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Capacity Enhancement of the Quenched Li-Ni-Mn-Co Oxide High-voltage Li-ion Battery Positive Electrode

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Publication Details
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Abstract
Li-rich metal oxides, regarded as a high-voltage composite cathode, is currently one of the hottest positive electrode material for lithium-ion batteries, due to its high-capacity and high-energy performance. The crystallography, phase composition and morphology can be altered by synthesis parameters, which can influence drastically the capacity and cycling performance. In this work, we demonstrate Li1.207Ni0.127Mn0.54Co0.127O2, obtained by a co-precipitation method, exhibits super-high specific capacity up to 298 mAh g−1 and excellent capacity retention of ~100% up to 50 cycles. Using neutron powder diffraction and transmission X-ray microscopy, we have found that the cooling-treatments applied after sintering during synthesis are crucially important in controlling the phase composition and morphology of the cathodes, thereby influencing the electrochemical performance. Unique spherical microstructure, larger lattice, and higher content of Li-rich monoclinic component can be achieved in the rapid quenching process, whereas severe particle cracking along with the smaller lattice and lower monoclinic component content is obtained when natural cooling of the furnace is applied. Combined with electrochemical impedance spectra, a plausible mechanism is described for the poorer specific capacity and cycling stability of the composite cathodes.

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Capacity Enhancement in Quenched Li-Ni-Mn-Co-Based High-voltage Oxide Cathode for Li-ion Batteries

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ABSTRACT: Li-rich layered metal oxide, as known as high-voltage layered composite cathode, is now the hottest positive electrode material for lithium-ion batteries, due to its high-capacity and high-energy performance. It is also known that the crystallography, phase composition, and morphology, which are alternated by synthesis parameters, of the Li-rich layered metal oxide play important roles in the capacity and cycling performance. In this work, we demonstrate a Li$_{1.207}$Ni$_{0.127}$Mn$_{0.54}$Co$_{0.127}$O$_2$, obtained by a co-precipitation method, exhibits a super-high specific capacity up to 298 mAh g$^{-1}$ and excellent capacity retention of ~100% up to 50 cycles. Using neutron powder diffraction and synchrotron transmission microscopy, we find that the cooling-treatments applied after sintering during synthesis are crucially important in controlling the phase composition and morphology of the cathodes, thereby influencing the electrochemical performance. Unique spherical microstructure, larger lattice, and higher content of Li-rich monoclinic component can be achieved in the rapid quenching process, whereas severe particle cracking along with the smaller lattice and lower monoclinic component content is obtained when natural cooling of the furnace is applied. Combined with electrochemical impedance spectra, a plausible mechanism is described for the poorer specific capacity and cycling stability of the composite cathodes.

KEYWORDS: Li-rich high voltage cathode, Quenching, Neutron diffraction, Transmission X-ray microscopy

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1. INTRODUCTION

Novel routes need to be discovered to address the challenge brought about by the advancement of technology and continuous depletion of resources for energy generation. Electrochemical energy storage devices have been studied widely to subdue energy scarcity. Research on energy storage systems, like supercapacitors and batteries, have been growing to accommodate themselves as the most convenient way of storage devices. In particular, Li-ion batteries (LIBs) have been found with the highest energy density among the classes of batteries. After its first commercial use by Sony in 1991, LIBs became the vital component in portable electronic devices, ranging from microelectronics to hybrid vehicles. In this context, LiCoO$_2$ has been widely used as the cathode in the commercial batteries, where the insufficient capacity performance, scarcity of Co, and its high cost cannot satisfy the existing and emerging technology and have stimulated the scientific attempts to develop varieties of novel cathode materials with higher capacity and energy density. For example, lithium nickel cobalt manganese oxides LiNi$_{1-x-y}$Co$_x$Mn$_y$O$_2$ ($0 \leq x \leq 0.5$, $0 \leq y \leq 0.3$) exhibited volumetric energy density higher than LiFePO$_4$ and LiMn$_2$O$_4$. (2.54–3.26 Wh cm$^{-3}$). Also the specific capacity obtained practically is in the range 140–180 mAh/g. Li-rich oxides represented as Li$_{1+y}$M$_{1-y}$O$_2$ ($M = $ Co, Mn, Ni), constituted of two-component zLi$_3$MnO$_3$ and (1-z) LiMO$_2$ ($M = $ Co, Mn, Ni), is capable of delivering specific capacity of >250 mAh g$^{-1}$ also can minimize the Co content.

