**Effect of Composition on the Voltage Fade Phenomenon in Lithium-, Manganese-Rich
 $x\text{LiMnO}_3 \cdot (1-x)\text{LiNi}_a\text{Mn}_b\text{Co}_c\text{O}_2$: A Combinatorial Synthesis Approach**

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Abstract

The effect of composition on the voltage fade phenomenon was probed using combinatorial synthesis methods. In compositions that have the general formula,

$(\text{Li}_2\text{MnO}_3)_a(\text{LiNiO}_2)_b(\text{LiMnO}_2)_c(\text{LiCoO}_2)_d$, where $0 \leq a \leq 0.83$, $0.15 \leq b \leq 0.42$, $0 \leq c \leq 0.85$, and

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$0 \leq d \leq 0.30$ ($a + b + c + d = 1$), the dependence of features in the x-ray diffraction pattern and of voltage fade on composition were identified and mapped.

The observed values of voltage fade indicated that it displayed some sensitivity to composition, but that the sensitivity was not large. The values of voltage fade were found to be amenable to statistical modeling. The model indicated that it may be possible to lower the value of voltage fade below 0.01% by adjusting the composition of the system; however, the composition is not expected to have the layered-layered structure.

Introduction

Lithium-, manganese-rich, nickel-manganese-cobalt (LMR-NMC) oxides are of great interest for use in a new generation of high-capacity lithium (Li) ion batteries targeting plug-in hybrid and electric vehicle applications. Most LMR-NMC cathodes can deliver $\sim 250 \text{ mAh g}^{-1}$ or more. This capacity density is almost double the practical capacity of other cathode materials, such as LiMn_2O_4 , LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [1–4].

LMR-NMC oxides can be thought of as composite materials consisting of atomically integrated Li_2MnO_3 and $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$ components and can be written as $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$ [5, 6]. In LMR-NMC, Li_2MnO_3 is integrated into the LiMO_2 layered structure to stabilize it so that more Li ions can be reversibly extracted from or inserted into the layered regions of the material without collapsing the structure [7]. Upon charge above approximately 4.5 V vs. Li, the samples become activated and displayed much higher capacity than can be explained by the Li

contained in the layered component alone. However, the average voltage decreases continuously upon subsequent cycling which, in turn, lowers the energy available in the cell. This phenomenon is commonly referred to as *voltage fade*.

In principle, the properties of these materials can be affected by composition. Dahn, et al. [8–10] showed how composition affected the phases present in the pseudo-ternaries, Li-Mn-Ni and Li-Co-Mn oxides. Their results show that the chemistry and structure of the ternary materials is, indeed, very rich. In their combinatorial work, the phases detected depended on cooling rate, oxygen partial pressure (air vs. 1 atm), and composition in the high-lithium corner of the phase diagram. For example, a continuous solid solution was not formed along the $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2 - \text{Li}_2\text{MnO}_3$ line when the material was made under 1 atm O_2 with slow cooling. Instead, multiple phases with layered structures were formed. When synthesized in air, the samples tended to be single-phase [8].

Very little systematic probing of the dependence of voltage fade on composition has been reported in the literature. For this work, we used combinatorial synthesis to explore the phase distributions and electrochemical performance of more than 100 LMR-NMC oxides with high Li content ($\text{Li}/\Sigma(\text{TM}) > 1$) and different transition metal (TM) ratios. To facilitate the analysis of the studied materials as a pseudo-quaternary system, we chose to represent them as $a(\text{Li}_2\text{MnO}_3) \cdot b(\text{LiNiO}_2) \cdot c(\text{LiMnO}_2) \cdot d(\text{LiCoO}_2)$, where $a + b + c + d = 1$, instead of in the more common, composite representation, $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}(\text{Ni}_\alpha\text{Mn}_\beta\text{Co}_\gamma)\text{O}_2$. Rather than providing an accurate description of the end members of the expected phase distribution in our samples, this formalism simply provides enough degrees of freedom to accommodate arbitrary Li and TM

ratios, while forcing the 1:1 oxygen:cation stoichiometry expected for LMR-NMC layered-layered systems. In addition, it builds in the assumption that excess Li is going to be accommodated by the formation of Li_2MnO_3 -like domains [5, 6].

