Ultrasonic-assisted co-precipitation to synthesize lithium-rich cathode $\text{Li}_{1.3}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_{2+d}$ materials for lithium-ion batteries

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Abstract

Lithium-rich, composite-layered, transition metal oxides have been intensively investigated recently. However, poor rate capability has severely hindered the commercial development of these materials. We produce nanoscale hydroxide precursors for these cathodes using ultrasonic-assisted co-precipitation. The ultrasonic irradiation of a liquid leads to the generation of a cavitation phenomenon comprised of unique reaction fields, which assists in the synthesis of nanoparticle materials. This is confirmed by scanning and transmission electron microscopy. X-ray diffraction and Rietveld refinement results indicate that the ultrasonic-assisted $\text{Li}_{1.3}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_{2+d}$ material has a larger lithium slab space. Electrochemical studies indicate that the ultrasonic-assisted material exhibits a higher initial discharge capacity (251.2 mAh g^{-1} at 0.1 C) and better cycling performance (200.4 mAh g^{-1} after 50 cycles) compared with the material synthesized using traditional co-precipitation. Surprisingly, the ultrasonic-assisted material has a stable capacity of 140 mAh g^{-1} at 5 C and 115 mAh g^{-1} at 10 C after 50 cycles. First-principles calculations are used to confirm that the specific lattice structure leads to a faster lithium-ion mobility speed.

Keywords: Lithium-ion battery; Cathode material; Ultrasonic-assisted co-precipitation; Rate capability

1 Introduction

Lithium-ion batteries are and will remain one of the most important energy storage devices. Cathodes are important for high-energy density and better rate capability. As promising cathode materials, layered Li-rich transition metal oxides have been extensively investigated recently¹⁻⁴. However, these materials have modest capacity when discharged at a high rate. Good cathode materials must have a high reversible storage capacity and undergo rapid solid-state Li^+ transport. Therefore, materials with very fast Li^+ diffusivity are needed to produce batteries capable of satisfying high power demands.

Reducing the particle size to the nanoscale level is considered an effective way to improve the rate capability because of a shortening of the Li^+ diffusion pathway and an increase in the electrolyte contact area^{5, 6}. Additionally, lattice parameters are known to be an important factor in Li^+ mobility in these layered structures^{7, 8}. Therefore, modifying the morphology and controlling the lattice parameters of a material is a reasonable strategy towards improving the rate capability of a battery.

Ultrasonic techniques have been extensively used to synthesize nanostructured materials^{9, 10}. Under ultrasonic conditions, micrometer-sized bubbles form and expand during the rarefaction phase and collapse during the compression phase. This process leads to a dramatic increase in temperature and pressure¹¹. The generated cavitation phenomenon, which comprises a unique reaction environment, has been used to synthesize nanoscale materials.

The layered structure of Li-rich transition metal oxides, shown in Fig. 1, consists of layers of transition metal cations that are separated from the Li layers by oxygen. As Li^+ moves along a two-dimensional layer between the Li slab, the spacing of the oxygen layers around the Li layer is critical for Li^+ motion. Li^+ diffusion in the oxide is an important factor that determines the rate

capability at which a battery can be charged and discharged.

In this paper, we discuss the morphological and crystallographic differences between $\text{Li}_{1.3}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_{2+d}$ materials synthesized by ultrasonic-assisted co-precipitation (UC) and traditional co-precipitation (TC). The homogeneous nanoscale particles synthesized by UC have a relatively large external surface area and a long c -lattice parameter, which can dramatically improve the rate capability of batteries.

In parallel with experimental studies, density functional theory (DFT) calculations were performed to determine the Li^+ hopping barrier (activation barrier). The activation barrier is defined as the difference in energy at the activated state and the energy at the initial equilibrium state of the hop. The activated state is located at the maximum energy point along the minimum energy path between the end points of the hop¹². The impact of the a (or b)-lattice parameters on the activation barrier is considerably smaller than that of the c -lattice parameter¹³. The Li^+ activation barrier of both materials was calculated to determine the rate capability of the materials.