Complexities of these Li-rich systems aren’t so well understood especially, the phase composition of the composite during electrochemical cycling is still under disputation. Each of the metal component of such Li-rich oxides are capable of influencing the performance of the electrode e.g. Ni being the main redox species though can enhance the reversible capacity, has detrimental effect on structural and thermal stabilities. Similarly, Mn can improve the interfacial
impedance and superior electrochemical and thermal performances are observed at an optimal ratio of Co:Mn, 1:2. During electrochemical process, including oxidation of Ni\(^{2+}\) and Co\(^{3+}\) to Ni\(^{4+}\) and Co\(^{4+}\), the Mn in Li\(_2\)MnO\(_3\) undergoes an oxygen evolution or activation process to contribute capacity upon charging in the first cycle,\(^5\)

\[
\text{Li}_2\text{MnO}_3 \rightarrow \text{MnO}_2 + 2\text{Li}^+ + 1/2\text{O}_2 \uparrow + 2\text{e}^- \quad (1)
\]

After activation, the structural transformation of the layered material to a spinel phase may induce capacity fading. Castel, et al. with the help of differential electrochemical mass spectrometry observed evolution of CO\(_2\) between 4.2 and 4.7 V indicating the start of the oxidative decomposition of the electrolyte.\(^6\) They also claim rate of CO\(_2\) reaccelerates once O\(_2\) evolves at 4.7 V and at 5.0 V rate of evolution of both CO\(_2\) and O\(_2\) reach their maxima. Armstrong et. al. have combined neutron powder diffraction which show that the loss of oxygen generally occur in the first cycle from the surface of the Li\(_2\)MnO\(_3\) followed by diffusion of metal ions existing on the surface to bulk and occupy vacancies created by Li removal.\(^7\) Since such gas evolution is an inherent property of such Li-rich systems, several operando techniques have been utilized to examine the effect of oxygen and CO\(_2\) on the electrochemical process.\(^8\)-\(^9\) The issues with oxygen stoichiometry has been addressed with a surface reconstruction mechanism that occur after the first cycle by Lin et. al.\(^10\) Hence understanding the effect of oxygen stoichiometry is very crucial for such Li-rich materials.