Previous studies have covered distributions at different $p\text{O}_2$ and cooling rates. In this work, we focused on voltage fade of layered-layered compositions. First, we identified those compositions in the Li-rich ($\text{Li}/\Sigma(\text{TM}) > 1$) corner of the Gibbs tetrahedron that would result in a simple layered-layered diffraction pattern. Then, we subjected layered-layered samples to electrochemical characterization, following established voltage fade protocols, and provide a statistical model of the effect of stoichiometry on voltage fade in this phase field.

Experimental

Materials.

Oxides of the general formula, $\text{Li}_{1+a}\text{Ni}_b\text{Mn}_{a+c}\text{Co}_d\text{O}_2$, with $0 \leq a \leq 0.83$, $0.15 \leq b \leq 0.42$, $0 \leq c \leq 0.85$, and $0 \leq d \leq 0.30$ (see Table S1) and $a + b + c + d = 1$, were synthesized as described below. In addition, the commercially available high energy cathode material $\text{Li}_{1.2}\text{Ni}_{0.19}\text{Mn}_{0.69}\text{Co}_{0.12}\text{O}_2$ (HE5050; $a = 0.45$, $b = 0.19$, $c = 0.24$, and $d = 0.12$) was purchased from TODA America, Inc. and included in this work as a reference point.

Figure 1 shows the automated synthesis platform — a Freeslate, Inc., core module deck (CM3) that is located at Argonne National Laboratory's (Argonne's) High Throughput Research

Laboratory. The CM3 is designed to perform solid and liquid handling as well as to process samples with on-deck heating, cooling, and stirring. Multi-well plates consisting of eight 20-mL glass vials were used. For each target composition, four batches were prepared in order to produce sufficient material for electrochemical characterization in coin cells. Lithium acetate, manganese acetate, cobalt acetate, and nickel acetate were used. All acetates were purum grade (Sigma-Aldrich, >99%). Individual, aqueous stock solutions of 1 M Li, Mn, and Co acetates were prepared. The nickel precursor was first dispensed as powder using a classic hopper (25 mL). An integrated, automated balance (± 0.2 mg accuracy) was used to weigh the solids. Sample vials were transported to and from the balance using a vial gripper. The platform was equipped with an extended syringe tip for transferring solutions and a rinsing/washing station. Between transfers, the syringe was rinsed with water to prevent cross-contamination. To accelerate dissolution of the nickel salt, the samples were stirred at 300 rpm, heated to 50°C, and then slowly cooled to room temperature. Each batch of material was transferred to a hot/stirring plate set at 120°C and allowed to dry in a fume hood.

Each batch was heated from ambient temperature to 200°C over the course of 1 hour; then heated to 300°C over the course of 30 hours, and, finally, held at 300°C for 10 hours to finish the decomposition process. The powder was ground by mortar/pestle. All four batches of each target composition were then packed in a 5- × 7.5-cm Al₂O₃ dish and calcined in air using the following heating profile: heating to 850°C over the course of 10 hours and holding the sample at 850°C for another 15 hours.

All materials made in this study were analyzed for chemical composition. The materials were dissolved in nitric acid (Optima grade) and diluted with deionized water to produce metal concentrations in the range of 1–2 mg mL⁻¹. Elemental composition ($\pm 5\%$) was determined using inductance-coupled plasma mass spectrometry. The response of the spectrometer was calibrated using standard solutions of each metal.

Each sample was characterized by x-ray diffraction (XRD). XRD patterns were acquired using a Rigaku Miniplex diffractometer using Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$) or using synchrotron radiation (Argonne's Advanced Photon Source, beamline 11-ID-C, $\lambda = 0.108 \text{ \AA}$). For the sake of facile comparisons, all values of 2θ were converted to values corresponding to Cu K α_1 radiation.

