Sensitivity of Bulk Magnetism to Off-Stoichiometry in the Next Generation Cathode Material LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$

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We present a structural and magnetic study on two batches of polycrystalline LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$ (commonly known as Li NMC 811), a Ni-rich Li battery cathode material, using elemental analysis, X-ray and neutron diffraction, bulk magnetometry, and polarised neutron scattering measurements. We find that the samples, labelled S1 and S2, have the composition Li$_{2-y}$Ni$_{0.8+y}$Mn$_{0.1+y}$Co$_{0.1+y}$O$_2$, with $x = 0.025(2)$, $y = 0.120(2)$ for S1 and $x = 0.002(2)$, $y = 0.004(2)$ for S2, corresponding to different concentrations of magnetic ions and excess Ni$^{2+}$ in the Li$^+$ layers. Both samples show a peak in the zero-field cooled (ZFC) dc susceptibility at 8 K but the temperature at which the ZFC and FC (field-cooled) curves deviate is substantially different. Ac susceptibility measurements indicate a frequency-dependent transition in S1 and a frequency-independent transition in S2. Our results demonstrate the extreme sensitivity of bulk magnetic measurements to off-stoichiometry of the magnetic transition metal ions in Li NMC 811 and indicate that such measurements can be used to benchmark sample quality for Ni-rich Li ion battery cathode materials.

I. INTRODUCTION

LiNiO$_2$, a layered transition metal (TM) oxide with $S = 1/2$ Ni$^{3+}$ ions on a triangular lattice [Fig. 1(a)], has been widely investigated as a quantum spin liquid candidate. However, the nature of its magnetic ground state remains controversial after decades of investigation [1–6]. This is because LiNiO$_2$ is extremely prone to off-stoichiometry and excess of Ni$^{2+}$ in Li$^+$ layers. Studies have shown that it is not possible to synthesise perfectly stoichiometric LiNiO$_2$, and instead the formula is Li$_{1-x}$Ni$_{1+y}$O$_2$ with $x \approx 0.004$ in the best quality samples [7–11]. This results in $2xS = 1$ Ni$^{2+}$ spins in order to maintain charge balance. Additionally, due to the similarity in Li$^+$ and Ni$^{2+}$ radii, $x$ Ni$^{2+}$ tend to migrate from the transition metal (TM) to the Li$^+$ layers. These factors have two crucial consequences for the magnetism. First, the presence of different magnetic species ($S = 1/2$ and $S = 1$) in amounts dependent on the degree of off-stoichiometry results in the magnetic ground state being highly sample-dependent. Second, the excess Ni$^{2+}$ in the Li$^+$ layers changes the competing interactions: in addition to the intra-layer ($J$) and inter-layer ($J'$) interactions, there are interactions between the spins in the Li$^+$ layers and those in the TM layers ($J''$) [Fig. 1(b)]. This may cause the spins to order magnetically or freeze instead of remaining in a dynamic liquid-like state [6,12]. A previous muon spin relaxation ($\mu$SR) and magnetometry study on Li$_{1-x}$Ni$_{1+y}$O$_2$ with $x = 0.02$, 0.03 found static ferromagnetic order for $x = 0.03$ below $\sim 50$ K and a disordered antiferromagnetic state for $x = 0.02$ below $\sim 20$ K [13]. Another $\mu$SR study on quasi-stoichiometric LiNiO$_2$ ($x = 0.004$) found a disordered, slowly fluctuating state below 12 K [14]. Thus the magnetic ground state varies significantly with slight changes in the off-stoichiometry $x$.

LiNiO$_2$ has also been investigated as a Li ion battery cathode material as it is cheaper and less toxic than the commercially established LiCoO$_2$ [15–18]. However, safety issues due to thermal instability severely limit its practical applicability [19]. Additionally, the inherent off-stoichiometry and migration of Ni$^{2+}$ to the Li$^+$ layers leads to irreversible capacity loss on long-term cycling [18,20]. Therefore the focus has shifted towards Ni-rich compositions from the family of Li ion TM oxides with the general formula LiNi$_y$Mn$_{1-y}$Co$_2$O$_2$, $x + y + z = 1$, commonly known as Li NMC oxides [20,22]. Being Ni-rich, these materials inherit the tendency for off-stoichiometry and Ni$^{2+}$ excess in Li$^+$ layers associated with LiNiO$_2$, which can significantly affect their performance in batteries [23].

