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Synthesis and thermal decomposition kinetics of LiNiO_2 ^①

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[Abstract] A layered LiNiO_2 with high crystallinity was synthesized by sintering the finely prepared mixture of lithium hydroxide and nickel hydroxide in the oxygen atmosphere. The electrochemical properties of LiNiO_2 show that it has a reversible capacity of more than $168 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. It was found that with increasing temperature, LiNiO_2 decomposed in air followed with three reaction stages, the apparent activation energies were $747.18 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$, $932.46 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $1126.97 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ respectively, and the kinetic equations of the three reaction stages were obtained.

[Key words] lithium ion batteries; LiNiO_2 ; electrochemistry; decomposition; kinetics

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1 INTRODUCTION

Lithium ion battery is a newly developed rechargeable battery subsequent to MH/Ni battery^[1], with the characteristics of higher voltage, larger capacity, lower self-discharging rate, longer cycle life, and so on. In order to improve the properties and reduce the cost of Lithium ion battery, many scholars focused attention on the research of anode insert materials^[2]. LiCoO_2 , LiNiO_2 , and LiMn_2O_4 are three promising anode insert materials. Among them, LiCoO_2 with good electrochemical properties can be prepared easily, but it is with very high cost; LiMn_2O_4 has lower Lithium inserting capacity and two discharging plane stages, which make LiMn_2O_4 unsuitable for practical application. So, LiNiO_2 with lower price and better electrochemical properties becomes the hot point of research^[3, 4].

In this paper, the preparation of LiNiO_2 and the electrochemical properties of the well-prepared LiNiO_2 were investigated. The thermal decomposition of LiNiO_2 in the air was also studied by means of DTA and XRD.

2 EXPERIMENTAL

2.1 Preparation of LiNiO_2

First, the ball-milled mixture of LiOH (AR) and Ni(OH)_2 (AR) was dried for 10 h at 150°C , pressed into blocks under 20 MPa, and pretreated at $550\sim 650^\circ\text{C}$ for 4~12 h. Then the pretreated product was ground into fine powder and repressed into block samples. Finally, the samples have been sintered at the temperature of $650\sim 750^\circ\text{C}$ for 5~15 h.

2.2 Measurements

Using the prepared LiNiO_2 as the anode material, the lithium metal plate as the cathode, 1 mol/L $\text{LiClO}_4/\text{PC} + \text{DME}$ (1:1) as an electrolyte, Celgard-2300 polypropylene as the cell septum, nickel net as the flow concentrator of anode, carbon powder as a conductive agent, and PVDF as a binder, the experimental batteries were assembled to measure the electrochemical properties of LiNiO_2 with DC-5 Battery Testing Instrument. The testing of charge and discharge cycle was carried out at the constant current density of $10 \text{ A} \cdot \text{m}^{-2}$. The microstructure of LiNiO_2 was observed with JSM-6301F Field Emission Scanning Electron Microscope.

The DTA curves of the samples were obtained by means of USA-Perkin-Elmer Differential Thermal Analyzer. In the experimental process, each sample of $17.50 \pm 1.5 \text{ mg}$ was put into a Pt-Au crucible, and five samples were measured in the air flowing at the rate of $25\sim 30 \text{ mL} \cdot \text{min}^{-1}$, with heating rates of 5, 10, 15, 20, $30^\circ\text{C} \cdot \text{min}^{-1}$ respectively. Coupled with DTA curves of the samples, LiNiO_2 has been sintered for 30 min at 720°C , 950°C and 1150°C separately, and then quickly cooled to determine the phase composition with D/MAX-3B X-ray Diffractometer (Japan Rigaku).

3 RESULTS AND DISCUSSION

3.1 Electrochemical properties of LiNiO_2

In the research, various lithium compounds and nickelous compounds were chosen to be the raw materials to synthesize LiNiO_2 , under the same preparing conditions as described before. The products prepared

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with different raw materials and their electrochemical properties are shown in Table 1.

Table 1 Electrochemical properties of products prepared with different raw materials

Raw materials	Product	Reversible discharging capacity/(mAh·g ⁻¹)
Li ₂ CO ₃ + Ni(OH) ₂	Li ₂ Ni ₈ O ₁₀	25
Li ₂ (CH ₃ COO) + Ni(OH) ₂	Li ₂ Ni ₈ O ₁₀	40
LiOH·H ₂ O+ β-Ni(OH) ₂	LiNiO ₂	90
LiOH·H ₂ O+ Ni ₂ O ₃	LiNiO ₂	70
LiOH·H ₂ O+ Ni ₂ CO ₃	Li ₂ Ni ₈ O ₁₀	35
LiOH·H ₂ O+ α-Ni(OH) ₂	LiNiO ₂	52
Li ₂ CO ₃ + Ni ₂ CO ₃	Li ₂ Ni ₈ O ₁₀	20
Li ₂ (CH ₃ COO) + Ni ₂ CO ₃	Li ₂ Ni ₈ O ₁₀	24

Table 1 shows that under the producing conditions given in this research, LiOH·H₂O and β-Ni(OH)₂ are the favorite raw materials to synthesize high quality LiNiO₂.

An appropriate producing condition of LiNiO₂ was obtained by orthogonal experiment designing of 4 factors and 3 levels, that is, L₉(3⁴). The factors and levels considered and the experimental results of L₉(3⁴) are shown in Table 2 and Table 3, respectively.

According to the above experimental data, it was found that from A, C, B to D, the four factors follow the increasing influence on the electrochemical property of LiNiO₂: the optimum combination of 4 factors and 3 levers was D₃, B₃, C₂, A₂. That was pretreatment of raw materials at 650 °C for 12 h and synthesis at 720 °C for 5 h, with mole ratio of Li to Ni at 1.1:1.0. Several verification of experiments were carried

Table 2 Factors and levels of orthogonal experiment

Levels	Factors			
	Mole ratio of Li to Ni	Pretreatment temperature/ °C	Synthesis temperature/ °C	Pretreatment time & synthesis time
1	1.0: 1.0	550	690	4 h, 15 h
2	1.1: 1.0	600	720	8 h, 10 h
3	1.2: 1.0	650	750	12 h, 5 h

Table 3 Results of orthogonal experiment

No.	A Mole ratio of Li to Ni	B Pretreatment temperature	C Synthesis temperature	D Pretreatment time & synthesis time	Reversible discharging capacity / (mAh·g ⁻¹)
1	1(1.0: 1.0)	1(550 °C)	1(690 °C)	1(4 h, 15 h)	14
2	1(1.0: 1.0)	2(600 °C)	2(720 °C)	2(8 h, 10 h)	85
3	1(1.0: 1.0)	3(650 °C)	3(750 °C)	3(12 h, 5 h)	86
4	2(1.1: 1.0)	1(550 °C)	2(720 °C)	3(12 h, 5 h)	82
5	2(1.1: 1.0)	2(600 °C)	3(750 °C)	1(4 h, 15 h)	45
6	2(1.1: 1.0)	3(650 °C)	1(690 °C)	2(8 h, 10 h)	95
7	3(1.2: 1.0)	1(550 °C)	3(750 °C)	2(8 h, 10 h)	34
8	3(1.2: 1.0)	2(600 °C)	1(690 °C)	3(12 h, 5 h)	82
9	3(1.2: 1.0)	3(650 °C)	2(720 °C)	1(4 h, 15 h)	63
I	185	130	191	112	
II	222	212	230	214	
III	179	244	165	250	
\bar{K}_1	61.67	43.33	63.67	40.67	
\bar{K}_2	74.00	70.67	76.67	71.33	
\bar{K}_3	59.67	81.33	55.00	83.33	
R	14.33	38.00	21.67	42.66	

out under the optimum combination conditions. The results of electrochemical property test show that the new LiNiO_2 prepared by the verified experiment has an average reversible discharging capacity of $168 \text{ mAh} \cdot \text{g}^{-1}$. Within the voltage of 2.5~ 4.2 V, the testing of charge and discharge cycles at constant current of $10 \text{ A} \cdot \text{m}^{-2}$ is shown in Fig. 1.