Electrochemical characterization.

Only those materials which crystallized in the layered-layered structure were characterized electrochemically. Candidate materials were made into laminates using binders, solvents, additives, and techniques which have been described elsewhere [11]. Portions of the laminates were assembled into coin cells (Hohsen, size 2032) in an argon-filled glove box for electrochemical measurements. The electrolyte consisted of a 1.2-M LiPF₆ solution in ethylene carbonate-ethylmethyl carbonate (3:7 by weight). The negative electrode was lithium foil. A total of 58 cells were made and cycled.

Galvanostatic charge-discharge measurements were performed with Argonne's standard voltage fade protocol [12, 13], in which the cells are charged and discharged at 10 mA g⁻¹ in the first cycle and 20 mA g⁻¹ in the following cycles. The first charge (activation) and discharge subcycles were defined as Charge0 and Discharge0, respectively. The voltage limits for the

cycling were 4.7 and 2.0 V for charge and discharge, respectively. In this study, the coin cells were cycled at ambient temperature.

Ten-minute current interrupts were used in all subcycles after Discharge0. In the charge subcycles, they were at 3.5, 3.9, and 4.3 V; in the discharge subcycle, they were at 4.0, 3.6, and 3.2 V. The *iR*-free values of the open current voltage (OCV) at these voltage points were taken from the last point during the interrupt period.

Data reduction and calculations.

Composition mapping. Selected crystallographic features of the XRD patterns were tracked as a function of composition in a pseudoquaternary Gibbs tetrahedron. The elemental analysis data were recast as mole fractions of Li_2MnO_3 , LiNiO_2 , LiMnO_2 , and LiCoO_2 .

To obtain a representation of the Gibbs tetrahedron in Cartesian space and for plotting convenience, we defined the location of its vertices as [1, 1, 1] for Li_2MnO_3 , [1, -1, -1] for LiNiO_2 , [-1, 1, -1] for LiMnO_2 , and [-1, -1, 1] for LiCoO_2 . The Cartesian coordinates of a point inside the Gibbs tetrahedron, representing a given composition,

$a(\text{Li}_2\text{MnO}_3) \bullet b(\text{LiNiO}_2) \bullet c(\text{LiMnO}_2) \bullet d(\text{LiCoO}_2)$, are obtained by application of the lever rule of mixtures.

$$\begin{cases} x = a + b - c - d \\ y = a - b + c - d \\ z = a - b - c + d \end{cases} \quad \text{Eq. 1}$$

Eq. 1 can be easily inverted to obtain the composition associated with a given point in Cartesian space, Eq. 2.

$$\begin{cases} a = (1 + x + y + z)/4 \\ b = (1 + x - y - z)/4 \\ c = (1 - x + y - z)/4 \\ d = (1 - x - y + z)/4 \end{cases} \quad \text{Eq. 2}$$

Note that Eq. 3 will yield valid compositions with end-member fractions adding up to 1 for Cartesian coordinates lying inside the Gibbs tetrahedron.

Compositions displaying each crystallographic feature of interest were mapped onto regions in the phase field, and later approximated as convex¹ hulls [14] in Cartesian space. These fully triangulated hulls were calculated using the Quickhull algorithm [15] and rendered in three dimensions using the SharpGL interface [16] to OpenGL [17]. The vertices of the convex hulls returned from the Quickhull algorithm were converted from (x, y, z) to (a, b, c, d) using Eq. 2.

In order to facilitate representation of the calculated hulls, we decomposed the Gibbs tetrahedron into a series of constant- d planes. First, a composition mesh with 100 steps per axis was constructed to span the Gibbs tetrahedron. Then, for each mesh point and hull the following algorithm was used to determine whether the mesh point belonged to the hull. Each point in the mesh was labeled according to which hulls it belonged, and the resulting matrix constituted a map of the spatial extent of the hulls. Constant- d (LiCoO₂ composition) slices were created by

¹ A convex set is one for which any linear combination of two elements belonging to the set also belongs to the set.

taking the subset of the mesh points with a given d value (specifically, $d = 0, 0.05, 0.10, 0.15$, and 0.20) and plotting them in Gibbs triangles using a color map to indicate to which hulls each point belongs (see Fig. 5, below).