In this paper, we focus on the next-generation Li ion battery cathode material LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$, commonly known as Li NMC 811. We present an investigation of the bulk magnetic properties, crystal structure and chemical composition of two different samples of Li NMC 811 using elemental analysis, powder X-ray and neutron diffraction, bulk magnetic measurements, and polarised neutron diffraction. We show that the magnetic susceptibility is extremely sensitive to slight changes in the stoichiometry, consistent with previous reports on LiNiO$_2$ [7,9,24,25]. This indicates that bulk magnetic measurements can be a powerful tool to benchmark sample quality for industrial-scale production of Ni-rich Li ion bat-
Electrochemical characterisation of 

**II. EXPERIMENTAL METHODS**

Two batches of polycrystalline samples of LiNMC 811 were obtained from Targray, each being purchased on a separate occasion. The samples will be referred to as S1 (Targray, Batch 1) and S2 (Targray, Batch 2) throughout this manuscript. Since LiNMC 811 is known to be sensitive to moisture [20, 26], the samples were stored in an Ar-atmosphere glovebox. All subsequent sample handling was in an Ar-atmosphere glovebox unless otherwise noted.

Elemental analysis was performed using inductively-coupled plasma optical emission spectroscopy (ICP-OES, Thermoscientific 7400 Duo). Aqueous solutions were prepared by dissolving $\sim$10 mg of the as-received LiNMC 811 powder in 1 ml of freshly prepared, concentrated aqua regia (3:1 hydrochloric to nitric acid, trace element grade, Fisher Scientific) overnight and subsequently diluting with deionized water (Millipore) to $\sim$1-10 ppm by mass for the measurement. The concentration of a given element in the solutions was determined by comparing the emission of the sample solutions to a calibration line generated from a concentration series using a multielemental standard (VWR, Aristar®) at each wavelength of interest. The emission wavelengths were selected such that there was no interference from other measured elements, elements in the standard or the matrix solution (2% nitric acid). The transition metals each had multiple wavelengths which were suitable for the ICP-OES measurement and the results at each wavelength were averaged to obtain the molar value of ions in solution. The composition of the powders was calculated by assuming that the molar fraction of transition metals was 1. The Li concentration was calculated by dividing the total moles of Li by the total moles of transition metals.

Room temperature powder X-Ray diffraction (PXRD) scans for structural analysis were collected over $5^\circ \leq 2\theta \leq 150^\circ$ ($\Delta 2\theta = 0.004^\circ$) using the 111 beamline at Diamond Light Source ($\lambda = 0.826$ Å). Room temperature powder neutron diffraction (PND) experiments for structural characterisation were carried out on the GEM diffractometer, ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, United Kingdom. The absorption correction for the time-of-flight (TOF) PND data was carried out using the Mantid program [27] and cross-checked using the GudrunN software [28]. The structural Rietveld refinements [29] were carried out using the Fullprof suite of programs [30]. The background was modelled using a Chebyshev polynomial and the peak shape was modelled using a pseudo-Voigt function for the PXRD data and an Ikeda-Carpenter function for the TOF PND data.

Magnetic dc susceptibility measurements were performed on a Quantum Design Magnetic Properties Measurement System (MPMS) with a Superconducting Quantum Interference Device (SQUID) magnetometer. The zero-field cooled (ZFC) and field-cooled (FC) susceptibility $\chi(T)$ was measured in a field of 100 Oe in the temperature range 2-300 K to investigate the presence of magnetic ordering. ZFC measurements were also carried out at 1000 Oe in the same temperature range to perform Curie-Weiss fits. In a field of 1000 Oe, the isothermal magnetisation $M(H)$ curve is linear at all $T$ and so $\chi(T)$ can be approximated by the linear relation $\chi(T) \approx M/H$. Isothermal magnetisation measurements in the field range $\mu_0 H = 0$-9 T for selected temperatures were carried out using the ACMS (AC Measurement System) option on a Quantum Design Physical Properties Measurement System (PPMS). ZFC ac susceptibility measurements in the temperature range 2-60 K were carried out using the same PPMS option with a dc field of 20 Oe and a driving field of 3 Oe at frequencies between 1-10 kHz.

Polarised neutron diffraction measurements for the S2 sample were carried out on the D7 diffractometer at the Institut Laue-Langevin, France, with $\lambda = 4.8$ Å. A sample of mass 7 g was loaded in an annular Al can of diameter 20 mm with an 18 mm cylindrical insert to minimise the effect of absorption from Li in our natural abundance samples. Scans were collected at 1.5 K and 20 K for 10 hours each. The data was processed in LAMP [31] to separate the nuclear coherent, nuclear-spin incoherent, and magnetic scattering contributions.

