Review article

Entropic stabilization in lithium-rich transition metal layered oxides – A perspective

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A B S T R A C T

In this paper we offer a new perspective on how the principles of high entropy design for oxide materials can be applied to lithium rich transition metal oxide cathodes. We discuss the structure, unique properties, and synthetic dependence of lithium rich transition metal oxide cathodes as well as some background on high entropy oxides. We then discuss the benefits of entropic stabilization in reducing the rigor and increasing the consistency of synthesizing phase pure cathodes materials. We draw parallels between the established temperature, time and transformation relationships used in synthesis of materials and electrochemistry to propose a voltage, time, and transformation analogue that can be used to help explore the phase transformations of lithium rich transition metal oxide cathodes over cycling. This proposed voltage, time, and transformation system is then used to explore the use of entropic stabilization of lithium rich transition metal oxide cathodes during electrochemical cycling. Finally, considerations for the design and limitations of entropic stabilization for lithium rich transition metal oxide cathodes are discussed, and solutions are offered.

Introduction to LRLOs

The lithium rich layered oxides (LRLO) cathodes are an ouroboros of structure and property relationships. The LRLO category of cathodes was initially notable due to high capacities, high voltages, and relatively low-cost compositions [23–27]. However, as time progressed, they became more well known for their challenges such as fading voltages and capacities, poor rate capabilities, and poor thermal stabilities [23, 25,28–30]. As seen in Fig. 1 Michael Thackeray, *et. al.* first noted the chemical and electrochemical behaviors of the Li_2MnO_3 material, the precursor of LRLO materials, in 1991 [1]. Further experimentation with Li_2MnO_3 resulted in its use to stabilize other layered lithium transition metal oxides, as seen in the work of Numata *et. al.* who successful stabilized $LiCoO_2$ with Li_2MnO_3 [2]. Further investigation of the structure of the resultant class of LRLO materials resulted in two rival structural interpretations. Thackeray proposed a two-phase structure with a mixture of a R-3 m component phase of $LiNi_{0.5}Mn_{0.5}O_2$, and a C2/m component phase of Li_2MnO_3; Dahn proposed a single R-3 m phase material, see Fig. 2(b), Figure SI1, and Figure SI2 [3,4]. Later structural refinement by Ceder, *et. al.* demonstrated that the arrangement of transition metals within the transition metal layer for both of the proposed structures could explain the observed XRD patterns, see Fig. 2 (c) and Figure SI3 [5]. Publication of the Gibbs Diagram by Dahn *et. al.* demonstrated how LRLO materials lie in a two-phase existence region between an R-3 m ($Li[Ni_{0.5}Mn_{0.5}]O_2$) phase, and a C2/m (Li_2MnO_3 phase, which highlighted how compositionally dependent the structure of LRLO materials are [12,13].

As the structural ambiguity remained, more observations were being made on the unique features of LRLO cathodes, such as their poor capacity and voltage cycle stability. The loss of voltage and capacity over multiple cycles was initially addressed by the use of a surface coatings [6]. The surfaces of LRLO materials were known to be unstable with observation of spinel or spinel-like phase forming over the course of cycling [8]. With surface coatings, which would stabilize LRLO surfaces and prevent side reactions, as well as spinel growth, voltage decay was observed, indicating that voltage decay was rooted in the bulk of the LRLO materials [6,8]. Migration of the transition metal ions in the bulk of the LRLO materials was first proposed in 2013 by Gallagher *et. al.* as the mechanism behind voltage fade, and this was later confirmed by direct observation by Li *et. al.* [14,21]. The migration of transition metals being the mechanism of voltage fade was consistent with the observed phase instability of the LRLO materials. This instability means

upon repeated cycling and the associated transition metal migration LRLO materials undergo phase decomposition into defect phases [12].

The phase instability of LRLO cathodes is also represented in the 4.5 V plateau seen in the first charge profile of with potentials at or above 4.5 V. This plateau is a representation of the LRLO materials undergoing a previously thought irreversible structural transformation, where transition metal ordering is lost, and oxygen becomes electrochemically active [7,22]. The electrochemical activation of oxygen was first proposed as an explanation for the greater than theoretical capacities seen in LRLO materials [7]. There are several competing contemporary explanations for the origin and cause of this additional capacity, though a majority of them ascribe the electrochemical activation of oxygen as critical for this process [9–11,15,16,18,19]. Additionally, as previously mentioned this process was believed to be entirely irreversible, until the discovery that simple thermal treatment could reverse the phase transformation, however, at time of writing the structural transformation remains electrochemically irreversible [22]. The discovery of the activation processing being reversible, as opposed to irreversible,

indicates that electrochemically active LLRO is metastable [22].

The metastability of electrochemically active LRLO materials offers several key insights into the mechanistic origins as well as for strategies for mitigating or eliminating phase instability. The electrochemically irreversible energy in the activation of LRLO materials is lost during the creation of defects accompanying the phase transition from the pristine material into the metastable material [22]. These defects also serve as the origin structural instability, voltage fade, and capacity loss in LRLO materials. The metastability of electrochemically active LRLO materials also offers the possibility of increasing the phase stability of these materials through entropic stabilization techniques.

Entropic stabilization in oxides

Entropy is critical in stabilizing a myriad of materials and structures from the membranes that make up life [31], to providing toughness and resilience for new alloys [32,33]. The discovery of high entropy alloys (HEA) demonstrated that entropic stabilization can be achieved through
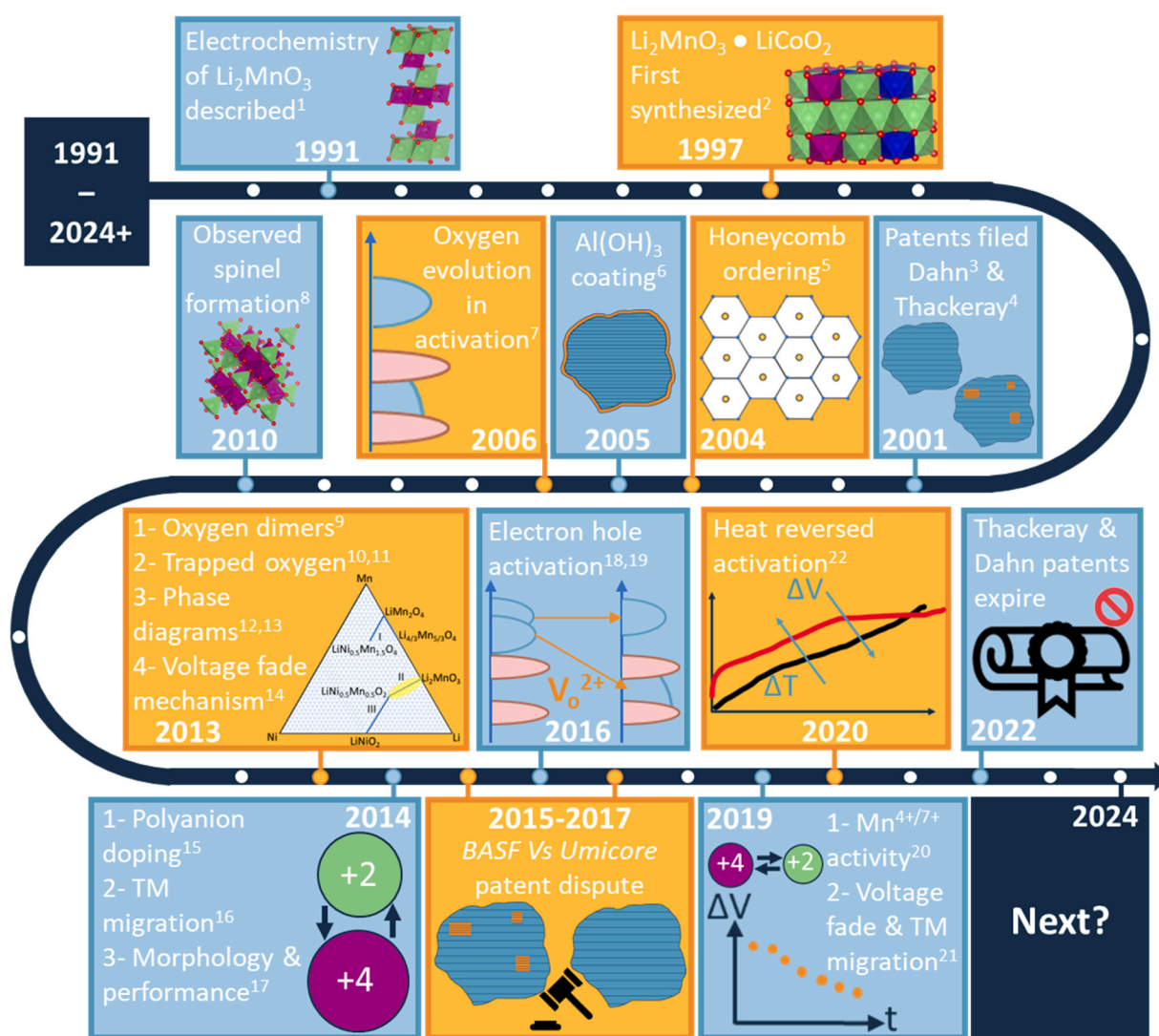