Fig. 2 presents a schematic of a convex hull (a regular tetrahedron, in this example) bounded by the vertices A, B, C , and D . Two points of interest — I and E — lie, respectively, inside and outside of the hull. In order to determine whether a point is inside or outside the hull, the center of the hull (point O) was, first, calculated by averaging the coordinates of all of its vertices. Second, for a given triangular facet, such as ΔABC shown in gray in Fig. 2, the vector normal to this facet, $\vec{n} = \overrightarrow{AB} \times \overrightarrow{AC}$ was calculated. For each point P ($P \in \{E, I\}$, in this case), the dot product $p = \vec{n} \cdot \overrightarrow{AP}$ was evaluated. If $p = 0$, then the point P lies on the ΔABC facet and is, by definition, inside the hull. Otherwise, the sign of p is compared with that of the dot product, $p_O = \vec{n} \cdot \overrightarrow{AO}$. If the signs of p and p_O are equal, then P is on the interior side of the bounding plane containing the ΔABC facet. If the signs of p and p_O are opposite, then P is outside the hull. This test was repeated for all points in the mesh and all bounding facets of the hull; points lying on the interior side of all facets were included as inside the hull.

Electrochemical data. The current-interrupt data were extracted from the cycling data, as described above. Because it had current-interrupt information, the discharge subcycle after Discharge0 was used as the $t = 0$ reference point for data reduction. The FORECAST function in Microsoft® Excel® was used to estimate the values of the OCV at 50% state of charge (SOC) using the measured values as input. The decrease in voltage was then calculated as the

difference of the OCV at time $t = 0$ and $t = 20$ cycles. The relative change in $OCV_{50\% \text{ SOC}}$ was calculated using Eq. 3 [18].

$$\Delta OCV_{50\%} = \frac{OCV_{50\%,0 \text{ cycles}} - OCV_{50\%,20 \text{ cycles}}}{OCV_{50\%,0 \text{ cycles}}} \times 100\% \quad \text{Eq. 3}$$

When more than one value of $\Delta OCV_{50\%}$ was available, they were averaged. The averaging was needed so that the polynomial fitting, described below, would not be biased. From this point on, all of these values will be referred to as $\Delta OCV_{50\%}$. The values of $\Delta OCV_{50\%}$ were then used for subsequent calculations and analysis.

The dependence of the average values of $\Delta OCV_{50\%}$ on composition were modeled using the simplex-centroid methods described by Scheffé [19, 20]. Scheffé's full, 26-term polynomial for a four-component system is given in Eq. 4.

$$\begin{aligned} Y = & a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 + \\ & a_{34}x_3x_4 + a_{123}x_1x_2x_3 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 + a_{234}x_2x_3x_4 + b_{12}x_1x_2(x_1 - x_2) + \\ & b_{13}x_1x_3(x_1 - x_3) + b_{14}x_1x_4(x_1 - x_4) + b_{23}x_2x_3(x_2 - x_3) + b_{24}x_2x_4(x_2 - x_4) + \\ & b_{34}x_3x_4(x_3 - x_4), \end{aligned} \quad \text{Eq. 4}$$

where Y is the observed parameter, a_n and b_n are fitting parameters, and x_n ($n = 1..4$) is the mole fraction of component n .

A Visual Basic for Applications script was written to automate the fitting of the data to different Scheffé models using up to 15 of the 26 possible terms, where the 15-term limit was selected to guarantee that the polynomial fit was always overdetermined. The actual least squares fit of the data to each Scheffé model was performed using the LINEST function in Microsoft® Excel®. For each fit, the root mean square (RMS) error was calculated. Of the combinations tried, only a few had an r^2 value greater than 0.95, a small number of terms, a small standard deviation for each coefficient (ratio of standard deviation/coefficient < 0.4), and a minimum RMS error (<0.45).

