湿化学法合成 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 及其表征张晓雨¹ 江卫军² 朱晓沛² 其 鲁^{1,*}(¹ 北京大学化学与分子工程学院应用化学系, 北京 100871; ² 中信国安盟固利电源技术有限公司, 北京 102200)

摘要: 利用琥珀酸为螯合剂的湿化学法成功合成了一系列锂离子电池正极材料 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, 在合成过程中改变琥珀酸与金属离子摩尔比(R)并研究了这一参数对合成 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 材料物理及电化学性质的影响. 采用热重、X 射线衍射、Rietveld 精修、扫描电镜以及超导量子干涉仪对反应机理、材料的结构、形貌以及磁学性质进行了详细表征. 得到最佳合成条件为 $R=1$, 此时 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ 的阳离子混排度最低. 此外, 通过 Rietveld 精修得到该材料阳离子混排度的结果与通过磁学方法得到的结果定量相符, 如对于在 $R=1$ 条件下合成的样品, Rietveld 精修结果显示其阳离子混排度为 1.85%, 而超导量子干涉仪的测试结果为 1.80%. 当充放电区间为 3.0–4.3 V, 电流密度为 $0.2C$ ($1C=160 \text{ mA} \cdot \text{g}^{-1}$) 时, 该样品的首次放电容量为 $161 \text{ mAh} \cdot \text{g}^{-1}$, 库仑效率为 93.1%, 经过 50 次循环后, 容量保持率可达 91.3%.

关键词: 锂离子电池; $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$; 湿化学法; 阳离子混排; 磁学性质

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Characterization of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Synthesized by Wet-Chemical MethodZHANG Xiao-Yu¹ JIANG Wei-Jun² ZHU Xiao-Pei² QI Lu^{1,*}(¹ Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; ² CITIC Guoan Mengguli Power Source Technology Co., Ltd., Beijing 102200, P. R. China)

Abstract: A series of cathode materials $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ for lithium-ion batteries were successfully synthesized using succinic acid as a chelating agent by a wet-chemical method. We varied the succinic acid to metal-ion molar ratios (R) and investigated the effect of this parameter on the physical and electrochemical properties of the prepared $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. The reaction mechanism, structural, morphological, and magnetic properties of the powders were characterized in detail by thermogravimetry (TG), X-ray diffraction (XRD), Rietveld refinement, scanning electron microscopy (SEM), and superconducting quantum interface device (SQUID). We determine that the optimum conditions for the synthesis of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ assisted with succinic acid is $R=1$, at the lowest amount of cation mixing. In addition, measurement of the magnetic properties revealed a concentration of Ni on the $3b$ Wyckoff site of the lithium-ions in good agreement with the results from the Rietveld refinement on the XRD spectra. For $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ($R=1$), the Rietveld refinement showed that cation mixing in this sample was 1.85%, which is in quantitative agreement with that from the SQUID result (1.80%). It delivered an initial discharge capacity of $161 \text{ mAh} \cdot \text{g}^{-1}$ at a current rate of $0.2C$ ($1C=160 \text{ mA} \cdot \text{g}^{-1}$) and at a cut-off voltage of 3.0–4.3 V with a coulombic efficiency of 93.1% and its capacity retention was 91.3% after 50 cycles.

Key Words: Lithium-ion battery; $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$; Wet-chemical method; Cation mixing; Magnetic property

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Nowadays, lithium-ion batteries (LIB) have been widely used in portable power sources. Most LIB use LiCoO_2 as cathode material because of its simple synthesis, low irreversible capacity loss, and good cycling performance^[1-2]. However, due to high cost of LiCoO_2 , much effort has been made to develop other cheaper cathode materials and use them in price-sensitive and large-scale applications. Recently, a layer-structured compound $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (simplified as LNMCO), first introduced by Ohzuku's group in 2001^[3], has been considered as an attractive candidate of next-generation cathode material to replace LiCoO_2 due to its lower cost, more stable structure, larger capacity, and better thermal stability at charged state^[4-6]. The valence states of nickel, manganese, and cobalt ions in LNMCO powder are +2, +4, and +3, respectively, confirmed by X-ray photoelectron spectroscopy (XPS) study^[7]. For LNMCO, each transition metal plays its important role. The divalent nickel ions and trivalent cobalt ions are electroactive and the electrochemical reaction of lithium extraction/insertion takes place by oxidation/reduction of $\text{Ni}^{2+}/\text{Ni}^{4+}$ and $\text{Co}^{3+}/\text{Co}^{4+}$ ions depending on different cut-off voltages, while Mn^{4+} remains inactive but maintains the structural stability^[8].

