Effect of transition metal substitution on elastoplastic properties of LiMn$_2$O$_4$ spinel
Effect of Transition Metal Substitution on Elastoplastic Properties of LiMn$_2$O$_4$ Spinel

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LiMn$_2$O$_4$ (LMO) derivatives partially substituted with transition metals (e.g., Ni) have received attention for their higher energy density achieved at higher charge voltage than pure LMO, and may be attractive cathode candidates for emerging all solid state batteries. Accurate mechanical properties of these high voltage spinels are required for prediction of electrode and electrolyte fracture that may compromise battery lifetime and performance. Here, we quantified the Young’s elastic modulus $E$ and hardness $H$ for LMO, LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO), and LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO) spinel microparticles via instrumented grid nanoindentation. Elastic modulus $E$ and hardness $H$ increased by more than 40% (up to 145 and 11 GPa, respectively) as a result of Ni or Ni/Fe substitution; such substitution also reduces the lattice parameter and increases the oxidization state of Mn. These results demonstrate how changes in transition metal occupancy can significantly affect the mechanical properties of LMO spinel, and provide critical parameters for designing against fracture in all solid state batteries.

Keywords: High-voltage cathodes; spinel cathodes; battery mechanics; nanoindentation; all solid state batteries; electrochemomechanics

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1. INTRODUCTION

All solid state Li-ion batteries are predicted to enable energy-dense electrodes that otherwise face challenges in conventional batteries with liquid electrolytes [1,2]. For example, LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) exhibits an operating voltage around 4.7 V with respect to Li$^0$, leading to oxidation of typical organic liquid electrolytes at the cathode and limiting the commercial use of LMNO [3,4]. This electrolyte stability issue is potentially avoided in all solid state batteries, for which the side reactions may be kinetically stifled [5,6]. Furthermore, the use of a solid electrolyte is expected to reduce Li dendrite growth, common for Li metal anodes used with liquid electrolytes or graphite anodes at high charge rates. The high energy density offered by high-voltage cathodes such as LMNO may thereby be more fully realized in an all solid state battery.

However, the mechanical compatibility constraints inherent to solid state batteries will likely pose a series of new challenges. The concurrent volume changes of positive and negative electrodes during electrochemical cycling, by chemical expansion (~7 vol% for LMO [7,8]) or by electroplating for a Li anode, can produce significant strains that must be accommodated within the electroactive “stack” [9]. Resulting fracture in the electrolyte or at the electrode-electrolyte interface can disrupt Li ion flow and provide pathways for dendritic growth of Li. Likewise, fracture of the electrode materials, termed “electrochemical shock,” may result from stress buildup within the particles [10–12]. Such fracture is thought to diminish electrode performance in conventional batteries with liquid electrolytes by accelerating active material dissolution, consuming working Li by continued formation of the solid-electrolyte interphase, or slowing Li-ion diffusion within the active material [13–15]. The prevention of fracture during repeated cycling is therefore of great importance for maximizing the lifetime of both conventional and all solid state batteries, and a critical step in modeling and predicting this fracture is to quantify the elastic and plastic mechanical behavior of the electrode compounds.

In this study, we investigated the mechanical behavior of LiMn$_2$O$_4$ (LMO), LMNO, and LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO) cathodes. LMNO crystallizes in the cubic spinel structure, like LMO, but has 1 in 4 of the Mn atoms on the 16d sublattice replaced with Ni [16–18]. The introduction of Ni increases the average oxidation state of Mn to 4+, eliminating the Mn$^{3+}$/4+ redox couple at 4.0 V and replacing it with Ni$^{2+}$/4+ at 4.7 V. In batteries using liquid electrolytes, the persisting issue of transition metal dissolution into the electrolyte prompted investigations of further doping with additional metals such as Fe and Co [19–22]. As discussed in the literature [11,17,21], the addition of small amounts of Fe to produce LMNFO improves the surface chemistry of the spinel, mitigates phase transformations responsible for particle fracture [11], and improves Li$^+$ diffusivity. As most of these advantages of LMNFO also apply to all solid state batteries, in this study we chose to compare this compound to LMO and LMNO.

