

Chapter 2

Experimental and Theoretical Considerations

2.1 Sample Preparation

2.1.1 Synthesis of Combinatorial Samples

The method used to synthesize hundreds of samples across the pseudo-ternary systems was to make combinatorial arrays of milligram-scale oxides. Throughout this section, the method used to make samples in the Li–Mn–Ni–O system will be described. The only variation needed to make samples in the Li–Co–Mn–O system is to replace the nickel starting solution with a cobalt solution (both were nitrates in these studies). This method, developed by Carey and Dahn [10], was closely based on that typically used for large scale samples made in a tank reactor. Carey [10] mixed a total of 10 μL of roughly 2 M lithium nitrate (Aldrich, 98 %), manganese nitrate (Sigma-Aldrich, 97 %) and nickel nitrate (Sigma-Aldrich, 97 %) using a Cartesian Pixsys solution-processing robot shown in Fig. 2.1. Figure 2.2 (a) shows how these solutions were dispensed onto an alumina plate (Pi-Kem, 96 %) coated with stearic acid (Aldrich, 96 %) which served to bead the solutions. Carey then added ammonium bicarbonate (Alfa Aesar, 98 %) in excess to cause co-precipitation of Li, Mn and Ni carbonates. After drying at 55 °C, the sample was made up of the mixed carbonate and any other products of the reaction (in Chap. 3, this will be shown to be primarily ammonium carbonate). Carey then heated the samples to 800 °C for 3 h in air to form the oxides. Silicon (100) wafers were then covered in a tacky mixture of Trilene-65 (a polymer mixture made by Lion Copolymer) and cyclohexane. The wafer was placed over the alumina plates and flipped in order to transfer the samples onto the silicon wafer. The final products were shown to be the expected spinel oxides by XRD.

By contrast, for bulk samples, a precursor is made over the course of several hours by mixing manganese and nickel solutions in a tank reactor in the presence of a precipitator such as ammonium bicarbonate or ammonium hydroxide. The results of this co-precipitation reaction, after rinsing, is a mixed manganese–nickel compound (either hydroxide or carbonate) which is then mixed with a lithium salt (typically Li_2CO_3 or LiOH) and heated to high temperature to make the oxide material. The main differences between the combinatorial approach and the tank reactor method

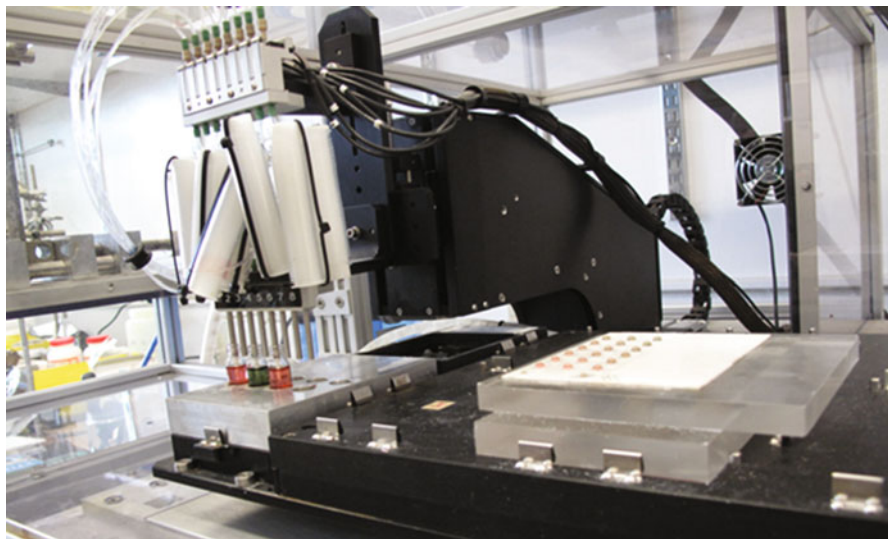


Fig. 2.1 The PixSis solution-dispensing robot used to make all combinatorial samples in this thesis. The three ceramic tips are pulling solutions from the vials in preparation for a dispense onto the partially filled alumina plate

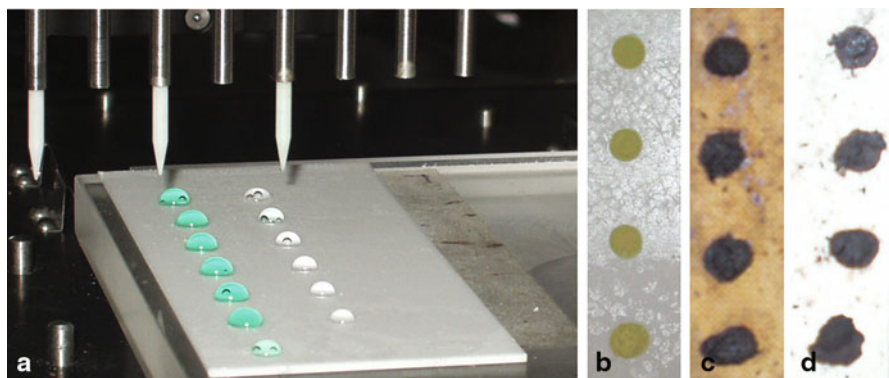


Fig. 2.2 **a** The PixSis solution-dispensing robot making samples with lithium and nickel. Spinel samples at various stages of synthesis. **b** After drying overnight. **c** After heating to 300 °C. **d** After heating to 800 °C in oxygen