2 Experimental

2.1 Material preparation

The $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor materials were synthesized by traditional co-precipitation and by ultrasonic-assisted co-precipitation. 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 starting materials to prepare the precursor. These materials were mixed in a water-jacketed, ultrasonic-assisted, continuous stirring tank reactor (UACSTR), as shown in Fig. 2. A 2 M transition metal solution with a Ni/Mn atomic ratio of 1/3 was pumped into the reactor at a speed of 0.5 L/h under N_2 atmosphere. At the same time, a 2 M NaOH solution and a desired amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution

were fed into the tank reactor to control the pH to 11. The reaction temperature was maintained at 60 °C and the agitation speed of the mixture in the reactor was kept at 1000 rpm. To synthesize the ultrasonic-assisted $\text{Ni}_{0.25}\text{Mn}_{0.75}(\text{OH})_2$ precursor, an ultrasonic horn was attached to the tank. The precursor materials were collected from the bottom outlet after the reaction time of 8-10 hours and washed with deionized water to remove residual sodium and sulfur species. They were then filtered and dried in a vacuum oven set at 80 °C overnight. Finally, the different precursor materials were mixed thoroughly with Li_2CO_3 and calcined at 600 °C for 6 h and then at 900 °C for 10 h in air to obtain the traditional co-precipitation and the ultrasonic-assisted co-precipitation $\text{Li}_{1.3}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_{2+d}$ materials (labeled TC-LNMO and UC-LNMO, respectively)

2.2 Material characterization

X-ray diffraction (XRD Rigaku Ultima IV-185) was used to identify the crystalline phase of the prepared materials. Diffraction patterns were recorded using Cu K α radiation (40 mA, 40 kV) over a 2 θ range of 10–80° at a rate of 0.6° min⁻¹. The collected XRD intensity data were analyzed by Rietveld refinement using Fullprof 2011. Scanning electron microscopy (SEM; FEI QUANTA 6000) and transmission electron microscopy (TEM; JEM 2010, 200 kV) were used to perform morphological studies. The BET surface area was determined using ASAP 2020 by measuring the rate of gas adsorption upon exposure to the materials, and the materials were dehydrated at 250 °C for 3 h and then cooled to room temperature. Aqua regia (HNO_3/HCl ratio:1/3) was used to digest the powder material into solution, and then the lithium and transition metal content of the materials were determined by inductively coupled plasma optical emission spectrometry (ICP-OES Varian 715-ES).

2.3 Electrochemical measurements and calculations

The synthesized cathode materials were mixed with acetylene black and a polyvinylidene

difluoride binder at a weight ratio of 80:10:10 and coated onto aluminum foil. Coin cells (type CR2025) were assembled within an argon-filled glove box and we used $\text{Li}_{1.3}\text{Ni}_{0.21}\text{Mn}_{0.64}\text{O}_{2+\text{d}}$ as the cathode, lithium metal as a counter electrode, and a Cellgard 2400 membrane as a separator. The electrolyte was LiPF_6 (1 M) dissolved in ethylene carbonate and dimethyl carbonate (1:1 by volume). Galvanostatic charge–discharge tests were all performed under constant current conditions using Land CT 2001A battery testers. The cells were evaluated from 2.0–4.8 V for the first cycle and then from 2.0–4.6 V in subsequent cycles at a constant current density of 0.1 C (20 mA g⁻¹) at room temperature to determine the cycling performance of the materials. Various rates (0.2, 1.0, 2.0, 5, and 10 C) were used to investigate the rate capability of the prepared materials. The potentials reported in this paper are relative to the Li / Li⁺ couple.

First-principles calculations were performed using the Materials Studio software as implemented in the CESTEP package (Accelrys, Inc.), which is based on DFT. The core electrons are represented by ultra-soft pseudopotentials¹⁴, and the Perdew–Wang (PW91) density functional was used for the exchange correlation¹⁵. Spin-polarized GGA+U approximations were used with U values of 5 eV and 5.96 eV for Mn ions and Ni ions, respectively¹⁶. The cutoff energy for the plane wave and density were set at 500 eV. A 3×3×1 Monkhorst-Pack k-points grid with a Gaussian smearing of 0.1 eV was used in a 2×2×1 superlattice.