Fig. 1. – A timeline of significant research milestones for lithium-rich cathode materials. These milestones are: Michael Thackeray's description of the first lithium-rich compounds [1], the first synthesis of Li_2MnO_3 stabilized cobalt analogue [2], the patents filed by Dahn [3] and Thackeray [4] with differing structural arguments, Ceder's publication of honeycomb ordering [5], the first use of coatings to successfully stabilize LRLOs [6], the oxygen activation theory [7], spinel formation observed and linked to voltage fade [8], Oxygen Dimer Theory [9], Trapped oxygen theory [10,11], publication of lithium-rich phase diagrams [12,13], proposed mechanism of voltage fade as TM migration [14], polyanion doping preformed in LRLO [15], oxygen vacancy and TM migration theory [16], link between morphology and performance of LRLO established [17], electron hole theory of activation [18,19], manganese oxidation theory [20], transition metal migration linked to voltage fading [21], reversibility of electrochemical activation through heat treatment [22].

the high mixing entropy from multiple components [32]. By the Boltzmann hypothesis the greater the number of available microstates increases the entropy, and by increasing the number of components the number of microstates increases. The gain in entropy arises from the number of components in a mixture and can be calculated by converting the mixing entropy to configurational entropy which measures the overall change in entropy per mole of each constituent element, see *Equation 1* for the process of deriving the configurational entropy [32].

Equation 1. – The derivation of configurational entropy, ΔS_{config}. Where k is Boltzmann's constant, ω is the number of microstates, n is the number of constituent elements of equimolarity, and R is the universal gas constant.

$$\Delta S_{config} = k\ln(\omega) = R\left(\frac{1}{n}\ln\left(\frac{1}{n}\right) + \ldots + \frac{1}{n}\ln\left(\frac{1}{n}\right)\right) = R\ln\left(\frac{1}{n}\right) = -R\ln(n)$$

The calculation of phase stability for these multicomponent alloys follows Gibb's rules, where for the formation of a stable phase, the Gibb's free energy of formation, ΔG_f, of the phase formation needs to be lower than zero. For this to happen the entropy of formation, ΔS_f, must be large enough to exceed the positive enthalpy of formation, ΔH_f, and dominate the Gibb's free energy of formation, ΔG_f where $\Delta G_f = \Delta H_f -$

$T\Delta S_f$ thereby stabilizing the formation of the alloys above a sufficiently high temperature. This definition of $|\Delta S_f T| >> |\Delta H_f|$ serves as the strictest definition of entropic stabilization [34]. Configurational entropy is the most direct mechanism for influencing the formation entropy of a material system. The expansion of the configurational entropy, as seen in *Equation 2*, while including the concentration of each constituent, is still based on idealized Boltzmann statistics and therefore fails to account for the possible interactions of other constituent elements that can have substantial influence on the enthalpy and entropy of the material [32,35,36]. For this purpose, convention set by Chang *et. al.* set the definition of high entropy alloys as those with 5 or more principle elements with concentrations between 35 and 5 at% with configurational entropies $\geq 1.5\,R$ such that any non-ideal factors are overcome [32].

Equation 2. – Ideal configuration entropy of non-equimolar phases is used to factor in the fraction, x, of each constituent element, i, for n constituent elements.

$$\Delta S_{config}(x_i) = -R\sum_{i=1}^{n} x_i \ln(x_i)$$

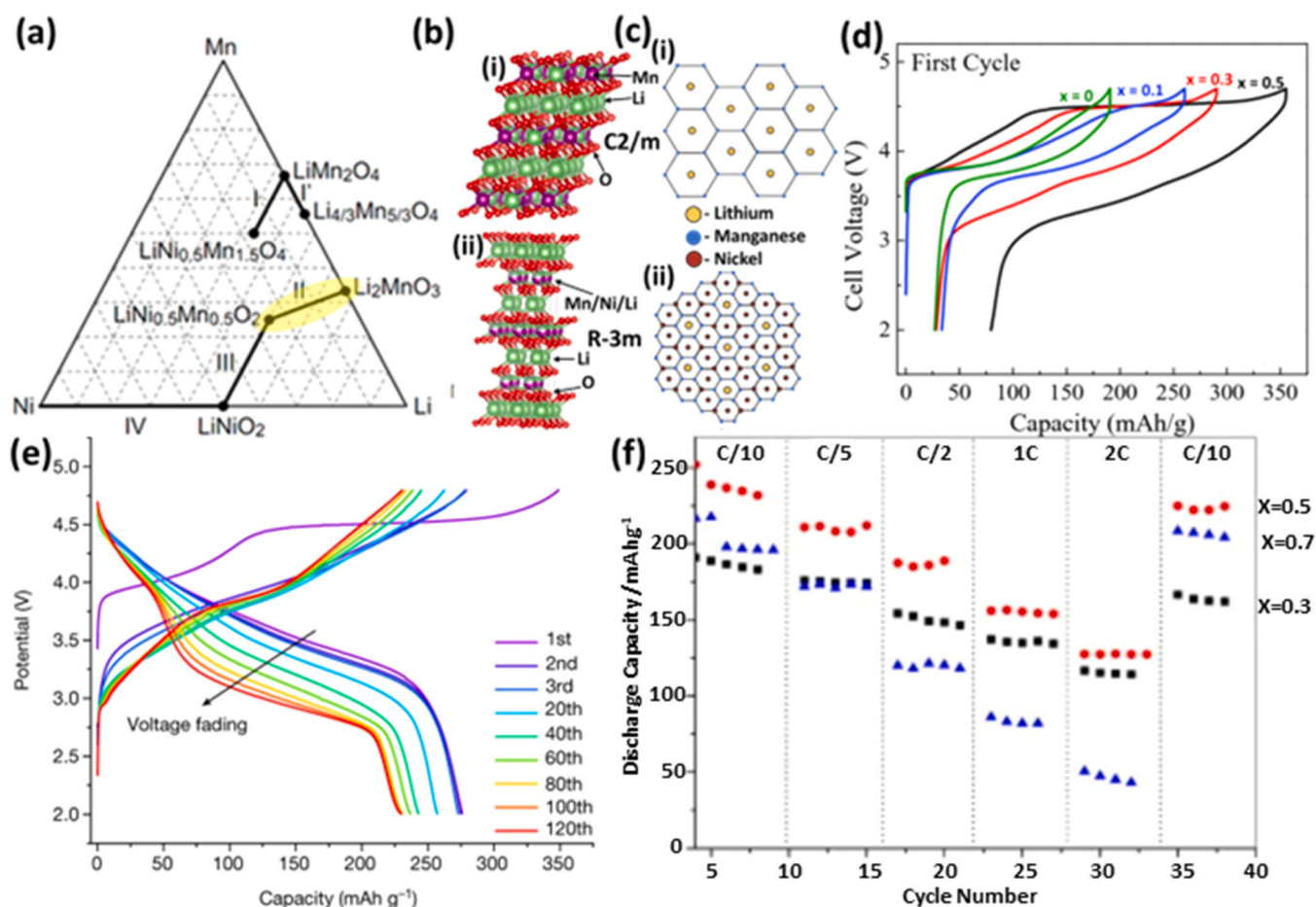Application of entropic stabilization expanded in 2015 with the