Results

One hundred and five compositions in the high-lithium region of the Li_2MnO_3 - LiNiO_2 - LiMnO_2 - LiCoO_2 system (see Table S1 in the supplemental material) were made to explore their crystallographic, and, if they crystallized with the layered-layered structure, their voltage fade characteristics.

XRD.

Fig. 3 shows the XRD pattern obtained from the HE5050 sample. The pattern displays a characteristic layered-layered structure [5, 6] consisting of a series of $R\bar{3}m$ reflections (labeled in the figure) and weak monoclinic superreflections in the $20^\circ \lesssim 2\theta \lesssim 25^\circ$ range (pointed to by an arrow in the figure), stemming from Li_2MnO_3 domains in the HE5050 crystals. In general,

samples with a $\text{Li}/\Sigma(\text{TM})$ ratio greater than about 1.3 displayed layered-layered XRD pattern; while those with a $\text{Li}/\Sigma(\text{TM})$ ratio lower than about 1.3 displayed additional features.

For example, Figs. 4a and 4b show the (synchrotron) XRD pattern recorded from sample 2-A ($\text{LiNi}_{0.18}\text{Mn}_{0.77}\text{Co}_{0.05}\text{O}_2$). In addition to the layered-layered pattern, there was a peak at $2\theta \approx 32.5^\circ$ and the (104) peak around $2\theta \approx 43^\circ$ had quite a rich structure (see Fig. 4b). The (104) peak was split into two clearly resolved components at $2\theta \approx 43.21^\circ$ and $2\theta \approx 43.56^\circ$ and had a satellite peak at $2\theta \approx 42.60^\circ$. The peak at $2\theta \approx 32.5^\circ$ was indexed as the $(220)_s^\dagger$ reflection of a cubic spinel, which had no $R\bar{3}m$ analog, in which case most of its intensity was due to TMs occupying the tetrahedral interstitials of the spinel lattice [21]. The splitting of the (104) peak was attributed to the strain induced by the monoclinic Li_2MnO_3 domains in the LMR-NMC structure [5, 6] and corresponded to monoclinic $(131)_M$ and $(20\bar{2})_M$ peaks, which, in bulk Li_2MnO_3 [ICSD# 165686], were found at $2\theta = 44.80^\circ$ and 44.64° , respectively. The satellite at $2\theta \approx 42.60^\circ$ had no monoclinic or layered analog and was usually attributed to the presence of an additional peak at lower 2θ due to a spinel phase [8]. However, we observed that the $(220)_s$ peak and the (104) satellite are not necessarily correlated. At least one of these two features was present in every sample not displaying a simple layered-layered XRD pattern, but not all such samples displayed both of them.

Rather than attempting to elucidate the composition-dependent crystal structure of these samples in full detail, which far exceeds the scope of this work, we limited ourselves to a phenomenological description of the composition ranges at which these additional XRD features

[†] The subscript on the Miller indices refers to crystal structure types. S=spinel, M=monoclinic. If no subscript is present, the indices refer to the layered-layered structure.

were present. First, we classified each recorded XRD pattern as being a simple layered-layered pattern (group 0), containing an additional (220)_s reflection (group 1), presenting a lower 2 θ satellite in the (104) peak (group 2), or both (group 3). This classification is summarized in Table S1. For example, the HE5050 XRD pattern, shown in Fig. 3, belongs to group 0 (layered-layered), while the pattern of LiNi_{0.18}Mn_{0.77}Co_{0.05}O₂, shown in Fig. 4, belongs to group 3 (both features). As stated above, no sample was found that (1) contained additional non-layered-layered features and (2) could not be classified as belonging to groups 1 to 3.

