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Strategies to Avert Electrochemical Shock and Their Demonstration in Spinel

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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_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. 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_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, fracture can be averted with particle sizes smaller than $\sim 1\ \mu\text{m}$. As a further critical test of the proposed mechanism, iron-doping was used to induce continuous solid solubility of lithium in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, and shown to virtually avert electrochemical shock, while having minimal impact on the electrode potential and capacity.

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Batteries based on ion-intercalation reactions—exemplified by lithium-ion batteries—enable high energy densities which are attractive for applications ranging from portable electronics to electrified transportation to grid-level storage. To achieve high storage capacities and energy density, ion-intercalation hosts must undergo large composition changes, which are often accompanied by large shape changes. These shape changes can result in electrochemical cycling-induced fracture, a phenomenon we have termed “electrochemical shock,” which contributes to impedance growth and performance degradation. Electrochemical shock has been observed in a variety of ion-intercalation materials with widely varying compositions and crystal structures^{1–7} and it can cause severe deleterious effects on battery performance, manifested as impedance growth upon cycling. This has been clearly demonstrated during early cycling (first 500 cycles) of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) cathodes, for example.³

Previously, we and others showed that electrochemical shock in intercalation electrodes can be C-rate dependent, such as occurs when steep gradients in ion concentration generate diffusion-induced stresses sufficient to cause fracture.^{8,9} Alternatively, electrochemical shock can occur by C-rate independent mechanisms, such as anisotropic shape changes in polycrystalline aggregates (e.g. secondary particles); this mechanism depends on crystal symmetry and state-of-charge, but not on cycling rate. Layered LiCoO_2 and isostructural derivative compounds such as $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ are a few examples amongst many in which electrochemical shock is dominated by the C-rate independent anisotropic shape change mechanism.^{10,11} (In distinguishing C-rate dependent vs. independent, we consider the rate dependence of a mechanism, not of a material. We have adopted a convention of calling C-rate independent any electrochemical shock mechanism that persists to arbitrarily small C-rates. Therefore, if electrochemical shock is observed during low C-rate cycling, this is clear evidence that a C-rate independent mechanism is active. At sufficiently high C-rates, the C-rate dependent concentration gradient mechanism will be simultaneously active and the observed damage accumulation in a given material may not be C-rate independent.) This classification scheme applies most directly to materials that undergo brittle fracture, such as most oxide and polyanion intercalation compounds. While micromechanical failure is also the main limitation to capacity utilization and cycle life in Si-based anodes, the mechanical deformation mechanisms in alloying electrodes are qualitatively different

due to the enormous strains and resultant plastic deformation which occurs.^{12–24}

Based on this understanding of electrochemical shock mechanisms, it might be hypothesized that $\text{Li}_x\text{M}_2\text{O}_4$ spinels, which typically retain cubic crystal symmetry throughout electrochemical cycling in the composition range of $x \leq 1$, do not exhibit severe electrochemical shock. In this work, we show that this hypothesis is incorrect: using acoustic emission^{10,25–29} to enable non-destructive *operando* measurements of damage accumulation during electrochemical cycling, we find that $\text{Li}_x\text{Mn}_2\text{O}_4$ and $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ —each of which remains cubic and exhibits isotropic shape as x varies—both exhibit 10^2 greater cumulative acoustic emission than comparably prepared LiCoO_2 electrodes (experimental results are shown Figure 1a, with the experimental apparatus illustrated in the inset). Monolithic sintered electrodes free of conductive additives and binders (all electrodes shown in Figure 1a have comparable porosity $\sim 25\%$ and thickness $500\ \mu\text{m}$) show this trend most clearly, and the low current rate of the experiments (C/50) indicates that the damage occurs by a C-rate independent electrochemical shock mechanism. The huge difference in acoustic emission between layered LiCoO_2 and the cubic spinels LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ indicates that different C-rate independent electrochemical shock mechanisms are active in layered and spinel materials. Low C-rate electrochemical shock in the spinels is further corroborated by post-mortem scanning electron microscopy (Figure 1b) of conventional cast composite electrodes of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, which shows individual electrode particles are fractured after two C/20 cycles. We find that electrochemical shock in these cubic spinels is due to coherency stresses arising from first-order cubic-to-cubic phase transformations; while previous modeling work has suggested that coherency stresses may drive C-rate independent electrochemical shock, the present work provides the first direct experimental study of this phenomenon, including demonstrations of two mitigation strategies.