Fig. 2. – **Representation of how the unique structure of LRLO materials is related to the oxygen activation as well as the historical limitation of phase instability and rate capability.** (a) The Gibbs diagram of the pseudo-ternary Li-Ni-Mn system, with the highlighted region demonstrating where on the diagram LRLO's exist. (b) The structures of the (i) R-3 m and (ii) C2/m phases. (c) Representation of the transition metal layer ordering in (i) C2/m and (ii) R-3 m phases. (d) The 1st cycles charge/discharge curves of Li/xLi$_2$MnO$_3$●(1-x)LiMn$_{0.5}$Ni$_{0.5}$O$_2$ cells between 4.7 – 2.0 V at 5 mA/g and 30 °C, where x = 0.1 and 0.5. (e) The voltage vs capacity curve over time demonstrating the loss of capacity and voltage over the course of repeated cycling.
(a) Adapted with permission from {reference 12} Copyright 2013 American Chemical Society. (b) Adapted with permission from {reference 38}. (c) Reproduced with permission from {reference 40} Copyright 2005 American Chemical Society. (d) Reproduced with permission from {reference 43}. (e) (f) Cycling behavior of xLi$_2$MnO$_3$●(1-x)LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ particle of compositions x = 0.3, 0.5, and 0.7, at various rates ranging from C/10–2 C with voltage range of 2.0 – 4.8 V, reproduced from [44].

initial discovery of high entropy oxides (HEO) by *Rost et. al.* demonstrating the assumptions made in classical HEA cannot be directly applied to oxides [34,37]. Oxide materials consist of a minimum of two distinct sublattices, the cationic sublattice and the oxygen sublattice, both of which can contribute to the configurational entropy of the resultant oxide. For HEO systems the maximum configurational entropy therefore scales not only with the number of constituent elements, but also the number of sublattices and their respective multiplicities as seen in *Equation 3*. Therefore, HEO can have less than 5 constituent elements and still exceed the $\Delta S_{config} \geq 1.5$ R threshold. In realistic materials systems, such as the LRLO cathodes, the lithium and oxygen sublattices are not heavily substituted, leaving the transition metal sublattice the primary driver of configurational entropy. This limits the overall entropy per sublattice of a potential entropy stabilized LRLO systems to 0.375 R of entropy per sublattice of LRLO in the case of $\Delta S_{config} = 1.5$ R. Which raises the question of if the per mole configurational entropy is sufficient to fulfill the strict requirement for entropic stabilization, such that $|\Delta S_f T| >> |\Delta H_f|$.

Equation 3. – The ideal configuration entropy for multiple sublattices, where m is the multiplicity of sublattice j, and s is the total number of sublattices.

$$\Delta S_{config}(x_{i,j}) = -R \sum_{j=1}^{s} m_j \left(\sum_{i=1}^{n} x_i, jln(x_{i,j}) \right)$$

The challenges imposed by applying the $\Delta S_{config} \geq 1.5$ R standard from HEAs on HEOs demonstrate that HEOs need separate definitions. Therefore, for this publication we will use the strict definition of entropic stabilization, where a single-phase material is stabilized due to the dominance of entropy in the thermodynamics of formation, such that $|\Delta S_f T| >> |\Delta H_f|$, instead of the $\Delta S_{config} \geq 1.5$ R benchmark. Prioritizing entropic stabilization provides more clarity as it links the definition to experimentally verifiable tests. These tests were first outlined by *Rost et. al.* and are described as follows: 1) the phase formation reaction is endothermic, 2) the phase formation is reversible, 3) the stabilized phase has a distinct crystal structure [34]. For more detailed descriptions of these tests refer to Supplemental Note 1. It is important to note that while these tests can help identify and confirm the entropic stabilization of an oxide material, there are other sources of entropy outside of the classical configuration entropy, as described in Supplemental Note 2, and each of these additional forms of entropy can complicate the previously mentioned tests. Many of these additional sources of entropy also arise from statistical distribution of microstates, and therefore for the rest of this this paper we will use chemical entropy to refer the configurational entropy that arises from the number and concentration of chemical constituents, as seen in *Equation 3*.

Structure and activation of LRLOs

The structure of LRLO cathode materials makes them an ideal candidate for the employ of entropic stabilization techniques. As seen in Fig. 2(a) LRLO cathodes exist in a two-phase regions of the Gibbs diagram with end member oxides of C2/m Li_2MnO_3 (see Fig. 2(b)i) and R-3 m $Li[Mx]O_2$ where Mx is a stand-in for transition metal(s) such as the most commonly used Mn, Ni, and Co, with compositions varied to maintain an average +3 oxidation state (see Fig. 2(b)ii). As a result, there a large range of possible transition metal and lithium metal configurations, with localized ordering able to resemble constituent phase, as seen in Fig. 2(c). This ordering results in many of the unique properties of LRLO cathodes, as discussed in Supplemental Note 3. For example ordering of lithium in the transition metal layers can form Li_2MnO_3 like regions which are directly correlated with many of the unique properties such as high capacities, activation, voltage fade and intrinsic voltage hysteresis [38–40]. This is particularly highlighted by the previous work of Delmas *et. al.* on the relationships between the

composition, structure and performance of LRLO materials. The disorder optimized composition of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ provides an excellent example of how these relationships can be leveraged, and as such this composition is an ideal starting point for any future ES-LRLO composition(s) [41].

The third tests of an entropically stabilized oxide specify that an entropically stabilized oxide must form a single phase that is structurally distinct from the end members [36,42]. Therefore, any entropically stabilized LRLO (ES-LRLO) cathode must be a single phase. The proposed R-3 m structure with transition metal superlattice peaks would therefore satisfy the requirements for structural distinction and phase purity [3,36,42]. For this purpose, the remainder of this publication will refer to LRLO cathodes as single-phase R-3 m, as the two-phase interpretation cannot satisfy the requirements for entropic stabilization. However, regardless of the model, the electrochemical activation of LRLO cathode represents a phase transformation, that results in the loss of the pristine structure and the associated transition metal ordering.