Since the electrochemical performance is affected by the oxygen stoichiometry and is affected by the cooling process during synthesis. In the current report, we present the effects of cooling rate on the phase composition, and morphology, as well as the electrochemical performance of Li\(_{1.207}\)Ni\(_{0.127}\)Mn\(_{0.54}\)Co\(_{0.127}\)O\(_2\) through comparing the samples, which were synthesized using the same experimental conditions but varying cooling rates. The improved electrochemical
performance in the quenched sample is observed and the enhancement mechanism is discussed in details.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of precursor. Co-precipitation method was used to synthesize Li-rich cathode material \( \text{Li}_{1.207}\text{Ni}_{0.127}\text{Mn}_{0.54}\text{Co}_{0.127}\text{O}_2 \). All the chemicals used are AR grade and were weighed according to the stoichiometric ratio. Briefly, Manganese sulfate \((\text{MnSO}_4 \cdot \text{H}_2\text{O})\) 0.172 mol (29.079 g), Nickel sulfate \((\text{NiSO}_4 \cdot 6\text{H}_2\text{O})\) 0.043 mol (11.303 g), and Cobalt sulfate \((\text{CoSO}_4 \cdot \text{H}_2\text{O})\) 0.043 mol (7.441 g) were placed in 100 mL of de-ionized water and dispersed in an ultrasonic vibration shaker. \( \text{Na}_2\text{CO}_3 \), 0.2581 mol (28.724 g), was dissolved in 300 mL of de-ionized water, 24 mL of aqueous ammonia, and diluted to 500 mL. A 500-mL DI water was heated to 50 °C (± 2 °C). \( \text{CO}_2 \) was introduced into the reaction vessel at a pH of 5.5. Diluted aqueous ammonia was added to adjust the pH to ~8. The aqueous solution of all the metal ions and \( \text{Na}_2\text{CO}_3 \) were added dropwise to the reaction vessel, maintaining the stirring speed of 500 rpm. A continuous flow of \( \text{CO}_2 \) was allowed to maintain the pH at ~7 to 7.5. The pH, temperature, and stirring were maintained for 24 hours. Finally, the mixture was filtered with suction and washed repeatedly with DI water. The product was dried at a vacuum at 70 °C to obtain the precursor for the cathode material. The X-ray diffraction (XRD) pattern of the precursor (Figure S1) showed very sharp peaks of the precursor, indicating the crystalline nature of the precursor material. The pattern has been indexed with the carbonates from Ni, Mn and Co. \( \text{Li}_{1.207}\text{Ni}_{0.127}\text{Mn}_{0.54}\text{Co}_{0.127}\text{O}_2 \) was obtained by mixing 443.38 mg of Li carbonate with 1046.16 mg of precursor powder using a mortar. The powder mixture was annealed at 900 °C for 12 hours at a heating rate of 5 °C/min. Two samples were obtained after sintering, one through quenching, that is, directly removing from the furnace at 900 °C to a Cu plate and the other through a natural cooling process, hereafter termed as LMNCOQ and LMNCONQ.

2.2. Assembling of cells. The electrode was coated using a slurry of active mass, polyvinylidene difluoride (PVDF) as binder, and Super P as conductive carbon in a ratio of 8:1:1. The slurry was coated on an Al foil and dried overnight at 70 °C. Electrodes of 12 mm
diameter were punched through the coated Al foil and used as cathodes with the Li foil as the anode and 1.0 M LiPF$_6$; EC/DMC = 1:1wt% as the electrolyte. The final battery was assembled using a 2032 coin-type coin cell, a Celgard separator in an Ar-filled glove box with a moisture level < 0.1 ppm.

3. CHARACTERIZATIONS

The as-synthesized powders was characterized using a Bruker D2 PHASER XRD with Cu Kα radiation ($\lambda = 1.54178$ Å) and data was recorded within the 2θ range from 15°–80° at a step size of 0.02 with 2-sec exposure. Moreover, high-resolution neutron powder diffraction (NPD) patterns were recorded using ECHIDNA at Open Pool Australian Light-water (OPAL) research reactor at the Australian Nuclear Science and Technology Organization (ANSTO). The neutron beam wavelengths were 1.6215(1) and 2.4393(2) Å, which were determined using the La$_{11}$B$_6$ NIST standard reference material (SRM) 660b. NPD data were obtained in the 2θ angular range from 2.75° to 163.95° with a step size of 0.125°. GSAS-II was employed to perform joint Rietveld analysis of the model with XRD and the two high-resolution ND data. The background coefficients, zero, peak shape parameters, lattice parameters, phase scale, and elemental composition were optimized. Scanning electron microscopy (SEM) images were collected from a JEOL JSM-6700F field-emission SEM to observe the morphologies of the electrode materials. Transmission X-ray microscopy (TXM) facility of BL01B1 beamline at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu City, Taiwan provides 2D micrograph and 3D tomography with spatial resolution of 50 nm at an X-ray energy of 8 keV. This TXM is equipped with Zernike phase contrast for the X-ray absorption lacking specimens. The field of view of the image is $15 \times 15$ mm$^2$. After acquiring series of 2D micrographs with the sample rotated stepwise azimuthally, the 3D tomography was reconstructed by applying a
filtered back-projection algorithm based on 151 sequential image frames taken with the azimuth angle rotating from -75° to +75° in this experiment. The final 3D tomography structures were generated using Amira 3D software to enhance the visualization.