However, cation mixing still remains a big problem for this material, since the ionic radius of Ni^{2+} (0.069 nm) is close to that of Li^+ (0.076 nm)^[9]. A partial occupation of Ni^{2+} by Li^+ and Ni^{2+} generates a disorder in the structure and this could restrict the motion of Li^+ ions within the layers of the oxide, which leads to the tendency for the capacity to fade during long cycling^[10]. Therefore, one aim of this work is to decrease the cation mixing by adjusting different acid to metal ion molar ratios (R) during the synthesis through wet-chemical method.

Moreover, It has been shown that magnetic experiment is quite a powerful tool to check the quality of samples and structural properties at nanoscopic scale, especially in the case of cathode materials for LIB^[11-14] and it is possible to correlate the magnetic and structural properties of LNMCO^[15-16]. In particular, we have shown that the Ni^{2+} ion in substitution for Li^+ on the $3b$ lattice site, $\text{Ni}^{2+}(3b)$ generates a ferromagnetic interaction with the Mn^{4+} ions nearest neighbours on $3a$ sites, and this $\text{Ni}^{2+}(3b)$ – $\text{Mn}^{4+}(3a)$ ferromagnetic interaction is responsible for the formation of a ferromagnetic cluster centred on the $\text{Ni}^{2+}(3b)$ defect^[17]. The magnetic moment resulting from these ferromagnetic clusters can be detected from the magnetic measurements, from which the concentration of the $\text{Ni}^{2+}(3b)$ defects can be derived and compared with the concentration deduced from Rietveld refinement of XRD spectra. This correlation between magnetic and structural properties makes possible the determination of the concentration of $\text{Ni}^{2+}(3b)$ defects with very good accuracy^[18]. We then use the same procedure in this work.

In addition, although wet-chemical method has been used to synthesize LNMCO, using different chelating agents, e.g., citric acid and oxalic acid^[19-23], and succinic acid is also one of the widely used chelating agents for the synthesis of oxides, the synthesis of LNMCO assisted by succinic acid and the effect of its

content on magnetic properties, especially on the relationship between structural and magnetic properties of LNMCO, has not been reported to the best of our knowledge. Therefore, varying the succinic acid to metal ion molar ratio and this effect on the structural, morphological, electrochemical, particularly on the magnetic properties of LNMCO, are studied detailedly in this paper.

1 Experimental

1.1 Sample synthesis

The synthesis occurred from metal acetates *via* inorganic polymerization reactions in the solution^[24-26]. This wet-chemical route was assisted by succinic acid (AR, Sigma-Aldrich product) as a polymeric agent, using appropriate molar ratios of lithium, nickel, manganese, and cobalt acetate as starting materials to synthesize LNMCO compound. Stoichiometric amounts of acetate hydrates of $\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ (AR), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), Sigma-Aldrich products, were dissolved in distilled water and mixed homogeneously with an aqueous solution of succinic acid, varying the molar ratio (R) of acid to metal-ion. The resulting solution was mixed by magnetic stirring at 80 °C for 6 h to obtain a clear viscous gel. The gel was dried in an oven at 120 °C for 12 h. The as-prepared precursor was pre-calcined at 450 °C for 4 h to convert the metal carboxylates to oxides. After cooling down to room temperature, the obtained powder was grounded in an agate mortar and then sintered at 900 °C in air for 15 h without pelleting to get the final LNMCO.

1.2 Apparatus

Thermogravimetry (TG) experiment was performed using a Q50 (TA, USA) instrument analyzer to monitor the mass loss/gain and heat treatment processes under a flow of dry air with a heating rate of 10 °C $\cdot$ min⁻¹. Measurements were carried out in the temperature range of 25 °C $\leq T \leq$ 750 °C.

