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

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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+yNiCoMnO2 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. © 2017 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Novel routes to address challenges in the advancement of electrochemical energy storage technology have been currently a growing interest. In particular, Li-ion batteries (LIBs) exhibit the highest energy density among commercialized batteries [1]; these batteries are a vital component in portable energy for applications ranging from microelectronics to hybrid vehicles. LiCoO2 has been widely used as the positive electrode in first-generation commercial LIBs. However, limited capacity and scarcity of Co result in the inability to satisfy existing and emerging LIB applications. Stability of the charged electrode materials and urge for higher specific capacity are also serious concerns. Consequently, the research and development of novel positive electrode materials with high energy density have attracted interest. For example, lithium nickel cobalt manganese oxides (LiNi1–x–yCo1–yMn2O4, 0 < x < 0.5, 0 < y ≤ 0.3) exhibit volumetric energy densities higher than those of LiFePO4 and LiMn2O4 (2.54–3.26 Wh cm⁻³) with practical specific capacity in the range of 140–180 mAh g⁻¹ [2,3]. Li-rich oxides, such as Li1+yLi1/2MnO2 (M = Co, Mn, Ni); consist of two components, namely, zLi2MnO3 and (1-z)LiMO2 (M = Co, Mn, Ni); these oxides can deliver specific capacities (>250 mAh g⁻¹) and can be tailored to reduce Co content [4,5].

The complexities of the phase composition of these Li-rich systems, specifically during electrochemical cycling, are not well-understood. Each electrode phase can influence the battery performance. For example, Ni, the main redox species, can
enhance the reversible capacity, but it presents a detrimental effect on structural and thermal stabilities. Similarly, Mn can improve the interfacial impedance and deliver superior electrochemical and thermal performances at an optimal ratio of Co: Mn, that is, 1:2 [6]. During electrochemical processes, including the oxidation of Ni4+ and Co4+ to Ni4+ and Co4+, respectively, the Li2MnO3 component undergoes oxygen evolution or activation process to contribute capacity upon charging in the first cycle [7].

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

After activation, a structural transformation in some layered materials to a spinel phase may induce capacity fading. Castel et al. used differential electrochemical mass spectrometry and observed CO2 evolution between 4.2 V and 4.7 V; this gas evolution indicates the start of the oxidative decomposition of electrolyte [8]. Furthermore, the rate of CO2 generation accelerates with O2 evolution at 4.7 V. At 5.0 V, the rates of evolution of both CO2 and O2 reach their maxima. Armstrong et al. used neutron powder diffraction (NPD) to show that oxygen loss generally occurs in the first cycle from the surface of Li2MnO3; subsequently, the metal ions on the surface diffuse to the bulk and occupy the vacancies created by Li removal [9]. Gas evolution is an inherent property of such Li-rich systems; thus, several \textit{operando} techniques have been utilized to examine the effect of oxygen and CO2 on electrochemical processes [10,11]. Lin et al. [12] addressed the issues with oxygen stoichiometry via a surface reconstruction mechanism occurring after the first cycle. Hence, understanding the effect of oxygen stoichiometry on properties is considerably crucial for advancing such Li-rich materials. The oxygen stoichiometry in such Li-rich materials is affected by the cooling process during synthesis [13,14]. In the present study, we present the effects of cooling rate on the phase composition, morphology, and electrochemical performance of Li1.207Ni0.127Mn0.54Co0.127O2. The samples synthesized using the same experimental conditions but at different cooling rates are compared. Improved electrochemical performance is achieved via quenching. This work presents and discusses the electrode performance enhancement mechanism.