Cyclic voltammograms were recorded at a scan rate of 0.1 mV/s at a potential window between 2-4.7V. Charge discharge cycles were recorded at 0.1C rate (1 C = 250 mA g⁻¹) within a potential window of 2-4.7V. Electrochemical impedance spectra (EIS) were recorded in the frequency range of 0.1 Hz to 1 MHz at an AC perturbation of 10 mV using CHI instruments model. The Impedance spectra were fitted using ZView program to get the equivalent circuit. The charge/discharge cycle test was conducted using the AcuTech Battery cycler.

4. RESULTS AND DISCUSSION

X-ray powder diffraction patterns of the LMNCOQ and LMNCONQ samples are alike with narrow and intense peaks, indicating both the samples are well crystalline (Figure 1 a & c). Both XRD profiles are consistent with α-NaFeO₂ structure and space group R̅3m (ICDD PDF # 00-056-0147). A clean-cut splitting in the 006/102 and 108/110 planes points out that both the quenched and unquenched samples have a high degree of ordered hexagonal layered structure.¹²⁻¹³ The collected XRD patterns of both LMNCOQ and LMNCONQ showed very weak peaks at 2θ values between 20°–35°, which were indexed by the C2/m space group again suggest the ordering of Li ions with transition metal ions in the transition metal layers and hence further indicated the presence of a second Li₂MnO₃ phase. Such weak peaks were also observed using in-situ X-ray measurement on the Li₁.₂Co₀.₁Mn₀.₅₅Ni₀.₁₅O₂ sample earlier.¹⁴ A general representation for such Li-rich oxides have been given in earlier reports e.g. xLi₂MnO₃.(1-x)LiMO₂.¹⁵ Transition metals, like Ni, Mn, and Co, were present in both the LMNCOQ and LMNCONQ samples with different oxidation states, and the migration of Li ion in the crystal
was greatly affected. Being of similar ionic radii Li$^+$ and Ni$^{2+}$, partial occupation of Li ion lattice sites by Ni$^{2+}$ blocks diffusion of Li ion pathway on a short-range scale.$^{16}$ As the detection of Li by X-rays is limited because of its low scattering factor, the high-resolution NPD of as-prepared samples were also collected and a joint structural refinement were carried out using two NPD ($\lambda$ = 1.6215(1) and 2.4393(2) Å) (Figure 1b & d and ESI figure 2) and one XRD (Cu Kα) patterns for each sample.

The phase fractions are summarized in table 1, showing rhombohedral phase ($R\overline{3}m$) is dominant in both the LMNCOQ and LMNCONQ samples with 73.5% and 77.5%, respectively, while the monoclinic phase ($C2/m$) is almost 1/3 of the whole composition at 26.5% and 22.5% for LMNCOQ and LMNCONQ, respectively. A closer view of the lattice parameters of both the quenched and unquenched samples showed slight variations in both the $R\overline{3}m$ and $C2/m$ phases. A high c/a value is preferred for well-defined hexagonal layered structures. In the case of LMNCOQ, the c/a ratio was 4.9986, which was higher than the LMNCONQ sample with a c/a ratio 4.9963. Hence, LMNCOQ has a more layered structure than the LMNCONQ sample. This observation further indicates the effect of fast cooling on the ordering of the crystal lattice.