The remainder of this paper is organized as follows. First, we present a model and experiments that demonstrate electrochemical shock in the cubic spinels occurs due to coherency stresses in first-order cubic-to-cubic phase transformations. Second, we develop and demonstrate two methods by which this electrochemical shock can be averted: A) by particle size reduction; B) doping to remove the phase transformation. The first demonstration is shown with *operando* acoustic emission measurements that correlate to a phase transformation and a micromechanical model of coherency stresses associated with lattice parameter misfit between distinct cubic phases which coexist over part of the electrochemical cycling window. At the

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Figure 1. (a) Acoustic comparisons of monolithic sintered electrodes charged at C/50 rate with (inset) schematic of the experimental apparatus (b) SEM image of fractured $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particle from conventional electrode.

interface between the two co-existing phases, spatially localized lattice parameter variations can generate large coherency stresses and drive fracture. This conclusion leads to the two strategies to avoid electrochemical shock. In the first of these, we demonstrate with modeling and experiment a strong sensitivity to particle size, such that electrochemical shock can be averted by reducing primary crystallite sizes to $\sim 1 \mu\text{m}$ or less. In a second and more powerful approach, we show that doping to remove the first-order phase transformations can completely avert coherency stress electrochemical shock. This strategy is demonstrated through iron-doping of the high-voltage spinel, e.g. $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$, to produce continuous solid solubility of lithium over the relevant composition window, thereby allowing even coarse particles of this material to be electrochemically cycled without mechanical damage accumulation.

The phase behavior of the cubic Mn-based spinels with respect to Li concentration is complex. During electrochemical cycling of $\text{Li}_x\text{Mn}_2\text{O}_4$ in the 4V region ($0 \leq X \leq 1$), lithium is initially removed as a continuous solid solution for compositions $0.5 \leq X \leq 1$. Subsequent delithiation for compositions ($0.25 \leq X \leq 0.5$) occurs via a first-order cubic-to-cubic phase transformation with a linear misfit strain of 1.2% between the two coexisting cubic phases.³⁰ The high voltage spinel $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ also undergoes at least one first-order phase transformation; the phase-behavior of this compound is sensitive to Ni/Mn ordering on the transition metal cation sublattice, which in turn depends on the thermal history of the material.^{31–36} The $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials tested here are prepared in a manner known to produce a disordered Ni/Mn cation arrangement, resulting in phase-behavior mirroring that of $\text{Li}_x\text{Mn}_2\text{O}_4$: initial delithiation occurs

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

Using the established phase behavior and known mechanical properties of LiMn_2O_4 , we estimate a critical primary crystallite size of $1.10 \mu\text{m}$, 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 .³⁷ The relevant materials properties used in the calculation are a bulk modulus of 119 GPa,³⁸ a surface energy of 0.58 J m^{-2} (this is the minimum surface energy of LiMn_2O_4 and is for the Li-terminated (001) plane³⁹), 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 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel, but the critical primary crystallite size for the high voltage spinel should be similar to that of the conventional LiMn_2O_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.⁴⁰ 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_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ 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 $\text{Li}_x\text{M}_2\text{O}_4$). Figure 2a compares the observed C/50 acoustic emission from the conventional spinel LiMn_2O_4 at two different primary crystallite sizes: fine material of $\sim 1 \mu\text{m}$ and coarse material of 2–5 μm . Figure 2b shows a corresponding comparison of the C/50 acoustic emission from high voltage $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel at two different primary crystallite sizes: fine materials of $\sim 500 \text{ nm}$ and coarse material of 2–5 μm . For both LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ 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 $\sim 1\%$ 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, $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$, 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 $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$ at different lithium compositions X , prepared electrochemically in composite pellet electrodes charged at a 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 $\sim 4\%$ for complete delithiation. For comparison, literature data of the composition-dependent lattice parameter for disordered, undoped, $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ are also shown in Figure 3.³⁴ 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 $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$,⁴¹ the lattice param-

Figure 2. First cycle C/50 acoustic emission data from composite spinel electrodes: (a) LiMn_2O_4 and (b) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.

ter variations and phase behavior of this material have not previously been reported to our knowledge.