For structural analysis of LNMCO, samples were characterized with X-ray diffraction (XRD) on a Philips (Netherlands) X'Pert PRO MRD (PW3050) diffractometer equipped with a Cu anticathode (Cu K_α radiation, $\lambda=0.154056$ nm) at room temperature. XRD patterns were collected under Bragg-Brentano geometry at 2θ with a step of 0.02° in the range of 10°–80° and were refined by the Rietveld method using the GSAS/EXPGUI package^[27]. For morphology analysis of LNMCO, a scanning electron microscope (SEM) study of the samples was performed using a JEOL (Japan) JSM-5600LV electron microscope.

The magnetic measurements (susceptibility and magnetization) were performed with a fully automated superconducting quantum interface device (SQUID) magnetometer (Quantum Design MPMS XL, USA) in the temperature range of 4–300 K. Powders were placed into small plastic vial, placed in a holder and finally inserted into the helium cryostat of the SQUID apparatus. The temperature dependence of the susceptibility data was recorded during heating of the sample using two modes: zero field cooling (ZFC) and field cooling (FC), to determine the mag-

netic behavior. The procedure is based on performing two consecutive magnetization measurements: in ZFC the sample is first cooled down in the absence of magnetic field, then a magnetic field $H=10$ kOe is applied, and the ZFC magnetic susceptibility $M(H)/H$ is measured where M is the magnetization measured upon heating. In the FC experiments, the same magnetic field is applied first at room temperature; the FC susceptibility is measured upon cooling. No difference, i.e., no magnetic irreversibility effect has been detected between ZFC and FC measurements in any of the samples. Magnetic curves $M(H)$ have been measured in an applied magnetic field in a range of 0–30 kOe.

Charge-discharge tests were performed on coin type cell (CR2032). Composite positive electrode was prepared by thoroughly mixing the active material (90% (w , mass fraction)) with carbon black (2% (w)), acetylene black (2% (w)), polyvinylidene fluoride (6% (w)) in N -methyl-pyrrolidinone and spread onto aluminium foils then dried at 120 °C for 24 h in vacuum. Cells were then assembled in an argon-filled glove box (Braun, Germany) using foils of Li metal as counter electrode and Celgard 2400 as separator. The electrolyte was 1.0 mol·L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, volume ratio). The cells were galvanostatically cycled at 0.2C (1C=160 mA·g⁻¹) between 3.0 V and 4.3 V (*versus* Li/Li⁺) on a Land CT2001A battery tester (Wuhan Jinnuo Electronics Co., Ltd., China) at room temperature.

2 Results and discussion

2.1 TG analysis of LNMCO precursor

When acetate of an electropositive transition metal dissolves in succinic acid, there is a finite release of the acetate anion into solution. The basic species, acetate anion, can allow the dissolution of metal acetates. The formation of a chelation complex is important to prevent the segregation or precipitation of metal ions. The acetate ligand, succinic acid, has oxygen atoms and hydrogen atoms which can participate in hydrogen bonding. As a result, metal acetates are trapped in a glassy state by an extended network of hydrogen bonds. At the same time, succinic acid binds to the metal acetates and replaces the water of hydration in the complex to give acid-acetate species^[28]. Succinic acid also acts as fuel and provides local heat for the formation of compound during the decomposition process because of its self-igniting property, accelerating the decomposition of acetate ions. Therefore, varying the acid to metal ion molar ratio (R) can affect the decomposition/formation reaction. As an example, Fig.1 shows the TG analysis curve of the precursor of LNMCO synthesized *via* $R=0.5$. Several mass loss stages are observed in this TG curve. The first mass loss stage occurs at ca 223 °C, which would be attributed to departure of residual water. After the departure of the remaining water molecule at ca 330 °C, the anhydrous metal acetate can be decomposed into both metal oxide and gases such as carbon dioxide by further thermal treatment in air^[29–30]. It was reported that chelating agent (carboxylic-based acid) provoked decomposition during the synthesis of oxide