The SEM images of both samples show marked difference in their morphologies (Figure 2). The LMNCOQ sample transformed into solid spheres, whereas the LMNCONQ sample broke into different shaped morphologies. This clearly suggests the effect of cooling rate on the morphologies of the samples. A closer view of the bulk of the spherical structure (inset) shows densely packed swallow trenches. The regular trenched pattern further suggests the high-crystallinity of both the samples. Furthermore void of LMNCOQ sample was uniform distributed, both at the inner and outer parts of the sphere, whereas the LMNCONQ sample showed radial pore-structure pattern, concentric circles pore-pattern and crack propagation in the
bulk of the sample. Such distinction in their microstructure can influence the electrode performance in the LIBs.

The statistical analysis conducted on the data obtained from the particle size analyzer is reported in table 2. Both samples show variations in their mean diameters and hence confirm the alteration caused by quenching and controlled cooling from high temperature further. The mean diameter of the LMNCOQ sample was ~19 μm, with a standard deviation of 8.5. The LMNCONQ sample was composed of spheres with a mean diameter of 23 μm and standard deviation of 7.1. The particle size analysis showed the shrinkage in the diameter of the sphere during quenching. Such volume contraction made the sphere denser than the unquenched one. As observed in the XRD, the Li-ion concentration in the transition metal plane in the quenched sample was enhanced, and the further contraction in size allowed the passage of Li-ion faster than the unquenched sample.

We have recorded the TXM images using soft X-ray band to prove the rigid spherical microstructure in the LMNCOQ sample compared to the LMNCONQ sample further (Figure 3). The exposure time of 2D imaging and 3D tomography for this experiment is 60 sec and 2.5 hour, respectively. Combining both the 2D and 3D TXM images, it shows that LMNCOQ sample composed of solid sphere with random pore distribution (dark part in 3a, c and Figure 3a SI). Nevertheless, LMNCONQ sample broke into pieces as shown in the Zernike phase contrast mode in figure 3b SI and 3D tomographic images in figure 3b and d. The images revealed streaks of the pore structures (bright parts except the outmost bright ring in (SI figure 3a). The pores emerge along the radial direction, several concentric-circles-pore pattern and some large pores in case of LMNCONQ sample. The full tomography of LMNCOQ and LMNCONQ were made into movies and presented in the supplemental information.
5. ELECTROCHEMICAL ANALYSIS

The electrochemical properties of the LMNCOQ and LMNCONQ were examined using cyclic voltammetry at a scan rate of 0.1 mV s\(^{-1}\) in a potential window of 2 V to 4.7 V. As reported earlier, the transition metal cations present in both the samples involved in the redox reactions were Ni\(^{2+}\) and Co\(^{3+}\) in the LiMO\(_2\), while Mn remained in its initial oxidation state of 4+. This observation was confirmed from the 1\(^{st}\) cycle of cathodic and anodic peaks centered at ~3.7 V and 4.1 V, respectively which resulted from the oxidation of Ni\(^{2+}\) and Co\(^{3+}\) to Ni\(^{4+}\) and Co\(^{4+}\), respectively. Profile of the voltammograms are in consistent with that of recorded by Whittingham et al. A peak > 3.5 V has been assigned to the phase transformation in the oxide Li\(_2\)MnO\(_3\) from layer to spinel-like nano-domain structure similar to that of Li\(_x\)Mn\(_y\)O\(_2\) phase. In the cathodic scan, the reduction of Ni\(^{4+}\) and Co\(^{4+}\) is evident from the peaks at ~2.75 V.\(^{17}\)