Although to our knowledge $E$ and $H$ for LMNO and LMNFO have not been characterized previously, the mechanical properties of LMO have been reported extensively in the literature and serve as a useful reference. For LMO, $E$ has been quantified by pressure-controlled X-ray diffraction (XRD) [23,24], the vibrating reed technique [25,26], and computation [27–29]. Those studies have yielded numerical values spanning more than an order of magnitude. $E$ and $H$ of LMO have also been measured by nanoindentation for both particles and thin films [30–32], including the
effects of delithiation on these properties [31]. Fracture toughness $K_{ic}$ of LMO was measured by Mughal et al. via a focused ion beam technique [33]. Here, we used instrumented nanoindentation to measure $E$ and $H$ in the LMO spinel family of cathode materials, analyzing mechanical responses of individual cathode microparticles within a mechanically defined matrix. For undoped, stoichiometric LMO, $E$ of 100 +/- 8 GPa and $H$ of 7.5 +/- 0.9 GPa agree well with prior nanoindentation studies [30,31]. For LMNO, $E$ and $H$ increased to 136 +/- 12 GPa and 10.1 +/- 1.9 GPa, respectively. The qualitative trend is consistent with the lattice parameter reduction occurring upon an increase in the Mn$^{3+}$/Mn$^{4+}$ ratio [19]. Finally, for LMNFO containing 0.08 Fe per formula unit, $E$ and $H$ were 145 +/- 15 GPa and 11.0 +/- 1.8 GPa, respectively, indicating a small increase in elastoplastic properties as compared with LMNO. Thus, up to 40% resistance to reversible deformation (elastic modulus) and 40% resistance to permanent deformation and flow (hardening) are induced by 25 at% substitution of Ni for Mn. These findings establish baseline values for the mechanical properties of the fully lithiated compositions of these spinels.

2. EXPERIMENTAL

2.1 Sample preparation.

Commercial LMO powder (Toda Kogyo Corp., Japan) was used for LMO samples, with a primary crystallite size of 1-2 μm as characterized by scanning electron microscopy (XL30 ESEM, FEI, Hillsboro, OR). Powders LMNO and LMNFO were prepared by ball milling stoichiometric amounts of LiCO$_3$, Mn$_2$O$_3$, NiO, and Fe$_3$O$_4$ in acetone for 24 h, pouring the slurry onto Al foil to dry, and calcining the dried product for 12 h at 900°C [11]. Samples were then ground by hand in a mortar and pestle and analyzed via XRD (PANalytical X’Pert Pro diffractometer) to verify the identity of the powder, as discussed in the Supplementary Material. To minimize the effect of finite particle dimensions in the indentation experiments [34–36], all samples were uniaxially pressed into pellets for 2 min at 140 MPa and coarsened at 950°C in 12-24 h segments to attain an abundance of particles of diameters of 8-10 μm (see Figure 1a). Additional coarsening treatments yielded diminishing returns in increasing particle diameter. The powder was ground and re-pressed between each coarsening step.

Sintering to achieve 50-100 μm grain size and fully dense compacts was not possible for LMO and its derivatives, though previously demonstrated by us for LiCoO$_2$ (LCO) powder [37,38]. Thus, each spinel powder sample was mixed with a thermosetting phenol formaldehyde resin matrix (Bakelite) to enable direct mechanical testing of microscale spinel particles within a well-defined composite. The mixed powder of resin and spinel of a given composition was formed into a disk of diameter 3.2 cm via hot mounting at 155°C and ~32 MPa, then cooled to room temperature. The resulting composite was polished to provide a flat testing surface using SiC sandpaper of decreasing grits (800, 1200, 2400, 4000) with water lubrication, and diamond polishing pads (UltraPrep, Buehler Limited, Lake Bluff, IL) of 3 μm, 1 μm and 0.5 μm grit sizes with no additional lubrication. Samples were rinsed with water between each polishing step. Figure 1b illustrates representative clusters of agglomerated LMO particles in the thermoset matrix after polishing. Before mechanical characterization, samples were
adhered to a steel plate with low-viscosity cyanoacrylate for magnetic sample mounting on the indentation stage.

A reference sample of LCO particles was also prepared for mechanical characterization. A dense compact was produced by pressing, sintering, and coarsening as described previously [38], then crushed with a mortar and pestle into a powder. The size similarity between the coarsened grains and resulting particles post-grinding suggested that the grains of the sintered compact became the loose particles upon grinding. Although some LCO particles exceeded the size of the LMO-based spinel particles, as quantified by optical microscopy, a subset of LCO particles was of the desired diameter of 8-10 µm. The LCO powder was mixed with thermoset resin powder, heated, polished, and mounted using the same procedure as was used for the spinel powders. For LCO, $E$ and $H$ have been established previously by Qu et al. [37] on dense sintered compacts comprising ~100 µm grain diameters (and thus no mounting matrix), as discussed in the Supplementary Material.