Fig.1 Thermogravimetric analysis profile for the precursor of LNMCO synthesized with succinic acid to metal ion molar ratio of $R=0.5$

powders and the gel precursor burned because the decomposed acetate ions acted as an oxidizer^[24–26], so the mass loss in the third step is observed around 376 °C which corresponds to the decomposition of succinic acid and acetate ions xerogel. After 450 °C, there is little mass loss, so in this work, we choose 450 °C as the heating temperature for pre-calcination. The reaction pathway can thus be given as follows:

2.2 Structural and morphological analysis of LNMCO

Fig.2 shows the XRD patterns of LNMCO materials synthesized by wet-chemistry with calcination at 900 °C in air for 15 h *via* different R values. From now on, all the experiments in this work will be focussed on the optimization of the parameter R . The Bragg lines are well indexed in the $R\bar{3}m$ space group with the hexagonal sitting. No impurity phases are detected and the powders are well crystallized in the α -NaFeO₂ type structure. As seen in Fig.2, the (006)/(102) and (108)/(110) doublets are well separated, which indicates a good hexagonal ordering of LNMCO^[31]. The narrow diffraction peaks of the pattern indicate a high crystallinity of the LNMCO powder and suggest a homogeneous distribution of the cations within the structure. The lattice

Fig.2 XRD patterns of LNMCO powders synthesized with different succinic acid to metal ion molar ratios (R)

parameters were obtained by analysis of the XRD data and the results were summarized in Table 1. The lattice parameter, a , is related to average metal–metal intraslab distance, the lattice parameter, c , is related to the average metal–metal inter-slab distance; and the trigonal distortion, c/a , is related to the hexagonal structure disorder. For layered compounds, higher value of c/a is desirable for better hexagonal structure^[7]. The trigonal distortion c/a is the largest for LNMCO $R=1$, which is used as a criterion of optimized material. In addition, the integrated intensity ratio of (003) to (104) peak, I_{003}/I_{104} , has been considered as an indicator of the degree of cation mixing^[32]. The higher the ratio is, the lower the cation mixing is. It is also believed that the lower value of $(I_{006}+I_{102})/I_{101}$ is another indicator of better hexagonal ordering^[33–34]. The lowest value of $(I_{006}+I_{102})/I_{101}$, together with the highest value of I_{103}/I_{104} is obtained for $R=1$, which suggests that this is the optimized value of this synthesis parameter. As a result, varying R value has a direct effect on the structural properties of LNMCO, since the self-igniting property of succinic acid can influence the oxygen partial pressure during synthesis. The sudden variation in the oxygen partial pressure, especially during the burning of the succinic acid, has an impact on LNMCO formation. When R value is low, it cannot provide enough local heat for the formation of precursor. However, when R value is too high, the local temperature increases too much in a short period of time and the partial pressure of oxygen decreases due to the increased CO_2 , which results in the insufficient oxidation of ions and ferromagnetic defects that can aggravate the cation mixing during the formation of LNMCO.

The Rietveld refinement has been made with the constraints that the lithium ion and the nickel-manganese-cobalt ions occupy the $3b$ (0, 0, 0) and $3a$ (0, 0, 1/2) Wyckoff sites, respectively, while the oxygen anions occupy the $6c$ (0, 0, z_{oxy}) position (z_{oxy} will be refined). In addition, we assume that each cationic site is fully occupied and the number of cations equals to that of anions, so

Table 1 Structural data of the $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ samples synthesized with different R values

Item	Value			
R	0.5	1	2	3
a/nm	0.28638(3)	0.28613(2)	0.28671(1)	0.28698(3)
c/nm	1.42517(2)	1.42496(2)	1.42548(3)	1.42597(4)
c/a	4.9765	4.9801	4.9719	4.9689
V/nm^3	0.10122(2)	0.10103(1)	0.10148(1)	0.10170(3)
I_{003}/I_{104}	1.293	1.429	1.149	1.087
$(I_{006}+I_{102})/I_{101}$	0.421	0.405	0.443	0.455
$y(\text{Ni}(3b))$ (%)	2.06	1.85	2.62	3.38
z_{oxy}	0.2590(1)	0.2593(2)	0.2588(2)	0.2584(3)
$S(\text{MO}_2)/\text{nm}^a$	0.2119	0.2110	0.2125	0.2137
$I(\text{LiO}_2)/\text{nm}^b$	0.2632	0.2640	0.2627	0.2616
R_p (%)	9.14	9.25	9.35	11.13
R_{wp} (%)	12.76	12.87	13.24	14.78
$R(F^2)$	0.1842	0.1898	0.2079	0.2248
χ^2	1.219	1.266	1.218	1.643