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 $\sim 5\text{--}7\ \mu\text{m}$ to the undoped high voltage spinel; despite the large primary crystallite sizes, the iron-doped $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$ 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;⁸ 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 transformation 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_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. 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.^{42–45} 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 $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ 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.^{41,46,47} 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

Figure 3. Lattice parameter data for $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$ (present results) and undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (literature data from Ref. 34) illustrating the qualitative difference in phase behavior. Both spinels are disordered on the transition metal cation sublattice. Dashed lines are guides to the eye.

non-equilibrium paths—has been previously identified as a route to electrode materials with enhanced rate capability,^{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 LiPF₆ salt (all from Sigma-Aldrich). All cells used 2 pieces of Tonen E20MMS separator and a 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 into pellets in a $\frac{1}{2}$ inch die at 140 MPa and held for 1 minute to obtain 0.5 mm thick electrodes. All electrodes were held in place on the positive coin cell can with a conductive binder that is a mixture of PVDF, Ketjen black ECP and vapor grown carbon fiber (VGCF) in NMP; this binder reduces the contact resistance and is particularly necessary for the sintered electrode experiments. To enable comparison between the sintered and composite electrode experiments, it was used for the composite electrodes as well. This binder was cured overnight at 120°C in a vacuum oven before transferring the electrodes to an Argon filled glove box where the coin cells are assembled and sealed. The resulting half-cells were cycled on a MACCOR 4000 tester at constant current C/50 to a maximum voltage of 5.0 V vs. Li⁺/Li. The composite electrodes used for composition-dependent lattice parameter measurements were prepared in an identical manner, but with a formulation of 80/10/10 (wt%) of active / Super P / Kynar 2101 binder. These samples were electrochemically delithiated in composite pellet electrodes charged at a C/50 rate to 4.9 V vs. Li⁺/Li, then discharged at C/50 to the specified state of charge.

Electrode and material processing.— We compare LiMn₂O₄ and LiMn_{1.5}Ni_{0.5}O₄ active materials with different particle size by using commercial materials as received and material coarsened during sintering. LiMn₂O₄ was sourced from Toda Kogyo and LiMn_{1.5}Ni_{0.5}O₄ material SP-10 was sourced from NEI Corporation (Somerset, NJ). LiCoO₂ 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 (LiMn₂O₄ and LiMn_{1.5}Ni_{0.5}O₄) or 1.5h (LiCoO₂) 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}O₄ was synthesized by solid-state reaction from stoichiometric amounts of Li₂CO₃, Fe₃O₄, Mn₂O₃, and NiO sourced from Sigma-Aldrich. The precursors were ball-milled in acetone for 24h and then calcined in air at 900°C for 24h with heating and cooling rates of 5°C min⁻¹.

Electron microscopy.— The morphology and characteristic particle sizes of the as-received and coarsened powders were observed by scanning electron microscopy, using the secondary electron imaging mode of a JEOL 5910 instrument with low accelerating voltages of 5–10 kV and are shown in Supporting Figure S2. The post mortem microscopy of LiMn_{1.5}Ni_{0.5}O₄ electrodes was conducted using a higher resolution FEI/Philips ESEM with a field emission element using typical accelerating voltages of 20 kV.

Acoustic emission.— Acoustic emission measurements were performed using a Physical Acoustics Corp. μ DISP instrument controlled by AEWin software on a laptop PC. A micro-30 sensor was attached to the positive electrode side of coin cell, using vacuum grease as a

couplant and held in place with rubber bands. Between the sensor and controller, a 2/4/6 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.

X-Ray diffraction.— X-Ray diffraction measurements were taken on a PANalytical X'Pert Pro instrument using copper K α tube-source radiation. Measurements were collected with the high-speed optics in a Bragg-Brentano θ – 2θ geometry over an angular range of 15–80° 2 θ . Powder samples were mounted in 16 mm diameter wells centered on the open Eulerian cradle. Fixed $\frac{1}{2}^\circ$ 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 HighScorePlus 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_{1.5}Fe_{0.5}O₄.

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