Figure 1 (a) Scanning electron micrograph of synthesized LiMn$_{1.3}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ particles after high-temperature coarsening treatments. Particle diameter ranged 8-10 µm. (b) Coarsened LiMn$_2$O$_4$ embedded in thermoset matrix and polished. (c) Representative load-depth curves acquired via load-controlled nanoindentionation exhibiting particle-dominated, matrix-dominated, and composite responses. Maximum indentation depth and extent of viscoelastic behavior both increase with matrix influence.
2.2 Nanomechanical characterization

Mechanical properties $E$ and $H$ were obtained by carrying out instrumented nanoindentation (Hysitron, Inc. Triboindenter, Minneapolis, MN) in grid patterns over the ceramic/polymer composite surface using a diamond Berkovich probe. This method has been validated previously by us and others for natural and engineered composites [39,40], and was further validated in the present study via testing of the LCO particle reference sample; see Supplementary Material.

Indentation grids on the spinel samples were acquired over regions composed of many particles of ~10 µm diameter as in Figure 1b, selected via optical microscopy within the instrumented indenter. These grids were selected to maximize the degree of particle phase encountered by the indentations, but a mixture of particle- and matrix-dominated measurements was expected. The thermoset polymeric resin matrix exhibited lower $E$ (~10 GPa, also measured via indentation); this was known to be lower than that expected of metal oxide materials. This matrix was chosen to enable secure particle mounting and polishing as required for indentation without significant spinel sample manipulation with temperature or chemicals. This mechanical contrast between the metal oxide particles and the polymer matrix also facilitated statistical clustering to distinguish particle-dominated and matrix-dominated mechanical responses.

As shown in Figure 1c, the $P$-$h$ (load-depth) responses for particle- and matrix-dominated measurements are distinguishable qualitatively by the steepness of the loading profile, maximum depth $h_{\text{max}}$, and extent of creep occurring at $h_{\text{max}}$. For the reference LCO sample, groups of particles with particle size 8-10 µm were targeted for comparison with the spinel samples of similar particle diameter. Indentation centers within each grid were spaced by 6-8 µm for all samples, and maximum load of 600 µN was achieved at a constant loading rate over 10 s, followed by holding at maximum load for 3 s and unloading over another 10 s. For LMO, indentations were also conducted at 1200 µN, 1800 µN, and 2400 µN to investigate whether the indentations occurred in a regime where the measured elastic modulus was sensitive to the ratio of maximum depth to particle radius $h_{\text{max}}/R$ as discussed by Yan et al. [36] Although load-independence was observed for LMO as discussed below and in the Supplementary Material, we conservatively applied the lowest maximum load (600 µN) to maximize data acquisition dominated by particle contributions. This range of maximum loads resulted in maximum depths within the spinel particles of 30 – 120 nm.

A fused quartz sample was used to calibrate machine compliance and indenter probe geometry (area function), including calibrations at maximum depths (30 – 120 nm) typically achieved in the spinel particles.

2.3 Nanomechanical Data Analysis

Mechanical data were analyzed in two steps. First, the Young’s elastic modulus $E$ and hardness $H$ were calculated for each load-depth profile as described below, according to established and automated methods. Second, these data were analyzed via clustering algorithms to identify the particle-dominated mechanical responses. This approach was combined with alternative examinations of the data, including cumulative distribution functions (CDFs), to obtain quantitatively consistent results for $E$ and $H$ of each material.
For each load-depth profile acquired, reduced modulus $E_r$ was calculated via the Oliver-Pharr method [41–43], relating the initial unloading response $dP/dh$ to the elastic response:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{1}{A} \frac{dP}{dh}$$

Eq. 1

where $P$, $h$, and $A$ correspond to the variables load, displacement, and projected indentation area, respectively. The Young’s elastic modulus $E$ of the material sample was calculated from $E_r$ by accounting for the mechanical properties of the diamond indenter:

$$\frac{1}{E_r} = \frac{(1 - v^2)}{E} + \frac{(1 - v_i^2)}{E_i}$$

Eq. 2

where $E_i$ and Poisson’s ratio $v_i$ of the diamond indenter were taken to be 1070 GPa and 0.07, respectively, and the Poisson’s ratio $v$ of the sample was taken to be 0.3. Hardness was calculated as the ratio of the maximum applied load to the projected indentation contact area at this load:

$$H = \frac{P_{max}}{A}$$

Eq. 3

All raw load-depth responses were viewed and recorded, and $E_r$ and $H$ for all samples were calculated by an automated script in the Hysitron software according to the Oliver-Pharr method. Afterward, several grids of $E$ data were superimposed on images obtained with the Hysitron optics to confirm spatial correlation between particle phase and high $E$ measurement.

