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Effect of particle size and crystallinity on the charge and discharge property of layered $LiNi_{0.5}Mn_{0.5}O_2$

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ABSTRACT

Layered structure $LiNi_{0.5}Mn_{0.5}O_2$ powders are prepared by hydroxide co-precipitation method. The samples are sintered at temperatures from 750 to 1000 °C. The galvanostatic charge and discharge tests show that the samples prepared at 800 and 850 °C deliver higher specific capacity than other samples sintered at higher temperatures. Three factors affecting the final electrochemical performances are discussed. XRD and SEM analyses show that the crystallinity and particle size increase with increasing sintering temperature, whereas, the cation disorder keeps constant. So the two factors, crystallinity and particle size, are considered playing important roles in determination the final performance of these samples sintered at different temperatures. Moreover, the integrated intensity ratios of the (003) to (104) reflections are not suggested as an indication of cation disorder directly.

1. Introduction

$LiCoO_2$ has been used as a mature cathode material for decades since it was commercialized by Sony. Obviously, it is an excellent cathode material with high energy density and low irreversible capacity [1,2]. But Co is a toxic and expensive element. So, it's necessary and worth to remove or replace it. Following the reports of greatly improved electrochemical performance of layered $LiNi_{0.5}Mn_{0.5}O_2$ [3,4], a tremendous number of studies have been carried out all over the world [5–8]. The layered $LiNi_{0.5}Mn_{0.5}O_2$ has many advantages, such as high theoretical capacity and excellent cyclic performance [4,9,10], good structure stability [11], and low cost. So, it has been considered a promising material to replace $LiCoO_2$ [3,11,12].

However, it also has some problems to be overcome, such as low rate capacity and the cation disorder (Li/Ni exchange) [10,13–15]. It is reported that all $LiNi_{0.5}Mn_{0.5}O_2$ materials synthesized by regular routes suffer from 8 to 12% exchange of Li and Ni, which will result in the lower rate capacities [12,16,17]. But the samples prepared by ionic exchange have only about 4% Li/Ni disorder, and they exhibit greatly enhanced specific capacities both at low and high current densities [12]. Besides cation disorder, the particle size and crystallinity will affect the final performance of the samples. However, because more attentions are paid on the cation distribution, the effects of the last two factors are always ignored. For example, Lu etc. reported that the cation disorder decreases with raising the calcination temperature from 900 to 1000 °C [18]. Meanwhile, they published a very systematic study work on $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$, while they reported that $LiNi_{0.5}Mn_{0.5}O_2$ sintered at 800 °C showed a slightly larger specific capacity, better capacity retention and smaller charge-discharge polarization than that prepared at 900 °C, with little explanation [9]. In most published papers, the effect of cation disorder is emphasized, and the effects of particle size and crystallinity are ignored. Until recently, the impact of particle size and crystallinity are emphasized in the cases of $LiNi_{0.45}Mn_{0.45}Co_{0.1}O_2$ and $Li_{1.4}Ni_{0.5}Mn_{0.5}O_2$ [19,20].

In order to understand the impact of the three factors on the electrochemical performances of $LiNi_{0.5}Mn_{0.5}O_2$, the powders are prepared by hydroxide co-precipitation method, with the heating temperatures varying from 750 to 1000 °C. We carefully study the Li/Ni ordering, crystallinity and particle size of the powders

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prepared under different heating conditions, and their relationships to the electrochemical behaviors.

2. Experimental

Transition metal hydroxide powders $Ni_{0.5}Mn_{0.5}(OH)_2$ were prepared by co-precipitation method [21]. An aqueous solution of $NiSO_4 \cdot 6H_2O$, $MnSO_4 \cdot 4H_2O$ (molar ratio of Ni^{2+}:$Mn^{2+} = 1$:1) NaOH, and aqueous ammonia were selected as starting materials to synthesize the precipitate. The resulting precipitate was washed, filtered for several times and dried at 80 °C in air. The dried precipitate was mixed with stoichiometric amount of $LiOH \cdot H_2O$ (5 wt% in excess) by ball milling. The obtained mixture was preheated at 480 °C for 3 h and then heated at 750, 800, 850, 900, 950, and 1000 °C for 12 h in air, denoted as S750, S800, S850, S900, S950 and S1000, respectively. To study the different calcination time impact on the morphology, part of the precursor was preheated at 480 °C for 3 h, and then heated at 1000 °C for 2 h in air, denoted as S1000(2).

The XRD measurements were carried out using a Rigaku TTRIII X-ray diffractometer equipped on graphite monochromatized high-intensity Cu K radiation in steps of 0.02° and holding at each step for 0.4 s. To calibrate the lattice parameters more accurately, high purity silicon (99.999 wt%) is selected as the internal standard. And lattice parameters are calculated from the XRD patterns with the software of Jade 7.0.