are that in the combinatorial approach, all three metals are mixed at the same time, the co-precipitation reaction times are short, there is stearic acid present and the samples are not rinsed after the co-precipitation. The main consequence of the short reaction times is that particles are smaller than those seen typically for bulk samples, especially with the short 3 h heating times. This can be seen by examining the crystallite size in Chap. 3 and in the SEM images in Chap. 6. The fact that particles are small may allow phase separation to occur more rapidly in these samples, thereby confirming

the changes seen in the combinatorial samples also occur in bulk samples is critical and is dealt with in Chap. 7. The main consequence of having stearic acid present is that there are contaminants in the samples, though some contaminants are also due to not rinsing the samples after the co-precipitation reaction, and all were found to disappear during synthesis. Figure 2.2 (b)–(d) shows the samples at various stages of heating. After drying at 55 °C, the stearic acid can be seen on the substrate, while at 300 °C, decomposition of the stearic acid begins. The fact that the substrate appears clean after heating to 800 °C shows that decomposition of the stearic acid does reach completion. There is no evidence that the contaminants during heating affect the final products, nor is there any evidence of there being consequences to mixing all three metals in one step, but again it is important to confirm that the tank reactor method gives comparable results to those obtained for the combinatorial samples, and so bulk and combinatorial samples will be compared throughout this thesis.

Chapter 3 shows the results of testing a number of variables in order to optimize the combinatorial synthesis method to minimize lithium loss. These variables were: the substrate used (alumina, alumina coated with LiAlO_2 and magnesia), the precipitator used (ammonium bicarbonate or ammonium hydroxide), the atmosphere used during heating (air or pure oxygen), the amount of solutions dispensed (10 or 20 μL) and the temperature at which the samples are heated (200, 300, 400 . . . 1000 °C). The sources of all chemicals were the same as those listed above, and ammonium hydroxide was obtained from Fisher while magnesia plates were obtained from Ceramtec. All substrates were first coated with stearic acid. The best combination obtained in that study was used throughout the rest of the thesis and proceeds as follows. Each combinatorial sample, with a mass of approximately 2 mg, was made by dispensing a total of 20 μL of 1.78 M solutions with the solution-processing robot. The concentrations were measured to within 2 % using atomic absorption as described later in this chapter. The three solutions were lithium, manganese and nickel nitrates, and the amounts of each were varied in order to map out the Gibbs triangle. The substrate used during heating was alumina. After dispensing the nitrates, 23 μL of 2 M ammonium bicarbonate was added, thereby ensuring that it was in excess for all samples. The samples were then dried overnight at 55 °C before being heated for 3 h at 800 °C. Some samples were heated in air in a box furnace while others were heated in a tube furnace under a flow of at least 30 mL/min of oxygen. Four cooling rates were used. The first involved turning off the power to the furnace which will be referred to as regular cooling. At high temperatures, this resulted in an approximate cooling rate of 8 °C/min and an overall rate of about 5 °C/min. This cooling method is comparable to that used in the making of commercial electrodes. The second cooling method was to quench the samples by transferring the alumina plate from the furnace onto a steel slab as quickly as possible. A Mastercraft infrared temperature sensor was used to determine that the quenched samples reached 100 °C within 1 min after removal from the furnace. This corresponds to a cooling rate of roughly 10 °C/sec. A second quenching method was used wherein samples were transferred into liquid nitrogen. This cooling occurs at the order of a few seconds such that a cooling rate of about 100 °C/sec was obtained. The final cooling rate, used occasionally, was to cool the samples at a controlled rate of 1 °C/min and will be referred to as slow cooling.

Fig. 2.3 The Li–Mn–Ni oxide triangle illustrating how samples are synthesized over entire composition range in a ternary system

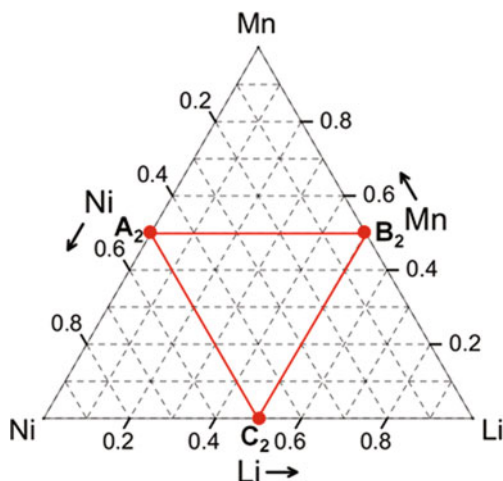


Figure 2.3 illustrates the methodology involved in making samples throughout the Li–Ni–Mn Gibbs triangle. Samples were made at every intersection point of the dashed lines, which resulted in 66 different compositions within the triangle. This was accomplished by making three plates, each holding a 6×6 array of samples. The plates were first cut in half in order to fit into the tube furnace. The three arrays corresponded to samples within each of the three parallelograms shown in Fig. 2.3: $\text{NiA}_2\text{B}_2\text{C}_2$, $\text{LiC}_2\text{A}_2\text{B}_2$ and $\text{MnB}_2\text{C}_2\text{A}_2$. This gave 21 compositions that were repeated on each of the three plates which served as a reproducibility check. Thus, this method results in a total of 108 samples made at 66 compositions. For each system, this mapping was done first. Then, as required, arrays were made over narrower ranges in order to zoom in on compositions of interest. In all cases, there were some duplicate samples to confirm reproducibility (usually duplicating a few samples from the original 66).