The specific capacities of the LMNCOQ and LMNCONQ electrodes were evaluated from the constant current charge/discharge measurements. Both the electrodes were subjected to lithiation/delithiation in a potential window of 2–4.7V at a current density of 0.1 C. Figure 5 shows that both the samples exhibited similar profiles in the 1\(^{st}\) charge cycle with an irreversible plateau near 4.5 V against the Li metal. This can be attributed to the loss of oxygen and simultaneous Li extraction. The specific capacities calculated from the 1\(^{st}\) cycle of charging were 332 and 318 mAh\(^{-1}\) for LMNCOQ and LMNCONQ, respectively. The discharge capacities of both electrodes in the 1\(^{st}\) cycle were evaluated as 298 and 232 mAh\(^{-1}\) for LMNCOQ and LMNCONQ, respectively. The excess capacity from the theoretical value can be caused by the Li\(^+\) extraction from Li\(_2\)O that formed during the cycle. The first-cycle coloumbic efficiencies were found to be 89% and 72% for the LMNCOQ and LMNCONQ samples, respectively.
Quenched LMNCOQ and unquenched LMNCONQ samples were tested at extended cycles to understand the effect of morphology on the long cycle test. The charge/discharge cycles were repeated for 50 cycles at 0.1 C rate. Figure 6a shows the specific capacity of the electrodes during 50 cycles. The LMNCOQ electrode exhibited the lowest specific capacity of 280 mAh g\(^{-1}\), while the LMNCONQ electrode decayed much faster at \(~204\) mAh g\(^{-1}\) during the 50 cycles. However the average capacity of the cell for the whole 50 cycles is found to be 295 mAh g\(^{-1}\) and 253 mAh g\(^{-1}\) for LMNCOQ and LMNCONQ. Decay in the specific capacity of both the samples can be attributed to the morphological and structural modifications achieved during the cooling process. As reported by Liu et al., NPD revealed with the help of operando that the ‘c’ parameter of the layered Li\(_2\)MNO\(_3\) phase expands during charging, while the ‘a’ parameter of the lattice decreases around 3.0 V. Irreversible oxygen evolution from the rhombohedral lattice occurred above 4.5 V (Li\(^+/\)Li).\(^{18}\) The operando examination further revealed that the two-phase reaction caused the decay in capacity. In the case of the LMNCONQ sample, the fast capacity fading can be addressed in the line of the two phase reactions and variation in lattice parameter.

The rate capability of both the quenched and unquenched electrodes were examined by cycling the electrodes at different current densities as shown in Figure 6b. The quenched LMNCOQ sample exhibits less variation upon carrying out the charge/discharge cycles at 0.1 C, 0.5 C, and 1 C each for the four cycles. Same electrodes were used for all the current densities. The LMNCONQ electrode showed continuous decay in the specific capacity with continuous cycles. The rapid decay at higher currents in the case of non-quenched samples can be ascribed from the enhanced catalytic activity of the sample. A schematic of the interaction between the electrolyte and the active transition metal ions is shown in Figure 7. The radial-pore pattern, concentric-circles-pore pattern and cracks which were formed during the natural cooling of the sample
enhanced the surface active sites and hence increased the reaction kinetics. These hierarchical structure with internal porous structure can increase the utilization of the cathode material and initiate new lithium storage space in the pores, leading to higher capacity. Homogeneously distributed pores in the quenched sample there by create a uniform centres for the Li ion active sites. Hy et al. used in-situ surface enhanced Raman spectroscopy where they observed surface reactions involving oxygen from the Li-rich cathode during electrochemical cycling. The Li$_2$O that formed on the cathode lead to the generation of H$_2$O together with LiOH and to the changes within the electrolyte, which eventually resulted in diminished performance.$^{19}$