Li NMC 811 electrodes for electrochemical characterisa-
TABLE I. Composition from ICP-OES for samples S1 and S2.

| Element | S1       | S2       |
|---------|----------|----------|
| Li      | 1.06(5)  | 1.01(3)  |
| Ni      | 0.80(2)  | 0.80(2)  |
| Mn      | 0.10(2)  | 0.10(2)  |
| Co      | 0.10(2)  | 0.10(2)  |

The slurry of S1 and S2 were prepared by mixing 90 wt% Li NMC 811 powder, 5 wt% polyvinylidene difluoride (PVDF) binder, 5 wt% carbon black (Timcal SuperP Li) and a desired amount of the NMP (1-Methyl-2-pyrrolidinone, anhydrous, 99.5%, Sigma-Aldrich) solvent in a Thinky planetary mixer at 2000 rpm for 10 minutes in total (5 minutes per cycle and two cycles). The slurry was coated onto an Al foil and pre-dried at 100 °C for 1 hour in a dry-room (~ -55 °C dew point). Dried Li NMC 811 laminates were punched into circular disks with a diameter of 14 mm, which were further dried at 120 °C for 12 hours under dynamic vacuum (~ 10^-2 mbar) in a Büchi oven. 2032 coin cells (Cambridge Energy Solution) were assembled in an Ar-atmosphere (O_2 < 1 ppm, H_2O < 1 ppm) glovebox consisting of a 14 mm diameter Li NMC 811 cathode, 16 mm diameter Celgard 3031 separator and 15 mm diameter Li metal. 50 mL electrolyte (1 M LiPF_6, ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3/7, Soul-Brain MI) was added to each coin cell. Battery cyclings were conducted on an Arbin battery cycler at room temperature between 3.0 V and 4.4 V at various rates. C-rates were defined based on a reversible capacity of 200 mAh g^{-1}, for instance, for the C/5 rate (5 hours for one charge or discharge process), a current density of 40 mA g^{-1} was applied.

III. RESULTS

A. Elemental analysis

The composition of both samples as determined from ICP-OES is given in Table I and the details of the error analysis are given in Appendix A. Both samples were found to have the ideal transition metal (TM) stoichiometry within error. Sample S1 is found to have a slight Li excess as compared to the nominal stoichiometry.

B. Room temperature PXRD and PND

The room temperature PXRD data for S1 and S2 indicated that the samples were phase pure and adopt the crystal structure of Li NMC oxides (space group \textit{R}3\textit{m}) with no indication of lowering of symmetry [33]. The room temperature PND data were consistent with this; however, closer inspection of the data plotted on a logarithmic intensity scale indicated a very small Li_2CO_3 impurity peak for S1, while no such peak was visible for S2. This is consistent with the higher Li content seen in elemental analysis for S1. The amount of Li_2CO_3 for S1 from the refinement was found to be 0.2(3) wt% and hence was not considered in further structural analysis.

The crystal structure was refined using a combined Rietveld refinement with the room temperature PXRD and TOF PND data using a structural model based on LiNiO_2, space group \textit{R}3\textit{m} [32]. PXRD is sensitive to the TMs (mainly Ni because of its higher concentration) while PND is much more sensitive to the contrast between Li (coherent scattering length of its higher concentration) while PND is much more sensitive to the contrast between Li (coherent scattering length of its higher concentration) while PND is much more sensitive to the contrast between Li (coherent scattering length of its higher concentration).

The PXRD data was adjusted to satisfy the following two conditions simultaneously: a) the total weighting of the PXRD and 5-bank PND refinements summed to 1 (each PND bank was assigned the same weighting); b) the weighted residual of the PXRD refinement was equal to that of the PND refinement, such that the PXRD and PND data contributed equally to the refinement. The refinement of the chemical composition is discussed later in Section III.D.

Representative fits to the PXRD and TOF PND data are shown in Figure 2 and the refined structural parameters are compiled in Table II. Li-deficient LiNiO_2 with the formula Li_{1-x}Ni_{1+x}O_2, x > 0.38, crystallises in a cubic rock salt structure (c/a = 2√6 = 4.889) with Li/Ni disordered on the 4a site; however, as the quantity of Li increases, it transforms to a hexagonal structure consisting of alternating layers of LiO_6 and NiO_6 octahedra and the c/a value increases with the layering of the material [18]. The c/a ratio for our samples of Li NMC 811 (4.944(3) for S1 and 4.946(2) for S2) is consistent with a layered hexagonal structure. Though less than that of a well-layered compound like LiCoO_2 (c/a = 4.99) [34, 35], it is consistent with the typical values for the parent compound LiNiO_2 (c/a = 4.93) [17, 24].