2.1.2 Synthesis of Bulk Samples

Three different synthesis methods were used to make bulk samples. The simplest was to use a solid-state reaction such as that used in Chap. 3 to make LiNiO_2 . This involved grinding $\text{NiO}_{(\text{s})}$ (Nova Met, 98 %) with $\text{LiOH}_{(\text{s})}$ (Sigma-Aldrich, 98 %) and heating to high temperature in air. The second bulk synthesis method mimicked the combinatorial method on a larger scale. This involved mL-scale (usually a total of about 20–40 mL) mixtures of lithium, manganese and nickel nitrates (from the same sources as in the combinatorial synthesis). Excess ammonium bicarbonate was then added to the mixtures in a beaker and stirred for a few minutes. After drying overnight at 55 °C, the samples were heated to 400 °C for about 30 min to drive-off the ammonium carbonate and any other products of the reaction. The samples were

then ground and heated for 5 h in air or a flow of oxygen, and either quenched, regular cooled or slow cooled. The resulting samples had masses of approximately 1–2 g. This method will be referred to as the “one-pot” synthesis and was used to determine the impact of the high surface area to volume ratio in the combinatorial samples.

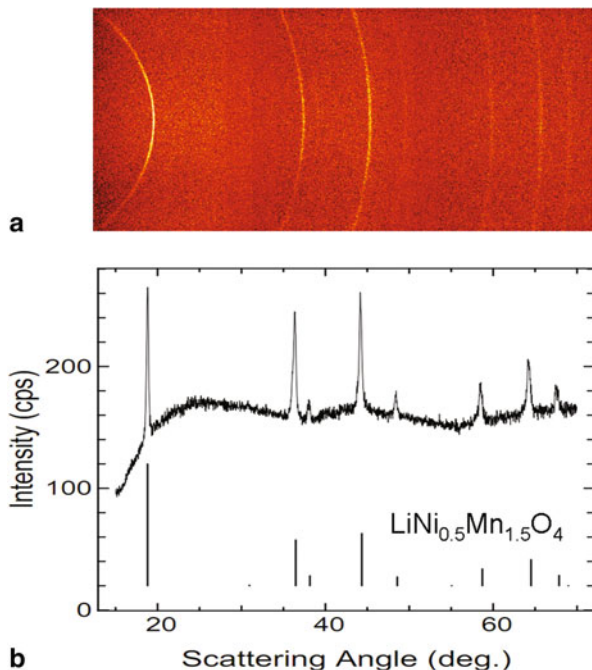
To ensure that the results obtained both by the combinatorial method and the one-pot synthesis are significant for other synthesis routes, bulk samples were also made using a tank reactor as described in Ref. [58]. These samples were made by Aaron Rowe and his contributions to this project will be pointed out explicitly throughout this thesis. A continuously stirred tank reactor was used to make mixed manganese–nickel hydroxide precursors. The metal precursor solutions were made using $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (both 99 % from Aldrich Chemical Co) in such a way that a variety of nickel to manganese ratios were obtained. The tank reactor was used to mix NH_4OH with the metal sulfate solutions at a constant pH of 10.3 throughout the 10 h reaction under a flow of nitrogen. The precursor was then rinsed with distilled water and dried at 140°C before being mixed with varying amounts of Li_2CO_3 to yield the desired stoichiometry. These mixtures were heated to 900°C for 10 h in a box furnace and then either quenched to room temperature between two copper plates or cooled at a slower controlled rate of $5^\circ\text{C}/\text{min}$ (which is comparable to the regular cooling rate used for the combinatorial samples and will be referred to as such).

2.2 X-Ray Diffraction

2.2.1 *High Throughput X-Ray Diffraction (XRD) of Combinatorial Samples*

Due to the large number of combinatorial samples, a Bruker D8 Discover X-Ray system was used to characterize the vast majority of the combinatorial samples. All X-ray diffractometers used during this project use $\text{Cu-K}\alpha$ radiation. The Bruker system has a collimated 0.5 mm wide beam, a Göbel mirror and an area detector. Each scan was made up of three frames with a 30 % overlap and each frame is obtained by counting for 300 s. Figure 2.4 shows typical results after stitching the frames together as well as the outcome of integrating along the arcs. This gave a scattering angle range of $15\text{--}70^\circ$ and required approximately 15 min per sample. The Bruker D8 diffractometer is equipped with a sample translation stage that allows motion in the x, y and z directions such that the scattering patterns from samples in the combinatorial arrays were automatically measured in sequence. As described previously, the samples were first transferred onto a silicon (100) single crystal which served as a zero-background holder during the XRD scans as long as the Bragg condition for the Si(400) peak was avoided. Although the peak positions determined using the Bruker diffractometer were extremely accurate, the scattered intensities were affected by the stitching of frames and the integration along arcs. As such, Rietveld refinement generally failed for scans produced in this way. The next section describes the diffractometers used when Rietveld refinement was essential.