3 Results and discussion

3.1 XRD structure characterization

Figure 3 shows the XRD pattern and the Rietveld refinement results for both UC-LNMO and TC-LNMO, and the refined crystallographic data are listed in Table 1. The most prominent reflections in the diffraction pattern are indexed as the α -NaFeO₂ structure and $R\bar{3}m$ symmetry. The crystal

structure models of both materials were refined using the high-symmetry $R\bar{3}m$ space group rather than the low-symmetry $C2/m$ space group. The superlattice reflections region from 20.5° to 22° was excluded, which corresponds to Li^+ , Ni^{2+} , and Mn^{4+} ordering in the transition metal layer, which is in agreement with other reports^{17, 18}. Low R values indicate satisfactory refinement. The lattice parameters of UC-LNMO were calculated to be $c=14.2662$ (13) Å, $a=2.8617$ (2) Å with $R_p=8.38$, $R_{wp}=13.8$, and $R_{exp}=4.79$. The refinement results show that the c -lattice parameter of UC-LNMO is larger than that of TC-LNMO by 0.03 Å, which indicates a wider Li slab spacing for the UC-LNMO material.

3.2. ICP and BET surface area analysis

The atomic ratio Li: Ni: Mn for both materials was 1.3: 0.21: 0.64, which indicates that both materials have approximately the same molar ratio of Li and transition metal ions, and the amount of different elements is consistent with the stoichiometric ratio.

The BET surface area test was used to determine the surface area of the materials by measuring the rate of gas adsorption upon exposure to the materials of interest. Because of the acoustic cavitation effect, the UC-LNMO material is homogenous and contains relatively small particles, as shown in the latter material's SEM and TEM analyses. A comparison of the surface area of TC-LNMO ($2.974\text{ m}^2\text{ g}^{-1}$) with that of UC-LNMO ($4.396\text{ m}^2\text{ g}^{-1}$) reveals that the latter is 48% larger. Therefore, the Li^+ transport distance through the UC-LNMO material particles is shorter and the electrolyte contact area is larger, which enables a higher intercalation/deintercalation rate and hence higher power.

3.3. SEM and TEM morphological analyses

Differences in the morphology and particle size between the two materials are evident, as shown in the SEM and TEM images in Figs. 4 and 5. The images in Fig. 4 (a) and (b) indicate that the TC-LNMO particles are secondary particles composed of primary nanoplates. The nanoscale primary

plates agglomerate with each other to form approximately 10- μ m spherical particles. The electrolyte likely penetrates the pores between the plates and enters the agglomerates. In contrast, the UC-LNMO particles shown in Fig. 4 (c) and (d) are homogenous rice-like nanoparticles of 100–300 nm in size. The agglomeration phenomenon is less obvious in the UC-LNMO particles. From the TEM images in Fig. 5, we can confirm that the primary particles of both materials are nanoscale in size. The TC-LNMO materials are secondary particles that consist of nanoplate pieces while the UC-LNMO materials are well dispersed primary nanoparticles. Electrolyte wettability was more effective because of the decrease in dimension, which is expected to enhance the rate performance of the material. The SEM and TEM images of both materials agree well with the BET surface area results. This suggests that the strong shock waves that are generated during ultrasonic cavitation affect the particle size¹⁹. However, the specific mechanism of ultrasonic waves on the formation of particles in these materials still needs investigation.

3.4. First-principles calculations

The migration of Li^+ in the crystal lattice can follow two different pathways²⁰, and these are labeled Path (a) and Path (b) in Fig. 6. From first-principles calculations, the activation barriers of the two migration paths decrease as the *c*-lattice parameter increases, which is in good agreement with Kang's study²¹. The length of the *c*-lattice parameter impacts the Li motion barrier because the Li slab distance changes as the *c*-lattice parameter changes. Because transition metal (Ni, Mn)-O bonding is much stiffer than Li-O bonding, most of the change in the *c*-lattice parameter is accommodated by the Li slab distance¹³. The calculated activation barrier for Li^+ migration in both pathways in the UC-LNMO and TC-LNMO materials is shown in Table 2. Apparently, the activation barrier for the UC-LNMO material is smaller than that of the TC-LNMO material by 288.5 meV and 3.05 meV for

the two mobility pathways, respectively, which means that the UC-LNMO material has higher Li^+ diffusivity.