Repeated cycling of LRLO cathodes leads to the loss of transition metal ordering and the formation of defects in LRLO cathodes, see Fig. 3 (a). As seen in Fig. 2(e) the capacity and voltage of LRLO materials decrease over repeated cycling, and while only the initial activation cycle sees large degree of transition metal migration, each cycle will result in small changes to the transition metal ordering. Over time the culmination of these defects results in formation of defect phases which eventually phase segregate. These phases have different electrochemical behaviors from LRLO and reduce the capacity and reduce the system-wide kinetics of lithium migration [43]. This ordering of metallic ions is not limited to just the transition metal layer either, as the LRLO system includes common defects, such as Li^+/Ni^{2+} anti-site defects, which introduce a degree of interlayer ordering. Anti-site defects are often associated with poor rate capabilities, as Li^+/Ni^{2+} defects can block lithium diffusion channels [29,45]. However, as seen in Fig. 2(f) the degree of integrated Li_2MnO_3 and overall rate capability of a LRLO cathode have a non-linear relationship, demonstrating that more factors than composition and structure influence the rate capability [44]. From the entropic perspective the anti-site defect impacts the rate capability of an LRLO system by disrupting long-range ordering and increasing the degree of short-range ordering that decrease the diffusion of the lithium ions. This is consistent with the recent work of Ceder *et. al.* on entropically stabilized disordered rock-salt cathodes with high rate capabilities [46]. The work of Breitung *et. al.* on increasing the electrochemical performance of rock-salt oxyfluorides [47], and other cutting edge work on rock-salt systems also demonstrate the utility of entropic stabilization for energy materials [37,48]. Other commonly found defects from activation include stacking faults among the transition metal layers, dislocations, twin boundaries, and anti-site domains [49]. These defects are predominantly observed post activation, but continued cycling also results in more defect formation. These defects disrupt the long range and short range ordering of the LRLO cathodes resulting in distortions in the oxygen sublattice of LRLO materials [49]. The loss of ordering in the LRLO system might initially seem like an increase in the entropy of the LRLO materials, however the relationship between defects, ordering and entropy is more complex, as mentioned in Supplemental Note 4.

Defects impact the phase purity and homogeneity of the LRLO cathode material, which reduces the entropy. As discussed in Supplemental Note 1, one of the tests for a material to be a HEO is being a single phase with a distinct structure. The single-phase system is also inherently more entropically stable than a multi-phase system of similar chemical composition. The reason for this is phase entropy. Phase entropy will be defined as the entropy derived from the phase homogeneity and mixing of the system. The relationship between the phase entropy and chemical entropy is that the phase entropy is the size(s) and number of the space(s) in which the mixing of chemical entropy can occur. In a homogenous phase of x atomic positions the number of microstate configurations that an atom "a" in bulk "b" has access to is $x!$ while in the case of a phase inhomogeneity of y atomic positions, given that $x > y$, the
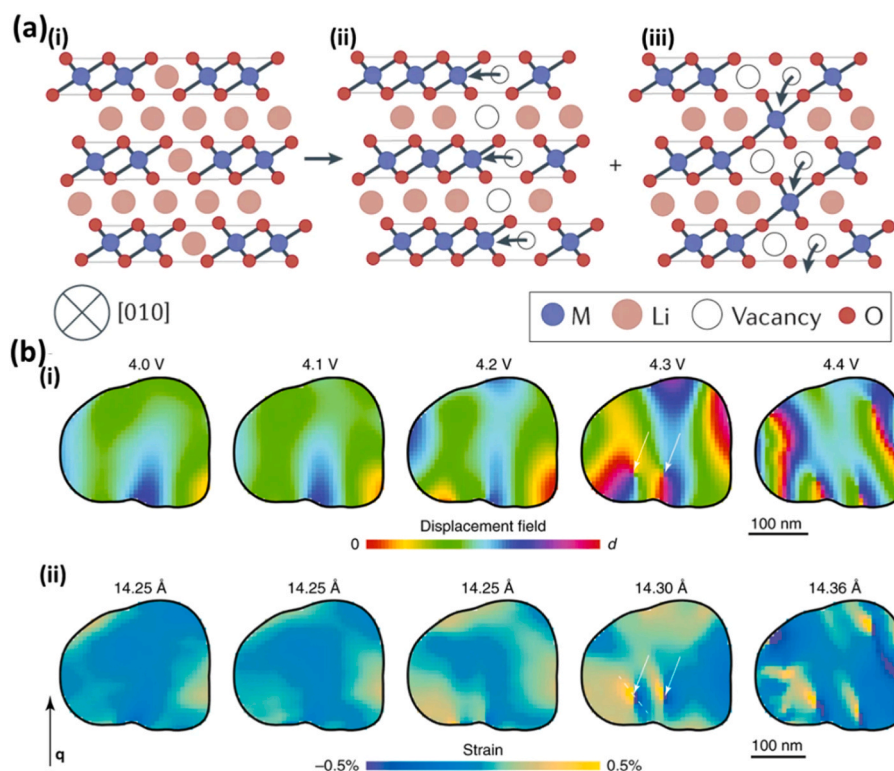
Fig. 3. – Summary of defects formed in LRLO materials. (a) The formation of lithium vacancies in LRLO materials during activation with (i) the pristine lattice before cycling, (ii) an in-plane migration of transition metals, (iii) an out-of- plane migration of transition metals that gives rise to anti-site defects. (b) In situ formation of dislocations in an LRLO particle, (i) the evolution of the displacement field along q as a function of voltage vs Li/Li$^+$, (ii) the strain along the (001) direction of the particle, which is perpendicular to the layers, with the average lattice constant displaced above.
(a) Reproduced with permission from {reference 49}. (b) Reproduced with permission from {reference 53}.

base matrix phase has *(x-y)!* microstates and the inhomogeneity has *y!* microstates for the atom of "*a*" to occupy. In these scenarios the total number of microstates has been reduced as $x! > ((x − y)! + y!)$. In LRLO materials the reduction of accessible microstates first occurs during the first cycle electrochemical activation.

As seen in Fig. 3(a) the defects created during activation are electrochemically irreversible and through disrupting the ordering of the LRLO cathode the defects block diffusion pathways resulting in the larger LRLO system being subdivided into several smaller domains, thereby reducing the entropy of the system [29,50–52]. This publication will refer to this as the "defect locking" of the domains. These defect locked domains will become more prevalent over the course of cycling until they begin to aggregate, and segregate creating defect phases. The formation of defect phases and the morphological heterogeneity they represent in the material leads to greater polarization during cycling, which induces stress in the cathode particles and eventually leads to cracking and material failure as describe in Fig. 3(b) [53,54]. Contemporary investigations are focused on how to mitigate or even prevent the formation of defects in LRLOs and the associated failure mechanisms by creating more resilient LRLO materials. Synthesizing these resilient LRLO materials however has proven difficult due to the high synthetic sensitivity of LRLO cathodes.

One additional advantage of high entropy design principles is that ES-LRLO cathodes will have greater defect resilience than non-entropically stabilized LRLO cathodes. As discussed in Supplemental Note 4 the introduction of multiple aliovalent consistent cations into the transition metal sublattice of an HEO materials, like LRLO cathodes, creates multiple localized environments in the oxygen sublattice that can be tuned to stabilize oxygen vacancies [55–58]. Being able to tune the stability of oxygen vacancies in LRLO cathodes will provide another mechanism for controlling the electrochemical activation of LRLO cathodes, potentially reducing the degree of electrochemically

irreversible capacity and increasing the degree of electrochemically accessible oxygen redox capacity. The diversity of oxidation states and ionic radii of a high entropy LRLO cathode will also result in a more mechanically robust lattice, that has higher dislocation tolerance and lower stacking fault energies [42,59–61]. This results in materials that have greater fracture toughness and are therefore less prone to the cracking induced failure. Further, the reduced mobility of the dislocations and stacking faults will increase the barrier for phase segregation, and reduce the amount of defect phases formed. Counter-intuitively a more entropic LRLO system will result in LRLO materials with greater defect tolerance, and greater tunability of the many unique properties of LRLO that these defects are responsible for. However, these benefits also come at a cost, as too many defects will result in loss of entropy, therefore design of high entropy LRLO materials must balance these factors.