2. EXPERIMENTAL SECTION

2.1. Precursor Synthesis

Co-precipitation method was used to synthesize the Li-rich electrode material, that is, Li1.207Ni0.127Mn0.54Co0.127O2 [14]. Synthesis of materials using co-precipitation method has the unique advantage of large-scale production of high-quality samples. All chemicals used were AR grade and weighed according to the stoichiometric ratio. Briefly, manganese sulfate (0.172 mol, 29.079 g), nickel sulfate (0.043 mol, 11.303 g), and cobalt sulfate (0.043 mol, 7.441 g) were placed in 100 mL of deionized (DI) water and dispersed in an ultrasonic bath. Na2CO3 (0.2581 mol, 28.724 g) was dissolved in 300 mL of DI water and 24 mL of aqueous ammonia; the mixture was then diluted to 500 mL. Approximately 500 mL of DI water was heated to 50 °C (± 2 °C) in a separate beaker, and CO2 was introduced to maintain the pH of the solution at 5.5. Diluted aqueous ammonia was added to adjust the pH to ~8. The aqueous solution of all the metal ions and the Na2CO3 were added dropwise to the reaction vessel. The stirring speed was maintained at 500 rpm. A continuous flow of CO2 was allowed to maintain the pH from ~7 to 7.5. The pH, temperature and stirring were maintained for 24 h. Finally, the mixture was filtered with suction and washed repeatedly with DI water. The product was dried under vacuum at 70 °C to obtain the precursor for the electrode material. The X-ray diffraction (XRD) pattern of the precursor (Fig. S1) shows remarkably sharp peaks, indicating the crystallization of particles in micrometric dimension. Standard JCPDS patterns of the precursors are also given for comparison of the product obtained before the final step. Li1.207Ni0.127Mn0.54Co0.127O2 was obtained by mixing 443.38 mg of Li2CO3 with 1046.16 mg of precursor powder using a mortar. The powder mixture was annealed at 900 °C for 12 h at a heating rate of 5 °C/min in an alumina crucible. Two samples were obtained after the annealing duration: one sample was obtained through quenching, where the sample was directly removed from the furnace at 900 °C to a Cu plate, and the other one was obtained through natural cooling inside the furnace; these samples were termed hereafter as LMNCOQ and LMNCONQ, respectively. The current approach of obtaining high-quality materials can be subjected to large-scale synthesis hence minimising the total cost.

2.2. Cell Assembly

The electrode was made using the quenched and unquenched samples as active material, Poly-vinylidene fluoride (PVDF) as binder, and Super P as conductive carbon; their ratio was 8:1:1 with a few drops of N-methyl-pyrroldione. The slurry was coated on an Al foil to 100 μm and dried overnight at 80 °C under vacuum. Electrodes of 12 mm diameter were punched through the coated Al foil and used as positive electrodes. Li foil was used as the negative electrode, and 1.0 M Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate (1:1 wt %) was the electrolyte. The final battery was assembled into a 2032 coin-type coin cell with Celgard as separator in an Ar-filled glove box with a moisture level <0.1 ppm.

2.3. Physical Characterization

The as-synthesized powders were characterized using a Bruker D2 PHASER XRD with Cu Kα radiation (λ = 1.54178 Å) in the 2θ range of 15°–80° at a step size of 0.02° and exposure time of 2 s. High-resolution NPD patterns were recorded using ECHIDNA at the Open Pool Australian Light-water research reactor of the Australian Nuclear Science and Technology Organization (ANSTO) [15]. The neutron beam wavelengths used were 1.6215 (1) and 2.4393 (2) Å, which were determined using the LaB6, NIST standard reference material (SRM) 660b. NPD data were obtained in the 2θ angular range of $3°$–163.95° with a step size of 0.125°. GSAS-II was employed to perform joint Rietveld analysis against XRD and the two high-resolution NPD datasets. Scanning electron microscopy (SEM) images were collected using a JEOL JSM-6700F field-emission SEM. Transmission X-ray microscopy (TXM) was performed at BL01B1 beamline at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu City, Taiwan. The spatial resolution was 50 nm using 8 keV X-rays, and the field of view was $15 \times 15 \text{mm}^2$. After acquiring a series of 2D micrographs via azimuthal rotation of the sample, 3D tomographical images were constructed by applying a filtered back-projection algorithm based on 151 sequential image frames taken with azimuthal sample rotation from $–75°$ to $+75°$. Final 3D images were generated using the Amira 3D software. The exposure time of 2D and 3D data acquisition was 60 s and 2.5 h, respectively.

2.4. Electrochemical Characterization

Cyclic voltammograms (CV) were recorded at a scan rate of 0.1 mV s$^{-1}$ at a potential range of 2–4.7 V. Charge/discharge cycles were recorded at 0.1 C rate (1C = 250 mA g$^{-1}$). Electrochemical impedance spectra (EIS) were recorded in the frequency ranging from 0.1 Hz to 1 MHz at an AC perturbation of 10 mV (CHI Instruments). The impedance spectra were fitted using the ZView software.
program to obtain the equivalent circuit. Charge/discharge cycles were conducted using the AcuTech Battery cycler.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

The powder diffraction patterns of the LMNCOQ and LMNCONQ samples are similar to one another; their narrow and intense peaks indicate good crystallinity (Figs. 1 and 2). The patterns are in agreement with the main phase comprising of \( \alpha\)-NaFeO\(_2\)-type structure with space group symmetry \( R\overline{3}m \) (ICDD PDF # 00-056-0147). Splitting of the 006/102 and 108/110 reflections illustrates that both the quenched and unquenched samples possess a hexagonal layered structure [16,17]. The collected XRD patterns of both LMNCOQ and LMNCONQ show considerably weak peaks at 2\( \theta \) values ranging within 20°–35°, which are indexed by the \( C2/m \) space group consistent with the presence of a second Li\(_2\)MnO\(_3\) phase [18]. This two-phase composition is typical for \( x\)Li\(_2\)MnO\(_3\). (1-x)LiMnO\(_2\) [19]. The similar ionic radii of Li\(^+\) and Ni\(^{2+}\) result in partial occupation of the Li sites in the Li layer by Ni\(^{2+}\), which can block the diffusion pathway for Li [20]. As the detection of Li by X-rays is limited in this system, the structure of the samples was refined using data from both high-resolution NPD datasets (\( \lambda = 1.6215 \) (1) and 2.4393 (2) Å) and the XRD data (Cu Ka) (Figs. 1 and 2); the goodness of fit was 2.02 and 2.06 for LMNCOQ and LMNCONQ, respectively. The phase fractions obtained are summarized in Table 1. The detailed parameters are given in Tables SI–S4. These results show that rhombohedral phase (\( R\overline{3}m \)) is dominant in both the LMNCOQ and LMNCONQ samples, which contain \(~75\%\) and \(~76\%\) of this phase, respectively; the remaining part of the samples is monoclinic phase (\( C2/m \)) at \(~25\%\).

Fig. 1. Rietveld profiles using XRD and NPD data for LMNCOQ.

Fig. 2. Rietveld profiles using XRD and NPD data for LMNCONQ.
and 24%, respectively. A c/a lattice parameter aspect ratio close to 5 is preferred for well-defined hexagonal layered structures, and both samples LMNCOQ and LMNCONQ exhibit such ordered structure [21].

Both samples show similar mean diameters (Table 2). The mean diameter of the LMNCOQ sample is 19.0 (8.5) μm and that of LMNCONQ is 23.0 (7.1) μm. SEM images of both samples show marked differences in their morphologies (Fig. 3). The LMNCOQ sample (Fig. 3a) is spherical in contrast to the morphologically less uniform LMNCONQ sample (Fig. 3b). A close view of the bulk of the LMNCOQ spherical particles (inset) reveals densely packed shallow trenches with a uniform distribution of voids in both the inner and outer parts of the sphere. On the contrary, the LMNCONQ sample exhibits a radially fragmented pore structure consisting of concentric circles (Fig. 3), which are characteristic of crack propagation in the sample bulk. Such microstructural differences can influence electrode performance in LIBs.

Both 2D and 3D TEM data reveal that LMNCOQ sample consists of spheres with a random pore distribution (dark sections in Figs. 4 a, 4c, and S2a). The LMNCONQ sample consists of broken pieces (Figs. 4 b, 4d, and S2b), which reveal the pore structures (bright parts except for the outmost bright ring in Fig. S2) emerging radially in concentric circles and large pores. The microstructural characterizations reveal novelty of the synthesis process to get organized porous network within materials.

