

## Fabrication of High Power $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Battery Cathodes by Nanostructuring

### Supporting information

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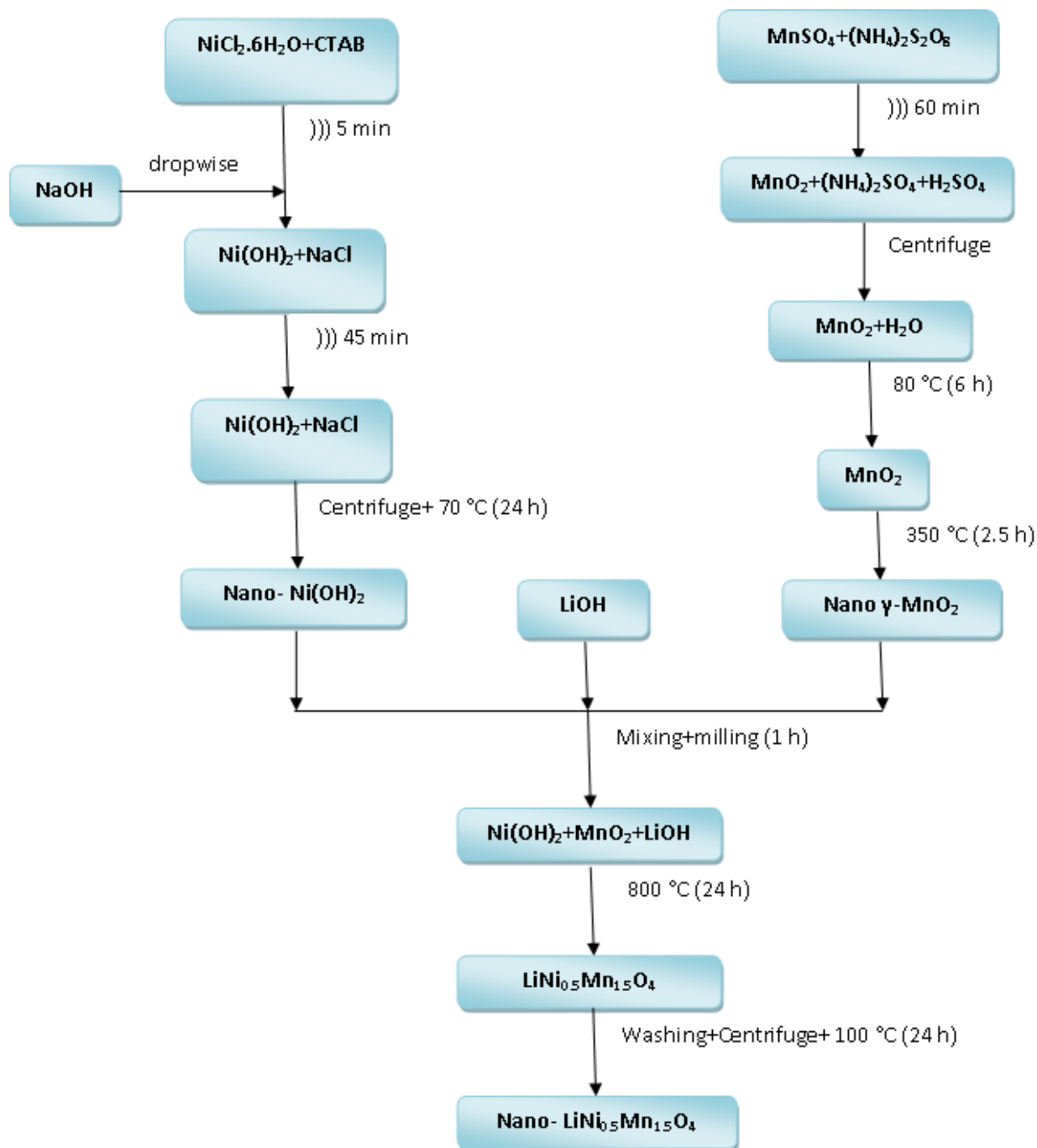
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### Supporting Introduction:

