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Synthesis of high capacity cathodes for lithium-ion batteries by morphology-tailored hydroxide co-precipitation



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HIGHLIGHTS

- A continuously stirred tank reactor was used to synthesize the precursor.
- Ammonia content has a significant effect on both the primary particle size and morphology of agglomerates.
- Li- and Mn- rich composite cathode materials synthesized based on these hydroxide precursors have a better tolerance to lithium.

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ABSTRACT

Nickel manganese hydroxide co-precipitation inside a continuous stirred tank reactor was studied with sodium hydroxide and ammonium hydroxide as the precipitation agents. The ammonium hydroxide concentration had an effect on the primary and secondary particle evolution. The two-step precipitation mechanism proposed earlier was experimentally confirmed. In cell tests, Li- and Mn-rich composite cathode materials based on the hydroxide precursors demonstrated good electrochemical performance in terms of cycle life over a wide range of lithium content.

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1. Introduction

As one of the most promising cathode materials with high energy density, Li- and Mn-rich composites have been investigated for over 10 years. [1,2] However, this material suffers from the drawback that a tradeoff is needed between rate performance and volumetric energy density.

The routine procedure for the synthesis of the composite cathode material involves two steps [3–12]: precursors are synthesized through co-precipitation reactions, then the precursors are

lithiated through high-temperature solid state reactions. Previous studies suggested that the properties of the Li- and Mn-rich cathode materials are greatly affected by the precursor, specifically, the composition, [2,6,13–16] particle morphology, [10,17,18] and size distributions. [19] Tailoring the precursor morphology is one effective way to tune the material to be a high power or high energy cathode.

Carbonate and hydroxide co-precipitations are the most popular methods to prepare the cathode precursors. Carbonate co-precipitations have the merits of facile morphology control and environmental friendliness. [10] However, before the steady state of the continuous reaction is reached, the particle usually becomes so large that the synthesized cathode cannot deliver decent rate capacity. [20] What is more, void layers between the adjacent rings in the onion-like particle morphology render the cathode materials too fragile to achieve high electrode density.

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Hydroxide co-precipitation does not have the limitations mentioned above; however, it is much more complex than the carbonate process, especially when a high manganese content composition is involved, for the following reasons. First, hydroxide precipitation can result in different structures. For example, both $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ can be α phase, β phase, or β_{bc} phase, which highly depends on the synthesis conditions. [21–24] The most reliable phase for the synthesis of Li- and Mn-rich cathode materials is β phase because its structure is impurity and defect free. Second, Mn_3O_4 always coexists with manganese hydroxide during the various stages of cathode synthesis (e.g., co-precipitation, precursor washing, lithiation). This is because in $\text{Mn}(\text{OH})_2$, Mn^{2+} can easily oxidize to Mn^{3+} and then becomes segregated in the form of mixed hydroxides. [10,25] Third, hydroxide primary particles tend to adopt lamellar or needle-like morphology, which poses a challenge in preparing densely packed secondary particles [26–28].

In this research, we studied the co-precipitation reaction with sodium and ammonium hydroxide for the formation of Li- and Mn-rich cathode materials, in particular, the effect of ammonia concentration on the growth of the primary and secondary particles. Although ammonia is widely used in precipitation reactions to (1) maintain a relatively stable pH, (2) achieve homogeneous distribution for different metal ions by chelating effect, [10,27,29–31] our study is the first systematic investigation to highlight its function as precursor morphology tailor by tuning (1) primary particle morphology (2) the packing behavior of the primary particles to form loosely or densely packed secondary particle. Coin cell tests of cathodes fabricated by the hydroxide co-precipitation demonstrated reasonable electrochemical performance.

2. Experiments

Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), sodium hydroxide (NaOH), and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as the starting materials to synthesize $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor in a continuously stirred tank reactor (CSTR). The feed rate of the transition metal solution was fixed at 16 ml min^{-1} , while the pumping rate of the base solution (mixture of NaOH and $\text{NH}_3 \cdot \text{H}_2\text{O}$) was controlled by a pH controller. The precipitation reaction was conducted at a constant temperature (60°C) and a fixed stirring speed (1000 rpm). An N_2 cover gas was introduced into the CSTR to prevent Mn^{2+} oxidation. The precursor materials were collected for 2 h after 8 h precipitation reaction. Longer reaction time may lead to better particle morphology and tap density, but determining the optimized reaction conditions is beyond the scope of this study.

The collected samples were washed with de-ionized water several times to remove residual sodium and sulfur species, then filtered and dried inside a vacuum oven set at 100°C for 24 h. Finally, Li- and Mn-rich cathode materials, $\text{Li}_x\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5+\delta}$ ($1.54 \leq x \leq 1.71$), were prepared through a solid state reaction between appropriate amounts of $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ and Li_2CO_3 at 900°C for 14 h.