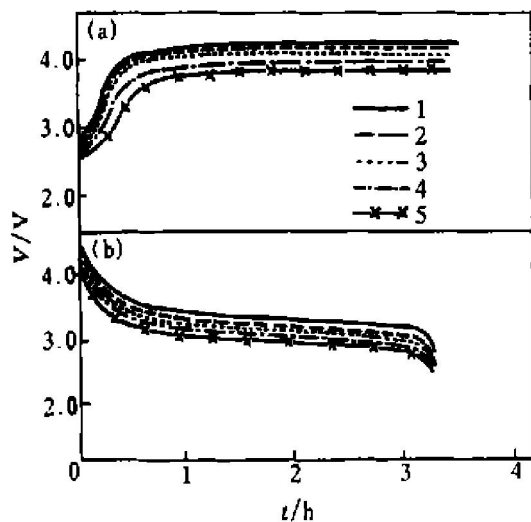


Fig. 1 Charge (a) and discharge (b) curves of LiNiO_2 (5 cycles)

The XRD results (Fig. 2) and the SEM photograph (Fig. 3) of LiNiO_2 show that a purer and layered LiNiO_2 with high crystallinity was prepared.

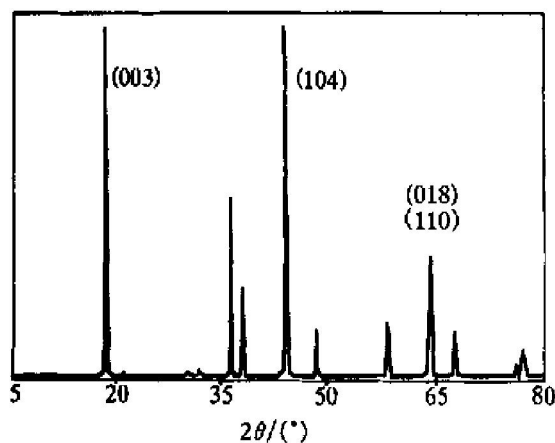


Fig. 2 XRD spectrum of LiNiO_2

3.2 Thermal decomposition of LiNiO_2

The DTA curve of LiNiO_2 at a temperature rising rate of $15 \text{ K} \cdot \text{min}^{-1}$ in the flowing air and the XRD spectra of LiNiO_2 decomposed product at different temperatures are given in Fig. 4 and Fig. 5, respectively.

Considered the XRD results shown in Fig. 5, the three endothermic peaks in DTA curve could deduce three decomposing stages of LiNiO_2 . At the first stage, LiNiO_2 decomposed into $\text{Li}_2\text{Ni}_8\text{O}_{10}$, Li_2O , and O_2 within $650 \sim 720^\circ\text{C}$. The reaction was supposed to be as