In the  $P4_332$  phase,  $\text{Ni}^{2+}$  ions take the 4b sites and  $\text{Mn}^{4+}$  ions take the 12d sites. On the other hand, in the  $Fd3m$  phase, both  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions take the 32e sites randomly. At low

temperature an ordered structure, with the  $P4_332$  (no oxygen deficiency) space group, and at high temperature a disordered structure with the  $Fd3m$  (weak oxygen deficiency) space group is formed [1]. Several comparative studies have been carried out on these two structures [1-5]. There are conflicting reports about these structures. Some researchers have shown that the  $Fd3m$  space group showed better electrochemical behaviors [1, 3, 6-9] and others have mentioned that the  $P4_332$  structure has better electrochemical behavior as the cathode in Li batteries [2, 10-12]. The disordered LNMO has a special electrochemical behavior; the oxygen deficiency leads to the presence of manganese in the Mn(III) oxidation state, which can be oxidized to Mn(IV) at around 4 V [6], thus reducing the specific energy and inducing the distortion of the spinel structure. Furthermore, in disordered LNMO, impurities such as NiO and  $Li_xNi_yO$  are generally observed. On the other hand, disordered LNMO shows higher electronic conductivity than the ordered stoichiometric phase due to the presence of the  $Mn^{3+/4+}$  redox couple and Ni/Mn disordering. Therefore, the preparation of the high energy ordered LNMO structure that also has high specific power (high rate capability) is a big challenge in this research area.

## Supporting Scheme:



**Scheme S1.** Schematic representation of the preparation of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

## Supporting Table:

**Table S1.** Rct ( $\Omega\cdot\text{cm}^2$ ) Fitted Values From EIS for Nano-Particles of LNMO at Different Applied Voltages (vs Li/Li<sup>+</sup>)

Voltage (V)	4.3	4.4	4.5	4.6	4.7	4.8	4.9	5.0
Rct ( $\Omega\text{ cm}^2$ )	35	30	27	21	7	11	14	19

**Table S2.** Comparison of different methods for the synthesis of LNMO as cathode materials.

	Synthesis method	Space group	Specific capacity (mAh g <sup>-1</sup> )	Voltage window (V)	Ref.
1	Solid state reaction	<i>P4<sub>3</sub>32</i>	134 (20 C)	3.0-5.0	[2]
2	Sol-gel	<i>P4<sub>3</sub>32</i>	100 (0.2 mAcm <sup>-2</sup> )	3.6-5.0	[17]
3	Solid state reaction	<i>P4<sub>3</sub>32</i>	98 (0.2 mAcm <sup>-2</sup> )	3.6-5.0	[17]
4	Molten salt	<i>Fd3m</i>	138 (0.15 C)	3.5-5.0	[46]
5	Molten salt	<i>P4<sub>3</sub>32</i>	140 (0.15 C)	3.5-5.0	[46]
6	Ultrasonic spray pyrolysis	<i>Fd3m</i>	230 (0.1 C)	2.0-5.0	[63]
7	Ultrasonic spray pyrolysis	<i>P4<sub>3</sub>32</i>	240 (0.1 C)	2.0-5.0	[63]
8	Solid state reaction	<i>Fd3m</i>	120 (0.2 C)	3.5-4.9	[64]
9	Solid state reaction	<i>P4<sub>3</sub>32</i>	90 (0.2C)	3.5-4.9	[64]
10	Resorcinol-formaldehyde assisted	<i>Fd3m</i>	118 (20 C)	3.5-5.0	[52]
11	Resorcinol-formaldehyde assisted	<i>P4<sub>3</sub>32</i>	80 (20 C)	3.5-5.0	[52]
12	Polymer-Assisted Synthesis	-	98 (15 C)	3.5-5.0	[18]
13	Ethylene glycol-assisted	<i>Fd3m</i>	117 (5 C)	3.5-4.9	[21]
14	Sucrose-aided combustion	-	40 (10 C)	3.4-5.2	[22]
15	Spray drying	<i>P4<sub>3</sub>32</i>	134 (0.15 C)	3.0-4.9	[41]
16	Flame synthesis	<i>Fd3m</i>	92 (14.9 mA g <sup>-1</sup> )	3.5-4.9	[47]
17	Solid state reaction	<i>P4<sub>3</sub>32</i>	40 (20 C)	3.5-5.0	[65]
18	Ultrasonic-assisted sol-gel	<i>Fd3m</i>	99 (15 C)	3.5-5.0	[66]
19	Sonochemical assisted	<i>P4<sub>3</sub>32</i>	100 (20 C)	4.5-5.0	<b>This Work</b>

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