TABLE II. Structural parameters for samples S1 and S2. All refinements were carried out in the space group \textit{R}3\textit{m}, with Li on the 3a sites (0,0,0), TM (Ni, Mn, Co) on the 3b sites (0,0,0.5), and O on the 6c (0,0,z) sites. The Mn^{4+} composition y and Ni^{4+} excess on the Li^{2+} site x were allowed to vary subject to the constraints discussed in the text.

| Parameter | S1       | S2       |
|-----------|----------|----------|
| a (Å)     | 2.8719(2) | 2.8727(3) |
| c (Å)     | 14.199(2) | 14.207(3) |
| c/a       | 4.944(3)  | 4.946(2)  |
| \(\chi^2\) | 0.025(2)  | 0.002(2)  |
| O (0,0,0) | 0.120(2)  | 0.094(2)  |
| TM (Ni/Mn/Co) (0,0,0.5) | 0.24095(9) | 0.24103(8) |
| \(B_{iso}(Å^2)\) | 5.3 | 5.7 |

\* in Li_{1-x}Ni_{0.9+x-y}Mn_xCo_{0.1}O_2
C. Bulk magnetic measurements

DC susceptibility $\chi(T)$ and isothermal magnetisation $M(H)$ measurements for S1 and S2 are shown in Figures 3 and 4, respectively. At low temperatures, both samples show a peak in the ZFC DC susceptibility at $T_g = 8.0(2)$ K [Fig. 3] and deviation in the ZFC-FC curves, indicating glassy behaviour. However, the temperature $T_{ZFC,FC}$ at which the ZFC-FC curves deviate is very different: 8.0(2) K for S1 and 122(2) K for S2. The isothermal magnetisation at $T = 2$ K ($T < T_g$) shows a slight hysteresis for both samples, consistent with a disordered ground state, whereas no hysteresis is observed at $T = 15$ K ($T > T_g$) [Fig. 4].

In a field of 1000 Oe, the reciprocal susceptibility $\chi^{-1}(T)$ is linear above 200 K and was used to fit the Curie-Weiss law, $\chi = \frac{C}{T - \theta_{CW}}$, where $C$ is the Curie constant and $\theta_{CW}$ is

| Parameter                  | S1       | S2       | Sample in Ref. 36 |
|----------------------------|----------|----------|-------------------|
| $T_g$ (K)                  | 8.0(2)   | 8.0(2)   | 20                |
| $T_{ZFC,FC}$ (K)           | 8.0(2)   | 122(2)   | 55                |
| $\theta_{CW}$ (K)          | -8(1)    | -10(3)   | -25               |
| $\mu_{eff}$ ($\mu_B$/f.u.)| 2.26(3)  | 2.08(2)  | 2.07              |

| TABLE III. Bulk magnetic properties for both batches of LiNMC811 and comparison with the LiNMC811 sample in Ref. 36. Curie-Weiss fits were carried out in the temperature range 200-300 K in an applied field of 1000 Oe. Assuming ideal stoichiometry LiNi$_{0.1}$Ni$_{0.7}$Mn$_{0.1}$Co$_{0.1}$O$_2$, the theoretical magnetic moment per formula unit (f.u.) $\mu_{th} = 2.10 \mu_B$/f.u. |
clear frequency dependence, \( \frac{\Delta T_g}{T_g \Delta(\log \omega)} = 0.01 \), consistent with spin-glass-like behaviour [37]. However, the transitions in sample S2 show no frequency dependence. The imaginary component of the ac susceptibility, \( \chi''(T) \), shows additional peaks at 20 K and 35 K in both samples [Fig. 5 inset]. A previous study on LiNMC 811 reported a frequency-dependent peak at 24 < T < 70 K, consistent with our measurements [36]. Such additional peaks in \( \chi''(T) \) at frequencies up to 1 kHz have also been reported for other Li ion battery cathode materials such as LiNi0.5Mn0.5O2 and LiNi0.4Mn0.6Co0.2O2, and have been attributed to spin reorientation transitions [38].