Fig. 2.4 **a** The X-Ray diffraction (XRD) image obtained after stitching three frames together for a spinel sample. **b** The result of integrating along the arcs while the vertical lines correspond to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel (JCPDS #80-2162)



2.2.2 X-Ray Diffraction of Bulk Samples

The X-ray scattering patterns from bulk samples as well as from a few combinatorial samples were collected using either a JD-2000 diffractometer or a Siemens D-5000 diffractometer. Both are equipped with a Cu-target X-ray tube and a diffracted beam monochromator, though the D-5000 also has a Soller slit to minimize out-of-plane scattering. These scans could be fitted accurately using Rietveld refinement to obtain values for lattice parameters as well as site occupations. Rietveld refinement was performed on single-phase samples only using the software Rietica. The information required was the space group and site occupations, though the occupations were often left as variables in the refinements. The function used for the peak shape was pseudo-Voigt (described in the next section). The primary outputs of the refinements were lattice parameters, site occupations, fitted peak widths and fit quality parameters such as the Bragg factor. In order to account for the average vibrations of the atoms, an overall thermal parameter was allowed to be refined.

2.3 Fitting of Combinatorial X-Ray Diffraction Patterns

Several challenges present themselves with respect to the analysis of XRD data obtained from the high-throughput Bruker machine. The peak intensities are distorted such that Rietveld refinement fails. Carey extracted precise lattice parameters by

fitting the top of peaks only [10]. However, this is not feasible when there are multiple phases present for which overlapping peaks result in shifts in apparent peak positions and only using peaks that have no overlap would result in poor precision. To overcome this, an in-house software was written in Yorick to fit the entire scans using a nonlinear least squares fitting algorithm [59]. Fitting the entire patterns had the added benefit of extracting peak width information that was used to calculate crystallite sizes and strains.

Using a degree six polynomial to describe the background was found to converge very slowly. This was resolved by using a cubic function and two broad asymmetric Gaussians centered near 20 and 45 ° to describe the background. This procedure was found to work well for all samples, including spinel samples where manganese fluorescence gives rise to a complicated background when the three frames are stitched together as shown in Fig. 2.4 (b).

In the program, each experimental peak was described by the convolution of the sample scattering with the machine broadening as outlined by Warren [60]:

$$I_k(2\theta) = \int F_k(2\theta - z)M(z)dz \quad (2.1)$$

where 2θ is the scattering angle, F_k is the sample scattering due to the k -th peak, and M is the machine broadening normalized to have an area of unity. The integration over z , the scattering angle of the machine broadening, was done numerically. The sample scattering was described with a pseudo-Voigt function:

$$F_k(2\theta) = I_k^\circ [\eta C(2\theta, 2\theta_k, H_k) + (1 - \eta)G(2\theta, 2\theta_k, H_k)] \quad (2.2)$$

where I_k° is the integrated peak intensity of the k -th peak, H_k is the full width at half maximum (FWHM), $2\theta_k$ is the position of the center of the peak, η is the Lorentzian component and is kept constant for all scattering angles, and C and G are the Lorentzian and Gaussian functions, respectively, each normalized to have an area of unity. The peak intensities were fitting parameters, thereby avoiding problems with distortions due to the stitching of frames. The position of each peak was calculated from the h , k and l values given in the Joint Committee on Powder Diffraction Standards (JCPDS) database and from the adjustable lattice parameters. The $K\alpha_1$ and $K\alpha_2$ peaks were included in a 2:1 ratio in the calculation in order to fit the high angle peaks accurately.

The machine broadening function, M , was determined by measuring the scattering from corundum (NIST standard 1976a), the expected scattering from which is given in JCPDS #46-1212. The scan was fit using pseudo-Voigt functions with $\eta = 0.5$ and letting the FWHM of each peak, $H(\theta)$, be a fitting parameter. Although corundum is not commonly used as a standard for machine broadening, it is sufficient to describe the extensive broadening obtained with the 0.5 mm wide beam. This was determined by measuring the scattering from a silicon wafer which was ground. The results gave peak widths comparable to those obtained with the corundum, however the five peaks showed far more scatter such that corundum proved to be the better standard. Figure 2.5 shows that the resulting peak widths can be described by the Williamson–Hall expression : $H(\theta) \cdot \cos\theta = A + B\sin\theta$, where A and B are constants. The

slope, B , is negative because the scattering volume decreases for frames with higher incident angles and there is no analyzer monochromator. There is also an evidence of slight plateaus in the Williamson–Hall plot corresponding to the stitching of frames, but this problem is minimized by the 30 % overlap, and the linear fit does describe the data well over the scattering angle range, 15–70° used throughout this project.

In order to extract values for crystallite size and micro-strain, the integral breadth method outlined by Klug and Alexander was used [25]. This involved assuming that the size contribution was Lorentzian and describing the strain broadening with a Gaussian function. The integral breadth of the k th peak was obtained by dividing the area of the pseudo-Voigt function by its height, which yields:

$$\beta_k = H_k/\alpha \quad (2.3)$$

where

$$\alpha = 2[\eta/\pi + (1 - \eta)\sqrt{\ln 2/\pi}]. \quad (2.4)$$

Utilizing the quadratic approximation [25, 61], and solving for the full width at half maximum gives:

$$H_k = \frac{\alpha}{2} \left[\frac{K\lambda}{L\cos\theta} + \sqrt{\left(\frac{K\lambda}{L\cos\theta} \right)^2 + 64e^2 \tan^2\theta} \right] \quad (2.5)$$

where L is the average crystallite size, the root-mean-square micro-strain is $\sqrt{\langle e^2 \rangle} = e/1.25$, and the usual approximation of $K = 1$ was made. The quadratic approximation is generally considered to give values for size and strain that are close to those obtained by Fourier methods without requiring extensive computations [61]. The micro-strain includes all contributions due to nonuniform lattice distortions, dislocations, stacking faults and local structural defects such as vacancies and interstitial atoms. In the case of $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$, fluctuations in lithium content within a grain have been observed in the early phases of synthesis in samples with lower lithium content ($x < 0.6$) [62]. A nonhomogeneous lithium distribution within grains would result in lattice distortions, thereby contributing to the strain. As a result, the strain parameter is of particular interest during synthesis of the samples and is therefore followed closely in Chap. 3.