Entropy stabilization in synthesis

As previously discussed, the structure of LRLO material is highly route dependent, with small variations in synthetic parameters resulting in a lack of phase purity. The Gibbs landscape for the LRLO synthesis therefore closely resembles that seen in Fig. 4(a)i, with multiple local energy minima that can lead to stable multiphase end products. In ES-LRLO materials this Gibbs landscape would begin to resemble Fig. 4 (a)ii, stabilizing the formation of the single-phase material. This increased phase stability will reduce the synthesis burden of making phase pure and high quality LRLO cathodes [12,13,22,34,62–64].

To achieve the entropic stabilization of LRLO cathodes during synthesis the chemical and phase entropies must be explored. The chemical entropy is the main way of increasing the entropy of the LRLO system during synthesis and can be accomplished through increasing the number of constituent elements in the transition metal sublattice of
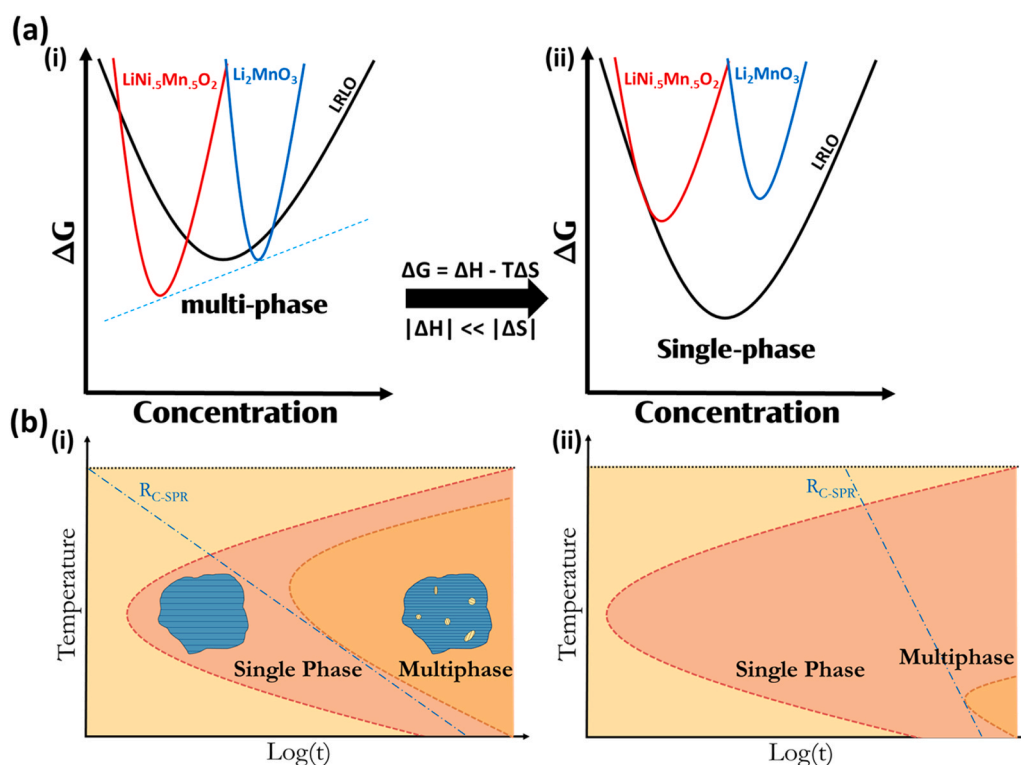
Fig. 4. – Through increasing the entropy of LRLOs the stability envelope of phase pure single-phase material can be increased. (a) Schematic of the Gibbs free energy profile for the synthesis of LRLO cathodes from compared to their constituent Li_2MnO_3 and $LiNi_{.5}Mn_{0.5}O_2$ phases, and the corresponding conversion to a more single phase dominate synthesis where $|\Delta S| >> |\Delta H|$. (b) TTT diagrams of (i) a non-entropically stabilized LRLO cathode, (ii) an entropically stabilized LRLO cathode. For TEM evidence of the phase separation during synthesis see Figure SI5. See Figure SI6 for larger global scale TTT diagram.

LRLO materials, as seen in *Equation 3* and Fig. 5(b). The other mechanism of influencing the entropy of these systems is through the temperature. As seen in the Gibbs free energy equation entropy can only dominate the enthalpy of formation at sufficiently high temperatures. Many entropically stabilized systems are therefore only stable at fairly high temperatures and therefore require quenching to maintain their single high entropy phase [65,66]. As seen in Fig. 5(c) the distribution of elements in a rapidly quenched material is more uniform than the clustering and phase segregating slowly cooled material. Therefore, to preserve the phase entropy of any ES-LRLO materials the temperature of synthesis must be sufficiently high to allow for the dominance of the chemical entropy. However, the relationship between chemical entropy and temperature is a two-way street. Fig. 4(b) shows a zoom-ins time--temperature-transformation plots of the LRLO cathode systems, demonstrating that the envelope of single-phase stability increases as the single-phase material becomes more entropically stabilized. This larger contribution from the entropy can result in decreasing the critical stabilization temperature for the single-phase region and even remove the necessity of thermal controls like quenching to achieve phase stability [67].

As previously discussed, the chemical entropy is built off an assumption of perfect entropic mixing, which is non-realistic in synthesis. As seen in Fig. 5(a) three different synthesis techniques for the same composition of LRLO resulted in only one phase pure material. These results highlight how while the chemical entropy of a system can be high the poor mixing of the system can still result in LRLO materials with poor phase purity and by extension poor phase entropy. The differences seen in Fig. 5(a) should that the sol-gel and co-precipitation methods resulted in materials with chemical segregation to the surfaces which would reduce the entropy of the resultant material, though it is important to note that all 3 of these synthesis methods can be conducted in manner that results in chemically homogenous final products [65–67]. These routes are also quite flexible and through

adjusting synthetic parameters the resultant particle morphologies can be adjusted for larger domain size in order to increase phase entropy. However, while these methods are adjusted to optimize for increased entropy the degree synthetic mixing remains as the most important factor, through adding more constituent elements there become more possibilities for non-idealized mixing and resultant phase segregation. Therefore, standardization of techniques that allow for large degrees of chemical mixing will be necessary for the wide implementation of ES-LRLO cathodes. It is also important to standardize and address the characterization methods used to evaluate the structure of the resultant materials. Many techniques lack the resolution to accurately determine the difference between the two structural analogues of LRLOS, and therefore a standard set of characterization results should be required for determination of is a resultant materials has fully achieved the phase purity [49].