^a $S(\text{MO}_2)=2(1/3-z_{\text{oxy}})c$; ^b $I(\text{LiO}_2)=c/3-S(\text{MO}_2)$

the overall charge neutrality is maintained. Furthermore, we assumed the existence of a small amount of nickel ions in the lithium sites, since the smaller difference in size between the Ni^{2+} (0.069 nm) and the Li^+ ions (0.076 nm) in contrast with other cations ($r(\text{Mn}^{4+})=0.053$ nm, $r(\text{Co}^{3+})=0.054$ nm in an octahedral environment^[9]). Therefore, we defined the formula as $[\text{Li}_{1-y}\text{Ni}_y]_{3b}[\text{Li}_y\text{Ni}_{1/3-y}\text{Mn}_{1/3}\text{Co}_{1/3}]_{3a}\text{O}_2$ for Rietveld refinement: the occupancy parameter y of the Ni^{2+} ions at the $3b$ sites was refined and constrained to be equal to that of Li^+ ions at the $3a$ sites, with the total nickel occupancy ratio constrained to 1/3. The results of the Rietveld refinement of the XRD patterns are also summarized in Table 1 as a function of R . Since the radius of Ni^{2+} is smaller than that of Li^+ , Ni^{2+} ions on $3b$ sites leads to an increase of the parameter a . Moreover, the presence of the Ni^{2+} ions in lithium plane leads to the stronger electrostatic attraction between oxygen and $\text{Li}^+/\text{Ni}^{2+}$ ions in the LiO_2 inter-slab plane, hence the decrease of the LiO_2 inter-slab space, $I(\text{LiO}_2)$, the correlated increase of the thickness $S(\text{MO}_2)$ of the MO_2 slabs, and the increase of c .

As seen from Table 1, we find a , c , $S(\text{MO}_2)$ are minimum and $I(\text{LiO}_2)$ is maximum for $R=1$, which confirms that this is the optimized value for this parameter. These correlated variations of a , c , $S(\text{MO}_2)$ and $I(\text{LiO}_2)$ are then additional proofs that $R=1$ is the optimized value for succinate route. Indeed, the amount of $\text{Li}^+/\text{Ni}^{2+}$ cation mixing is the lowest in this case ($y=1.85\%$), which is better than the results in Refs.[21,35]. The Rietveld fit of the XRD pattern for this sample is shown in Fig.3.

The morphologies of powders were investigated by SEM. Fig. 4(a–d) shows the SEM images of LNMCO compounds synthesized *via* succinic acid route with different R values. The SEM pictures also show that the primary particles are stuck into agglomerates. The sample synthesized *via* the optimal value $R=1$ (Fig.4b), with minimum cation mixing and optimum structural integrity, seems to have a more uniform size distribution of particles than the others, which can facilitate the diffusion of lithium-ion, so higher specific capacity and better capacity retention can

Fig.3 Rietveld refinement patterns of LNMCO synthesized at $R=1$ *via* wet-chemical method

The cross marks show observed X-ray diffraction intensities and the solid line (in red on the web version) represents calculated intensities. The curve at the bottom (in blue on the web version) is the difference between the calculated and observed intensities on the same scale.

Fig.4 SEM images of LNMCO synthesized with different R values

R : (a) 0.5, (b) 1, (c) 2, (d) 3

be expected.

2.3 Magnetic properties of LNMCO

The temperature dependence of the reciprocal magnetic susceptibility, $\chi_m^{-1} = H/M$ is presented in Fig.5 for all the samples.

Fig.5 Plots of the reciprocal magnetic susceptibility χ_m^{-1} for samples synthesized with different R values

Data were collected with a magnetic field $H=10$ kOe.