In order to estimate the minimum crystallite size that can be resolved with the combinatorial X-ray machine, the broadening of the machine peaks due to crystallites of various sizes was calculated by using the Scherrer equation and assuming the peaks were Gaussian to minimize the broadening. A similar calculation was made for strain, assuming crystallites of infinite size. Figure 2.5 shows the results of these calculations and shows that the Bruker XRD system resolves crystallite sizes precisely up to 100 nm; however, above this point, machine broadening begins to dominate and any size greater than 150 nm cannot be determined. For larger crystallites, it would be necessary to use a smaller beam spot (0.3 mm or even 0.1 mm are commonly used), but this was avoided here, since it would have greatly increased the required count

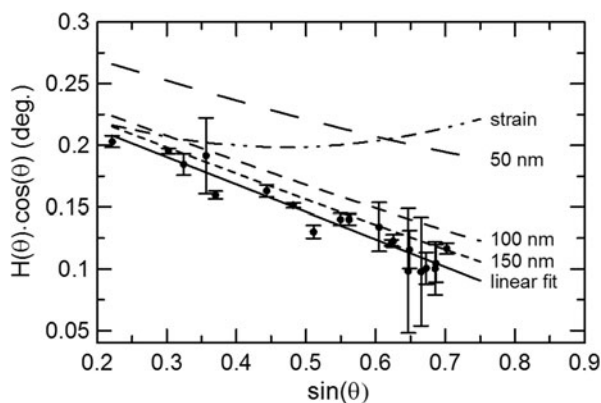


Fig. 2.5 Williamson-Hall plot for corundum obtained with the Bruker XRD machine with a beam spot of 0.5 mm. The *solid line* is a linear fit and is used to define the machine broadening. *Dashed lines* are obtained assuming peaks are Gaussian and using the Scherrer equation to describe the size broadening. The *dotted-dashed line* is obtained similarly, assuming an infinite crystallite with a strain of 1.0×10^{-3}

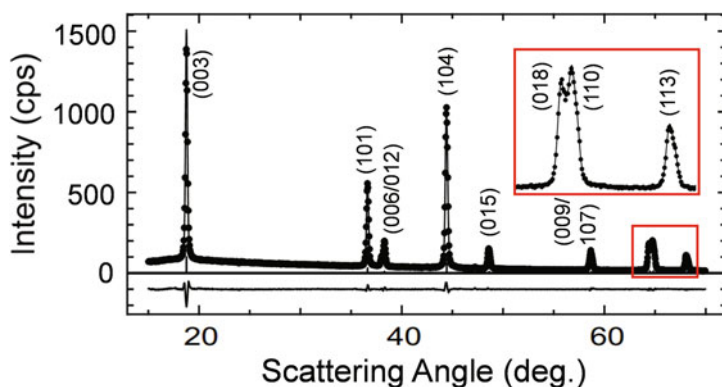


Fig. 2.6 The fit obtained for a combinatorial sample of LiNiO_2 . This reflects the quality of fit typically obtained for XRD scans of the combinatorial samples taken with the Bruker diffractometer. For clarity, only every third data point is included as *closed circles* while the result of the fit is shown as a *solid line* and the difference plot is shown below

time. Figure 2.5 also shows that a strain value of 1×10^{-3} can be readily resolved. Any strain value below 0.1×10^{-3} was considered too small to be measured accurately.

Figure 2.6 shows a typical scan obtained for a combinatorial lithium-nickel oxide sample measured with the Bruker machine along with the fit produced by the in-house software. The peaks fitted the experimental data extremely well such that the lattice parameters and the size/strain values extracted from the fitting routine were well constrained. For clarity, all XRD patterns shown throughout the rest of this thesis have the fitted background subtracted from the experimental patterns. This allows for easy comparison of many samples stacked in the same plot.

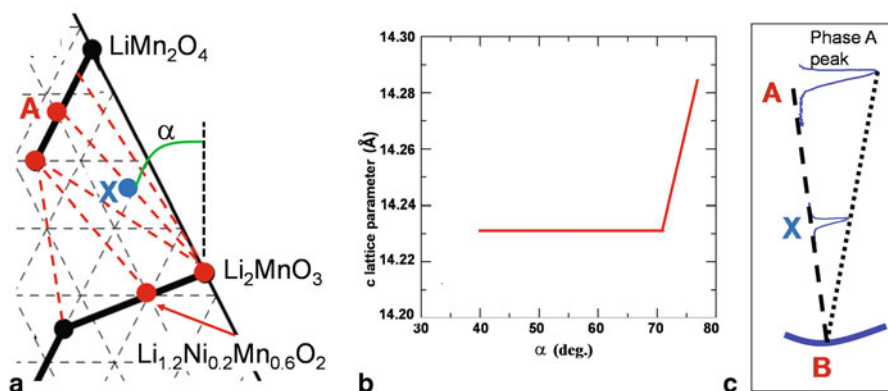


Fig. 2.7 **a** A section of the Li–Ni–Mn–O phase diagram showing previously known single-phase regions. *Red dashed lines* represent proposed tie-lines. **b** An illustration of how lattice parameter values can be used to determine the direction of tie-lines in two-phase regions. **c** A schematic of using the lever rule in a two-phase region to determine the location of a point *B* on the boundary of the single-phase region (e.g. if *a* is correct, point *B* should be Li_2MnO_3)

The program was written to be able to fit multiphase samples. The calculated pattern was therefore a linear combination of the functions representing each of the single phases. Thus, the fitting of multiphase scans generated lattice parameters and integrated peak areas for each phase. The size and/or strain was examined in Chaps. 3 and 4 only. For all other combinatorial results, phase compositions (obtained from the calculated peak areas) and lattice parameters were extracted. As shown in the next section, this information is sufficient to generate precise phase diagrams.