Implementing entropic stabilization techniques in the synthesis of LRLO materials will need to be accomplished through controlling the composition to maximize the chemical entropy of the system. As previously mentioned initial definitions of high entropy materials stipulated the necessity for 5 principle elements of 5 at. percent or higher to reach the point of entropic stabilization [32,33]. Reaching this point can also be accomplished through the use of multiple dopant elements with concentrations below 5 at. percent. This means for LRLO systems to reach the point of entropic stabilization at least one additional principal element is needed, for Co containing LRLO systems, or several dopants. Extensive previous work has been done on dopants for LRLO systems that can further speed up the process of determining what elements to select when making ES-LRLO cathodes [69]. These ES-LRLO cathodes will therefore enter the closed electrochemical system with higher chemical and phase entropies, which will result in enhanced electrochemical performance.
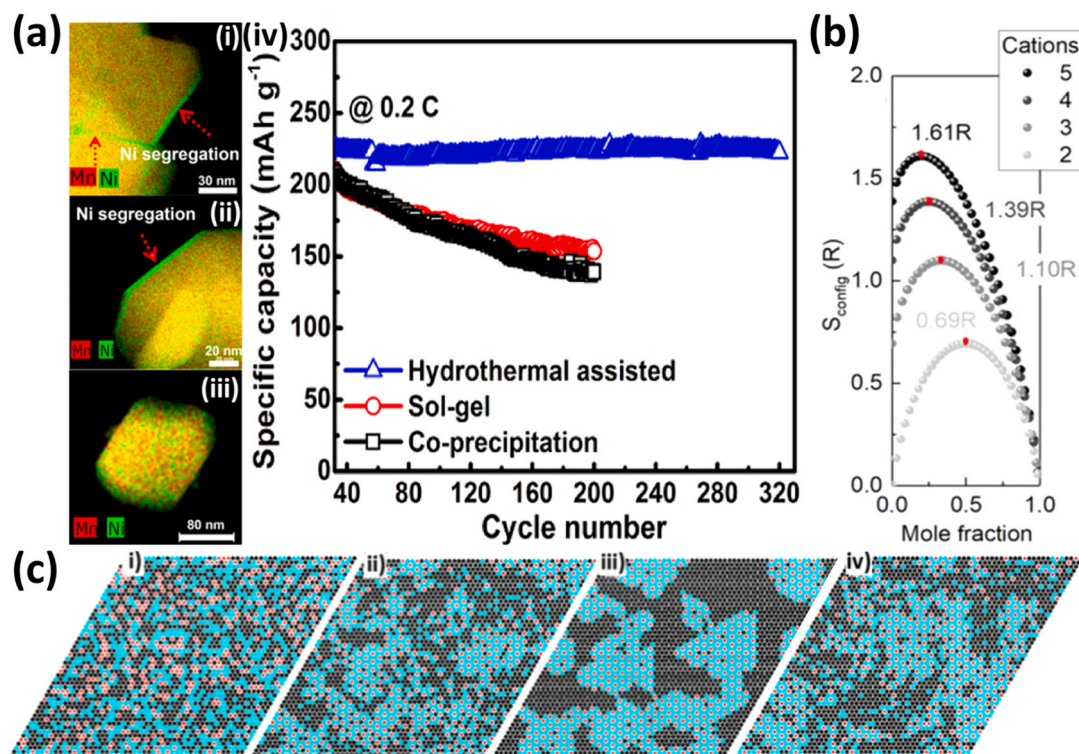
Fig. 5. – The synthesis dependence of LRLO materials can be mitigated through increasing the entropy of the LRLO materials. (a) EDS maps of Li [Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ cathode particles made through either (i) co-precipitation, (ii) sol-gel, (iii) Hydrothermal routes, and (iv) the specific capacity vs cycle number data for the resultant cathode materials. (c) Results from Monte Carlo simulations of the transition metal layer for the simulated slow cooling of Li [Li$_{0.167}$Co$_{0.25}$Mn$_{0.583}$]O$_2$ with i) instant quench from high temperature, ii) quench from an intermediate temperature ~800 °C, iii) quench from a temperature of ~160 °C, and iv) simulated annealing at the intermediate temperature from ii. In this representation cobalt, manganese and lithium are represented by black circles, cyan crosses and red circles, respectively.

(a) Adapted with permission from {reference 39} Copyright 2014 American Chemical Society. (b) (b) A graphical depiction of the dependence of configurational entropy on the number of components in the material, reproduced from [68]. (c) Figure reproduced from [13].

Entropy stabilization in electrochemical cycling

The electrochemical cycling of an intercalation material can be thought of as analogous to its synthesis. Both processes have external forces that drive reactions in the material causing physio-chemical changes. In synthesis this force is a thermal gradient, and in cycling it is a potential gradient. The phase segregation of LRLO materials in synthesis is due to their thermodynamic instability. Similarly, LRLO cathodes are not electrochemically phase stable, undergoing phase segregation during electrochemical cycling as seen in Fig. 6(a) [70]. The electrochemical phase instability of LRLOs contributes to the gradual voltage and capacity fading, eventually leading to cell failure [70]. The determination of whether or not entropic stabilization is viable in electrochemical phase transformations requires the electrochemical phase transformation to fulfil the same metrics: reversibility, phase distinction, and endothermicity [71]. The initial reversibility requirement is fulfilled by LRLO cathodes, as electrochemical activation and phase degradation of repeated cycling are both reversible [22].

Understanding the entropy landscape of the LRLO system during activation and during electrochemical cycling is critical for understanding why LRLO cathodes pass the reversibility requirement of entropic stabilization. Previous work done by Meng *et. al.* found that the activation process of LRLO cathodes results in a metastable material, and that the respective phase transformation is not electrochemically reversible, but is thermally reversible [22]. As seen in Fig. 7(b) the electrochemically activated LRLO phase can be converted back to a pristine state by meeting the minimum temperature around 300 °C [22]. This indicates that the reversal process has a minimum activation energy [22]. This thermal process also results in the restoration of the

superlattice ordering of the LRLO cathode as evidenced by the super-lattice peaks seen in the XRD patterns of the treated LRLO materials in Fig. 6**(c)**. Furthermore, repeated cycling of LRLO cathodes can also be reversed by the thermal treatment process, as seen in Figs. 6(e), and 6(f). This indicates that process of phase segregation is similar to that of electrochemical activation, as they are reversible through the same process. It is important to note that LRLO cathodes are not a closed system and the loss of materials such as lithium and oxygen from activation, or transition metals through dissolution, will cause some amount of irreversibility. The success of this thermal process in reversing the electrochemical phase reaction demonstrates these phase trans-formations pass the first test of entropic stabilization, reversibility [34, 71]. Reversibility also hints that an electrochemical process for reversing this phase transformation might exist, however this will require further investigation. Further the use of a thermal process to reverse an electrochemically driven phase transformation suggests that electrochemical and thermal processes are more analogous than previously thought.