### D. Determination of chemical composition

We now discuss refinement of the chemical composition of the two LiNMC 811 samples. The refinement was subject to the following constraints: a) charge balance; b) the the 3a, 3b and 6 crystallographic sites (corresponding to Li, TM and O respectively) were fully occupied; c) the magnetic moment was consistent with \( \mu_{eff} \), the magnetic moment obtained from the Curie-Weiss fit [Table III]; d) the composition of the TM ions were consistent with the values obtained from elemental analysis within error. We further reduced the number of free parameters by noting that, since Co3+ has \( S = 0 \), its composition cannot be constrained using magnetometry. Hence the Co composition was fixed to the nominal value 0.1, consistent with elemental analysis. Previous neutron diffraction studies on LiNiO2 have examined the possibility of Li/Ni site disorder such as \{Li1−xNi\}3a[Ni1−yLi]3bO2 and \{Li1−xNi\}3a[Ni1−yLi]3bO2 and ruled it out for near-stoichiometric samples [32] [39]. Our refinements also indicate the absence of Li+ in the TM layers and so a single parameter \( x \) was used to refine the Ni2+ excess in the Li+ layers. The composition Li1−xNi0.98+y−zMnCo0.1O2 was refined for a range of \( (x, y) \) values consistent with the above constraints and the final values were chosen corresponding to the refinement with the minimum \( \chi^2 \). Both samples of Li NMC 811 are slightly Li-deficient, consistent with previous studies on LiNiO2; however, their compositions are different. Sample S1 has the formula Li0.975(2)Ni0.805(4)Mn0.120(2)Co0.1O2 while S2 has the formula Li0.996(2)Ni0.810(4)Mn0.094(2)Co0.1O2, corresponding to Ni2+ excess in the Li+ layers of 2.5(2)% and 0.2(2)%, respectively.

### E. Polarised neutron diffraction

Neutron scattering experiments using XYZ polarisation analysis on the D7 instrument at the ILL enable separation of the nuclear coherent, nuclear-spin incoherent, and magnetic scattering contributions from the sample. Thus they are ideal for investigating diffuse scattering in disordered magnetic systems [40]. Our ac susceptibility measurements indicated a static magnetically-disordered state for S2 and so polarised neutron scattering measurements were carried out to investigate the nature of the transition at 8 K. Figure 6(a) shows the
magnetic scattering as a function of momentum transfer $Q$ for S2 at 1.5 K (below $T_g = 8$ K) and 20 K (above $T_g = 8$ K). The negative intensity at $Q \approx 1.3$ Å$^{-1}$ is an artifact from the subtraction of the nuclear Bragg peak and does not have any physical significance. No magnetic Bragg peaks are observed, consistent with the absence of long-range magnetic order; however, there is a broad diffuse feature at low $Q$ indicative of short-range spin correlations. A previous inelastic neutron scattering study on Li$_{1-x}$Ni$_{1+x}$O$_2$, $x = 0.029(1)$, reported a decrease in the inelastic channel and an increase in the elastic line on cooling through $T_g = 15$ K, consistent with spin freezing [6]. The elastic scattering at 1.7 K in [6] showed no magnetic Bragg peaks, only broad magnetic diffuse scattering at low $Q$. The feature observed in our magnetic scattering for S2 is qualitatively similar to this previous report on LiNiO$_2$; however, it was not possible to carry out quantitative modelling of the magnetic interactions due to the weak magnetic scattering and contributions from multiple magnetic species.

The nuclear coherent scattering intensity at $T = 20$ K is plotted on a logarithmic scale as a function of $Q$ in Figure (b). Several very weak peaks from an impurity phase are observed along with the single nuclear Bragg peak from the main phase; these were identified to be from Li$_2$CO$_3$. This Li$_2$CO$_3$ phase was beyond the detection limit of the PXRD and PND data for S2 used for our structural Rietveld refinements; however, it is observed here due to the separation of the coherent and incoherent nuclear contributions, which improves the signal-to-noise ratio in the coherent Bragg scattering. Due to the limited $Q$ range and the presence of only a single nuclear Bragg peak from the main phase, it was not possible to carry out a structural refinement to quantify the exact amount of Li$_2$CO$_3$; however, based on our structural analysis for S1 (for which the Li$_2$CO$_3$ impurity was visible in the PND data plotted on a logarithmic scale), we can place an upper bound of 0.2(3) wt%.

**IV. DISCUSSION**

We now discuss the key features of our bulk magnetic measurements and structural refinements on the two commercial samples of Li NMC 811.