2.4 Methods to Generate the Phase Diagrams

The information extracted from the XRD scans includes: phase types (layered, spinel, rocksalt . . .), lattice parameters and the peak areas of each peak for all phases present. These are sufficient to determine the boundaries of the single-phase regions and the nature of the co-existence regions. Figure 2.7 (a) shows the proposed tie-lines lying between the spinel and layered regions in the Li–Mn–Ni–O system as discussed in the introduction. This will be used here to illustrate how the XRD patterns could be used to confirm that the proposed diagram was correct. Firstly, all XRD patterns obtained would have to be visually consistent with the phase diagram. This simply means that no signs of a second phase existed in scans of samples in the single-phase region, and no samples lying in the co-existence regions appeared single-phase (as will be shown in Chaps. 5 and 6, this proposed phase diagram fails on both counts). However, visual inspection of XRD scans was insufficient to precisely identify the boundaries of the single-phase region. The next step was to carefully examine the values of the lattice parameters obtained in the co-existence region and to compare

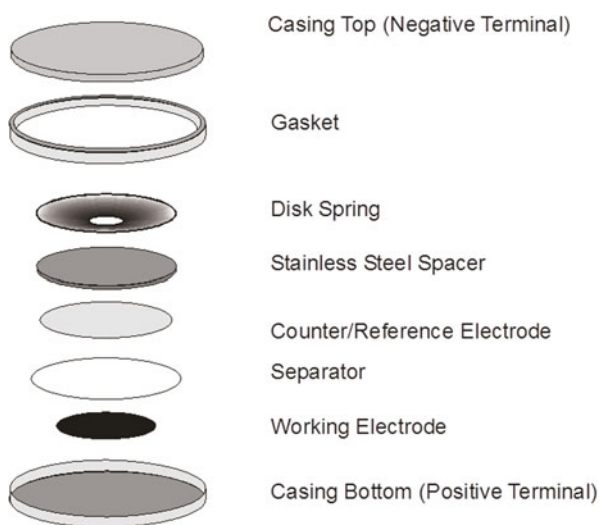
them to those found for single-phase samples. In the proposed phase diagram, tie-lines fan out from Li_2MnO_3 up to an angle of about $\alpha = 70^\circ$. This implies that up to this angle, the value of the layered lattice parameters in the two-phase samples should be equal to those of Li_2MnO_3 . Figure 2.7 (b) illustrates the expected plot of the c lattice parameter as a function of α based on the proposed tie-lines. Since $c = 14.23 \text{ \AA}$ for Li_2MnO_3 when fitted as a hexagonal structure, as shown in Chap. 6, such a graph would confirm that the tie-lines fan-out from Li_2MnO_3 . Plots of this type were extremely useful in demonstrating the directions of tie-lines in the Li–Mn–Ni–O system and were used throughout this thesis. In three-phase regions, there is no variation in the phases present; only the amount of each phase varies. As such, the fitted lattice parameters should remain constant throughout the three-phase region.

In order to work out the boundaries of the single-phase regions, the lever rule was used. Figure 2.7 (c) illustrates the use of the lever rule for sample X lying on a tie-line between phases A and B. Extrapolating to where the integrated peak intensity of the phase A peaks would be zero yields point B. If the proposed phase diagram is correct, point B would coincide with Li_2MnO_3 . In practice, the distance from A to B was calculated using the mathematical form of the lever rule which states that the fraction of phase A is equal to $d(X,B)/d(A,B)$. This allows for the calculation of the position of point B, which can then be compared to the position of Li_2MnO_3 . This same method was used to determine the positions of the corners of three-phase regions as will be demonstrated in Chap. 6. It should be noted that microabsorption effects were not taken into account in the calculations. This is justified for the combinatorial samples with small particle sizes, as will be demonstrated in Sect. 5.4. Therefore, even without Rietveld refinement, the XRD patterns can be used to identify the boundaries of single-phase regions, the direction of tie-lines in two-phase regions and the extent of three-phase regions. The large number of scans in the single-phase regions also provided lattice parameters over wide composition ranges which were expressed as contour plots in Chaps. 5, 6 and 7. These contour plots should be of considerable use to researchers working in these systems.

2.5 Electrochemical Tests

Coin cells were made from a few bulk samples in order to determine the electrochemical performance of materials of interest. Figure 2.8 shows the parts involved in assembling a standard coin cell. Electrochemical tests were carried out using a standard 2325 coin cell with the positive electrode being cycled against a lithium counter electrode (Chemetall Foote Corp.). The electrolyte used was 1 M LiPF_6 in 1:2 ethylene carbonate:diethyl carbonate (Novolyte Corp., now part of BASF). The positive electrodes contained 5 % polyvinylidene-fluoride binder (Kynar 301P, Elf Atochem) and 5 % carbon black (TIMCAL). Two identical cells were typically made. The details of the coin cell design are included in Ref. [63]. The cycling conditions varied from experiment to experiment and will be stated explicitly in the results sections.