In applying principal component analysis (PCA) to distinguish particle-dominated from matrix-dominated indentation responses, we selected three important characteristics to define each measurement: computed $E$, computed $H$, and creep displacement. Creep displacement was defined for each $P$-$h$ profile by the total displacement at maximum load, as indicated in Figure 1c. Quadratic fit quality [30] and $h_{max}$ were also considered initially, but reduced the quality of the clustering procedure. The dimensionality of the data was then reduced from 3 to 2 by the “pca” procedure in MATLAB, with which two axes are selected to display the data in the directions of highest variance. The new axes of the data are linear combinations of the original 3 axes. The resulting data displayed on a 2-axis plot were then grouped into clusters using the “kmeans” algorithm in MATLAB.

All mechanical property data are reported as mean +/- standard deviation. When comparing means obtained with different variances and sample sizes $n$, Welch’s $t$-test was used to identify differences with statistical significance.

3. RESULTS AND DISCUSSION
3.1 Distribution of $E$ and $H$ measurements with particle and matrix influence

Due to the finite particle size and a large difference between particle and matrix stiffness, the cumulative distribution functions (CDFs) shown in Figure 2(a-b) indicate a wide range of measured $E$ and $H$. The measurements varied continuously between the particle and matrix modulus endpoints without exhibiting distinct regions belonging to each phase, suggesting that the majority of measurements are influenced by both the matrix and particle phases. However, despite an apparent scarcity of pure particle measurements, a qualitative difference in mechanical behavior is clear between the Ni/Fe substituted spinels and pure LMO samples. For both $E$ and $H$, the measurements for LMNO and LMNFO tended toward significantly higher particle-dominated endpoints, indicating an increase in $E$ and $H$ for these spinels as compared with LMO.

Multiple analyses were used to ascertain that the qualitative $E$ and $H$ increases in Figure 2(a-b) were not caused by inconsistent sampling errors, such as unequal particle size distributions or overly high indentation loads. As shown in the Supplementary Material, $E$ and $H$ indentation grids were acquired for the LMO sample at 600, 1200, 1800, and 2400 $\mu$N loading, and the corresponding CDFs converge at both the low and high ends of the measured $E$ spectrum. The consistency of the CDFs indicates that the sensitivity to peak load and $h_{\text{max}}/R$ is low in this load range. Furthermore, the agreement of $E$ in the high-modulus range at all peak loads indicates that the data do indeed converge to the elastic modulus of LMO. Further confirmation of the observed trend can be obtained by viewing the data trends in $E$ vs. $h_{\text{max}}$, creep vs. $h_{\text{max}}$ format, and by comparing the CDFs to the reference LiCoO$_2$ sample. These analyses are detailed in the Supplementary Material.

3.2 Selection of particle-dominated measurements for quantification of $E$ and $H$

Although the experiments discussed above demonstrate that the particle-dominated regime is accessible in our measurements, quantification of $E$ and $H$ for the LMO-based phases from these spectra required further treatment of the data. As no discontinuity is apparent in our CDFs, the data do not lend themselves to visually obvious, objective separation between matrix- and particle-dominated measurements. Therefore, we used a principal component analysis (PCA) and clustering technique to identify the designated particle-dominated measurements for each sample. PCA included computed $E$, computed $H$, and creep displacement as described in Methods.

Figure 2(c-e) shows the indentations of each sample in the optimized component space, with particle-dominated measurements clustered at higher magnitudes of “component 1” as indicated by the dashed verticals. We also conducted sensitivity tests to vary the number of clusters $k$ between 3 and 7 until the particle-dominated cluster was invariant with further cluster additions. At $k = 5$ for all samples, a cluster was consistently identified in a region of high data density at the particle-dominated extreme of the data. The members of these clusters exhibit the expected qualitative features of the particle phase – high $E$, high $H$, and low creep displacement (as compared with the other data points within that sample set). Although this method is useful for defining groups at the extreme of each data set, the grouping of the data into five clusters does not have physical meaning. Only two phases exist, with a range of measurements between them, and the clustering at the data extremes is caused by the convergence of data to the particle and
matrix limits. Details of the \( k \) sensitivity test are discussed further in the Supplementary Material.