Fig.6 Isothermal plots of the magnetization $M(H)$ for the LNMCO sample synthesized with different R values

The magnetization curves are reported in Fig.6(a–d) for samples with the “optimized” value $R=1$, and the other three samples. Above 150 K, the curve $\chi_m^{-1}-T$ shows a paramagnetic (PM) behavior and the magnetization is linear in field for all the samples, so that χ_m^{-1} is meaningful, i.e., $H/M = \partial H / \partial M$. The quasi-linear variations of χ_m^{-1} with T at the susceptibility can be described by a Curie-Weiss law $\chi_m^{-1} = (T - \Theta_p) / C_p$, with Θ_p the Curie-Weiss temperature, and C_p the Curie constant related to the effective magnetic moment μ_{eff} by the relation $C_p = N \cdot \mu_{\text{eff}}^2 / (3k_B)$ with k_B the Boltzmann constant and N the number of metal ions in one mole of product. The values of the two fitting parameters Θ_p and μ_{eff} obtained for the different acid to metal ion ratios R are reported in Table 2. Θ_p is negative in all the compounds and this is an intrinsic property due to the fact that intrinsic magnetic interactions are mainly the intra-layer superexchange interactions mediated via oxygen at 90° bonding angle, and they are dominantly anti-ferromagnetic (AFM)^[14]. Taking into account that the magnetic moments carried by Ni^{2+} and Mn^{4+} are $2.83\mu_B$ and $3.87\mu_B$, respectively in this material while Co^{3+} is diamagnetic^[36–38], the theoretic

Table 2 Magnetic properties of LNMCO synthesized with different R values

R	$C_p/(\text{emu} \cdot \text{K} \cdot \text{mol}^{-1})$	Θ_p/K	μ_{eff}/μ_B	$M_s/(\text{emu} \cdot \text{mol}^{-1})$	$y(\text{Ni}^{2+}(3b))$
0.5	0.97	-89	2.80	211	2.28%
1	0.94	-77	2.75	167	1.80%
2	1.03	-101	2.88	260	2.75%
3	1.08	-115	2.95	360	3.59%

cal value of μ_{eff} in absence of $\text{Ni}^{2+}(3b)$ defects would be:

$$\mu_{\text{theor}} = [(1/3) \times 2.83^2 + (1/3) \times 3.87^2 + (1/3) \times 0]^{1/2} \mu_B = 2.77 \mu_B$$

The experimental value of μ_{eff} for the $R=1$ sample is close to this theoretical value. For the other samples, however, μ_{eff} is found to be larger. To understand this effect, we note that the magnetization curves are no longer linear below 80 K. Note in this case, $H/M \neq \partial H / \partial M$, so that χ_m^{-1} in Fig.6(a-d) does not have any physical meaning at these low temperatures. Nevertheless, we have reported the data in Fig.6(a-d) since it will be useful to the discussion. For the moment, we just note that these deviations from linearity are related to the onset of a remanent magnetization at low temperature, evidenced in the magnetization curves of the $R=3$ in Fig.6(d). Following the prior works^[14-16], we attribute this feature to the $\text{Ni}^{2+}(3b)$ defects. The substitution of Li by Ni on a $3b$ site generates a 180° interlayer $\text{Mn}^{4+}(3a)\text{-O-Ni}^{2+}(3b)$ superexchange interactions which is ferromagnetic (FM) after the Goodenough rules^[17]. This interaction is strong enough to generate a ferromagnetic spin freezing of the $\text{Mn}^{4+}(3a)\text{-O-Ni}^{2+}(3b)$ pair that is responsible for the onset of remanent magnetization at low temperature. This interaction is actually strong enough to induce a ferromagnetic spin-freezing of such pairs at low temperature. We can then estimate the amount of $\text{Ni}^{2+}(3a)$ defects as the ratio of the magnetic moment at saturation (M_s) of the ferromagnetic component of the magnetization, to the moment at saturation that the sample would have if all the Mn and Ni ions were saturated ferromagnetically, namely $(1/3)g \cdot \mu_B \cdot (S_{\text{Mn}} + S_{\text{Ni}}) = (5/3)\mu_B = 1.67\mu_B$ per chemical formula, since the Mn^{4+} and Ni^{2+} carry a spin $S_{\text{Mn}}=3/2$ and $S_{\text{Ni}}=1$. The gyromagnetic factor g is 2, since the orbital momentum is quenched by crystal field effects, and the factor $1/3$ comes from the fact that there is only $1/3$ Ni-Mn pair per chemical formula. M_s has been estimated from the linear extrapolation to $H \rightarrow 0$ of the isothermal magnetization curve $M(H)$ at $T=4.2$ K taken in the range $20 \text{ kOe} < H < 30 \text{ kOe}$. The lowest temperature and this range of the highest field available in the experiments have been chosen to be sure that the ferromagnetic component is saturated. Despite this precaution, it should be noticed that the curvature of the magnetic curves below 20 kOe does not guarantee that the full saturation of the ferromagnetic component has been achieved even at higher field, and even at 4.2 K. Nevertheless, the result for the estimation of the rate of substitution y deduced from this magnetic analysis reported in Table 2, is in remarkable agreement with the result deduced from Rietveld refinement for all the samples investigated, which validates the analysis. For instance, in the case of the sample with $R=1$, we find $M_s=167 \text{ emu} \cdot \text{mol}^{-1}$ (Fig.6(b)), which amounts to a magnetic moment per formula $0.03\mu_B$. So the concentration