3.5. Electrochemical performance

The electrochemical performance of the UC-LNMO and TC-LNMO electrodes were evaluated from 2.0–4.8 V at 0.1 C for the first cycle and then from 2.0–4.6 V in subsequent cycles at different constant current densities. Figure 7 (a) shows the first charge and discharge profiles of the UC-LNMO and TC-LNMO electrodes at 0.1 C in a voltage window of 2–4.8 V. The discharge capacities of the UC-LNMO and TC-LNMO electrodes are 251 mAh g^{-1} and 235.6 mAh g^{-1} , respectively. Both electrodes exhibit a sloping region followed by a long 4.5 V plateau during the first charge process. The initial capacity at less than 4.4 V is due to the oxidation of Ni^{2+} to Ni^{4+} , and the capacity observed in the plateau region between 4.4 and 4.8 V comes from the activation of Li_2MnO_3 , which is in agreement with previous reports²²⁻²⁴. The cycling performance of both electrodes at 0.1 C is shown in Fig. 7 (b). The cells were initially cycled between 2 and 4.8 V for 1 cycle at 0.1 C to activate the Li_2MnO_3 component, and then cycled from 2 to 4.6 V in subsequent cycles. The UC-LNMO electrode gave a reversible capacity of 200.4 mAh g^{-1} after 50 cycles, which is higher than the TC-LNMO electrode with 180 mAh g^{-1} . Over the initial 10 cycles, the discharge capacities of both electrodes remained almost the same while the capacity of the TC-LNMO electrode decreased significantly in subsequent cycles. Almost 100% Coulombic efficiency was maintained for both electrodes over 50 cycles.

Figure 8 compares the charge and discharge profiles at 0.1 C for the 1st, 2nd, 10th, 20th, 30th, 40th, and 50th cycles of the TC-LNMO and UC-LNMO electrodes. All the curves have the sloping feature of layered oxide cathode materials as well as a voltage depression region upon an increase in cycle number²⁵. To investigate the capacity fade mechanism and voltage depression, differential

capacity vs. voltage plots of both electrodes at various cycle numbers are shown in Fig. 9. After the initial electrochemical activation of the Li_2MnO_3 component at higher than 4.5 V, a reversible redox reaction at about 3.2 V for both electrodes occurs and this becomes apparent in subsequent cycles. Additionally, the redox peak at 3.2 V for the UC-LNMO electrode is more evident than that of the TC-LNMO electrode in the corresponding cycle, indicating that a higher discharge capacity was delivered by the UC-LNMO electrode. The redox peaks of the layered component at about 3.75 V weakened slowly meaning that the layered structure of both materials transformed into a spinel component upon cycling, resulting in a gradual decrease in voltage and capacity²⁶. Recent studies found that modifications or heterogeneous distribution in the composition could suppress the voltage fade to some extent^{27,28}.

The rate performance of the UC-LNMO and TC-LNMO electrodes is shown in Figs. 10 and 11. After activation at 0.1 C in the first cycle, both the electrodes were cycled between 2 and 4.6 V at 0.1 C, 0.2 C, 1 C, 2 C, and 5 C and back to 0.1 C for five cycles, and the results are shown in Fig. 10. As the current density increases the discharge capacity gradually decreases for both electrodes. The effect of current density on the discharge capacity of both electrodes is not significant at 0.1 C and 0.2 C. On the contrary, with an increase in current density the UC-LNMO electrode delivers an apparent higher capacity (144.8 mAh g^{-1} at 5 C) than the TC-LNMO electrode (110.2 mAh g^{-1} at 5 C). To demonstrate the rate capability of the UC-LNMO electrode, the cycling performance of the UC-LNMO electrode at various high rates (1 C, 2 C, 5 C, and 10 C) over 50 cycles were evaluated and the results are shown in Fig. 11. All the cells were cycled between 2.0 and 4.6 V with the same charge and discharge current densities from 1 C to 10 C after activation at 0.1 C in the first cycle. The results show that the UC-LNMO electrode has good stability under all the current densities tested. At 1 C, the electrode

delivers a capacity of 166.3 mAh g⁻¹ after 50 cycles. Discharge capacities as high as 140 mAh g⁻¹ at 5 C and 115 mAh g⁻¹ at 10 C were obtained after 50 cycles with high capacity retention and almost no capacity fading, and this can be attributed to the nanoscale size of the particles and the larger lithium layer distance in the lattice structure, as discussed above.