Fig. 2.8 A schematic of the components used in making a typical coin cell for electrochemical testing



2.6 Thermo-Gravimetric Analysis

As a consequence of the high surface area to volume ratio, the combinatorial samples were very sensitive to surface reactions. The mass changes resulting from these reactions were studied using a thermo-gravimetric analyzer (TGA). The TGA was useful in the study of lithium loss during synthesis as will be discussed in Chap. 3. A typical TGA run involved heating approximately 10 mg of sample in a small alumina cup in a TA Instrument, SDT-Q600 TGA under a gas flow of 50 mL/min. These samples were approximately five times larger than those made by the solution-dispensing robot and so the TGA results can be considered to be an ideal limit for the behavior of the combinatorial samples (i.e., the combinatorial samples would lose slightly more lithium than those heated in the TGA). The lithium loss experiments were repeated in flows of argon, air and oxygen in order to identify the role played by the atmosphere.

2.7 Elemental Analysis

With lithium being lost during heating of the combinatorial samples in certain regions of the Li–Mn–Ni Gibbs triangle, the composition of a sample is not necessarily the same before and after heating. As such, either atomic absorption (AA) or inductively coupled plasma optical emission spectroscopy (ICP) have been used as elemental analysis in order to determine the actual compositions of samples. To do this for combinatorial samples, the samples were transferred into 2 mL vials with the use of a transfer plate that clamps the substrate to the vials thereby, preventing mixing of neighboring samples. To each vial, approximately 0.5 mL of a solution of 25 % nitric

acid and 75 % hydrochloric acid was added to dissolve the samples. The solutions were then analyzed by Dan Chevalier (Minerals Engineering Centre, Dalhousie University) to give the concentrations of nickel, lithium and manganese, accurate to 5 % for the small samples. The same method was used for bulk samples, though slightly more powder was used to improve the precision of the measurements. For the starting solutions used with the solution-processing robot, AA measurements were repeated three times such that the uncertainty was 2 %.

2.8 Scanning Electron Microscopy

Scanning electron microscopy (SEM) allows the viewing of particles as small as 50 nm in length. As will be discussed in the next chapter, the crystallites made in combinatorial samples heated to 800 °C typically fall in this range such that the SEM was useful in order to get a better idea of whether or not phase separation had occurred. To this end, a few samples were imaged by Ramesh Shunmugasundaram using a Hitachi S-4700 field emission scanning electron microscope with an accelerating voltage of 10 kV and an emission current of 15 μ A.

2.9 Redox Titration

As mentioned in the introduction, the oxidation states of the transition metals in the electrode material have a large effect on the electrochemistry. It proved useful to use redox titrations in order to determine the average oxidation state of the nickel and manganese for the materials discussed in Chap. 8. This involved two redox titrations, both using potassium permanganate. The first involved adding the potassium permanganate to the samples (both dissolved in acid) in order to determine the total amount of manganese present. The second titration involved first mixing the dissolved sample with ferrous ammonium sulfate in order to reduce nickel and manganese to the 2+ oxidation state while oxidizing some iron to 3+ state. The subsequent titration with potassium permanganate then reduced iron back to 2+. The two measurements allowed the determination of the average manganese oxidation state (assuming all nickel was in the 2+ state). As such, a result for the manganese oxidation state greater than 4.0 would imply some Ni^{3+} was present. It is important to notice that this method cannot distinguish between a $\text{Ni}^{2+}\text{--Mn}^{4+}$ pair and a $\text{Ni}^{3+}\text{--Mn}^{3+}$ pair, since this approach essentially counts the number of oxidation states above 2+. To make the distinction between these two combinations, manganese X-ray absorption spectra were taken as described in the next section. The titrations were performed by Oliver Schilling of Erachem Comilog.

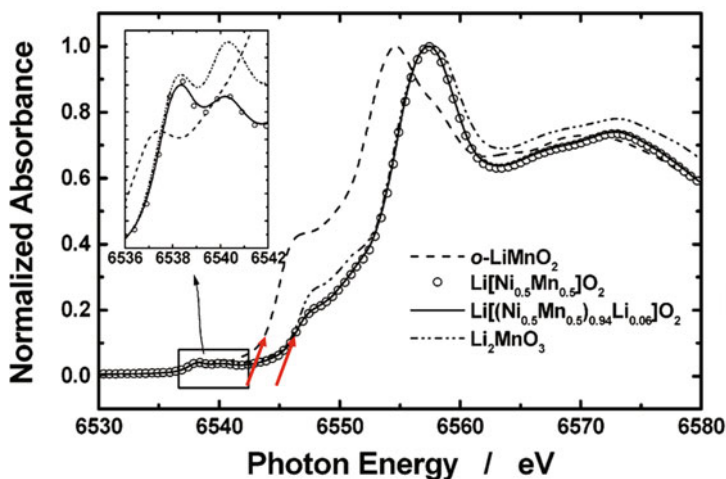


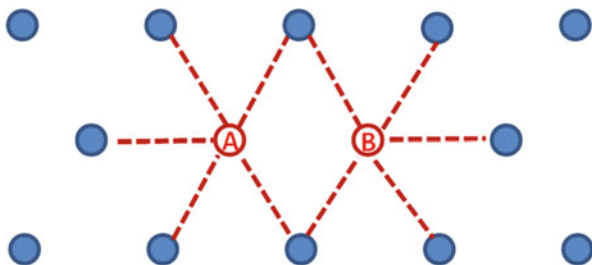
Fig. 2.9 X-ray absorption near-edge structure (XANES) spectra reproduced from Ref. [64] with permission from the American Chemical Society. The *red arrows* mark the rough positions of the main absorption edges

2.10 X-Ray Absorption Spectroscopy

The X-ray absorption spectra of materials are sensitive to both the local and long range electronic structure of the material. Fitting the spectra is rather complex, but information about the oxidation state of each metal can be extracted relatively easily by comparison with known reference materials. Comparing two spectra of materials with similar structures means that the differences seen are primarily due to the electronic configuration of the atom in question.