Fig.7 Initial charge-discharge profiles of LNMCO samples synthesized with different R values

of Ni^{2+} at $3b$ sites can be calculated as $0.03\mu_B/1.67\mu_B=1.80\%$, which is the lowest value among all the samples and agrees well with the results obtained from Rietveld refinement. In the paramagnetic regime, the ferromagnetic $\text{Mn}^{4+}(3a)\text{-O-Ni}^{2+}(3b)$ pairing enhances the effective magnetic moment of the material. This is the reason for the increasing large value of μ_{eff} upon increasing departure of the parameter R from its optimized value $R=1$, i.e., upon increasing y .

2.4 Electrochemical properties of LNMCO

Fig.7 shows the initial charge-discharge curves of LNMCO cathode synthesized with different R values at $32 \text{ mA} \cdot \text{g}^{-1}$ ($0.2C$) rate between 3.0 V and 4.3 V versus Li/Li^+ at room temperature. As shown in Fig.7, the prepared LNMCO materials display smooth charge-discharge curves without any plateaus, which indicates no spinel-related phases forming during cycling. As seen from Table 3, the initial discharge capacity of LNMCO samples are $155 \text{ mAh} \cdot \text{g}^{-1}$ ($R=0.5$), $161 \text{ mAh} \cdot \text{g}^{-1}$ ($R=1$), $149 \text{ mAh} \cdot \text{g}^{-1}$ ($R=2$), and $141 \text{ mAh} \cdot \text{g}^{-1}$ ($R=3$), respectively. The coulombic efficiencies are 90.6% ($R=0.5$), 93.1% ($R=1$), 90.3% ($R=2$), and 89.2% ($R=3$).

Fig.8 shows the differential capacity ($\partial Q / \partial E$) vs cell potential (E) of the Li/LNMCO ($R=1$) coin cell calculated from data presented in Fig.7. Upon charging the cell displays a major oxidation peak at 3.79 V, while the reduction peak occurs at 3.68 V upon discharging. As reported many times in the literature, the oxidation peak at ca 3.8 V with the corresponding reduction peak at 3.7 V is typical for the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction in the Li-Ni-Mn-Co oxide lattice^[5,14]. However, the asymmetry toward the high potential side is due to the partial redox contribution from Co^{3+} to Co^{4+} that corresponds to the second electron transfer.