Four convex hulls were calculated—representing Li₂MnO₃-only, Li₂MnO₃+(220)_s peak, Li₂MnO₃+ (104) satellite peak, and Li₂MnO₃+(220)_s peak+ (104) satellite peak. For the sake of simplicity, they will be referred to as hull0, hull1, hull2, and hull3, respectively. From an analysis of these results, it was clear that the four hulls intersect.

Isopotential planes through the hulls at constant x_{LiCoO_2} are shown in Fig. 5. Due to the Quickhull algorithm, there was overlap of the four hulls, especially at $x_{LiCoO_2} = 0$ and 0.05. Imposing the limitations shown in Table S1 regarding the combination of structural features actually observed, produces Fig. 6. Fig. 6 also shows the effect of adding LiCoO₂ to the distribution of structural features. With the addition of LiCoO₂, the general tendency was for the regions to merge, meaning that there were fewer structural differences.

Comparing the results shown in Fig. 6(a) with those discussed in Ref. [8] is not straightforward. The two groups of materials were not made using the same conditions of temperature, oxygen partial pressure, and cooling rate. For example, the samples in Ref. [8] were made at 850°C and

in 1 atm of oxygen; those in this study were made at 800°C and in air. Thus, there may be a larger contribution from Ni(3+) and from equilibration kinetics to the phase distributions seen in the former study.

Electrochemical Performance.

All compositions subject to electrochemical testing displayed voltage fade, as shown in Fig. 7, for a typical composition. The rationale for using the 50% SOC point in the discharge curves for further analysis was described in our earlier paper. Briefly, current interrupts, shown in Fig. 7, occurred at approximately 80, 50, and 20% SOC. The value of OCV at 50% was chosen because it changed more with cycle count than those at 80% SOC and was more likely to be more sensitive to change than those at 20% SOC [18]. Fig. 8 shows the results of plotting the values of $\Delta\text{OCV}_{50\%}$ vs. cycle count for several compositions produced.

From Fig. 8, the value of average $\Delta\text{OCV}_{50\%}$ displays sensitivity to composition. Here, the values of $\Delta\text{OCV}_{50\%}$ after 20 cycles range from ~1.00 to 4.25%. Some of the compositions displayed a greater degree of voltage fade than HE5050, while others showed less. That is, the degree of voltage fade ranged from about one-third of that of HE5050 to ~1.5 times it.

Fitting.

The principles behind Scheffé's statistic models should apply to any mixture. For example, a mixture-based, polynomial fit was used in a prior study on glass electrolytes [22]. A

methodology similar to that in Kucera, et al. [22] was used to fit the values of $\Delta\text{OCV}_{50\%}$. In all, 63,020 combinations of the fitting terms given in Eq. 5 were evaluated.

Four of these combinations were found to have a value of $r^2 > 0.97$; to have an RMS error < 0.45 ; to have a minimal standard deviation in the fitting coefficients; and to represent the data well. As a result of this selection process, an 11-term fit was selected, as shown in Eq. 5. The value of r^2 was 0.98 and the RMS error was 0.39, indicating a good fit. Table 1 gives the values of the fitting coefficients and their standard deviations.

Table 2 shows the comparison of the observed and calculated values of $\Delta\text{OCV}_{50\%}$. The values of the residual shown in Table 2 indicate that, indeed, Eq. 5 represents the values of $\Delta\text{OCV}_{50\%}$ well.

$$Y = \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_4 x_4 + \alpha_{14} x_1 x_4 + \alpha_{24} x_2 x_4 + \alpha_{34} x_3 x_4 + \alpha_{123} x_1 x_2 x_3 + \alpha_{124} x_1 x_2 x_4 + \alpha_{234} x_2 x_3 x_4 + \beta_{24} x_2 x_4 (x_2 - x_4) \quad \text{Eq. 5}$$

Since $\Delta\text{OCV}_{50\%}$ decreased on the order of 1–4% over the course of 20 cycles, these materials may have limited use in transportation applications. A value of $\Delta\text{OCV}_{50\%}$ orders of magnitude less would enhance the usefulness of the LMR-NMC materials. Eq. 5 was used to estimate the composition of materials which may have values of $\Delta\text{OCV}_{50\%}$ that are 100 and 1000 times less

than the values observed. The results of these calculations are shown in Table 3. No estimated compositions with smaller values of $\Delta\text{OCV}_{50\%}$ than that shown in Table 3 were found in the region of the Gibbs tetrahedron where it would be likely to form the layered-layered structure.

Discussion

The features observed in the XRD patterns were sensitive to composition. Indeed, examining the data in Table S1 shows other trends in the features observed in XRD patterns versus composition. At concentrations less than about $x_{\text{Li}_2\text{MnO}_3}=0.3$, features in addition to those associated with the layered-layered structure were seen. Above that concentration, they were not. These imply that a certain amount of Li_2MnO_3 was necessary to form the layered-layered phase.

As x_{LiNiO_2} increased from ~ 0.14 to ~ 0.20 , the tendency to observe XRD features associated only with the layered-layered structure increased. Beyond about $x_{\text{LiNiO}_2} \sim 0.25$, this tendency decreased. There seemed to be a limited range where the formation of the layered-layered was favored when x_{LiNiO_2} was varied.

In the range of compositions $x_{\text{LiMnO}_2}=0.0$ to ~ 0.40 , the XRD features associated with only the layered-layered phase tended to be seen. Above about $x_{\text{LiMnO}_2}=0.4$, again, apparent exsolution was seen.

Finally, from Fig. 6, as x_{LiCoO_2} increased, the number features observed tended to diminish, and the relative compositional space for the layered-layered structure tended to increase. Adding

LiCoO₂ may, thus, increase the range of “solid-solution” formation and stabilize the layered-layered structure. In compositions where $x_{\text{LiCoO}_2} > 0.20$, there seemed to be a limit where the LMR-NMC, layered-layered structure would form. This may be due to insufficient manganese concentrations.

Implicit in this work was the assumption that voltage fade is sensitive to composition. In theory, if the relationship between these parameters were understood, it may then be possible to control voltage fade by adjusting the composition. From the results described above, the voltage fade phenomenon displays some sensitivity to composition, but it does not change that much.

Even though the compound LiMnO₂ is known to convert into a spinel phase with cycling [23, 24], using the quaternary formalism, $a(\text{Li}_2\text{MnO}_3) \cdot b(\text{LiNiO}_2) \cdot c(\text{LiMnO}_2) \cdot d(\text{LiCoO}_2)$, facilitated fitting. The results of the fitting show that the values of $\Delta\text{OCV}_{50\%}$, that is, voltage fade, are amenable to statistical modeling. Although the 11-term polynomial is empirical at the outset (it was not based on the response of the end-member oxides), it is tempting to ascribe physical meaning to the terms. Here, positive coefficients indicate terms that favor voltage fade; on the other hand, negative coefficients indicate that terms hinder voltage fade. Of all single component, α_n , terms, only α_2 (i.e., LiNiO₂) is negative, indicating, to the first-order approximation, that Ni hinders voltage fade. It is also interesting to note that all the binary, α_{xy} terms are negative, indicating that “solid-solution” formation with LiCoO₂ has a similar effect. Higher-order effects can be seen in the coefficients of the ternary terms, α_{xyz} . Here, only one hinders the voltage fade process, α_{123} . The others favor it. Thus, the potentially higher Mn

concentration in the ternary “solid-solution,” $\text{Li}_2\text{MnO}_3\text{-LiNiO}_2\text{-LiMnO}_2$, as compared to $\text{Li}_2\text{MnO}_3\text{-LiNiO}_2\text{-LiCoO}_2$ and $\text{LiNiO}_2\text{-LiMnO}_2\text{-LiCoO}_2$, may hinder the voltage fade process.

The β_{24} term is interesting because it can hinder or favor voltage fade. It is positive, but it also depends on the difference, $x_2 - x_4$. It will favor voltage fade if $x_4 < x_2$ and will hinder voltage fade if $x_4 > x_2$, as was the case in the predicted composition in Table 3.

