We demonstrate that extensive electrochemical shock–electrochemical cycling induced fracture–occurs due to coherency stresses arising from first order cubic-to-cubic phase transformations in the spinels LiMn_{2}O_{4} and LiMn_{1.5}Ni_{0.5}O_{4}. Electrochemical shock occurs despite the isotropy of the shape changes in these materials. This electrochemical shock mechanism is strongly sensitive to particle size; for LiMn_{2}O_{4} and LiMn_{1.5}Ni_{0.5}O_{4}, fracture can be averted with particle sizes smaller than ~1 μm. As a further critical test of the proposed mechanism, iron-doping was used to induce continuous solid solubility of lithium in LiMn_{1.5}Ni_{0.5}O_{4}, and shown to virtually avert electrochemical shock, while having minimal impact on the electrode potential and capacity.

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through a solid solution, followed by a first-order phase transformation between two cubic phases with a linear misfit strain of ~1.0%. When the Ni/Mn transition metals are ordered, delithiation occurs through two distinct first-order phase transformations each with a linear misfit strain of ~1.0%.

Using the established phase behavior and known mechanical properties of LiMn$_2$O$_4$, we estimate a critical primary crystallite size of $1.10 \, \mu m$ below which coherency stress fracture is energetically unfavorable. Our analysis follows established approaches to interfacial fracture problems and a similar method was previously applied to study electrochemical shock of LiFePO$_4$. The relevant materials properties used in the calculation are a bulk modulus of 119 GPa, a surface energy of 0.58 J m$^{-2}$ (this is the minimum surface energy of LiMn$_2$O$_4$ and is for the Li-terminated (001) plane), and a Poisson’s ratio of 0.3, which is assumed; further details of these calculations are provided in the Supporting Information. To date, there have been no reports of these materials properties for the high voltage LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel, but the critical primary crystallite size for the high voltage spinel should be similar to that of the conventional LiMn$_2$O$_4$ spinel, due to the similar crystal chemistry and lattice parameter misfit in the two compounds. This critical crystallite size calculation considers only coherency stresses arising from two-phase coexistence and is therefore the critical size in the limit of zero C-rate. However, previous micromechanical modeling shows the dependency on C-rate to be extremely weak; the critical size differs by only a factor of 1.5 between C-rates of C/1000 and 1000C. Therefore, two-phase coherency stresses are the dominant source of stresses—and therefore the root cause of electrochemical shock—across all practical C-rates in these spinel materials.

The predicted critical primary crystallite size was confirmed using acoustic emission measurements of composite electrodes of LiMn$_2$O$_4$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ during low C-rate (C/50) first cycle charging (Figure 2). Cell voltage (upper panel) and cumulative acoustic counts (lower panel) are plotted as functions of lithium composition (X in Li$_X$Mn$_2$O$_4$). Figure 2a compares the observed C/50 acoustic emission from the conventional spinel LiMn$_2$O$_4$ at two different primary crystallite sizes: fine material of ~1 $\mu m$ and coarse material of 2–5 $\mu m$. Figure 2b shows a corresponding comparison of the C/50 acoustic emission from high voltage Li$_{1.5}$Mn$_{1.5}$Ni$_{0.5}$O$_4$ spinel at two different primary crystallite sizes: fine materials of ~500 nm and coarse material of 2–5 $\mu m$. For both LiMn$_2$O$_4$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$ spinel materials, fine primary crystallites show very little acoustic emission during the first C/50 charge cycle, while larger primary crystallites show significant acoustic emission, which is highly correlated with the two-phase regions where two distinct cubic phases with ~1% linear misfit strain coexist. These experimental observations demonstrate that electrochemical shock in these cubic spinel materials is a direct consequence of transformation strains which accompany the first-order phase transformations during electrochemical (de)lithiation.