The superior electrochemical performance of the LMNCOQ sample over the LMNCONQ was proven further from the electrochemical impedance spectra (EIS) (Figure 8). The spectra showed a depressed semicircle in the high frequency region, which accounted for the charge transfer process, and the linear part at the low frequency, which corresponded to the diffusion of Li-ions into the specimen. The raw data were simulated to obtain the desired equivalent circuit uncompensated electrolyte resistance ($R_s$), charge transfer resistance ($R_{ct}$), constant phase element (CPE), which counts the deviation from the ideal capacity element and the Warburg factor ($W_o$) which refer to the diffusion of ions at low frequencies using ZView program. The fitted parameters are listed in table 3. Though not much difference in the $R_s$ existed, the $R_{ct}$ showed significant variations in both the samples. The lower $R_{ct}$ in the case of the LMNCOQ sample indicated the easier passage of Li-ions through the grains of the crystallites. Higher $R_{ct}$ in case of unquenched sample can be correlated to the enormous grain boundaries present in it as shown in figure 9. In correlation with the TXM 3D images the diffusion of Li ions inside both the quenched and unquenched samples can be understood from the distribution of the pores within them. The lower $R_{ct}$ in quenched sample can be attributed to the uniform diffusion of Li
ions. The comparative analysis of the electrochemical performances between the quenched LMNCOQ and unquenched LMNCONQ electrodes showed that the LMNCOQ sample was more efficient than the LMNCONQ electrode. In addition to the high specific capacity, rate performance and cyclic stability were also enhanced when the material was quenched in air. This can be understood better with the detailed analysis of the structural, morphological stability, and Li-ion mobility in the crystal lattice. Previous report achieved the stabilization of such electrodes with multi-component transition metals by coating a thin layer of alumina or incorporating additives. However, we provided an approach to enhance the stability of electrodes without involving any external agents.

6. CONCLUSIONS

Li_{1.207}Ni_{0.127}Mn_{0.54}Co_{0.127}O_2, a unique spherical Li-rich material, was obtained via the coprecipitation method. The spheres were very regularly shaped with uniform pores when the reaction product was removed directly from high temperature, whereas exhibited radial-pore pattern, concentric-circles-pore pattern and cracked into pieces at natural cooling. This phenomenon motivated a new approach to understanding the variation in the composition of each of the samples. The rigid spherical materials showed excellent electrochemical capacities and capacity retention at higher currents than that of the slow-cooled sample. Impedance measurements further confirmed the superior conductivity, which may related to the volume contraction and Li-ion concentration in the fast-cooled sample. We believe our approach of obtaining highly uniform solid spheres can provide a method to synthesize dense electrode materials for high-power vehicles.

AUTHOR INFORMATION

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Anirudha Jena and Cho-Hsueh Lee have contributed equally.

Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

The supporting information is attached with the article contains XRD patterns of the precursor synthesized by co-precipitation method, the neutron patterns and the TXM images recorded in the Zernike phase contrast mode.

REFERENCES


ACS Appl. Mater. Interfaces xx, xx, xx


5. Koga, H.; Croguennec, L.; Ménétrier, M.; Mannessiez, P.; Weill, F.; Delmas, C.; Belin, S., Operando X-ray Absorption Study of the Redox Processes Involved upon Cycling of the Li-Rich Layered Oxide Li_{1.20}Mn_{0.54}Co_{0.13}Ni_{0.13}O_{2} in Li Ion Batteries. *J. Phys. Chem. C* **2014**, *118*, 5700-5709.


17. Bian, X.; Fu, Q.; Qiu, H.; Du, F.; Gao, Y.; Zhang, L.; Zou, B.; Chen, G.; Wei, Y., High-Performance Li(Li_{0.18}Ni_{0.15}Co_{0.15}Mn_{0.52})O_2@Li_4M_5O_{12} Heterostructured Cathode Material Coated with a Lithium Borate Oxide Glass Layer. Chem. Mater. 2015, 27, 5745-5754.


19. Hy, S.; Felix, F.; Rick, J.; Su, W.-N.; Hwang, B. J., Direct In situ Observation of Li_2O Evolution on Li-rich High-Capacity Cathode Material, Li[Ni_xLi_{(1-2x)/3}Mn_{(2-x)/3}]O_2 (0 ≤ x ≤ 0.5). J. Am. Chem. Soc. 2014, 136, 999–1007.