**3.2. Electrochemical Analysis.** The electrochemical properties of the LMNCOQ and LMNCONQ samples within coin cells were examined using CV at a scan rate of 0.1 mV s⁻¹ in the potential range of 2–4.7 V. As shown in Fig. 5, Ni²⁺ and Co³⁺ in the LiMn₂O₄ phase are both redox active, and Mn remains in its initial oxidation state of 4+ [22]. This observation is confirmed by the 1st cycle, in which cathodic and anodic peaks are centered at ~3.7 and 4.1 V, respectively. This result, which is consistent with that recorded by Whittingham et al., is also attributed to the oxidation of Ni²⁺ and Co³⁺ to Ni⁴⁺ and Co⁴⁺, respectively [23]. A peak >3.5 V is the phase transformation in the oxide Li₂MnO₃ from a layered structure to spinel-like nanodomain, which is similar to that of the Li₂Mn₃O₆ phase. In the cathodic scan, the reduction of Ni⁴⁺ and Co⁴⁺ is evident among peaks at ~2.75 V [24]. The performance of the electrode materials is very closely dependent on the thermal treatment given during their synthesis. A rise of polarization is in direct link to the rise in cell resistance [25]. Also, there may be the dissolution of transition metal ions at higher voltages which occupy the lattice sites.

The specific capacities of the LMNCOQ and LMNCONQ electrodes were evaluated from the constant current charge/discharge measurements. Both electrodes were subjected to lithiation/de-lithiation in the potential range of 2–4.7 V at a current density of 0.1 C. Fig. 6 shows that both samples exhibit similar profiles in the 1st charge cycle with an irreversible plateau near 4.5 V against the Li metal. This may be attributed to the loss of oxygen and simultaneous Li extraction. The specific capacities calculated from the 1st cycle of charging are 332 and 318 mAhg⁻¹ for LMNCOQ and LMNCONQ, respectively. The discharge capacities of both electrodes in the 1st cycle are 298 and 232 mAhg⁻¹ for LMNCOQ and LMNCONQ, respectively. The excess capacity from the theoretical value may result from the extraction of Li⁺ from the Li₂O phase formed [26]. The first-cycle coulombic efficiencies are 89% and 72% for the LMNCOQ and LMNCONQ samples, respectively. The low irreversibility and high capacity can be related to the structural stability of the quenched sample than that of the non-quenched sample. As reported earlier, [18] during initial charge step ~4.4 V, vacant Li sites created which is accompanied by the release of oxygen from the metal oxide layer on further charging. As described in the equation 1, one molar Li₂MnO₃ in the nanocomposite will produce two molar Li⁺ ions and one molar O₂ [27].

**Table 1**

<table>
<thead>
<tr>
<th>Phases</th>
<th>Parameters</th>
<th>Samples</th>
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<tr>
<td></td>
<td></td>
<td>LMNCOQ</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>mT</td>
<td>Li[Ni₀.₅Co₀.₅Mn₀.₅]O₂</td>
<td>a (Å)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c (Å)</td>
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<tr>
<td></td>
<td>Weight fraction %</td>
<td>75 (1)</td>
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| C2/m, Li₂MnO₃ | a (Å) | 4.944 (1) | 4.944 (1) |
| b (Å) | 8.555 (1) | 8.559 (1) |
| c (Å) | 5.034 (2) | 5.030 (1) |
| Weight fraction % | 109.36 (1) | 109.34 (1) |

**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean Diameter, μm</th>
<th>Standard Deviation, μm</th>
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<tbody>
<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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Fig. 3. Scanning electron microscopy images of (a) LMNCOQ and (b) LMNCONQ (scale bar, 1 μm).
Fig. 4. Transmission X-ray microscopic 3D tomography data of LMNCOQ and LMNCONQ (a) and (b), respectively. Internal dark sections of (c) and (d) show the pore distribution within the Li-rich materials after heat treatment.

Fig. 5. Cyclic Voltammogram curves of (a) LMNCOQ and (b) LMNCONQ at a scan rate of 0.1 mV s\(^{-1}\).
After the charge compensation, Li-ion reverts back during discharge ~3.5 V. Wang et al. have reported the irreversible capacity loss can be minimized by the synergistic effect of thin coating on the active electrode. Both Co$_3$O$_4$ and FePO$_4$ coated on Li$_2$MnO$_3$ reduces the irreversible capacity loss by hosting the de-intercalating Li-ions [27,28].