Examination of the composition in Table 3 shows that it is mainly LiCoO_2 . This composition is very close to $0.5(\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2) \bullet 0.5\text{LiCoO}_2$, which is expected to crystallize in a layered structure. However, the low (next to none) Li excess in the structure will result in low capacity and, hence, energy, which, in turn, will not be as attractive as the promise of a voltage-stable Li-rich phase.

Conclusions

The effect of composition on the voltage fade phenomenon was probed using combinatorial synthesis methods. In compositions that have the general formula,

$(\text{Li}_2\text{MnO}_3)_a(\text{LiNiO}_2)_b(\text{LiMnO}_2)_c(\text{LiCoO}_2)_d$, where $0 \leq a \leq 0.83$, $0.15 \leq b \leq 0.42$, $0 \leq c \leq 0.85$, and $0 \leq d \leq 0.30$ ($a + b + c + d = 1$), the dependence of features in the x-ray diffraction pattern and of voltage fade on composition identified and mapped.

The observed values of voltage fade indicated that it displayed some sensitivity to composition, but that the sensitivity was not large. The values of voltage fade were found to be amenable to

statistical modeling. The model indicated that lower values of voltage fade may be possible but probably not in a layered-layered composition.

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TABLES

Table 1.

Coefficient	Value (s.d.)
α_1	7.40 (0.94)
α_2	−10.34 (2.45)
α_3	20.61 (4.36)
α_4	458.49 (154.25)
α_{14}	−579.65 (177.08)
α_{24}	−1425.90 (440.86)
α_{34}	−682.54 (210.88)
α_{123}	−126.76 (38.630)
α_{124}	1597.56 (434.78)
α_{234}	1802.56 (533.94)
β_{24}	957.77 (362.82)

Table 2.

Code	Observed, %	Calculated, %	Residual
HE5050	3.11	3.06	0.05
3-E	2.89	3.06	0.73
3-F	3.01	2.80	0.20
3-G	3.00	2.92	0.08
4-G	3.53	3.64	−0.11
5-E	4.66	4.25	0.41
5-F	3.15	3.34	−0.19
5-G	2.34	3.04	−0.70
6-F	3.39	3.17	0.21
6-G	2.59	3.06	−0.47
7-E	3.25	3.39	−0.14
7-F	3.56	3.28	0.28
7-G	3.54	3.41	0.14
8-F	3.48	2.47	1.01
8-G	2.82	2.86	−0.04
12-D	3.04	2.53	0.51
12-E	1.79	2.62	−0.83
12-F	2.92	2.73	0.19
12-G	2.80	2.85	−0.04
16-D	3.57	3.56	0.02
16-E	2.45	2.59	−0.14
16-F	2.61	2.56	0.06
16-G	2.79	2.47	0.31
21-F	1.34	1.57	−0.23
21-G	1.58	1.51	0.08
L-59	1.09	0.87	0.12
L-60	1.22	1.18	−0.03
L-61	1.63	1.93	−0.64
L-62	1.60	2.25	−0.75
L-63	2.25	1.78	0.47
L-64	2.01	1.68	0.33

Table 3.

Mole fraction				$\Delta\text{OCV}_{50\%}, \%$
Li_2MnO_3	LiNiO_2	LiMnO_2	LiCoO_2	
0.06	0.26	0.24	0.44	7.66×10^{-3}

FIGURES

Fig 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

- Voltage fade depends on composition in LMR-NMC cathodes.
- A simplex-centroid model was developed to estimate voltage fade vs. composition.
- The model indicates that zero voltage fade in LMR-NMC cathodes may not be possible.

Effect of Composition on the Voltage Fade Phenomenon in Lithium-, Manganese-Rich $x\text{LiMnO}_3 \cdot (1-x)\text{LiNi}_a\text{Mn}_b\text{Co}_c\text{O}_2$: A Combinatorial Synthesis Approach

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