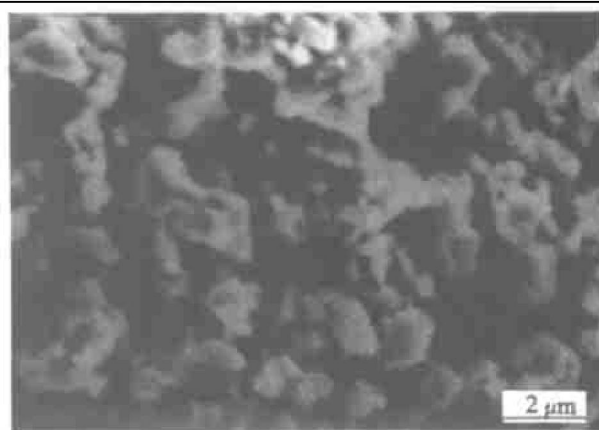


Fig. 3 SEM photograph of LiNiO_2

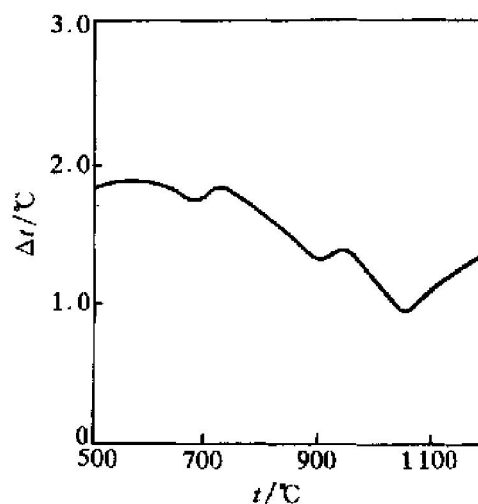


Fig. 4 DTA curve of LiNiO_2

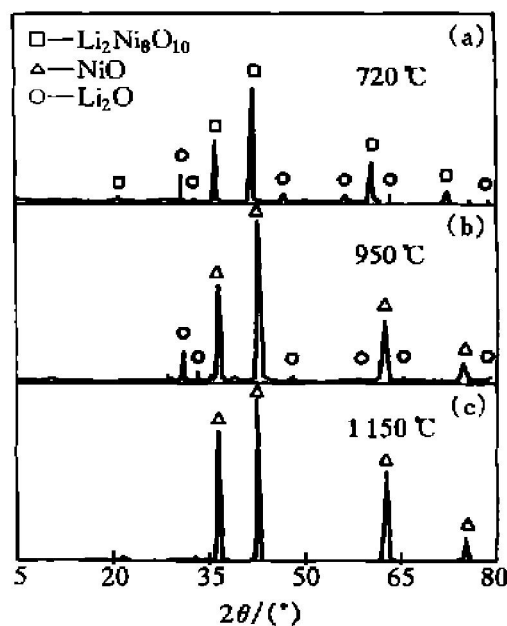
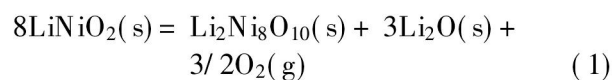
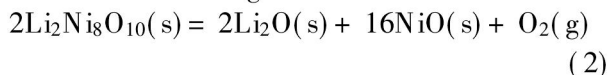


Fig. 5 XRD spectra of decomposed products of LiNiO_2 at different temperatures



In succession, $\text{Li}_2\text{Ni}_8\text{O}_{10}$ decomposed further into $\text{Li}_2\text{O}(\text{s})$, NiO , and O_2 as Eqn. (2) within 850~950 °C at the second stage:



At the third stage, the decomposed product — solid Li_2O volatilized as Eqn. (3) within 1000~1150 °C and the only remainder was NiO .



The decomposing process of LiNiO_2 could interpret why sometimes $\text{Li}_2\text{Ni}_8\text{O}_{10}$ instead of desired LiNiO_2 was obtained during the preparation. Products from different raw materials and preparing processes varied greatly in composition, microstructure and property. So the synthesis temperature should be chosen carefully to gain pure LiNiO_2 .

3.3 Decomposing kinetics of LiNiO_2

By means of Doyle-Ozawa method and Kissinger method, the reactive activation energy and reaction order were calculated according to DTA measurements at the heating rates of 5, 10, 15, 20, 30 °C·min⁻¹. And the formula of Doyle-Ozawa method^[5~8] is as

$$\lg \Phi_1 + 0.4567E/RT_1 = \lg \Phi_2 + 0.4567E/RT_2 = \dots = \text{Constant} \quad (4)$$

where E is reactive activation energy, Φ is heating rate. At a certain degree of reaction (abbreviated as α in Table 4), the relationship of $\lg \Phi_i$ to $1/T$ is linear and the slope of the line is minus $0.4567E/R$. The reactive activation energy E and the relation coefficient r of $\lg \Phi_i \sim 1/T$ line at different degrees of reaction are listed in Table 4.

Hence the apparent activation energies of the three endothermic peaks are obtained as 746.10 kJ·mol⁻¹, 937.90 kJ·mol⁻¹ and 1131.50 kJ·mol⁻¹ separately, by averaging the values in each E column.

The basic formula of Kissinger method^[9] is given as

$$\ln(\Phi/T_m^2) = (-E/R) d(1/T_m) \quad (5)$$

where T_m is the maximum temperature of a peak. The relationship between $\ln(\Phi/T_m^2)$ and $1/T_m$ is also linear, and the line slope is $-E/R$.