20. Wise, A. M.; Ban, C.; Weker, J. N.; Misra, S.; Cavanagh, A. S.; Wu, Z.; Li, Z.; Whittingham, M. S.; Xu, K.; George, S. M.; Toney, M. F., Effect of Al_2O_3 Coating on Stabilizing LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2 Cathodes. Chem. Mater. 2015, 27, 6146-6154.
Table Captions

Table 1. Fitted crystallographic parameters from refined XRDP and NPD

Table 2. Summarized particle size analysis

Table 3: Fitted parameters of LMNCOQ and LMNCONQ

Figure Captions

Figure 1: Rietveld-fit profiles using XRD and NPD data of the quenched and unquenched LMNCONQ.

Figure 2: SEM images of (a) LMNCOQ and (b) LMNCONQ (scale bar 1 μm)

Figure 3: TXM 3D Tomographic images of LMNCOQ and LMNCONQ (a) and (b), respectively. The internal dark parts of (c) and (d) show distribution of the pores within the Li-rich materials after heat treatment.

Figure 4: CV of (a) LMNCOQ and (b) LMNCONQ at a scan rate of 0.1 mV s⁻¹

Figure 5: Charge–discharge cycles of (a) LMNCOQ and (b) LMNCONQ at a rate of 0.1 C.

Figure 6: (a) Specific capacity of LMNCOQ and LMNCONQ recorded for 50 cycles at 0.1 C rate. (b) Rate capability of LMNCOQ and LMNCONQ samples at 0.1 C, 0.5 C, and 1 C.

Figure 7: Schematic of the interaction between the electrolyte and the samples.
Figure 8: Electrochemical impedance spectrum of LMNCOQ and LMNCONQ

Table 1.

<p>| Phases | Parameters | Samples | | | |
|---|---|---|---|---|
| R-3m | Li(Ni_{0.2}Co_{0.2}Mn_{0.6})O_2 | $a$ (Å) | 2.8521(1) | 2.8515(1) |
| | | $c$ (Å) | 14.2566(5) | 14.2472(5) |
| | | Weight fraction % | 73.5(5) | 77.5(5) |
| C2/m, Li_2MnO_3 | $a$ (Å) | 4.945(1) | 4.945(2) |
| | $b$ (Å) | 8.554(1) | 8.549(1) |
| | $c$ (Å) | 5.034(1) | 5.028(1) |
| | $\beta$ (°) | 109.35(1) | 109.37(2) |
| | Weight fraction % | 26.5(5) | 22.5(5) |</p>
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<th>Sample</th>
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<td>μm</td>
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<tr>
<td>LMNCOQ</td>
<td>19</td>
<td>8.5</td>
</tr>
<tr>
<td>LMNCONQ</td>
<td>22</td>
<td>7</td>
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Table 3.

<table>
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<th></th>
<th>Rs</th>
<th>Rct</th>
<th>Capacity</th>
</tr>
</thead>
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<tr>
<td>(Ohm)</td>
<td>(Ohm)</td>
<td>(mAh g(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>LMNCOQ</td>
<td>5</td>
<td>209</td>
<td>298</td>
</tr>
<tr>
<td>LMNCONQ</td>
<td>4</td>
<td>307</td>
<td>232</td>
</tr>
</tbody>
</table>
Figure 1:

(a) XRPD $R_{wp} = 6.23\%$

(b) XRPD $R_{wp} = 6.17\%$

(c) NPD ($\lambda = 1.62176(7) \, \text{Å}$) $R_{wp} = 5.18\%$

(d) NPD ($\lambda = 1.62176(7) \, \text{Å}$) $R_{wp} = 7.10\%$
Figure 2:
Figure 3:
Figure 4:
Figure 5:

(a) [Graph showing voltage vs. capacity with curves for 1st and 2nd iterations]

(b) [Graph showing voltage vs. capacity with curves for 1st and 2nd iterations]
Figure 6:

(a) Comparison of specific capacity (mAh/g) for LMNCOQ and LMNCONQ materials over a range of cycle numbers.

(b) Specific capacity (mAh/g) for different rates (0.1 C, 0.5 C, 1 C) over a range of cycle numbers for LMNCOQ and LMNCONQ materials.
Figure 7:
Figure 8: