Flame Aerosol Synthesis and Electrochemical Characterisation of Ni-rich Layered Cathode Materials for Li-ion Batteries

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Abstract

We report on the synthesis of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 (NCM811) Li-ion battery cathode materials using an aerosol of micron-size aqueous metal nitrate solution droplets delivered to non-premixed flames. The objective is to investigate the effect of Ni mole fraction and the aerosol preheating and flame synthesis temperatures on the particle properties and electrochemistry by comparing NCM811 with LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2 (NCM111). It is found that the solution composition strongly influences precursor precipitation and oxidation and the resultant particle morphology. NCM111 solutions form predominantly spherical particles from single droplets, whereas Ni-rich solutions form irregularly-shaped particles because the lower solubility of Ni nitrate and its high concentration causes rapid precipitation at the droplet surface and subsequent formation and collapse of shell-like structures in the flame. After annealing, NCM111 retains the secondary particle structure, but NCM811 forms irregular shapes with a broad size distribution of primary features because the higher decomposition temperature of NCM811 precursor solutions limits the oxidation and particle formation in the aerosol phase. It is also found that aerosol preheating and flame temperatures play critical roles in determining the electrochemical properties of the final annealed product. The best NCM811 cycling performance was achieved using higher aerosol preheating temperatures (450K) and lower synthesis temperatures (1350K). These conditions promote single-mode solid particle formation which increases the size of the primary particles and enhances the uniformity of the primary particle size distribution, thereby improving structural stability without using high synthesis temperatures that damage the ordering of the layered crystal structure.

Keywords Ni-rich cathode; Flame aerosol synthesis; Lithium-ion batteries; Layered materials; particle formation
1. Introduction

A promising cathode material for the next generation of Li-ion batteries is Ni-rich particles, e.g. LiNi$_{1-x}Co_xMn_yO$_2, where x+y<0.2, due to their higher specific capacity [1, 2]. More importantly, reduced use of cobalt is necessary because cobalt is expensive and derived from mines in countries like the Democratic Republic of the Congo at a reportedly very high human health risk [3]. The need for Ni-rich cathode materials is therefore growing, and growing especially quickly in order to also meet the increased demand for Li-ion battery technology in general [4]. In part this is driven by the supposed electrification of transport, especially light-duty passenger vehicles, to reduce CO$_2$ emissions and eliminate pollutants directly from the car exhaust. The form of electrification is much debated and will logically depend on the primary source of electricity generation in the specific country or region [5] as well as multiple economic factors. However, in highly populated areas, besides simply reducing primary use and downsizing passenger cars, various types of hybridisation or even full electrification will take place. This and other basic renewable energy storage needs motivate the scientific community and industry to produce performance Li-ion battery materials with a high energy density, including Ni-rich cathodes.

Currently most commercially-available LiNi$_{1-x}Co_xMn_yO$_2 (NCM) is produced using the co-precipitation method [6]. Starting solutions of metal sulphates plus NaOH and ammonia for pH control are pumped into a tank reactor. The resulting precipitates must be sequentially washed, dried, ground, mixed with a lithium precursor, and calcined. Advantages are the uniform secondary particle size and crystal purity. Disadvantages include the necessity for tightly controlled liquid mixing rates to achieve transition metal ion homogeneity, multi-step processing, long processing times of several days, and large volumes of ion-containing liquid wastes. Alternative synthesis methods for Li-ion battery cathode materials are needed.

Aerosol synthesis is one such alternative, which encompasses both methods targeting ultrafine nanoparticle formation from the gas phase, i.e. starting with metal precursors in the gas or liquid phase and delivering these to some high temperature or plasma environment; and processes normally targeting formation of larger micron-size particles from single precursor solution droplets, i.e. spray drying or pyrolysis in flames, diffusion dryers or hot-wall reactors. The benefits and drawbacks are highly dependent on the exact realisation of the process but as advantages we can list controllable particle morphology and size spanning the nanoscale to several microns; a reduced number of processing steps, especially for direct aerosol deposition processes e.g. Ref. [7]; tailored and reproducible chemical composition in each particle; and a relatively environmentally clean process, even when flames are used as the heat source. A further and often touted advantage of aerosol processes is that they are scalable, but there are limitations imposed by the process energy input for heating large gas volumes and/or high cost of precursors with appropriate thermochemical properties. An appraisal of some important factors in the context of scaling NCM production is provided in Ref. [8]. Nevertheless, the insights derived from lab-scale aerosol synthesis experiments are essential to understand the influence of chemistry and
heat and mass transfer phenomena on the final material properties, which where feasible then informs the design of larger pilot-scale and ultimately industrial processes.

In light of these promising features, aerosol processes have been widely used to produce electrode materials for Li-ion batteries. Examples of anode materials include synthesis of Si nanoparticles [9] and MnO$_2$-C nanocomposites [10, 11] in hot-wall reactors and Li$_4$Ti$_5$O$_{12}$ (LTO) nanoparticles in spray flames [7, 12, 13]. LTO is stable during cycling and therefore particles on the order 10’s nm provide excellent electrochemical performance by overcoming the ordinarily slow Li$^+$ migration by reducing the diffusion pathlength. Turning our attention to cathode materials, spinel LiMn$_2$O$_4$ and LiFe$_2$O$_4$ [12] and LiFePO$_4$-C composite [14, 15] nanoparticles have also been synthesised in spray flames. Similarly, LiFePO$_4$ has a good inherent stability but poor electronic conductivity and Li-ion diffusivity, and again the highly porous nanostructured materials characteristic of the gas-to-particle formation route are favourable. However, some cathode materials, in particular the Ni-rich materials at the focus of this study, are extremely reactive in the charged state [16] and so cathodes with a very large exposed surface area are in fact detrimental to performance. Instead, as outlined in the following paragraph, targeting the formation of micron-scale cathode particles from single droplets (the droplet-to-particle formation route) may be preferable.