The morphology and particle size of the samples were observed by scanning electron microscopy (NoVa™ Nano SEM 250). Thermogravimetric analyses (TGA, NETZSCH STA449F3) for the mixture was carried out in air from 30 to 1000 °C at a heating rate of 10 °C/min. Surface chemical composition of the prepared samples were investigated by X-ray photoelectroscopy (PHI 5000, VersaProbe-II), The C1s line at 284.8 eV was used as a reference for calibration of XPS peaks.

The electrochemical characterizations were carried out using CR2032 coin-type half cells. Using metallic lithium as the counter and reference electrodes and 1 M $LiPF_6$ in ethyl carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 vol %). The cathodes for the battery test cell were made from the cathode materials, super P carbon black, and polyvinylidene fluoride (PVdF) binder in a weight ratio of 80:10:10. The electrodes were prepared by coating a cathode-slurry onto an Al foil followed by drying at 80 °C for 12 h in the vacuum oven. After pressed by the roller, disks of 1.33 cm^2 were punched out of the foil. Cells were cycled galvanostatically using a LAND-BT2013A battery testing system. The samples were charged at a current density of 20 mA g^{-1} and subsequently discharged by applying different current density.

3. Results and discussion

3.1. Chemical analysis of transition metals double oxides

Characterized by chemical analysis, the contents of the chemical compositions of the prepared nickel manganese double hydroxide are very close to the theoretical one, which implies that the molar ratio of Ni to Mn is close to the designed value. The exact values are list in Table 1.

Table 1
Chemical composition analysis of the prepared nickel manganese double hydroxide powder.

Sample	Ni wt%	Mn wt%	Ni:Mn (molar ratio)
Theoretical value	32.31	30.24	0.5:0.5
Actual value	31.77	30.44	0.49:0.50

3.2. TG analysis

Fig. 1 shows the TGA curve of the prepared nickel manganese double hydroxide and the mixture of the hydroxide and $LiOH \cdot H_2O$. The prepared nickel manganese double hydroxide (dashed line in Fig. 1) has a gradual decrease in mass with increasing temperature up to 220 °C, corresponding to the elimination of bound water of the powders. When further heated, two sharp decrease in mass that reach maxima in differential mass loss at ~280 and ~750 °C appear. The weight loss at ~280 °C should be attributed to the decomposition of the nickel manganese double hydroxide and the concurrent formation of $NiMnO_3$. And the high temperature feature at ~750 °C is consistent with the additional loss of oxygen to form $(NiMn)_3O_8$ [22–24].

The solid line in Fig. 1 shows TGA curves of the mixture of the prepared nickel manganese double hydroxide and $LiOH \cdot H_2O$. Combined with the results of the hydroxide, the rapid weight loss below ~120 °C can be mainly ascribed to the loss of structural water of $LiOH \cdot H_2O$, and in the region from ~120 to ~450 °C, the continuous mass loss could be related to the decomposition of the reactants and the combination of the decomposed oxides to form spinel lithium manganese nickel oxides. As the temperature increases above ~500 °C—~750 °C, a continuous decrease in mass is observed, this is an evidence supporting the point that the transformation of spinel phase to layered lithium manganese nickel oxides, as Dahn's group [9] has discussed that the sample prepared at 600 °C may adopt spinel-type structure and at high temperatures the samples are layered. Thus, in this paper, all the samples are prepared at temperatures no lower than 750 °C.

3.3. Structure

Fig. 2 shows XRD patterns of the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ powders at different calcination temperatures. The XRD patterns can be indexed on the basis of the α-$NaFeO_2$ structure (space group $R\bar{3}m$) and no remarkable secondary phase can be observed in the patterns. When the synthesis temperature increases, the intensities of all the peaks also increase and the peaks become sharper reflecting the increasing particle size and crystallinity. The crystallinity mainly refers to the degree of structural perfection of the

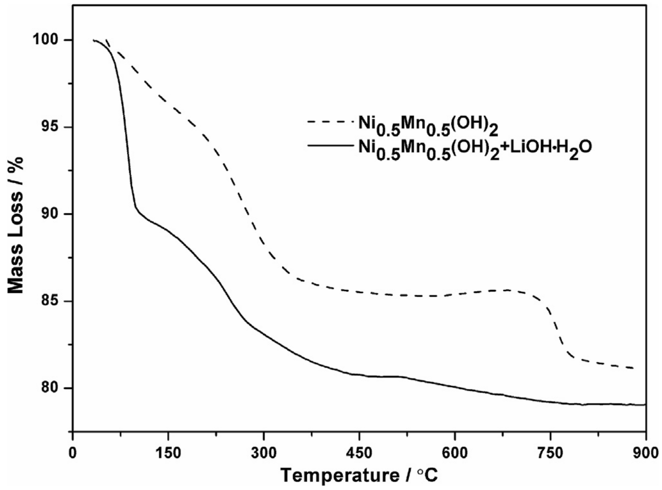

Fig. 1. TGA curves of the Ni, Mn double oxide prepared by co-precipitation (dash line) and the mixture of the hydroxide and $LiOH \cdot H_2O$ (solid line).