LMNCOQ and LMNCONQ were tested in coin cells over 50 cycles at 0.1C (Fig. 7a). The LMNCOQ electrode exhibits the lowest specific capacity of 280 mAh g$^{-1}$ within 50 cycles compared with that for the LMNCONQ electrode at ~144 mAh g$^{-1}$. Since the LMNCONQ sample shows drastic degradation after 50 cycles, the net cycle's number is limited to 50 cycles.

The rate capability of both the quenched and unquenched electrodes was examined by cycling coin cells containing the electrodes at different current densities (Fig. 7b). The quenched LMNCOQ sample exhibits less capacity decline on cycling at the higher currents of 0.5C and 1C compared with the LMNCONQ electrode, which exhibits continuous decay. The rapid decay at high currents of non-quenched samples may be explained by the different morphologies; fragments and cracks formed during the natural cooling of the sample act as additional active surface areas that cause particle fracture and segregation after extended cycling (Fig. 8). This mechanism is supported by the work of Hy et al. who used in situ surface-enhanced Raman spectroscopy to observe the surface reactions of oxygen in the Li-rich material during electrochemical cycling; the formed Li$_2$O causes the generation of H$_2$O and LiOH, which results in decreased performance [29]. By contrast, the homogeneous distribution of pores in the quenched sample creates uniform paths for Li-ion access, thereby avoiding this segregation.

The superior electrochemical performance of the LMNCOQ sample over LMNCONQ is also shown in the EIS data (Fig. 9). The spectra show a depressed semicircle in the high-frequency region, which accounts for the charge-transfer processes. The linear part in the low-frequency region corresponds to the diffusion of Li ions. The raw data were simulated to obtain an equivalent circuit using electrolyte resistance ($R_e$), charge transfer resistance ($R_{ct}$), a constant phase element accounting for the deviation from the ideal capacity element, and the Warburg factor, which refers to the diffusion of ions at low frequencies. The fitted parameters are listed in Table 3. $R_e$ values show no considerable difference, whereas $R_{ct}$ shows significant variation between the samples. The low $R_{ct}$ in the
LMNCOQ sample indicates an easy passage of Li ions through the grains of the crystallites. A high $R_\text{ct}$ in the unquenched sample is correlated with the presence of a large number of grain boundaries. The 3D TXM data clearly show a pore distribution in the quenched sample that is favorable for the uniform diffusion of Li ions and consistent with a low $R_\text{ct}$. The quenched LMNCOQ sample shows a higher efficiency in electrochemical performances than that of unquenched LMNCONQ electrodes. Moreover, LMNCOQ sample exhibits higher specific capacity, rate performance, and cycle stability than LMNCONQ. As reported earlier, the Li-rich electrodes are stabilized with multicomponent transition metals by coating a thin layer of alumina or incorporating additives [30]. A controlled cooling process as reported by Kang et al. [13] can accommodate the capacity retention as the Li and transition metals redistribute during slow cooling, which results in the formation of monoclinic and cubic spinel phases. A fine control over the phase fraction by quench and slow cool can enable further improvements in the performance.

### 4. CONCLUSIONS

We have synthesized a composite positive electrode material $\text{Li}_{1.207}\text{Ni}_{0.127}\text{Mn}_{0.54}\text{Co}_{0.127}\text{O}_2$ via air quenching for Li-ion battery. This material exhibits a spherical morphology, in which particles are uniform in size and pore structure. This distinct morphology enhances electrochemical capacity and capacity retention at higher currents compared with the material prepared using the traditional slow-cooling approach. Our study reveals an easy diffusion of Li through the quenched sample. This type of morphology also prevents the formation of particle cracks during the natural cooling of the sample. Consequently, the subsequent particle segregation causing capacity decay after an extended cycling is avoided. Therefore, air quenching is a simple and effective method for producing this material with a morphology that is considerably favorable for enhanced electrochemical performance. Use of X-ray microscopic 3D imaging can effectively enhance the capability of understanding intriguing bulk pore structures.

**Conflict of interest**

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017.03.163.

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