Using such a process, examples of cathode materials that have been produced are spinel LiMn$_2$O$_4$ [17] and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ [18], Li-rich materials [19-21], LiCoPO$_4$-C composites [22] and layered LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ (hereafter referred to as NCM111) [8, 23-25], using precursor solutions which are atomised into droplets on the 1-10 µm scale and delivered to self-supporting flames or tube furnaces. Several observations can be made. First, metal (normally including lithium) nitrate, acetate or chloride precursors are dissolved in water, which overall is a much cheaper solution than using high-volatility metal alkoxides often employed in spray flames. Second, the flames or tubular furnaces serve essentially as a heat source which evaporates the solvent from the droplets and oxidises the precursors to form individual (secondary) micron-scale particles made up of smaller (primary) crystallites. The precursor concentration is normally maximised for efficiency, and then the droplet diameter controls the secondary particle size in a suitable size range (although there are exceptions: studies synthesizing LiCoO$_2$, e.g. Refs. [26, 27], seemingly generated fine nanoparticles via a gas-phase route; and larger 1-10 µm particles were produced using a slurry of micron-size particles sprayed into a flame-heated reactor [28]). Third, the as-prepared materials are almost always annealed in furnaces to achieve highly-crystalline materials free of impurity phases with suitable electrochemical performance. Even extended high temperature residence times >10 s in tube furnaces is not sufficient to form the final product, because of slow bulk diffusion in highly viscous droplets [29] and the long time required for crystal growth. Fourth, none of the cited studies have examined the role of the synthesis temperature on the electrochemical performance and instead focused on annealing conditions. Fifth and finally, to the best of our knowledge NCM811 has not been synthesised via an aerosol route before and thus the effect of increasing Ni concentration on the particle formation in high temperature aerosol processes is unknown.
To address the last two points, here we demonstrate the synthesis of NCM811 cathode materials using a liquid-fed aerosol route in a slot burner. The objectives are 1) to investigate the influence of increased Ni content and synthesis conditions on the particle formation mechanism and material properties of the as-prepared and annealed cathode materials, in comparison to NCM111; 2) to determine how the synthesis conditions can be tailored to improve the electrochemical performance of NCM811. Throughout, we focus on NCM811, and where appropriate results are compared to NCM111 prepared under the same synthesis conditions.

Section 2 details the experimental setup, synthesis conditions and characterisation methods. Section 3 first details the influence of Ni content and synthesis conditions on the morphology, crystallinity and composition of the cathode materials. Secondly we provide electrochemical data and link the synthesis conditions to the electrochemical performance of the NCM811 materials.

2. Experimental setup

2.1 Precursors, flame synthesis apparatus and annealing conditions
Precursors used consisted of metal nitrates (>97% purity, Sigma-Aldrich). Ni(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O and Mn(NO$_3$)$_2$·4H$_2$O were weighed in the required proportions (molar ratios of 1:1:1 for NCM111, 8:1:1 for NCM811) and dissolved in deionised water at a precursor concentration of 1 mol total transition metal nitrates / L solution. LiNO$_3$ was then added at a concentration of 1.05 mol Li nitrate / L solution, that is, 5% in excess of stoichiometry, to compensate for Li loss during synthesis and reduce Ni$^{2+}$/Li$^+$ mixing in the layered structure [6].

The experimental setup is shown in Fig. 1. The main elements are the atomiser, preheater, non-premixed slot burner and collection system. Liquid precursor solutions were added to a polymer vessel and positioned in a water bath containing the atomiser unit, consisting of an array of ultrasonic transducers operating at 1.7 MHz. Ultrasound provides the driving force for atomisation of the precursor inside the vessel, generating a fine aerosol with a number-based mean diameter of 3.5 µm [30]. A flow of carrier gas comprising air enriched with oxygen transported the solution droplets at a rate of approximately 1 g droplets min$^{-1}$ to the preheating section, consisting of a 20 mm (inside diameter) stainless steel pipe maintained at a constant temperature (±10 K) using an external wrap heater. Following a warm-up period of 25 minutes, the aerosol was introduced into the reactor. The preheat temperatures stated in Table 1 are the gas temperatures at the exit of the preheating section and before the burner, as measured using a type K thermocouple.
The slot burner itself consists of a 45 mm wide steel housing surrounding four 6 mm slots through which the aerosol stream passes, five 1.5 mm slots for the fuel mixture (CH₄/N₂), and two 6 mm coflow slots (each fed with air at 1 SLPM) as shown in the top view of Fig. 1. All flows were metered using mass flow controllers, calibrated to within 1% accuracy. Three synthesis conditions were chosen according to the objective of understanding their effect on the particle formation, and these aerosol preheat and flame synthesis temperatures are indicated in Table 1. The flame synthesis temperature was adjusted using the fuel flowrate, and was estimated by calculating the adiabatic flame temperature of the mixed gases only. This estimate does not include the effects of droplet evaporation (assuming instead that all the water is evaporated in the flame, i.e. the limiting case of no preheating, results in a calculated reduction in the Table 1 flame temperatures of approximately 100 K), chemical conversion of the precursors, and radiative heat loss. Oxygen was added to the aerosol stream such that the total aerosol flow was fixed at 12.5 SLPM and the O₂/CH₄ ratio was a constant value of 4.3. Based on the flowrates and flame conditions the total residence time in the aerosol system varies between 0.8 and 1 s.
Table 1  Particle synthesis conditions

| Condition # | Aerosol preheat temperature, K | Flame synthesis temperature, K |
|-------------|---------------------------------|-------------------------------|
| 1           | 350                             | 1350                          |
| 2           | 350                             | 2250                          |
| 3           | 450                             | 1350                          |