The morphology and particle size distribution of the precursor and cathode materials were characterized with a cold field emission scanning electron microscope (SEM, Hitachi S-4700-II) and particle size analyzer (Cilas1090), respectively. Tap density of the precursor was measured with Autotap from Quantachrome. The crystal structures of the precursor and cathode materials were determined by powder X-ray diffraction (XRD) with a D5000 Siemens X-ray diffractometer, using a $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The samples were scanned from $2\theta = 5^\circ$ to 80° at a rate of $0.1^\circ/20 \text{ s}$. The chemical compositions were determined with inductively coupled plasma-mass spectroscopy (ICP-MS, Agilent Technologies 7700 series).

Electrochemical characterizations were conducted in CR2032 coin-type cells. Cathodes were composed of synthesized Li- and Mn-rich cathode materials (80 wt%), acetylene black (10 wt%), and polyvinylidene difluoride binder (10 wt%). A slurry of this mixture was coated onto an aluminum foil and dried at 85°C . The lithium cells were assembled inside a helium-filled glove box with lithium metal as the counter anode, Celgard 2325 membrane as the separator, and 1.2 M LiPF_6 dissolved in ethylene carbonate and ethyl methyl carbonate (3:7 volume ratio) as the electrolyte. The cells were tested with a 2.0–4.6 V voltage window and a C/3 discharge current. (In our calculations, the 1C rate is assumed to be equal to 200 mA g^{-1})

3. Results and discussion

Table 1 lists the experimental parameters used to synthesize $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursors. The only variation was the base solution composition. To explore the ammonia effect on the precipitation process, the molar ratio between sodium hydroxide and ammonium hydroxide (M_S/M_A) was gradually increased from 2:3 (experiment #1) to 4:1 (experiment #6). The tap densities of the dried precursors were also measured and are listed in Table 1. Most of the precursors have relatively low tap density ($<0.84 \text{ g cm}^{-3}$), except for that from experiment #2 (1.5 g cm^{-3}).

The tap density of the powder material is a reflection of the secondary particle size distribution and the primary particle packing within secondary particles. We found that ammonia concentration has a direct impact on both of the secondary particle growth rate and the primary particle packing. Evolutions of D50 particle size for four M_S/M_A ratios are compared in Fig. 1. Neither the low M_S/M_A ratio (2:3, red (in the web version) line in Fig. 1) nor the high M_S/M_A ratio (4:1, black line in Fig. 1) benefits the secondary particle growth. After 10 h reaction, the D50 values were still under $10 \mu\text{m}$ for these two ratios. At $M_S/M_A = 3:2$ (olive line in Fig. 1), D50 values increased with reaction time and stabilized between 10 and $11 \mu\text{m}$ after 5 h. Decrease of M_S/M_A to 1:1 significantly boosted the initial growth rate (blue (in the web version) line in Fig. 1): D50 quickly reached $23 \mu\text{m}$ from the initial $8 \mu\text{m}$ in the first 4 h, with an average growth rate of $4.28 \mu\text{m h}^{-1}$, after which, D50 rapidly shrunk to $9 \mu\text{m}$ and became stabilized at this size. One hypothesis is that when the agglomerates approach a critical size, the shear stress exerted on the agglomerates by the hydrodynamic motion becomes larger than the cohesive force among primary particles, and then the agglomerates break down to smaller fragments, resulting in smaller D50. Different stirring rates and agglomerate population densities within the reactor could affect the agglomeration growth rate significantly, which is beyond the purpose of this study and will be discussed in separate papers.

The above hypothesis is supported by Fig. 2, which shows the particle size distributions of hydroxide precursors collected for six M_S/M_A ratios. Most of the histogram curves have maxima at $0.3 \mu\text{m}$, $2 \mu\text{m}$, and $10 \mu\text{m}$, which correspond to -crystal nuclei, agglomerate fragments, and agglomerates, respectively. The peak intensity at

Table 1
Experimental conditions for the $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ co-precipitation reactions.

Experiment	T (°C)	Metal sulfate (M)	Control pH	RPM	NaOH/NH ₃ ·H ₂ O	Tap density (g cm ⁻³)
#1	60	2	11	1000	2:3	0.74
#2	60	2	11	1000	1:1	1.5
#3	60	2	11	1000	3:2	0.80
#4	60	2	11	1000	2	0.84
#5	60	2	11	1000	5:2	0.73
#6	60	2	11	1000	4:1	0.54

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