Figure 2 Cumulative distribution functions for (a) Young’s modulus and (b) hardness of all spinel samples. Young’s modulus, hardness and creep displacement data for (c) LiMn\(_2\)O\(_4\), (d) LiMn\(_{1.5}\)Ni\(_0.5\)O\(_4\), and (e) LiFe\(_{0.08}\)Mn\(_{1.5}\)Ni\(_{0.42}\)O\(_4\) are shown in a 2-dimensional space determined by principal component analysis. Clusters assigned to particle-dominated measurements are highlighted.

3.3 Comparison of samples based on particle-dominated measurements

The selected particle-dominated groups were used to compute \( E \) and \( H \) for each sample, and these results are shown in both Figure 3 and Table 1, where \( n \) is the number of independent indentation experiments represented within the particle-dominated cluster for each material. From these results, it is clear that both the elastic modulus and hardness of the Ni and Ni+Fe substituted derivatives were significantly higher than those of LiMn\(_2\)O\(_4\). This comparison confers a high degree of statistical significance (\( p < 0.0001, \) Welch’s t-test), and represents an approximately 40% increase in stiffness and hardness upon substitution with Ni to form either LMNO or LMNFO of these compositions.
Figure 3 Young’s modulus and hardness for LiMn$_2$O$_4$ (LMO), LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO), and LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO). Error bars are standard deviations. Asterisks denote statistical significance: p < 0.0001 (*), p ~ 0.03 (**), and p ~ 0.14(***).

Table 1. Young’s modulus $E$ and hardness $H$ for LiMn$_2$O$_4$ and its Ni/Fe substituted derivatives.

| Material                  | $E$ (GPa) | $H$ (GPa) | $n$ of cluster |
|---------------------------|-----------|-----------|----------------|
| LiMn$_2$O$_4$             | 100 +/- 8 | 7.5 +/- 0.9 | 23             |
| LiMn$_{1.5}$Ni$_{0.5}$O$_4$ | 136 +/- 12 | 10.1 +/- 1.9 | 19             |
| LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ | 145 +/- 15 | 11.0 +/- 1.8 | 23             |

This increase of $E$ and $H$ upon Ni substitution within LiMn$_2$O$_4$ is consistent with the change in lattice parameter and Mn$^{4+}$/Mn$^{3+}$ ratio. Amanieu et al. [31] observed an increase in $E$ and $H$ due to delithiation of pure LMO, which was attributed to increased Mn-O bond strength upon Mn$^{3+}$ oxidation to Mn$^{4+}$ and marked by a corresponding decrease in lattice parameter [44]. Likewise, the inclusion of Ni to form LiMn$_{1.5}$Ni$_{0.5}$O$_4$ causes Mn to be fully oxidized to Mn$^{4+}$ and results in a decreased lattice parameter [19,45]. Importantly, the increased stiffness and hardness of this candidate battery electrode material upon Ni doping indicates lower capability to accommodate strain in an all solid state battery, as well as increased elastic stress fields contributing to fracture within the electrode material for both conventional and all solid state applications [10,12,46,47].

Additionally, elastic modulus increased slightly as a result of Fe doping: mean $E$ of LMNFO was 7% higher than that of LMNO. This effect, though statistically significant (p ~ 0.03), represented a mildly increased stiffness of only 9 GPa for a partial doping of Fe on the Mn and Ni sites as indicated by LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$. The hardness
of the Fe-doped spinel was not statistically different from its Ni-substituted counterpart LMNO (p ~ 0.14). The physical basis by which Fe doping can further stiffen the spinel requires further study, though we note that experimental and computational studies of other complex metal oxides have attributed detectable changes in $E$ to lattice parameter changes associated with electronic and point defects [48]. By the same reasoning that LMNO should display higher $E$ and $H$ than LMO, the inclusion of Fe in LMNO lowers the Mn oxidation state and increases the lattice parameter [19], suggesting that at sufficient Fe doping the $E$ and $H$ for LMNFO be intermediate to that of LMO and LMNO. Despite apparently higher $E$, the propensity for electrochemical shock has been shown to decrease in LMNFO, but this has been attributed to reduction of phase transformation strain via modification of the phase diagram [11,21]. Although it is possible in principle for powder processing and particle morphology to contribute to such mechanical differences, we maintained particle coarsening and treatment conditions uniform among samples and found all spinel materials to exhibit indistinguishable particle morphology and size (see Supplementary Material). Thus, our findings indicate that Ni substitution of LiMn$_2$O$_4$ significantly and substantially increases the stiffness and hardness of this spinel candidate for active electrode materials in all solid state batteries, in the form of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ or LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$. Additional doping of Fe in a Ni substituted LMO derivative mildly increases stiffness but not hardness, and thus more detailed computational studies may elucidate how additional or different transition metals can affect these elastoplastic properties of LMNO.