The exhaust was housed in a 180 mm diameter quartz tube and particles were collected 320 mm downstream on glass fiber filters (Whatman GF/F, 90 mm diameter) assisted using a vacuum pump. The filter temperature was 450 K, measured for condition #1. The typical yield of these experiments was approximately 5 g hour⁻¹, with typical run times of 15-45 minutes. The as-prepared powders were promptly annealed in ceramic crucibles in a tube furnace at 1023 K for 18 hours under a constant flow of 0.25 SLPM of oxygen.

2.2 Material characterisation

As-prepared and annealed powders were imaged using a scanning electron microscope (SEM) (Verios 460, FEI). Where applicable, mean particle sizes were evaluated from over 100 particles and are given to the nearest 0.1 µm. The relative element ratios of Ni, Co and Mn in the annealed material was checked using an energy dispersive X-ray spectroscopy (EDXS) system (Oxford Instruments, with Aztec analysis software) coupled to the electron microscope. An X-ray photoelectron spectrometer (XPS) (K-Alpha, ThermoFisher) was used to determine the chemical composition of the surface of the materials. The uncertainty of the element composition was conservatively estimated as ±3%. The crystallinity of the annealed particles was probed using X-ray diffraction (XRD) (D8 Advance, Bruker) using a Cu Kα source. Backgrounds were fitted through the raw data and subtracted. The signal-to-noise ratio is in the range 50-100, as evaluated from the baseline noise relative to the diffraction peak intensity. Peak ratios of the 003 and 014 crystal planes and the full-width half-maximum (FWHM) values are provided with an uncertainty determined from repeat measurements of ±0.06 and ±0.02 respectively. A thermogravimetric analyser (TGA) (TGA-8000, PerkinElmer) was used to study the thermal decomposition of the precursor solutions. Solutions were heated at a rate of 25 K min⁻¹ in the range 300-1250 K using a sample flow of air at 30 ml min⁻¹. No fluctuations in the traces were visible and repeat runs with fresh solutions produced near-identical results.
2.3 Electrochemical characterisation

Cathodes were prepared by blending the active material (90%wt), conductive carbon (3%) and PVDF binder (7%), mixing with N-methyl-2-pyrrolidone solvent, and stirring for at least 4 hours. The resulting slurry was cast onto aluminium foil and dried in a vacuum oven. Cathodes were used as coated, with an active mass loading of ~6.5 mg cm$^{-2}$. Half-cells were assembled using an Li counterelectrode and a 15.5 µm membrane separator (Celgard) in a 2032 coin cell configuration with an electrolyte solution consisting of 1.2 M LiPF$_6$ in a 1:1:1 ethylene/dimethyl/diethyl carbonate solution.

To determine the charge/discharge characteristics of the cathode materials, the assembled cells were cycled between cutoff voltages of 2.8 and either 4.25 V or 4.3 V for NCM111 and NCM811 cells respectively. Cycling rates were constant at 80 mA g$^{-1}$ and 100 mA g$^{-1}$ for NCM111 and NCM811 respectively, using 0.1C (first cycle, taper cutoff C/50), 0.2C (second cycle) and 0.5C thereafter (C/20 taper cutoff). The repeatability of the derived electrochemical data was determined from the variation between two to six coin cells assembled for every synthesis condition, including cells fabricated from each of four batches of NCM811 powders synthesised in separate repeat experiments for synthesis condition #1. The average cell-to-cell variation in the first cycle efficiency, initial discharge capacity and discharge capacity after 25 cycles are ±1.8%, ±3.3% and ±5.2% respectively. To reduce this uncertainty, unless otherwise noted electrochemical data averaged for several cells is presented in Section 3.4.

3. Results and discussion

3.1 Effect of synthesis conditions and Ni content on particle size and morphology

Figure 2 shows as-prepared NCM111 and 811 particles prepared at each synthesis condition given in Table 1. At a temperature of 1350 K (condition #1) NCM111 particles are predominantly spherical with a mean diameter of 1.2 µm. This size is only slightly larger than a calculation based on the mean droplet size (3.5 µm), precursor concentration (1 mol L$^{-1}$) and product molar volume (20.4 cm$^3$ mol$^{-1}$ [31]), which predicts a final particle diameter of 1.0 µm. This is consistent with particle formation from single droplets. At higher synthesis temperatures (condition #2), a large number of fine nanoparticles are also present (see insets in the top left corner of each image shown in Figure 2). That the presence of the fine nanoparticles depends on the synthesis temperature suggests that these nanoparticles are not formed from single droplets, but instead via a gas-to-particle mechanism, where the precursor is vaporised and particles then form by nucleation and growth in the gas phase. For synthesis temperatures of 1350 K, increasing the preheating temperature from 350 K to 450 K (compare conditions #1 and 3) changes the mean particle size to 1.0 µm, a decrease of approximately 20%. Although occasional collapsed structures are visible in both samples, this decrease in average particle size suggests that higher preheating temperatures encourage the formation of denser particles with fewer voids.
Figure 2 SEM images for as-prepared NCM111 (top row) and NCM811 (bottom row) cathode powders prepared at three different synthesis conditions. Insets at a higher magnification are shown in the top left corner of each image.