If correct, this interpretation of the electrochemical shock mechanism in cubic spinels would suggest that electrochemical shock can be averted if all misfitting first-order phase transformations are suppressed. We tested this design strategy through iron-doping of the high voltage spinel, Li$_{1.5}$Mn$_{1.5}$Ni$_{0.5}$Fe$_{0.5}$O$_4$, which has continuous solid solubility of lithium over the electrochemical cycling window, as shown in Figure 3. Here the measured lattice parameters are shown for Li$_{1.5}$Mn$_{1.5}$Ni$_{0.5}$Fe$_{0.5}$O$_4$ at different lithium compositions X, prepared electrochemically in composite pellet electrodes charged at C/50 rate to 4.9 V vs. Li$^+$/Li, then discharged at C/50 to the specified state of charge; the lithium composition is determined coulometrically. At each composition, the X-ray diffraction pattern indicates a single phase to the limit of detection of the measurement and the total volume change is ~4% for complete delithiation. For comparison, literature data of the composition-dependent lattice parameter for disorders, undoped, Li$_{1.5}$Mn$_{1.5}$Ni$_{0.5}$O$_4$ are also shown in Figure 3. While the iron-doped material has been studied previously, and has been reported to have improved rate capability and capacity retention compared to undoped material Li$_{1.5}$Mn$_{1.5}$Ni$_{0.5}$O$_4$, the lattice parameter...
Acoustic emission measurements of the iron-doped high voltage spinel confirm that the change in phase-behavior qualitatively changes electrochemical shock relative to the undoped material. Figure 2b compares iron-doped high voltage spinel with primary crystallite sizes of ~5–7 μm to the undoped high voltage spinel; despite the large primary crystallite sizes, the iron-doped Li$_{x}$Mn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_{4}$ material shows essentially no acoustic emission during the first C/50 charge cycle. Thus, modest iron-doping results in a high voltage spinel with tremendously improved mechanical reliability while having minor impact on the electrochemical properties. At very high rates, this iron-doped spinel may be expected to undergo electrochemical shock due to the concentration gradient stresses; in fact, the isotropic shape change and continuous solid-solubility of the iron-doped material make it an ideal model system in which to experimentally study the concentration gradient mechanism for electrochemical shock.

To summarize the experimental results, when coherency stresses due to phase transition exist, particles above a critical size are subject to electrochemical shock at arbitrarily low C-rates. When the phase transformation is eliminated by doping, no low C-rate electrochemical shock occurs even at large particle sizes.

In conclusion, ion-intercalation materials with first-order phase transformations are subject to C-rate independent electrochemical shock through coherency stresses; this mechanism is demonstrated in two cubic spinel model systems, LiMn$_2$O$_4$ and LiMn$_{1.5}$Ni$_{0.5}$O$_4$. Electrochemical shock in phase transforming electrode materials is strongly sensitive to particle size, as predicted by micromechanical modeling and verified by experiment. Therefore, one strategy to avert electrochemical shock in phase transforming intercalation compounds is particle size control. However, while particle size reduction is effective in eliminating electrochemical shock (at least in the early cycles), this strategy does not completely relax the underlying stresses. Although the stresses in small particles are subcritical for early cycles, continued electrochemical cycling requires the propagation of a phase boundary that will continue to generate cyclic stresses. We suggest that this can be an additional factor leading to long-term degradation of ion-storage materials. For example, cyclic subcritical stresses can lead to fatigue failure, chemically-assisted fracture mechanisms such as stress-corrosion cracking, or both. These additional mechanisms remain to be explored. Further, the increased specific surface area of finer particles may accelerate undesirable side reactions, such as electrolyte decomposition.

A second strategy for averting electrochemical shock due to coherency stresses is to use chemical modifications to modulate the misfit strain between coexisting phases. We demonstrate that iron-doping of LiMn$_{1.5}$Ni$_{0.5}$O$_4$ changes the phase-behavior of the material to a continuous solid-solution with respect to lithium; the altered phase-behavior fundamentally changes the available electrochemical shock mechanisms and the iron-doped material is no longer subject to early cycle electrochemical shock through coherency stresses, enabling a wider range of particle sizes and C-rates to be used without mechanical damage. Previous experimental observations suggest that reduced misfit strain between coexisting cubic spinel phases promotes capacity retention. Based on the understanding of electrochemical shock in these materials, we suggest that reduced misfit strain helps prevent particle-level fracture, thereby minimizing impedance growth and the available surface area for deleterious side reactions, such as manganese-dissolution and/or electrolyte decomposition which further limit coulombic efficiency and cycle life. At high cycle number, single-phase materials—such as the iron-doped high voltage spinel—may be less susceptible to cyclic fatigue than phase transforming materials with reduced misfit strain, since no cyclic phase boundary propagation occurs. The larger particle sizes enabled by materials with continuous solid-solubility also reduce the available surface area for deleterious side reactions.