4. CONCLUSIONS

We report the first measurements of two key mechanical properties for LMNO and LMNFO spinels, elastic modulus relating to reversible deformation and hardness relating to plastic flow. Grid arrays of nanoindentation on spinel microparticles embedded in a polymer matrix provided $E$ and $H$ over a range of composite responses spanning from the matrix-dominated to particle-dominated regimes. PCA and two-dimensional clustering facilitated objective identification of particle-dominated measurements. From those data, we determine that $E$ and $H$ increase by ~40% upon Ni and Ni+Fe doping as compared to LMO, up to as much as 145 GPa and 11.0 GPa, respectively. These results demonstrate how the stiffness and resistance to permanent deformation of the manganese spinel family of cathodes is influenced by transition metal substitution on the 16d sites, and enable further investigations on the effects of stress distributions and fracture criteria for both conventional and all solid state battery systems.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.
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SUPPLEMENTARY MATERIAL

Effect of Transition Metal Substitution on Elastoplastic Properties of LiMn$_2$O$_4$ Spinel

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S.1. X-ray diffraction to confirm the identity of doped spinels

X-ray diffraction was conducted on the LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) and LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO) powder using a PANalytical X’Pert Pro diffractometer. The scan ranged from 15 to 80 °2Θ and the radiation source was Cu Kα. As LMNO and LMNFO were both synthesized starting from oxides and carbonates as discussed in the main text, XRD was used to confirm the spinel structure, as well as distinguish between LMNO and LMNFO. As explained in the literature [1,2], impurity phase Li$_x$Ni$_{1-x}$O occurs as a result of oxygen off-stoichiometry after cooling LMNO from high temperature. The XRD peaks associated with this impurity phase are circled in Figure S.A. Addition of Fe to the structure reduces the amount of Li$_x$Ni$_{1-x}$O, and accordingly we see that the impurity peaks are not present for LMNFO. The spinel crystal structure was confirmed for both samples.

![Figure S.A.](image-url) Spinel crystal structure of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) and LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO) confirmed by X-ray diffraction. Circled peaks belonging to the Li$_x$Ni$_{1-x}$O impurity phase are verified in LMNO but absent in LMNFO, as discussed by Liu et al.[1]
S.2. Comparison of reference LiCoO₂ particles to monolithic LiCoO₂

As stated in the manuscript, a LiCoO₂ (LCO) reference sample was prepared by grinding a sintered pellet and mounting it with Bakelite polymer. Particles of 8-10 µm width (comparable to the spinel samples) were targeted for indentation, to validate the capacity of this indentation approach on particles to attain accurately the Young’s modulus \(E\) and hardness \(H\) via grid indentation of particles embedded within a matrix. Magnitudes of \(E\) and \(H\) for dense, monolithic LCO samples with 50-100 µm grains have already been reported by us [3,4]. Specifically, Qu et al. [3] measured \(E\) and \(H\) for LCO as 174 +/- 25 GPa (mean +/- standard deviation) and 11.7 +/- 3.8 GPa. The cumulative distribution functions (CDFs) for \(E\) and \(H\) as acquired by the grid indentation method are shown in Figure S.B, with a solid vertical line indicating the mean \(E\) and \(H\) as measured by Qu et al. Swallow et al. [4] measured \(E\) and \(H\) as 178 +/- 5 GPa (mean +/- standard error of the mean) and 8.3 +/- 0.5 GPa. These values are indicated as dashed vertical lines in Figure S.B.

For \(E\), the CDFs extend well beyond the mean value reported by Qu et al. and Swallow et al., indicating that a robust particle-dominated response was measured on a subset of the indentations. For \(H\), the CDF extends well beyond \(H\) as reported by Swallow et al., but does not meet the \(H\) value reported by Qu et al. If we take Qu et al. as a reference, we therefore may expect that our method underestimates the true \(H\) of the particles. We may also expect that the effect of the substrate will be smaller for the spinel samples, as their \(E\) is found to be lower than that of LCO. Closer matching of matrix and particle stiffness reduces the influence of the substrate on the measured properties [5–7].