Figure 2.9 shows the X-ray absorption near-edge structure (XANES) spectra for manganese-containing samples near the Mn K-edge (obtained by exciting 1 s electrons) published by Myung et al. [64]. The position of the main absorption edge, marked for each spectrum with a red arrow, is sensitive to the oxidation state of the manganese atoms. Thus, the two reference materials (Li_2MnO_3 for 4+ and LiMnO_2 for 3+) were used by Myung to determine that the manganese atoms in the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_4$ sample were in the 4+ state. This simple analysis will be used in Chap. 8 to determine the oxidation state of the manganese atoms. The XANES spectra were collected by Paul Duchesne on the PNC-CAT beamline 20-BM at the Advanced Photon Source of Argonne National Labs. Incident X-rays were made monochromatic using a silicon (111) double-crystal system employing platinum mirrors for harmonic rejection. The samples were all measured in transmission mode at room temperature using ionization chamber detectors.

Fig. 2.10 An array of atoms illustrating the interactions used in the Monte Carlo simulations (*red lines*) when calculating the probability of accepting a move wherein atoms A and B are interchanged



2.11 Helium Pycnometry

Some of the materials studied in this thesis showed oxygen non-stoichiometry (either oxygen or metal vacancies). Precise density measurements were used to identify the concentrations of such vacancies. This required knowing the metallic compositions from ICP and the volume of the unit cell from XRD. A Micromeritics AccuPyc II 1340 Helium Pycnometer was used to measure the true volume of the samples. The pycnometer works by pressurizing an empty reference chamber and measuring this pressure before opening a valve between the reference and sample chambers and remeasuring the pressure again. Since the volumes of the empty chambers are known, Boyles' law was used to calculate the volume of the sample. A high precision scale was used to measure the mass of the sample. Multiple measurements with the pycnometer were used in order to calculate a statistical uncertainty. This approach was used in Chaps. 6 and 8.

2.12 Monte Carlo Simulations

As has been discussed, a significant portion of this thesis deals with phase transformations taking place during slow cooling. A Monte Carlo simulation was used to examine the changes that take place on the metal atom layers in the layered oxide materials during slow cooling. This was used on three occasions, in Chaps. 4, 8 and 9. In each case, a 50×50 hexagonal array was made with compositions matching the stoichiometry on the TM layer determined experimentally. The initial array was made assuming random occupation of all sites such that the starting configuration corresponded to infinite temperature where entropy wins out entirely over internal energy. For all simulations, the potential used for the energy of the system was the Coulombic potential for nearest neighbor (NN) interactions only and periodic boundary conditions were used. The effective charge of each atom was assumed to be proportional to its oxidation number. The simulation involved evaluating whether randomly chosen nearest neighbors might exchange position. Figure 2.10 shows the interactions involved in calculating the change in energy between the original configuration and the proposed one obtained by switching the atoms A and B. The effective charge of the i -th atom is $\delta \cdot n_i$, with n_i being the oxidation number of atom i in the

original structure and n'_i that of the atom in the structure after the proposed change. The change in energy due to such a move is:

$$\frac{\Delta E}{k_B T} = \beta_T \left(\sum_{i,j}^{NN} n'_i n'_j - \sum_{i,j}^{NN} n_i n_j \right) \quad (2.6)$$

where k_B is the Boltzmann constant, T is temperature, $\beta_T = \delta^2 / (4\pi\epsilon_o k_B T \cdot a)$, ϵ_o is the permittivity of free space and a is the in-plane lattice parameter. In this model, it was assumed that all nearest neighbors were separated by a distance a . The Metropolis rate equation [65] was used such that the probability of accepting a move is 1 if $\Delta E < 0$ and $e^{-\Delta E/k_B T}$ if $\Delta E > 0$. The simulation was run for increasing values of β_T (0.5, 1, 1.5 ... 5) in order to simulate slow cooling. At each temperature, 10000 Monte Carlo steps were performed (2500 attempted moves constituted a Monte Carlo step).

The third use of this simulation, discussed in Chap. 9, involved a situation where the lithium layer was not entirely filled with lithium. As such, interactions between the lithium and TM layers had to be taken into account. Again, only the six NN out-of-plane interactions were considered (three from the plane above, three from the plane below). The out-of-plane nearest neighbor lies $c/6$ away in the out-of-plane direction and $a/\sqrt{3}$ away in the in-plane direction such that the distance between out-of-plane nearest-neighbors is roughly 1.004 times larger than for in-plane neighbors based on $a = 2.90 \text{ \AA}$ and $c = 14.30 \text{ \AA}$ as obtained in Chap. 9. Thus, the in-plane and out-of-plane nearest neighbors are nearly equidistant and this correction was included in the calculations.

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