The ZFC transition temperature and ZFC-FC irreversibility in our Li NMC 811 samples is consistent with previous reports on LiNiO$_2$ samples with similar values of $x$ in Li$_{1-x}$Ni$_{1+x}$O$_2$ ($T_g = 9$ K) [6, 7], as well as other Ni-rich Li ion cathode materials such as LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (Li NCA) ($T_g = 6.5$ K) [41] and LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (Li NMC 622) ($T_g = 7.2$ K) [42]. This indicates that the magnetic properties are still dominated by the $S = \frac{1}{2}$ Ni$^{3+}$ and $S = 1$ Ni$^{2+}$ spins. The difference in $T_{ZFC-FC}$ in our samples can be attributed to the difference in composition, which alters the relative number of Ni$^{3+}$, Ni$^{2+}$, and Mn$^{4+}$, and hence the magnetic interactions. A previous study on a sample of Li NMC 811 had reported $T_g \approx 20$ K and $T_{ZFC-FC} \approx 50$ K; however, the Ni$^{2+}$ excess in the Li$^+$ layers (calculated using XRD) was 3.9% [36], which is greater than both our samples, and the Mn$^{4+}$ composition was not refined. Previous investigations on Li$_{1-x}$Ni$_{1+x}$O$_2$ have shown that even a slight change in composition can dramatically alter the transition temperature; for example, $T_g = 7.5$ K for $x = 0.004$ and 8.6 K for $x = 0.015$ [10]. The transition temperature for our samples, $T_g = 8$ K, is consistent with lower values of $x$ (2.5(2)% and 0.2(2)% for S1 and S2, respectively) as compared to the previous study.

Our bulk magnetic measurements demonstrate that the sample dependence of the magnetic properties widely reported for the parent material LiNiO$_2$ persists in Li NMC 811. The origin of the sample dependence in LiNiO$_2$ is the off-stoichiometry Li$_{1-x}$Ni$_{1+x}$O$_2$ and $x$, the Ni$^{2+}$ excess in the Li$^+$ layers. However, the situation is more complex in Li NMC 811 due to the presence of multiple magnetic species. For ideal stoichiometry, the formula can be written as LiNi$_{1.1}$Ni$_{0.7}$Mn$_{0.1}$Co$_{0.1}$O$_2$, the magnetic species being $S = \frac{1}{2}$ Ni$^{3+}$, $S = 1$ Ni$^{2+}$ and $S = \frac{3}{2}$ Mn$^{4+}$, whereas Co$^{3+}$ with $S = 0$ plays the role of non-magnetic site dilution in the TM layers. However, the composition for our samples is...
$\text{Li}_{1-x}\text{Ni}_{0.94+y}\text{Mn}_{x}\text{Co}_{1-y}\text{O}_2$, with $x = 0.025(2)$, $y = 0.120(2)$ for S1, and $x = 0.002(2)$, $y = 0.094(2)$ for S2. Thus the amount of each magnetic species present depends on the composition: $(0.9 - x)\text{Ni}^{3+} (S = \frac{1}{2})$, $(y + 2x)\text{Ni}^{2+} (S = 1)$ and $y \text{Mn}^{4+} (S = \frac{3}{2})$. Since $x$ and $y$ are both different for S1 and S2 (S2 is closer to nominal stoichiometry), the relative number of magnetic species is also different in these samples. Additionally, $x \text{Ni}^{2+}$ migrate to the Li$^+$ layers, introducing a competition between the inter-layer and intra-layer interactions dependent on $x$, analogous to LiNiO$_2$. Further, it has been observed that a higher deviation from nominal stoichiometry in $\text{Li}_{1-x}\text{Ni}_{1+y}\text{O}_2$ corresponds to a greater tendency for spin-glass-like behaviour [6]. Thus S1, which is more off-stoichiometric, exhibits a frequency dependent spin-glass-like transition whereas S2, close to ideal stoichiometry, shows no such frequency dependence in the ac susceptibility. Thus the differences in the bulk magnetic properties of S1 and S2 can be explained.

We find that a combination of elemental analysis, bulk magnetic measurements, and diffraction is essential to provide an accurate quantitative estimate of the composition for Li NMC 811. Previous studies have often set the composition to the values determined from elemental analysis and carried out structural refinements using X-ray diffraction data only [22,43]. Our results indicate that this approach may need to be treated with caution for Ni-rich compositions, which tend to be Li-deficient. Elemental analysis provides the average composition value for each element; that is, the contributions from the main phase (LiNMC 811) as well as any impurity phases (Li$_2$CO$_3$) are both included. PXRD is much less sensitive to the presence of light elements like Li, C, and O, and so no Li$_2$CO$_3$ impurity Bragg peaks are visible in the room temperature PXRD pattern. By contrast, PND is much more sensitive to the presence of these elements; our room temperature PND data for S1 and polarised neutron diffraction data at 20 K for S2 provide conclusive evidence for the presence of Li$_2$CO$_3$. Returning to our elemental analysis results, since the Li composition was equal to 1 (within error) and the neutron data confirms the presence of Li$_2$CO$_3$, we can conclude that the Li NMC 811 samples are indeed Li-deficient. This is consistent with our combined structural refinements. Recent high resolution powder diffraction studies on Li NMC oxides have also indicated the necessity of using PXRD and PND data to determine the stoichiometry accurately [23,45]. By including an additional constraint on the total magnetic moment from our bulk magnetic measurements, we are able to increase the accuracy of our refined compositions for Li, Ni, and Mn in Li NMC 811. Techniques such as Li nuclear magnetic resonance (NMR) could also be used to quantify the Li composition in Li NMC 811 more accurately as the signal would be well separated for paramagnetic (Li NMC 811) and diamagnetic (Li$_2$CO$_3$) Li-containing phases.