![Cumulative distribution function](image)
Figure S.B. Cumulative distribution functions (CDFs) for a) $E$ and b) $H$ of the LiCoO$_2$ (LCO) reference sample. The mean $E$ and $H$ for LCO were measured in other works on a monolithic sample with 50-100 µm grains. Values from Qu et al. [3] and Swallow et al. [4] are shown as solid and dashed vertical lines, respectively.

S.3. Load sensitivity test for LiMn$_2$O$_4$

All data used to calculate $E$ and $H$ for the materials in the study were derived from loading profiles at constant loading rate with maximum load of 600 µN. Although we intentionally chose a low load to maximize the particle response and prevent substrate effects and particle sink-in, a sensitivity test was necessary to determine the potential for systematic errors in our methods. We chose to use LiMn$_2$O$_4$ (LMO) for the sensitivity test. By detailed simulations, Yan et al. [7] determined the parameter $h_{\text{max}}/R$ (maximum depth / particle radius) to determine the effect of substrate when indenting a semi-spherical particle in a more compliant matrix. By our logic, as particle radius $R$ is not easily varied, changing $h_{\text{max}}$ by conducting deeper indentations at higher load is an effective way to test the sensitivity of our system to the $h_{\text{max}}/R$ parameter. In this sense, a load sensitivity test indicates whether small differences between particle size distributions (PSDs) for each sample will lead to large errors in the results.

Yan et al. also found that there exists a low-depth regime for particle indentations, such that the measured $E$ approaches the true $E$ of the particle (within +/- 10%) and becomes less sensitive to the $h_{\text{max}}/R$ parameter. Therefore, depth-independence of the particle-dominated measurements indicates that we have reached this regime of good agreement with the actual $E$ of the particle.

In Figure S.Ca, we note the distribution of measured $E$ as a function of $h_{\text{max}}$ at 600, 1200, 1800, and 2400 µN. We can observe clearly that, although we did not conduct depth-controlled indentations, variation of load led to variations in $h_{\text{max}}$ for the high-modulus, particle-dominated measurements. Furthermore, we see that $E$ of the high-modulus group does not change significantly for each load, suggesting that the measured $E$ is indeed independent of the applied load, and therefore the $h_{\text{max}}/R$ parameter. We verify this observation by viewing the data in CDF format in Figure S.Cb. Good agreement is reached for LMO indentations at all applied loads. This finding, combined
with the analysis of Yan et al., supports our expectation that the CDFs of the measured spinel samples extend to the accurate magnitude of $E$ for LMO.

**Figure S.C.** a) Young’s modulus vs. $h_{\text{max}}$ for grid indentations conducted on LiMn$_2$O$_4$ at 600, 1200, 1800, and 2400 µN maximum load. Maximum indentation depth increases with maximum applied load. b) Corresponding cumulative distribution functions for the same experiments. Both figures indicate that the particle-dominated indentations have low sensitivity to applied load and maximum depth variation.

**S.4. Comparison of $E$ vs. $h_{\text{max}}$ and creep vs. $h_{\text{max}}$ for spinel samples**

In the manuscript, we selected CDFs and principal component analysis (PCA) as our methods of comparing the raw $E$ and $H$ data for the doped and undoped spinels. Additional trends are visible by viewing the data as a function of maximum depth $h_{\text{max}}$. In Figure S.Da, $E$ vs. $h_{\text{max}}$ for all spinel samples is shown. From comparing the doped and undoped data sets, we note that (1) All samples converge at the matrix-dominated
measurements with high \( h_{\text{max}} \) and low \( E \); (2) the particle-dominated measurements of LMNO and LMNFO occur at significantly higher \( E \) as compared with LMO; and (3) The LMO data set diverges from the doped spinels at high \( E \), resulting in comparable \( h_{\text{max}} \) despite significantly lower \( E \) than the doped materials. The third observation supports our conclusion that undoped LMO exhibits a more compliant mechanical response, and confirms that systematic errors such as PSD discrepancies are not responsible for the observed difference. Artificially low \( E \) due to small particle size would likely cause the LMO data at higher \( E \) to fit within the envelope of the LMNO and LMNFO data in this plot.