4 Conclusions

A cathode precursor Ni_{0.25}Mn_{0.75}(OH)₂ was synthesized by traditional co-precipitation and by ultrasonic-assisted co-precipitation. After calcination with Li₂CO₃, lithium-rich layered Li_{1.3}Ni_{0.21}Mn_{0.64}O_{2+d} materials were obtained. From SEM and TEM results, the ultrasonic method produced nanoscale particles with homogenous morphology. XRD and the Rietveld refinement results indicate that the Li_{1.3}Ni_{0.21}Mn_{0.64}O_{2+d} material obtained by ultrasonic-assisted co-precipitation has a larger lithium slab width than that obtained by traditional co-precipitation. First-principles calculations confirmed that the larger lithium slab width contributes to smaller activation barriers, which means a higher Li⁺ diffusivity for the ultrasonic-assisted co-precipitation material. The cycling performance of both materials showed that the ultrasonic-assisted material has a higher initial discharge capacity (251.2 mAh g⁻¹ at 0.1 C) and better cycling performance (200.4 mAh g⁻¹ after 50 cycles) compared with the material synthesized by traditional co-precipitation (235.6 mAh g⁻¹ at 0.1 C, 180 mAh g⁻¹ after 50 cycles). The rate performance of both materials showed that the ultrasonic-assisted co-precipitation material can deliver capacities as high as 140 mAh g⁻¹ at 5 C and 115 mAh g⁻¹ at 10 C after 50 cycles with high capacity retention. The surprising rate capability comes from the nanoscale morphology and the larger lithium layer distance of the lattice structure, which is attributed to the acoustic cavitation effect of ultrasonic waves.

Acknowledgements

The experimental work of this study was supported by the National Science Foundation of China (NSFC 51302014), Beijing Nova Program (Z121103002512029), Beijing Excellent Talents Plan funding and the New Century Educational Talents Plan of the Chinese Education Ministry (NCET-12-0050). This work was also supported by the U.S. Department of Energy under Contract DE-AC0206CH11357 with the main support provided by the Vehicle Technologies Office, Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE). The authors especially thank US-China Electric Vehicle and Battery Technology between Argonne National Laboratory and Beijing Institute of Technology.

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Figures and Tables

Fig. 1. The layered structure consists of layers of transition metal cations separated from the Li layers by oxygen.

Fig. 2. Schematic drawing of the UACSTR system and the ultrasonic cavitation phenomenon.

Fig. 3. (a) XRD and (b) Rietveld refinement patterns for the UC-LNMO and TC-LNMO materials.

Fig. 4. SEM images of the TC-LNMO (a and b) and UC-LNMO (c and d) materials.

Fig. 5. TEM images of the UC-LNMO (a) and TC-LNMO (b) materials.

Fig. 6. The two lithium migration pathways in the layered LNMO.

(Blue balls represent lithium ions, red balls are oxygen ions, and white balls represent lithium vacancies.)

Fig. 7. (a) First charge/discharge curves and (b) cycling performance of the UC-LNMO

and TC-LNMO materials at 0.1 C.

Fig. 8. Charge/discharge profiles at 0.1 C for the 1st, 2nd, 10th, 20th, 30th, 40th, and 50th cycles of the UC-LNMO and TC-LNMO materials.

Fig. 9. Differential capacity vs. voltage of the UC-LNMO and TC-LNMO materials cycled at 0.1 C.

Fig. 10. Rate performance of the TC-LNMO and UC-LNMO materials at 0.1 C, 0.2 C, 1 C, 2 C, and 5 C and back to 0.1 C in sequence for each of the five cycles.

Fig. 11. Cycling stability of the UC-LNMO material at different current densities.

Table 1 Crystallographic parameters for the UC-LNMO and TC-LNMO materials.

Sample	Crystallographic Parameters				
	a (Å)	c (Å)	R_p	R_{wp}	R_{exp}
UC-LNMO	2.8617(2)	14.2662(13)	8.38	13.8	4.79
TC-LNMO	2.8559(1)	14.2349(8)	6.38	8.29	4.85

Table 2 Calculated activation barriers for Li migration in the different pathways for the UC-LNMO and TC-LNMO materials.

Sample	Activation barriers (meV)	
	Path (a)	Path (b)
UC-LNMO	694.41	176.697
TC-LNMO	982.93	179.75