According to Kissinger method, the reaction order can be calculated by

$$n = 1.26I^{1/2} \quad (6)$$

The computing method of peak shape factor I is the same as reported in Ref. [10]. The maximum temperature of a peak T_m , reaction order n and apparent activation energy E_a of each peak are listed in Table 5, according to DTA curves of different heating rates. The frequency factor A is gained by

$$(E_a\Phi)/(RT_m^2) = A n \exp(-E_a/RT_m) \cdot (1-\alpha) m^{n-1} \quad (7)$$

It is concluded from Table 4 and Table 5 that the advantage of using Doyle-Ozawa method is that the reactive activation energy in different reaction degrees can be obtained. But the values of the apparent activation energies calculated by these two methods are very close to each other correspondingly. So the apparent activation energies of the three reactions are determined as 747.18 ± 1.0 kJ·mol⁻¹, 932.46 ± 1.0 kJ·mol⁻¹ and 1126.97 ± 1.0 kJ·mol⁻¹, which are averages of each two corresponding values obtained by the two methods. From Table 5, three

Table 4 Reactive activation energy (E) and relation coefficient (r) of each endothermic peak in various degrees of reaction

Degree of reaction, α	First peak		Second peak		Third peak	
	$E/(\text{kJ}\cdot\text{mol}^{-1})$	r	$E/(\text{kJ}\cdot\text{mol}^{-1})$	r	$E/(\text{kJ}\cdot\text{mol}^{-1})$	r
0.1	928.0	-0.999	1121.0	-0.998	1281.0	-0.998
0.2	926.0	-0.997	1120.0	-0.998	1278.0	-0.997
0.3	750.0	-0.997	930.0	-0.997	1130.0	-0.999
0.4	750.0	-0.998	930.0	-0.999	1128.0	-0.998
0.5	724.0	-0.996	914.0	-0.997	1110.0	-0.996
0.6	723.0	-0.996	913.0	-0.996	1108.0	-0.997
0.7	685.0	-0.995	887.0	-0.995	1085.0	-0.998
0.8	685.0	-0.997	885.0	-0.997	1083.0	-0.996
0.9	650.0	-0.996	847.0	-0.997	1062.0	-0.997
1.0	640.0	-0.996	832.0	-0.996	1050.0	-0.997

Table 5 Apparent activation energy E_a , reaction order n and frequency factor A of each peak

Endothermic peak	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$	r	n	A
First peak	748.26	- 0.998	1.057	1.736×10^{39}
Second peak	927.01	- 0.997	0.844	1.806×10^{39}
Third peak	1 122.40	- 0.996	1.275	4.262×10^{42}

reaction rate equations are also deduced as^[11, 12]

$$\frac{d\alpha}{dt} = 1.736 \times 10^{39} \exp(-90000/T) \cdot (1-\alpha)^{1.057} \quad (8)$$

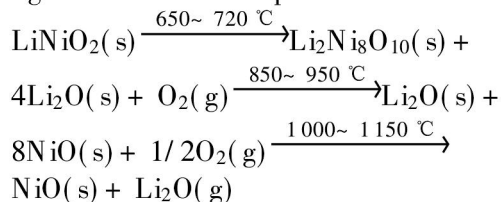
$$\frac{d\alpha}{dt} = 1.806 \times 10^{39} \exp(-111500/T) \cdot (1-\alpha)^{0.844} \quad (9)$$

$$\frac{d\alpha}{dt} = 4.262 \times 10^{42} \exp(-135000/T) \cdot (1-\alpha)^{1.275} \quad (10)$$

4 CONCLUSIONS

1) LiOH·H₂O and β-Ni(OH)₂ were chosen as proper raw materials to synthesize LiNiO₂. The reversible discharging capacity of LiNiO₂ prepared in the research could achieve a maximum 168 mAh·g⁻¹. XRD and SEM measurements show that a pure and layered LiNiO₂ with high crystallinity can be synthesized under the appropriate conditions.

2) The thermal decomposition of LiNiO₂ in the flowing air follows the steps as



So, the synthesis of LiNiO₂ should be controlled at appropriate temperature. Otherwise it is difficult to obtain pure LiNiO₂.

3) The apparent activation energies of the above three reactions are calculated to be $747.18 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$, $932.46 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ and $1126.97 \pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ by Doyle-Ozawa method and Kissinger method. The reaction rate equations are deduced as

$$\frac{d\alpha}{dt} = 1.736 \times 10^{39} \exp(-90000/T) \cdot (1-\alpha)^{1.057}$$

$$\frac{d\alpha}{dt} = 1.806 \times 10^{39} \exp(-111500/T) \cdot (1-\alpha)^{0.844}$$

$$\frac{d\alpha}{dt} = 4.262 \times 10^{42} \exp(-135000/T) \cdot$$

$$(1-\alpha)^{1.275}$$

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