In Figure S.Db, we compare creep at maximum indentation load vs. \( h_{\text{max}} \) for all spinel samples and the LCO reference sample. We can consider creep at maximum load, measured as shown in the schematic of Figure 1c in the main text, to be an independent indicator of substrate influence in each measurement. This is because creep is not expected to occur for a pure ceramic (linear elastic rather than viscoelastic) response, but in practice drift of the instrument signal is possible. Likewise, \( h_{\text{max}} \) should be an indicator of matrix influence, as shallow maximum indentation depths are also typical for the stiffer ceramic response. From Figure S.Db, we observe that a distinct group of data exists in the low-creep, low-depth region of the graph. These data correspond to the particle-dominated indentations. We see that the positions of these groups are comparable for all samples, including both the transition-metal substitute and unsubstituted LMO spinels. Therefore, indentations of consistent quality are available in all data sets to represent the particle phase. This observation further supports that our comparison of LMO, LMNO, and LMNFO is not detectably influenced by systematic errors or significant differences in measurement quality.
S.5. Selection of $k$ parameter for cluster analysis

The data derived by PCA, shown in Figure 2(c-e) of the main text, form an elongated envelope in the two-component space. At each end of the envelope, the data converge to the characteristics of the particle-dominated or matrix-dominated measurements. The k-means clustering analysis as applied to such a continuum cannot easily identify a clear group of particle-dominated indentations, as the data range continuously between the particle and matrix endpoints. As a result, we must make an arbitrary decision of where to cut off the particle-dominated data as they blend into the composite response. The decision in the case of clustering is simplified to choosing a number of clusters $k$. In the simplest example, choosing $k = 2$ roughly divides the data into two halves. Since we are not interested in the intermediate composite responses, $k = 3$ is the minimum number of clusters that can exclude the unwanted data.

In an effort to reduce the arbitrary aspect of choosing $k$, we conducted a sensitivity analysis in which $k$ was increased from 3 to 7 for the PCA-converted LMO, LMNO, and LMNFO data. As shown for LMNO in Figure S.E, the selected particle-dominated group decreased in size when we increased $k$ from 3 to 4, but stayed the same as $k$ increased from 4 to 7. The particle data remain intact and the clustering changes elsewhere in the rest of the data. After varying $k$ for all data sets, we found that all samples had consistent particle-dominated groups from $k = 5$ to $k = 7$. We therefore concluded that the best grouping of the particle measurements was obtained in this $k$ range, as the group was stable. We then used $k = 5$ to determine the particle-dominated measurements for $E$ and $H$ quantification, as indicated in the manuscript.
Figure S.E. Clustering procedure applied with \( k = 3 \) to \( k = 7 \) clusters for \( \text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4 \) after principal component analysis in MATLAB. The chosen particle-dominated group (circled) shrinks upon increasing \( k \) from 3 to 4, but is independent of the number of clusters between \( k = 4 \) and \( k = 7 \).

S.6. Comparison of particle size for LMO, LMNO, and LMNFO

Figure 1a in the manuscript showed a scanning electron microscope (SEM) image of LMNFO particles after coarsening treatments, demonstrating that an abundance of particles were available in the diameter range of 8-10 µm. For comparison, Figure S.F shows SEM images for LMO and LMNO after coarsening. In both images, the largest particles approach 10 µm width.

Comparison of the particles via optical microscope (OM) in the final form for indentation is shown in Figure S.G. The optical images demonstrate that the effective particles sizes and particle field layouts are comparable for the LMO, LMNO, and LMNFO samples. Using the ImageJ image analysis program, the large particles in each particle group were measured by drawing three skew lines across the exposed surface of each particle. The mean +/- standard deviation from measuring at least 4 such fields with 10 particles each were 6.4 +/- 1.0, 6.6 +/- 1.0, and 6.5 +/- 0.8 µm for LMO, LMNO, and LMNFO, respectively. We therefore conclude that the measurement conditions were comparable for all spinel samples.

The LCO reference sample is also shown in Figure S.G. Clearly, most of the particles are significantly larger than those of the spinel samples. Specific regions such as the particle group indicated by the circle were chosen for comparison to the spinel samples, as the particles were smaller and of comparable size to the spinels. The particle size in this region, as calculated by the same process, was 6.9 +/- 1.6 µm. This
comparison supports our assumption that the LCO reference sample can be used to demonstrate the accuracy of our grid indentation method.

Figure S.F. Scanning electron micrographs of coarsened LiMn$_2$O$_4$ (LMO) powder (left) and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (LMNO) powder (right). LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (LMNFO) is shown in Figure 1 of the main text. Large particles in these images occur at ~8-10 µm.
Figure S.G. Optical images of LiMn$_2$O$_4$ (top left), LiMn$_{1.5}$Ni$_{0.5}$O$_4$ (top right), LiMn$_{1.3}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ (bottom left), and LiCoO$_2$ (LCO) (bottom right). Images such as these were used to calculate particle size in typical indentation regions. The blue circle indicates a group of small particles chosen for the LCO reference.
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