The cycling performances of LNMCO samples are illustrated

Table 3 Electrochemical properties of LNMCO synthesized with different R values

	Capacity ($\text{mAh} \cdot \text{g}^{-1}$)			
	$R=0.5$	$R=1$	$R=2$	$R=3$
1st charge	171	173	165	158
1st discharge	155	161	149	141
coulombic efficiency	90.6%	93.1%	90.3%	89.2%
50th discharge	137	147	124	112
capacity retention	88.4%	91.3%	83.2%	79.4%

Fig.8 Differential capacity ($\partial Q/\partial E$) vs cell potential (E) of the Li//LNMCO ($R=1$) coin cell

Fig.9 Cycling performance of LNMCO samples synthesized with different R values

in Fig.9. The optimized sample ($R=1$) achieves higher initial discharge capacity ($161 \text{ mAh} \cdot \text{g}^{-1}$) and its capacity retention is 91.3% after 50 cycles, which correspond well with the results from structural and magnetic analyses before. Higher structural integrity and less cation mixing result in better electrochemical performance, which can be compared with that of LNMCO synthesized by other wet-chemical methods^[39–40], when using the same cut-off voltage (3.0–4.3 V) and current density ($32 \text{ mA} \cdot \text{g}^{-1}$) for electrochemical characterization.

3 Conclusions

The layered LNMCO was successfully synthesized *via* wet-chemical route assisted by succinic acid with different R values. XRD, SQUID, and charge-discharge characterizations show that the structural, magnetic, and electrochemical profiles are sensitive to the synthetic conditions, i.e., the R value that governs the cation mixing. The best performance of the LNMCO electrode has been obtained from an acid to metal ion ratio $R=1$ sintered at 900°C for 15 h. The amount of cation mixing estimated from the magnetization curve for $R=1$ is 1.80%, which agrees well with the Rietveld refinement result (1.85%). The LNMCO sample with $R=1$ shows the best reversibility with a coulombic efficiency of 93.1% for the first cycle. Its initial discharge capacity is $161 \text{ mAh} \cdot \text{g}^{-1}$ and its capacity retention is 91.3% after 50 cycles in the cut-off voltage of 3.0–4.3 V.

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第六届国际环境催化大会(ICEC6, 2010)

第六届国际环境催化大会(6th International Conference on Environmental Catalysis, ICEC6)将于2010年9月12-15日在北京召开。国际环境催化大会是环境催化领域的高学术水平的会议,具有很高的国际知名度。该大会于1995年在意大利比萨首次举行,随后分别于1998年在美国迈阿密、2001年在日本东京、2005年在德国海德堡、2008年在英国贝尔法斯特举行,已举办了5届,在环境催化领域产生了很大影响,促进了各国研究者之间的合作与交流。在全球气候变化、环境污染和能源危机等问题引起广泛关注的背景下,本届大会由中国科学院生态环境研究中心负责主办。中国科学院大连化学物理研究所李灿院士担任大会主席,中国科学院生态环境研究中心贺泓研究员担任大会组委会共同主席。

本届大会将继续承前几届大会的传统,展示近年来环境催化领域在科学和工程上所取得的最新研究进展,推进全球环境催化科学的交流及其在环境保护和发展新能源方面的应用,并为学术界和工业界研究者提供交流和学习平台。大会将邀请国内外著名学者和专家就环境催化领域的研究和应用前沿进展做精彩报告,详细信息请见会议网站 www.icec2010.org 或通过电子邮件与我们联系 info@icec2010.org。大会组委会诚挚邀请国内外环境催化领域的专家、学者、技术人员和相关企业参加本届大会。

1. 征文范围

- 1) 机动车尾气催化净化最新研究进展;
- 2) 用于空气和水质净化的催化科学和技术;
- 3) 可持续洁净能源转化过程中的催化科学和技术;
- 4) 温室气体的催化消除;
- 5) 涉及绿色化学的催化过程。

2. 征文要求

论文符合主题范围,且未在国内外学术期刊上正式发表。

论文详细摘要以A4纸不超过1页为宜。来稿经审阅后将编入会议论文集。优秀稿件经审稿后将在《Catalysis Today》上发表。欢迎登陆会议主网页(www.icec2010.org)投稿、注册和查看会议筹备进展情况。

3. 重要日期

2010年3月10日	论文投稿截止期
2010年6月30日	优惠注册截止期
2010年8月30日	酒店预订截止期

4. 联系方式

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