Temperature vs time plots are commonly used to map the phase transformations of a material during synthesis; voltage can be thought of as analogous to temperature and a voltage vs time plot can be used to map the electrochemical phase transformations of a material during electrochemical processes [72,73]. These voltage and time plots will be referred to as VTT-diagrams, and one can be seen in Fig. 7(a), and Figure SI8. Similarly to how a TTT-diagram acts as a guide to which phases are thermodynamically stable for a given time and temperature based off the Gibbs free energy, the VTT-diagram would also represent which phases are present at specific potentials based off their Gibbs free energy. Therefore any changes in a phase's entropy that significantly
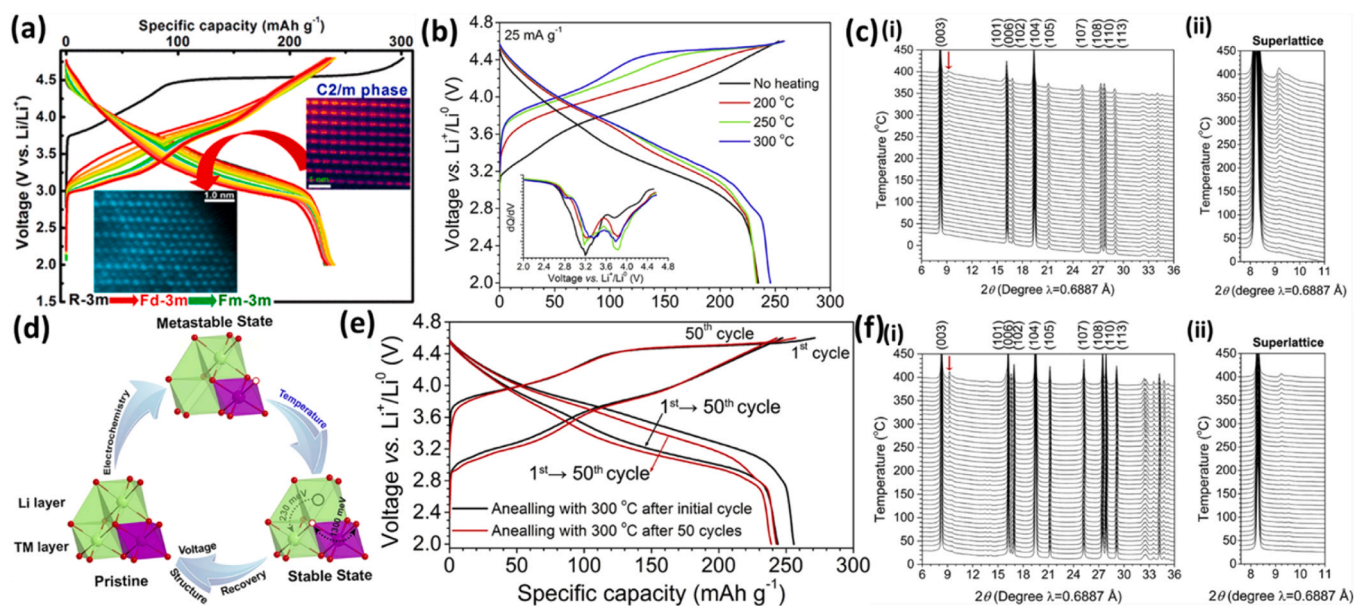
Fig. 6. – **The activation of the LRLO material is electrochemically irreversible but can be reversed through heating to 300°C, making the process reversible and the active LRLO phase metastable.** (a) The voltage profiles for LRLO materials over the course of several cycles demonstrating the loss of capacity and voltage over the course of cycling, inlays demonstrate the pristine and post cycling phase change. (b) Comparison of the electrochemical charge and discharge profiles of post first cycle LRLO materials after different thermal treatment with an inlay of those cycles' dq/dv. (c)&(f) (i) X-ray diffraction patterns of LRLO cathode material after being heated to temperature for 1 hour after (c) one initial cycle and (f) 50 cycles, (ii) close views on superlattice peaks. (d) A schematic representation of oxygen vacancy migration in LRLO material after cycling and after heat treatment, with the colors green, purple, and red representing lithium, manganese and oxygen respectively. (e) Comparison of the electrochemical charge and discharge profiles of LRLO materials that underwent 300 °C heat treatments after the initial cycle and 50 cycles.
(a) Reproduced with permission from [70]. (b) Reproduced with permission from [22]. (c) Both reproduced with permission from [22]. (d) Reproduced with permission from [22]. (e) Reproduced with permission from [22].
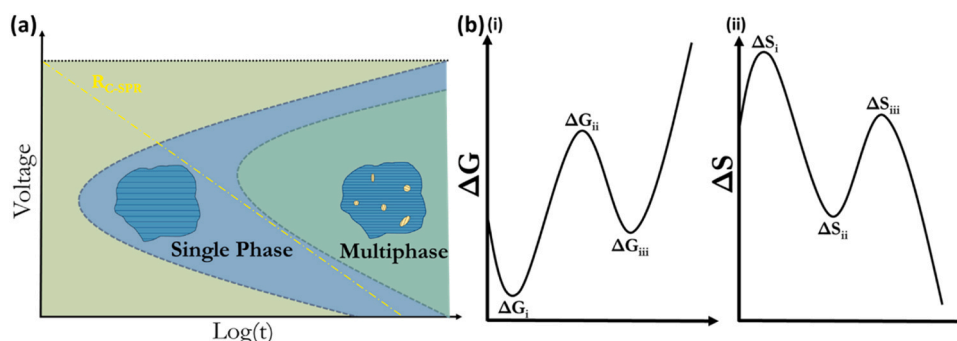

Fig. 7. – **The entropy of the system also influences the phase stability during electrochemical cycling.** (a) A VTT diagram, and analogue of the TTT diagram where temperature is replaced by voltage (state of charge), demonstrating how longer time at voltage will cause the material to phase segregate. For TEM demonstrations of the phase separation during cycling see Figure SI7. See Figure SI8 for larger VTT diagram. (b) (i) A Gibbs diagram representing the conversion from pristine LRLO to cycled LRLO [22], and (ii) the corresponding entropy profile of the same transformation.

increases its stability would be reflected in an expansion of that phase's single/active regions on the VTT-diagram, these results would be consistent with some previous result in sodium systems [74]. This means that through increasing the entropy of the LRLO material such that entropy dominates, the time at voltage (and the corresponding state of charge) an LRLO material is stable increases, which indicates greater electrochemical stability. Since potential for many lithium-ion systems is also directly related to the degree of lithiation this also indicates that these materials become more resistant the any lattice stresses associated with this. While the VTT diagram can also indicate the maximum voltage that a given material can tolerate while remaining in the phase stable window, this correlation between the lithiation and voltage means there is always an ultimate upper limit for lithiated phases. The cycling of materials at reduced voltages lead to longer cycle life and greater phase stability has been demonstrated by Dahn, *et. al.*, where the

cathode materials that were cycled with narrower voltage windows had greater lifetimes [75]. The use of VTT methodology would also indicate that there is a critical cycling protocol that optimizes the LRLO material time at voltage to stabilize the material in the single-phase region; this would be analogous to quenching in synthesis and is represented by the critical rate of phase stabilization, $R_{C\text{-}SPR}$, line in Fig. 7(a). However, this critical cycling however has not, to our knowledge, been experimentally verified.

In electrochemical cycling the stability of the phase means instead of two phases becoming a structural distinct single phase as in synthesis we instead want the single phase to not decompose into two or more distinct phase. But in order to meet the requirements for a candidate process the parent phase must be structural distinct from the daughter phases, which as seen in Fig. 6*(a)*, LRLO materials are structural distinct before and after cycling; the initial cycled and thermally treated phases are also

structurally distinct, as seen in Fig. 6(c) and Fig. 6(f).

The third test of the phase transformation being endothermic requires the careful calorimetric characterization of the electrochemical activation and continued cycling of both entropically stabilized and non-stabilized LRLO cathodes. The work of *Tarascon et. al.* has demonstrated that in model LRLO cathodes systems anionic redox results in heat generation and voltage hysteresis that causes lost electrochemical work to be lost as waste heat [64]. As previously discussed, the stabilization reaction should be endothermic, so for decomposition of the stabile phase the release of heat is consistent [36,42]. Further development of calorimetric techniques, developed by *Tarascon et. al.* and *Gasteiger et. al.,* would allow for accurate measurement of heat follow and entropic changes of these reactions in situ, allowing for invaluable information for the design of electrochemically viable ES-LRLO cathode materials [76–78].

Design and engineering strategy for entropy stabilization in LRLO

ES- LRLO cathodes will have a greater of phase purity and electrochemical phase stability. The design considerations for the maximization of ES-LRLO cathodes entropy requires careful consideration on the number and concentration of constituent elements. As seen in Fig. 8(a) LRLO cathodes with more consistent elements, ie Ni-Mn-Co, on average have a greater cycle lifetimes, which is consistent with these systems having greater chemical entropy than the Mn-Ni or Ni-Co based systems [79]. As seen in *Equation 3*, the concentration of these constituent elements is also critical for maximizing the system's chemical entropy, with Fig. 8(b) highlighting how even among stoichiometric LRLO systems, such as the $Li[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$ stoichiometry, the chemical entropy can be quite varied, with the higher entropy systems achieving higher capacities and greater cycle lives. While the number and relative concentration of primary constituent elements in the transition metal sublattice of LRLO cathodes are the primary drivers of the system's chemical entropy the use of other, dopant elements must also be carefully considered. Due to the unique environment of high entropy oxides like ES-LRLO cathodes even relatively small amounts of any constituent can have profound impacts on the properties of the final materials through the cocktail effect [62,72,73,80]. Once again, the expanding corpus of literature on the impact of various dopants on LRLO cathodes can elucidate the potential outcomes of adding any specific element to ES-LRLO cathodes. The binding energies, and oxidation states of each possible constituent element are particularly important. As seen in Fig. 8(c) the energy levels of an LRLO can be tuned to reduce the energy of an oxygen orbital, and maximize oxygen redox [81,82]. As previously discussed in Supplemental Notes 2 and 4 these constituent elements can also allow encourage or discourage the formation and stabilization of specific defect, like oxygen vacancies, which can allow for even greater degrees of property control. These new constituent elements would not only increase the chemical entropies of the resultant LRLO systems but could also be chosen based on the overlap of energy states in order to maximize any possible electronic or magnetic entropy that could arise from these interactions [42,60,83]. However, energy density also needs to be considered in these cases, as adding electrochemically inactive species, such as aluminum, might help with stabilization but will reduce the overall utility of the resultant cathode [45]. Design of ES-LRLO cathodes offers many exciting possibilities as each additional dopant element can through the cocktail effect cause new exciting properties.