Conclusions

The design criteria developed here for electrochemical shock resistance are generally applicable to all ion-intercalation materials with first-order phase transformations. Many ion-intercalation compounds undergo first-order phase transformations between misfitting phases and are subject to electrochemical shock if the electrode microstructure is not properly engineered. The design of materials that avoid misfitting, coherent phase transformations—through equilibrium or
non-equilibrium paths—has been previously identified as a route to electrode materials with enhanced rate capability;\textsuperscript{48–51} electrochemical shock resistance provides another motivation to engineer such electrode materials.

**Experimental**

**Electrochemical testing.**— Thick composite electrodes were prepared and mounted in 2016 coin cells (MTI Corporation, Richmond, CA). The electrolyte was a 1:1 mixture by volume of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1 M LiPF\(_6\) salt (all from Sigma-Aldrich). All cells used 2 pieces of Tonen E20MMS separator 1 Li metal (Alfa Aesar) negative electrode. Pellet-type composite electrodes were prepared with a composition 90/5/5 (wt\%) of active material / Super P / Kynar 2101 binder were prepared by mixing the powders in 1-methyl-2-pyrrolidinone (NMP) followed by drying on a hot plate overnight, and then grinding by hand in an agate mortar and pestle. The resulting composite powder was then uniaxially pressed to the specified state of charge.

**X-Ray diffraction.**— X-Ray diffraction measurements were taken on a PANalytical X'Pert Pro instrument using copper K\(_\alpha\) tube-source radiation. Measurements were collected with the high-speed optics in a Bragg-Brentano 0–\(2\theta\) geometry over an angular range of 15–80° 2\(\theta\). Powder samples were mounted in 16 mm diameter wells centered on the open Eulerian cradle. Fixed \(\frac{\pi}{4}\) slits were used for both the incident and diffracted beams. A 10 mm width limiting mask, 1° anti-scatter slit and 0.02 radian Soller slits were also used for all measurements. The measured patterns were profile fit in HighScore Plus using asymmetric peak shapes and widths. Lattice parameters were refined by first refining without sample displacement and then turning it on in the refinement. Fe-containing samples were most reliably refined by starting from a reference pattern for LiMn\(_2\)Fe\(_{0.5}\)O\(_4\).

**Electrode and material processing.**— We compare LiMn\(_2\)O\(_4\) and LiMn\(_{1.5}\)Ni\(_0.5\)O\(_4\) active materials with different particle size by using commercial materials as received and material coarsened during sintering. LiMn\(_2\)O\(_4\) was sourced from Toda Kogyo and LiMn\(_{1.5}\)Ni\(_0.5\)O\(_4\) material SP-10 was sourced from NEI Corporation (Somerset, NJ). LiCoO\(_2\) powder was sourced from AGC Seimi Chemical Co. Ltd. (Kanagawa, Japan) Sintered electrodes were prepared by pressing pellets of the active material in a \(\frac{1}{2}\) inch die at 140 MPa and held for 4 minutes. The resulting pellets were sintered at 950°C for 12 h (LiMn\(_2\)O\(_4\) and LiMn\(_{1.5}\)Ni\(_0.5\)O\(_4\)) or 1.5h (LiCoO\(_2\)) with a heating rate of 9°C min\(^{-1}\) and a furnace cool. Coarsened powders of the spinels were prepared by grinding the sintered electrode by hand in an agate mortar and pestle to yield a powder used to prepare a composite electrode. LiFe\(_{0.08}\)Mn\(_{1.5}\)Ni\(_{0.42}\)O\(_4\) was synthesized by solid-state reaction from stoichiometric amounts of Li\(_2\)CO\(_3\), Fe\(_3\)O\(_4\), Mn\(_2\)O\(_3\), and NiO (Kanagawa, Japan) Sintered electrodes were prepared by pressing pellets of the active material at 140 MPa and held for 1 minute to obtain 0.5 mm thick electrodes. All cells were held in place on the positive coin cell, using vacuum grease as a couplant and held in place with rubber bands. Between the sensor and controller, a 2/46 voltage pre-amplifier was set to 40 dB gain; no software gain was used. The raw data are collected with an analog frequency filter with a bandpass of 100 kHz to 2 MHz and analog to digital conversion is done at 1 MHz. The event threshold was set at 24 dB with a front-end filter that excludes events that register less than 3 counts; these test parameters were chosen to give minimal background, as measured on an identically prepared cell that is not electrochemically cycled.

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