For all conditions, in comparison with NCM111, NCM811 precursor solutions form particles with a markedly different morphology. For condition #1, the particles are inhomogeneous and partially coagulated, with fine nanoparticles visible on the surface. Increasing the synthesis temperature (condition #2) forms particles with a defined secondary structure on the micron-scale, although the morphology is still irregular. Significant gas-to-particle formation leading to a strongly bimodal distribution [30] is also observed. The metal nitrate precursors used here have a low vapour pressure and the solvent (water) preferentially evaporates during the preheating stage. Vaporisation of formed intermediates and/or product (e.g. Ref. [32]); or droplet explosion phenomena (e.g. Ref. [33]) are plausible mechanisms for the gas-to-particle particle formation at high flame temperatures. A higher preheating temperature (condition #3) has a pronounced effect on as-prepared NCM811 particles. The particles are recognisably formed from single droplets, with a mean particle size of approximately 1.3 µm and no visible nanoparticle formation. As for all synthesis conditions the morphology is still distorted and very different to the regular spherical structures formed by NCM111 solutions.

This difference between the morphology of as-prepared NCM111 and 811 particles can be explained by the variation in solubility of these transition metal nitrates and their relative concentrations in solution. As a droplet enters the high temperature environment, the solvent, in this case water, evaporates from the droplet surface. The concentration of the solute becomes higher at the surface, prompting the solute to diffuse toward the lower concentration region in the centre of the droplet. Under conditions of fast vaporisation where the rate of solvent evaporation is comparable to the rate of solute diffusion, a concentration gradient is established within the droplet [34, 35]. In general, both the severity
of the internal concentration gradient and the solubility characteristics of the solute influence whether the solute will initially precipitate homogeneously or at the periphery of the droplet.

Table 2 tabulates the solubility limits of aqueous metal nitrate precursor solutions used in these experiments, for two temperatures of 298 and 353 K [36]. Note that the data for Mn(NO$_3$)$_2$ at elevated temperatures is not directly available, but Ref. [37] reports that the solubility of Mn(NO$_3$)$_2$ tetrahydrate is apparently without measurable limit. At 353 K the solubilities of Ni and Co nitrate are at least a factor three lower than that of Li and Mn nitrates. The relative solution saturation may be defined as the ratio of concentration in the starting solution to the solubility limit [34, 35, 38]. Straightforward calculation shows that (1) in both 111 (0.033 mol Ni(NO$_3$)$_2$/100 ml water) and 811 (0.08 mol Ni(NO$_3$)$_2$/100 ml water) solutions Ni nitrate has the highest relative solution saturation of any of the transition metals; and (2) in 811 precursor solutions the starting Ni relative saturation is 0.15, whereas it is a factor two lower for 111 solutions. Therefore as the solute accumulates at the droplet surface, the high Ni nitrate content of 811 solutions will prompt earlier precipitation of the salt, forming a shell. This can inhibit evaporation of remaining water through the partially dried layer. As the particle continues through the flame, this layer can buckle and collapse, explaining the irregular shape of NCM811 particles in comparison to NCM111. These findings are supported by the results of experiments given in the Supporting Information (Figure S1), where particles were synthesised from the individual transition metal nitrates. Though this proposed mechanism offers some qualitative understanding, it should be noted other phenomena will play a role e.g. temperature-dependent supersaturation characteristics and variable diffusion of metal ions in highly concentrated solutions. Subsequent processes such as precursor melting and chemical reaction [39], superheating of trapped solvent [33], and the mechanical strength of solid crusts [35] may also influence the final morphology.

| Compound     | Solubility 298 K, mol/100 ml H$_2$O | Solubility 353 K, mol/100 ml H$_2$O |
|--------------|-----------------------------------|-----------------------------------|
| Mn(NO$_3$)$_2$ | 0.90                              | See caption                       |
| Co(NO$_3$)$_2$ | 0.56                              | 1.15                              |
| Ni(NO$_3$)$_2$ | 0.54                              | 1.04                              |
| LiNO$_3$      | 1.48                              | 2.97                              |

Figure 3 shows the materials corresponding to the exact same compositions and synthesis conditions in Figure 2 after annealing the samples at 1023 K for 18 hrs under 0.25 SLPM O$_2$. For all the NCM111 samples (shown in the top row, Figure 3), the spherical structure is maintained after annealing. For the NCM111 particles originally synthesised at low preheating temperatures (350 K, conditions #1 & 2), during annealing the fine nanoparticles that were formed from the gas phase are largely subsumed into
the larger particles formed from single droplets, though the inset figures (shown in the top left corner of each frame in Figure 3) shows that some nanoparticles remain, especially for the high temperature flame. For the same flame temperature (1350 K), after annealing the particles prepared at higher preheating temperature of 450 K have a noticeably smoother surface (compare inset figures for conditions #1 and 3, Figure 3).

Figure 3 SEM images for annealed NCM111 (top row) and NCM811 (bottom row) cathode powders prepared at three different synthesis conditions. Insets at a higher magnification are shown in the top left corner of each image.