Another key result of our study is to demonstrate the remarkable sensitivity of bulk magnetic measurements to variations in the composition $\text{Li}_{1-x}\text{Ni}_{0.94+y}\text{Mn}_{x}\text{Co}_{1-y}\text{O}_2$, particularly changes in $y$, the amount of $S = \frac{3}{2}$ Mn$^{4+}$, and $x$, the amount of Ni$^{2+}$ in the Li$^+$ layers. The presence of Ni$^{2+}$ excess in Li$^+$ layers in LiNiO$_2$ has been repeatedly linked to deterioration in cycling performance as the Ni$^{2+}$ significantly hinder Li$^+$ mobility [13]. Measurements comparing the electrochemical performance of S1 and S2, Appendix B suggest that the degree of Ni$^{2+}$ excess in Li$^+$ layers ($= 2.5(2)\%$ for S1 and $0.2(2)\%$ for S2 respectively) has no significant influence on the rate performance for Li NMC 811 samples with low levels of off-stoichiometry (upto 2-3% of Ni$^{2+}$ excess in Li$^+$ layers). Our results indicate that bulk magnetic measurements can serve as a powerful laboratory tool for benchmarking such ‘good quality’ samples of Li ion TM oxide battery cathode materials prior to carrying out long-term electrochemical cycling, particularly for Ni-rich systems which are prone to off-stoichiometry and migration of Ni$^{2+}$ into the Li$^+$ layers.

V. CONCLUSION

We have carried out elemental analysis, room temperature X-ray and neutron diffraction, bulk magnetic measurements, and polarised neutron scattering measurements on two powder samples of Li NMC 811 from a commercial supplier. Our combined PXRD and PND structural refinements using constraints from all these techniques show that the samples have the composition $\text{Li}_{0.975(2)}\text{Ni}_{0.805(4)}\text{Mn}_{0.120(2)}\text{Co}_{0.104(2)}\text{O}_2$ for S1 and $\text{Li}_{0.998(2)}\text{Ni}_{0.808(4)}\text{Mn}_{0.094(2)}\text{Co}_{0.104(2)}\text{O}_2$ for S2 respectively. Bulk magnetic measurements reveal a transition at 8 K for both samples, but the ZFC-FC curves deviate at very different temperatures: 8 K for S1 and 122 K for S2. The nature of the transition is also different: dynamic in S1 with a frequency dependence consistent with spin-glass-like behaviour, and frequency independent in S2. This is attributed to the fact that S1 is more off-stoichiometric and so shows a greater tendency for spin freezing, analogous with the parent compound $\text{Li}_{1-x}\text{Ni}_{1+y}\text{O}_2$.

Thus a combination of elemental analysis, diffraction, and bulk magnetic measurements can be used to distinguish high quality samples of Li NMC 811 and other Ni-rich Li ion battery cathode materials prior to cycling them in batteries.

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Appendix A: ICP-OES error analysis

To understand the error in the ICP-OES measurement, error calculations were made from the two largest sources of uncertainty: the error associated with the sample measurement and the error in the linear calibration. From these values, error calculations were performed at the 95% confidence level as discussed in [46]. The standard deviation of the sample measurement is simply the standard deviation of the three replicate measurements and represents how repeatable the individual measurement is for a given sample. The prediction interval, \( s(x_0) \), represents how accurate the instrument response is based on a linear relationship between the sample concentration and intensity at a given wavelength. The prediction interval can be calculated using equation \( A1 \):

\[
s(x_0) = \frac{\text{RSD}}{b} \sqrt{\frac{1}{N} + \frac{1}{n} + \frac{(\bar{y}_0 - \bar{y})^2}{b^2 \Sigma_{i=1}^{n} (x_i - \bar{x})^2}}
\]

where

- \( \text{RSD} \) = residual standard deviation of \( y \) with \( x \)
- \( n \) = number of calibration points = 4
- \( N \) = number of repeat calibration points / replicates = 3
- \( b \) = slope of linear calibration
- \( \bar{y}_0 \) = mean of \( N \) measurements of \( y \)-value (intensities) for the sample
- \( \bar{y} \) = mean of the \( y \)-values of the calibration standards
- \( x_i \) = \( x \)-value (concentration) of the standards
- \( \bar{x} \) = mean of the \( x_i \) values of the samples

