onto aluminium foils. Electrodes, with loading between 8 and 10 mg active material cm$^{-2}$, were dried for 24 h at 110 °C in electric oven under vacuum. CR2032 simulated half cells were then assembled in a helium filled dry box (<1 ppm $O_2/H_2O$) using foils of Li metal as counter electrodes and Celgard 3401 saturated with a 1 M $LiPF_6$ (electrolyte) in ethylene carbonate/diethyl carbonate (1:1, v/v). Several simulated cells containing each sample were assembled and tested, to ensure reproducibility.

## 3. Results and discussion

### *3.1. The choice of the reaction temperature of precipitation*

During the precipitation process, the crystals endured two steps: the formation of crystal nuclei and their growing up which includes each single crystal nucleus development and the agglomeration of some nuclei. The well formed and high-density particles can be prepared with the decrease of temperature for the lower nucleus concentration and lower growing rate [7]. For the reason of complexation of cobalt and nickel by ammonia, little precipitate can emerge when the temperature is low, which decreased the product capacity. When the feed rate is 20 ml min$^{-1}$, and molar ratio of the metal to ammonia is 2.5, Table 1 shows the concentrations of cobalt, nickel and manganese in the solution after reaction at different temperatures. While the reaction temperature increases, the concentrations of cobalt, nickel and manganese decrease promptly. Considering the importance of tap density of the final sample and product capacity, the reasonable reaction temperature should be chosen as 80 °C.

### *3.2. The effect of feed rate*

Feed rate is an important factor that can affect the possibility of industrialization. Lower feed rate decreases the production capacity, then increases the production cost. And lower feed rate decreases the nucleation speed and causes fewer nuclei to be formed. Although the speed of nuclei growth was also lowered, it was still higher than the nucleation speed. For the

Table 1

The concentration of cobalt, nickel and manganese in the solution and the tap density of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ at different temperatures

| Temperature (°C) | Cobalt (mg ml$^{-1}$) | Nickel (mg ml$^{-1}$) | Manganese (mg ml$^{-1}$) | Tap density of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (g cm$^{-3}$) |
|---|---|---|---|---|
| 60 | 8.41 | 13.52 | 0.47 | 2.32 |
| 70 | 2.19 | 5.28 | 0.12 | 2.21 |
| 80 | 0.93 | 2.06 | 0.05 | 2.19 |
| 90 | 0.27 | 0.84 | 0.02 | 1.77 |