For NCM811, on the other hand, annealing has a profound influence on the material morphology. Even for materials prepared at conditions #2 and 3, where the as-prepared NCM811 particles had a defined (if irregular) micron-scale single-particle morphology, annealing causes this structure to collapse. A similar overall morphological change for long annealing times (10-20 hr) of Li-rich Li$_{1.28}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ powders prepared using spray pyrolysis have also been noted [21]. For the layered NCM811 synthesised here, we confirmed that annealing for a shorter duration (4 hr) or reducing the Li content in the precursor solution do not noticeably affect the observed changes.

That said, the flame synthesis conditions clearly have a strong influence on the resultant annealed NCM811 morphology. For materials synthesised at 350 K preheating and 1350 K synthesis temperature (condition #1) the primary features have a large distribution of sizes, ranging from below 0.1 µm up to 0.8 µm (see insets in the top left corner of each frame in Figure 3). Increasing either the flame synthesis temperature (condition #2) or the preheating temperature (condition #3) leads to the formation of larger and contiguous primary features with a more uniform size distribution after annealing.

To understand these observations, the thermal decomposition of NCM111 and 811 precursor solutions was measured. Figure 4 shows TGA profiles tracking the mass reduction of each solution with
increasing temperature. During the initial water loss both profiles essentially follow each other to approximately 500 K, where visual inspection revealed that for these slow heating rates the solution was reduced to a gently bubbling slurry with no shell formation. Beyond 500 K the profiles for each solution depart slightly such that the calculated expected water loss to 21.9% mass is reached at a 25 K higher temperature for 811 solutions. After this point, as nitrate decomposition proceeds, the profiles depart more strongly as seen in the inset, and oxidation of 811 solutions is completed at just over 900 K, a temperature approximately 150 K higher than for 111 solutions (760 K).

These data can be compared with existing thermal decomposition data for the individual hydrated transition metal nitrates. Oxide formation for Mn, Co and Ni nitrates occurs at approximately 525 K [40], 625 K [41] and 675 K [41, 42], respectively. While this trend is consistent with our observation that the Ni-rich precursor solution completes oxidation at a higher temperature, by itself this cannot explain the difference since the measured temperatures for both solutions exceed the oxide formation temperature for Ni nitrate alone. In fact, the decomposition of Li nitrate completes at 975 K [42], which suggests the other transition metals may influence formation of the Li-containing layered oxide. For example, it has been previously observed that the presence of Mn nitrate drastically reduces the decomposition temperature of Li/Mn nitrate mixtures relative to Li nitrate alone due to a catalytic effect of MnO₂ [17, 43]. Therefore, the decreased manganese or cobalt concentration could also be responsible for the difference in the higher oxide formation temperature of Ni-rich precursor solutions.

These TGA results are consistent with measurements of the sample mass before and after annealing as shown in Table 3. For every flame condition, NCM811 samples lose a significantly higher fraction of the mass during annealing, partly because during flame synthesis thermal decomposition has not proceeded as far as for NCM111 solutions. However, transport processes specific to the aerosol also contribute. As explained above, rapid droplet evaporation coupled with the lower solubility of Ni nitrate
and its high concentration in NCM811 solutions causes shell formation. This has the effect of slowing diffusion through the partially-dried particle, thereby trapping the solvent, reducing the temperature and inhibiting oxidation. Even though every synthesis condition exceeds the final decomposition temperature of either solution by several hundred K, the short residence time in the high temperature zone is not sufficient to fully oxidise the precursors.

Table 3 Mass loss for cathode powders after annealing

| Condition | Annealing mass loss % |
|-----------|-----------------------|
|           | NCM811 | NCM111 |
| #1        | 28.0   | 21.7   |
| #2        | 12.5   | 10.0   |
| #3        | 21.8   | 17.0   |

These facts provide insight into how the synthesis conditions in the aerosol phase and the precursor chemistry influence the structure of the material after annealing. For example, for NCM111 precursor solutions thermal decomposition progresses farther during flame synthesis and so NCM111 retains the spherical structure after annealing in comparison to NCM811. Similarly, higher preheating or synthesis temperatures will advance thermal decomposition during flame synthesis, consistent with the reduced mass loss during annealing given in Table 3. This alters the effect of subsequent thermal treatment. For example, the partly-oxidised NCM811 prepared at a low synthesis temperatures (condition #1) leads to irregular oxidation and crystal growth during annealing, leading to the broad distribution of primary features. Increasing the aerosol preheating temperature (condition #3) serves to dry out the droplets ahead of the flame and so thermal decomposition progresses farther within each particle. Moreover, nanoparticle formation from the gas phase is suppressed by the increased preheating temperature. Subsequent oxidation and crystal growth during annealing is defined by the more uniform particle structure originally established in the flame, leading in this case to larger and regular primary features.

To summarise this section, for the same synthesis conditions NCM811 forms irregularly shaped particles because the lower solubility of Ni nitrate and its high concentration causes shell formation in the flame. The delayed thermal decomposition of NCM811 also causes a collapse of the material structure after annealing. However, the synthesis conditions still have a strong effect on the final (annealed) morphology of the cathode materials. In general, higher synthesis temperatures advance the progress of thermal decomposition in the aerosol phase. In this system, higher aerosol preheating temperatures also reduce nanoparticle formation from the gas phase. These variables can be used to improve the uniformity of the primary cathode structure.
3.2 Effect of synthesis conditions and Ni content on crystal structure

Figure 5 shows X-ray diffraction patterns for annealed NCM111 and 811 prepared at synthesis temperatures of 1350 K (condition #1) and 2250 K (condition #2). The diffraction peaks correspond to those of the ICDD data card for NCM111 (R3̅m) [31] and no peaks from any other crystal phases (e.g. M3O4-type spinel or MO-type rock salt) are visible. The fine splitting of the 018 and 110 planes indicates the highly crystalline layered structure.