To combine the error at each wavelength at the confidence level, the confidence interval was calculated for both the standard deviation of the sample measurement (\( \mu_{\lambda,n,s} = t_{N-1} \frac{SD_{\text{RSD}}}{\sqrt{N}} \)) and for the prediction interval (\( \mu_{\lambda,n,s(x_0)} = t_{n-2} s(x_0) \)) using a two sided t-statistic. In our case, both t-statistics have 2 degrees of freedom (\( t_{N-1} = t_{n-2} = 4.3 \)). The standard deviation of the sample measurement was then combined with the prediction interval to obtain the total error of the measurement at a given wavelength \( \mu_\lambda = \sqrt{\mu_{\lambda,n,s}^2 + \mu_{\lambda,n,s(x_0)}^2} \). The errors are given in Table IV. Since the concentrations of each element were measured at different wavelengths (2 for Co, 3 for Mn and 4 for Ni) and averaged to obtain the mean concentration in the measurement, the confidence interval for each wavelength was combined using \( \mu_{\text{element},k} = \frac{\mu_\lambda}{\sqrt{\text{No.of}\lambda}} \).

Finally, the confidence interval for each element was calculated using the expression \( \mu_{\text{element,composition}} = \sqrt{\mu_{\text{Ni,k}}^2 + \mu_{\text{Mn,k}}^2 + \mu_{\text{Co,k}}^2 + \mu_{\text{element,k}}^2} \) since the transition metals were assume to have a total fraction of 1 and the Li composition was calculated by dividing the number of moles of lithium by the number of moles of transition metal.

Appendix B: Electrochemical performance

We evaluated the electrochemical performance of S1 and S2 at various charge/discharge rates as the Ni\(^{2+}\) excess in the Li\(^+\) layers is expected to influence the Li ion diffusivity, and therefore impact the rate capability of the cathode material [47]. The experiments were carried out in half-cell configuration, i.e. with Li metal as the anode, and three cells per sample were tested. The average discharge capacities at various rates are show in Figure 7.

FIG. 7. Discharge capacities of S1 and S2 at various cycling rates between 3.0 V and 4.4 V vs. Li. The capacity is normalized to the mass of Li NMC 811, and the C-rate is calculated based on a reversible capacity of 200 mAh g\(^{-1}\). The error bars are calculated based on three cells for each sample.

Both samples show a discharge capacity of 210 mAh g\(^{-1}\) at C/20 rate, which is in good agreement with literature that Li NMC 811 cathodes typically show capacities above 200 mAh g\(^{-1}\) at slow rates [48]. S1 and S2 exhibit good rate capability, with no major capacity decreases until extremely high rates (i.e. 3C and 5C) and the capacity-rate profiles of the two samples are also very similar.

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TABLE IV. ICP-OES error analysis for samples S1 and S2.

| Element | Li  | Ni  | Ni  | Ni  | Mn  | Mn  | Mn  | Mn  | Co  | Co  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Wavelength (nm) | 610.362 | 216.556 | 221.647 | 230.3 | 231.6 | 257.61 | 259.373 | 260.569 | 228.616 | 237.862 |

| S1         | Mean | 1.057 | 0.802 | 0.796 | 0.796 | 0.795 | 0.799 | 1.000 | 1.012 | 0.102 | 0.103 |
|           | StDev (sample)(%) | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 |
|           | \( \mu_{\lambda} \) (%) | 4.3 | 0.9 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
|           | \( \mu_{\lambda, s} \) (%) | 0.5 | 0.7 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
|           | \( \mu_\lambda \) (%) | 2.1 | 2.9 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 | 3.7 |

| S2         | Mean | 1.007 | 0.803 | 0.800 | 0.798 | 0.797 | 0.799 | 0.799 | 0.100 | 0.102 | 0.101 |
|           | StDev (sample)(%) | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 | 9.96 |
|           | \( \mu_{\lambda} \) (%) | 5.4 | 0.5 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
|           | \( \mu_{\lambda, s} \) (%) | 0.6 | 0.8 | 1.0 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
|           | \( \mu_\lambda \) (%) | 2.7 | 3.4 | 4.4 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |

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