Figure 5 X-ray diffraction patterns for annealed NCM811 and 111 cathode materials prepared at synthesis conditions #1 and 2, and ICDD data card for LiNi0.33Mn0.33Co0.33O2

Table 4 shows the ratio of the integrated peak intensities of the 003 and 014 crystal planes extracted from the XRD data for each of the annealed NCM811 and 111 samples. Ni atoms can occupy the Li layer due to the similar atomic radii of Li⁺ and Ni²⁺ [4, 6, 44, 45] leading to the onset of formation of disordered phases, which causes reduced intensity of the 003 diffraction peak belonging to the layered structure (or even complete disappearance of the 003 peak for the formation of MO-type phase, e.g. NiO) [46]. In this way the 003/014 ratio can serve as a qualitative indicator for ion exchange in layered structure oxides [47]. For NCM111, the synthesis conditions have little detectable effect on the 003/014 ratio, indicating that for short residence times even high flame temperatures do not alter the degree of cationic disordering. For NCM811, however, there is a noticeable drop in the peak ratio for materials synthesised at the high flame temperature (condition #2). This finding will be compared to the electrochemistry in Section 3.4.
Table 4 003/014 diffraction peak ratios for all annealed cathode powders

| Condition | 003/014 diffraction peak ratio |
|-----------|--------------------------------|
|           | NCM811  | NCM111  |
| #1        | 0.88    | 0.82    |
| #2        | 0.67    | 0.79    |
| #3        | 0.87    | 0.81    |

Table 5 also shows the full-width half-maximum (FWHM) of the 003 diffraction peak for all annealed samples. The average crystal size is qualitatively reflected by the inverse of the peak width. The synthesis conditions affect the crystal size, where particularly for NCM111 higher synthesis temperatures (condition #2) noticeably favour the growth of larger crystals. Also, NCM811 evidently forms larger crystals than NCM111 for the same synthesis conditions. This provides an additional explanation for the loss of structure for the NCM811 samples relative to NCM111 during annealing. As the partially-oxidised samples undergo complete oxidation and crystal growth in the furnace, the ratio of the crystal size relative to the lengthscale of the aerosol system (~1 µm) could play a role in the observed structures. The larger crystal size for NCM811 leads to more prominent primary features and noticeable distortion of the secondary structure during annealing, whereas the smaller crystal size for NCM111 means that the spherical secondary particle structure can be maintained.

Table 5 Measured 003 plane diffraction peak width (full-width half maximum) for annealed cathode materials

| Condition | Diffraction peak width (deg. 2 theta) |
|-----------|--------------------------------------|
|           | NCM811  | NCM111  |
| #1        | 0.23    | 0.51    |
| #2        | 0.21    | 0.29    |
| #3        | 0.25    | 0.39    |

It is interesting to contrast these findings with the relative difference between balanced and Ni-rich NCM cathodes synthesised using the more common co-precipitation method. For example, one study noted that the primary particle size of the final product decreased with increasing Ni content [48], whereas in our materials produced using flame aerosol synthesis NCM811 has recognisably larger primary features than NCM111. The crystal formation and growth processes in each synthesis method occur on different time and length scales, as examples, in co-precipitated concentration gradient Ni-rich particles the formation kinetics causes the growth of aligned, nanoscale rod-like structures [1]; and
LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 prepared by low temperature spray drying and subsequent annealing has a finer structure than solid-state synthesis from the same precursors alone [49]. These differences can be exploited in aerosol synthesis methods to produce Ni-rich materials with optimised morphologies.

3.3 Effect of synthesis conditions and Ni content on chemical composition: bulk and surface

Table 6 displays the atomic ratios of transition metals derived from EDXS data for several cathode samples. Note that the data is normalised to the Ni concentration. For brevity we only present data for the variation of synthesis temperature for NCM811, and comparison to NCM111 at 1350 K (condition #1), for both as-prepared and annealed powders. The results indicate that the transition metal ratio is as designed in NCM111 which indicates balanced element concentrations relative to Ni. For NCM811 the designed ratios are Mn/Ni~Co/Ni~0.125, which are correct for cobalt. However, the Mn/Ni ratio is consistently lower than that expected even considering the EDXS experimental uncertainty (±3%, corresponding to a -1σ limit of Mn/Ni~0.09). It was verified by multiple repeat experiments with fresh precursors solutions that this is not due to error in the precursor preparation, and error caused by the uncertainty in the hydration state of Mn(NO_3)_2.xH_2O is negligible. This could be due to a Mn-rich core in the larger NCM811 secondary structure that is not captured in the EDXS interaction volume. There are no significant differences in the overall elemental content before and after annealing.

| Condition | Composition | Powder | Co   | Mn   | Ni  |
|-----------|-------------|--------|------|------|-----|
| #1, T=1350 K | NCM811      | as-prepared | 0.14 | 0.07 | 1.00 |
|           |             | annealed   | 0.17 | 0.10 | 1.00 |
|           | NCM111      | as-prepared | 0.99 | 1.08 | 1.00 |
|           |             | annealed   | 1.04 | 0.97 | 1.00 |
| #2, T=2250 K | NCM811      | as-prepared | 0.12 | 0.07 | 1.00 |
|           |             | annealed   | 0.10 | 0.06 | 1.00 |

As Table 7 and Figure 6 indicate, for the first 1-10 nm at the surface of the cathode powders there is both a marked deviation in the composition from the designed one and a significant difference before and after annealing. Mn is present in lower concentrations than expected or is even undetectable in all the as-prepared powder. For example, Figure 6(a) shows the Mn2p peak for as-prepared NCM111 synthesised at 1350 K (condition #1). The Mn/Ni ratio is 0.41 as shown in Table 7, significantly lower than the expected unity value as confirmed by the EDXS data for the bulk material (Table 6). It has been previously shown, in a low-temperature system similar to the preheating used in these experiments, that the order in which components reach saturation can be used to control the surface composition relative to the bulk composition [50]. Solutes with a lower solubility tend to precipitate earlier, which increases their relative concentration at the particle surface. In these samples, the low Mn concentration
at the surface can be explained by the much higher solubility of Mn nitrate relative to Ni nitrate. Ni nitrate precipitates first on the surface, enriching the Ni surface concentration relative to Mn. This interpretation of the surface composition data is also consistent with the observed particle morphology differences between as-prepared NCM111 and NCM811. For all samples, annealing increases the Mn content at the surface by diffusion within the particle, as exemplified by the Mn2p$_{1/2}$ peak at ~654 eV for NCM111 and 811 shown in Figure 6(a) and 6(b) respectively, but the Mn/Ni ratio remains below the designed values. This underscores the point that transport processes occurring during aerosol synthesis have a strong effect on the final product, even after annealing.

Table 7 Elemental transition metal ratios (relative to Ni) on the cathode surface

| Condition   | Composition | Powder   | Co   | Mn   | Ni   | N   | Carbonate |
|-------------|-------------|----------|------|------|------|-----|-----------|
| condition #1, T=1350 K | NCM811      | as-prepared | 0.12 | -    | 1.00 | 0.32| 1.23     |
|             |             | annealed  | 0.14 | 0.05 | 1.00 | -   | 0.37     |
|             | NCM111      | as-prepared | 1.01 | 0.41 | 1.00 | 0.49| 3.37     |
|             |             | annealed  | 0.99 | 0.68 | 1.00 | -   | 0.23     |
| condition #2, T=2250 K | NCM811      | as-prepared | 0.14 | 0.02 | 1.00 | -   | 1.81     |
|             |             | annealed  | 0.15 | 0.05 | 1.00 | -   | 0.91     |

Figure 6 XPS spectra for Mn in as-prepared and annealed cathode materials synthesised under condition #1. (a) and (b) are NCM111 and 811 respectively. Note the Mn2p$_{3/2}$ peak at ~642 eV overlaps with the Ni Auger peak [51] and was not used in the concentration calculation.

Nitrate is present on the surface of samples prepared at 1350 K (condition #1). Increasing the synthesis temperature to 2250 K (condition #2) is sufficient to completely remove nitrogen from the surface, also evident for all samples after annealing (see Table 7). Additionally, Ni-rich NCM powders can react with CO$_2$ which results in the formation of carbonate groups at the surface e.g. Li$_2$CO$_3$ [52]. Table 7 shows a significant carbonate fraction at the surface of the as-prepared samples, which is reduced following annealing.
3.4 Electrochemical performance

The initial charge/discharge profiles of coin cells made from the annealed NCM111 and 811 materials are as expected. Example cells produced from cathodes produced in flame conditions #1 and 2 indicate a characteristic voltage plateau, as shown in Figure 7. The measured specific discharge capacities for NCM111 compare favourably to materials prepared by aerosol processes [8, 23-25] and other synthesis methods [6]. The NCM811 cathodes show the intrinsic higher first discharge capacity (~180 mAh g⁻¹) compared with NCM111 (~150 mAh g⁻¹), and lower first cycle efficiency.

![Charge/discharge curves](image)

Figure 7 Charge/discharge curves of the first five cycles for single coin cells assembled from NCM811 (top) and NCM111 (bottom) cathode materials synthesised at flame conditions #1 (left) and 2 (right).

Table 8 tabulates the average first cycle efficiency (FCE) and specific capacity of cells produced for all the synthesis conditions. The data indicate that the variations in first-cycle electrochemical performance for both NCM111 and 811 for every synthesis condition are within the repeatability of the cell tests. For NCM811, this invariance of the first cycle behaviour with synthesis temperature is notable given the significant difference in the NCM811 morphology for the different synthesis conditions displayed in Figure 3.
Table 8 Average first cycle efficiency and discharge capacity of coin cells assembled from NCM811 and 111 cathodes prepared at different flame conditions

| Condition | NCM811 |  | NCM111 |  |
|-----------|--------|---|--------|---|
|           | FCE   | Discharge capacity | FCE | Discharge capacity |
|           | %     | mAh g$^{-1}$        | %   | mAh g$^{-1}$        |
| #1        | 83.6  | 179.4              | 91.3| 153.7              |
| #2        | 83.8  | 178.0              | 87.6| 144.1              |
| #3        | 85.6  | 185.5              | 90.9| 150.2              |

$^a$ cutoff voltage 4.3 V; $^b$ cutoff voltage 4.25 V

However, the average cycling results for NCM811 coin cells shown in Figure 8 reveal that the cycling behaviour strongly depends on the synthesis conditions. For NCM811 prepared at 2250 K (condition #2), the discharge capacity fades faster than the material prepared at 1350 K (condition #1). At these conditions NCM111 shows similar trends (data not shown). The best NCM811 cycling behaviour is achieved for materials produced using a higher preheating temperature but low overall synthesis temperature (condition #3), which show an average capacity retention of 85.0% after 25 cycles and 81.1% after 45 cycles (see Supplementary Information Figure S2).

Figure 8 Average cycling behaviour of coin cells assembled from NCM811 cathode materials produced for different preheating and flame conditions. The current density was 100 mA g$^{-1}$ (0.5 C) in the voltage range of 2.8-4.3 V.

These trends can be related to the NCM811 material morphology and the XRD results. NCM with higher nickel content is more reactive, especially in the delithiated state [4, 16]. Also, Ni-rich materials are subject to increased structural strain during cycling [2]. It was previously proposed that the smaller 100-200 nm primary particles synthesised by co-precipitation, for example, could therefore more easily undergo transformation of the crystalline structure and even breakup during repeated charge/discharge, which is also responsible for diminished cycling performance [48]. This partly explains the trends of
Figure 8 for these materials produced using aerosol synthesis. The wide range of primary particle sizes found for condition #1 (1350 K) means that the smallest particles suffer from increased surface reactions and collapse of the crystalline structure during cycling, leading to the observed capacity fade. For condition #2 the synthesis temperature is increased to 2250 K. In Ni-rich materials such high temperatures drives increased cationic mixing of Ni and Li ions between the transition metal and Li layers (as evidenced by the decreased 003/014 peak ratio), as well as prominent gas-to-particle formation in the flame, both leading to the poor cycling performance. The best NCM811 cycling behaviour is achieved for condition #3, where the synthesis temperature is 1350 K but the preheating temperature is increased to 450 K. This was observed to increase the size of the primary particles and enhance the uniformity of the primary particle size distribution. Therefore using higher preheating temperatures improves the structural stability without using high synthesis temperatures that damage the ordering of the layered structure. However, the capacity and cycling performance must still be significantly improved, by post-annealing and/or the aerosol processing conditions. These findings provide guidelines for further optimisation of the material via temperature control in the reactor. For example, staged preheating, lower peak synthesis temperatures and longer residence times should enhance the energy harvesting.

Conclusions

LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} (NCM811) cathode materials were prepared using a flame aerosol route. The effect of the synthesis conditions on the particle formation and electrochemical performance were examined and compared to LiNi_{0.33}Co_{0.33}Mn_{0.33}O_{2} (NCM111) particles prepared under the same conditions. It was found that:

(1) Solutions rich in nickel tend to form more irregularly-shaped particles from single droplets because the lower solubility of Ni nitrate causes earlier precipitation at the droplet surface and formation of a shell-like structure. This result is confirmed via XPS which indicates a lower than expected concentration of higher-solubility manganese at the surface of the as-prepared materials.

(2) Higher flame synthesis temperatures (2250 K) lead to a bimodal size distribution via additional gas-to-particle formation route. Electrically preheating the aerosol stream to 450 K before the flame promotes single mode solid particle formation by removing more solvent ahead of the flame, thereby prompting more homogeneous precipitation of the solute and improvement of the morphology of as-prepared NCM811 particles.

(3) After annealing, NCM111 materials retain the secondary particle structure, but NCM811 forms irregular shapes with a broad size distribution of primary features. TGA of the precursor solutions indicates that thermal decomposition completes at a higher temperature for Ni-rich solutions than balanced NCM111 solutions. The limited oxidation and particle formation of
NCM811 precursors in the aerosol phase, and the growth of larger NCM811 crystals as evidenced by XRD data, cause this collapse of the single-particle structure during annealing. Electrical preheating of the aerosol stream and adjusting the flame temperature can be used to control the morphology and crystallinity of the annealed product. (4) All the cathode materials show reasonable first cycle efficiency and initial discharge capacity, with NCM111 averaging 89.9% and 149.3 mAh g\(^{-1}\) and NCM811 84.3% and 181 mAh g\(^{-1}\) respectively. Though the synthesis conditions have little impact on the first cycle performance, there is a pronounced effect on the cycling behaviour of NCM811. A higher preheating temperature (450 K) and lower synthesis temperature (1350 K) improves the uniformity in primary particle size distribution and therefore the structural stability while avoiding high synthesis temperatures that damage the ordering of the layered crystal structure.

Aerosol synthesis offers multiple ways to control the length- and timescales over which transport processes occur. For instance in this study, which targets the droplet-to-particle formation route, the initial droplet size is a key parameter. We emphasise that the aerosol synthesis conditions have a pronounced effect on the final product, even after post-treatment at elevated temperatures and for extended times. Here therefore, despite the loss of secondary structure in Ni-rich materials after annealing, the flame conditions affect the primary particle size and the concentration of the transition metals varies within the material structure. This opens up possibilities to tailor the morphology and compositional gradients and thereby improve the cycle lifetime of Ni-rich materials, for example by choice of metal salt solubility, changing the droplet size, residence time control, or even in situ-surface modification via staged introduction of doping elements.

**Supporting Information**

SEM images of particles synthesised from aqueous solutions of Mn, Ni and Co nitrate, description of experiment and results, electrochemical data for NCM811 synthesised for flame condition #3. The Supporting Information is available free of charge on the ACS Publications website [http://pubs.acs.org/](http://pubs.acs.org/)

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