The design of ES-LRLO cathodes needs to also carefully consider the surfaces, as while any entropic stabilization effects would be predominantly expressed in the material bulk, the majority of entropy disrupting defects will occur from the material surfaces. The dominate surface interactions for LRLO cathodes will be with electrolytes, making it essential to understand the electrolyte/cathode interfaces. An electrolyte is stable within a specific potential range, known as its electrochemical stability window, which is predominately set by the energy difference between the lowest unoccupied molecular orbital (LUMO),
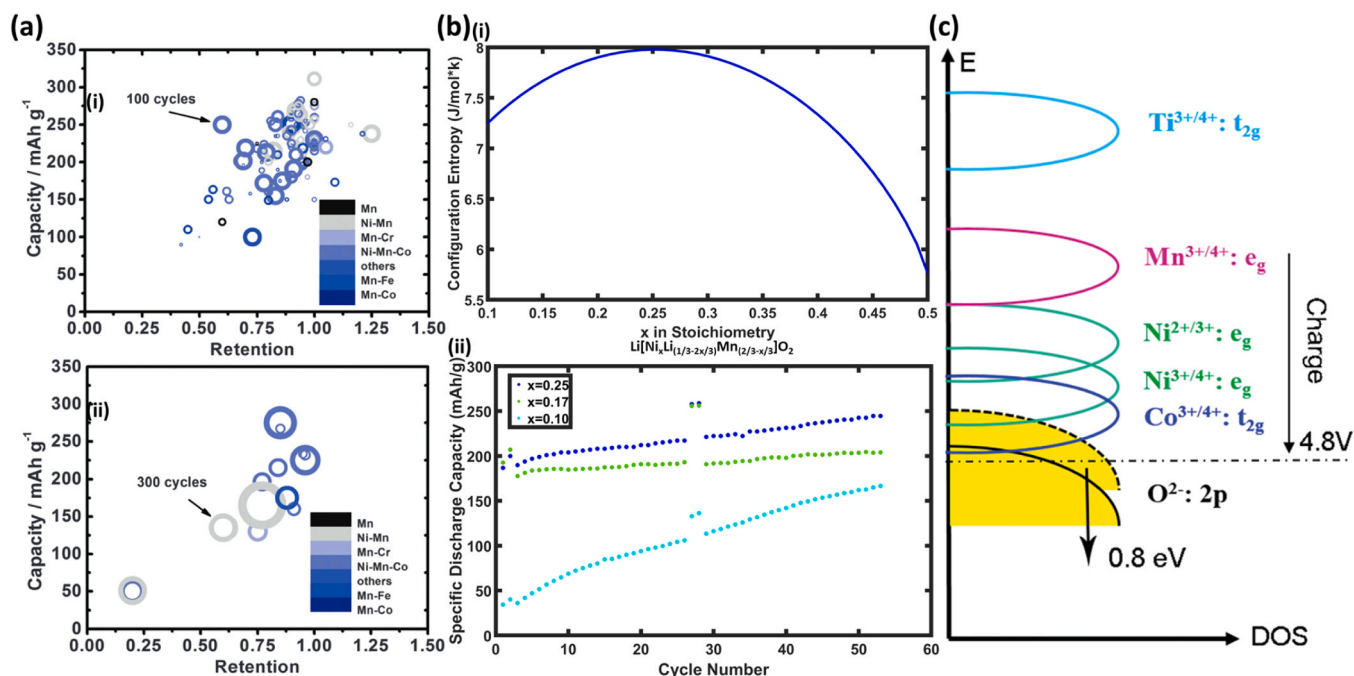

Fig. 8. – An outline of how many contemporary techniques for stabilizing LRLO techniques are related to the design principles for entropic stabilization. (a) The capacity and capacity retention of various LRLO composition at i) <100 cycles and b) >100 cycles. (b) (i) A chart of the compositional entropy of the $Li_x[Ni_xLi_{(1/3-2x/3)}Mn_{(2/3-x/3)}]O_2$ stoichiometric series vs the nickel composition, x. (ii) the capacity over time of LRLO materials of this stoichiometric series with varying x values. (c) Density of states diagram demonstrating the energies of many of the transition metal redox couples found in LRLOs, demonstrating how dopants such as BO_4/BO_3 can influence energy levels.
(a) Reproduced with permission from [79]. (b) Reproduced with permission from [65]. (c) Reproduced with permission from [81].

and the highest occupied molecular orbital (HOMO) of the electrolyte. During operation if the valance band of the cathode material is lower than the HOMO of the electrolyte, see Fig. 9(a), then charge transfer across this interface will result in electrons being pulled from the electrolyte causing decomposition [84,85]. This process can cause the creation of undesirable defects that could cause defect locking in the LRLO system, which can in turn reduce the phase entropy of the system. Due to the high operating potential of the LRLO cathodes, their valance bands tend to be quite low, making it difficult to find electrolytes that have HOMOs low enough to be compatible. Ideally, an electrolyte would have a HOMO lower than the valence band of the cathode, as seen in Fig. 9**(b)**, which would prevent decomposition reactions. Another view of this model is through electrochemical potential, $\tilde{\mu}_e$ [84,85]. The potential model of decomposition deal with the bulk potentials of the materials, and a representation can be seen in Fig. 9(c), where the large gap in electrochemical potentials stems from the mismatch of the electrolyte HOMO and cathode valance band levels [85].

Equation 4. – The Gibbs-Duhem Equation, where the change in chemical potential, μ_i for a species of gas, N_i, is summed for each component and found to be equal to the volume and pressure of the gas systems as well as the entropy and change in temperature.

$$\sum_i N_i \Delta\mu_i = V\Delta P - S\Delta T$$

There are a variety of strategies that could aid in minimizing the potential gap between liquid electrolytes, such as: energy level tuning in the cathode, the use of intermediate phases, higher voltage electrolytes, solid-state electrolytes, or liquefied gas electrolytes. As seen in Fig. 8(c) the energy levels of constituent ions in the LRLO materials can impact the potential of the cathode system [81]. Through the inclusion of 5 constituent metals, to ensure $|\Delta S| >> |\Delta H|$, the materials selection process can include constituents that tune the energy level of the LRLO cathode to be closer to that of the electrolytes. This would increase the shelf-life of the systems, but still have a negligible impact when charged to high voltage. The use of an intermediate phase, or surface coating, can be seen as a mixture of Figs. 9(a) and 9(b), where the electrolyte has a small potential gap between it and the intermediate phase, and the intermediate phase has small gap with the cathode, thereby protecting the cathode and the electrolyte from the larger, and more damaging, potential gap of electrolyte on cathode. This solution however can reduce the energy density of the materials, as these intermediate phases are not usually electrochemically active. The ability to use higher voltage liquid electrolytes and solid-state electrolytes are very similar, as both would
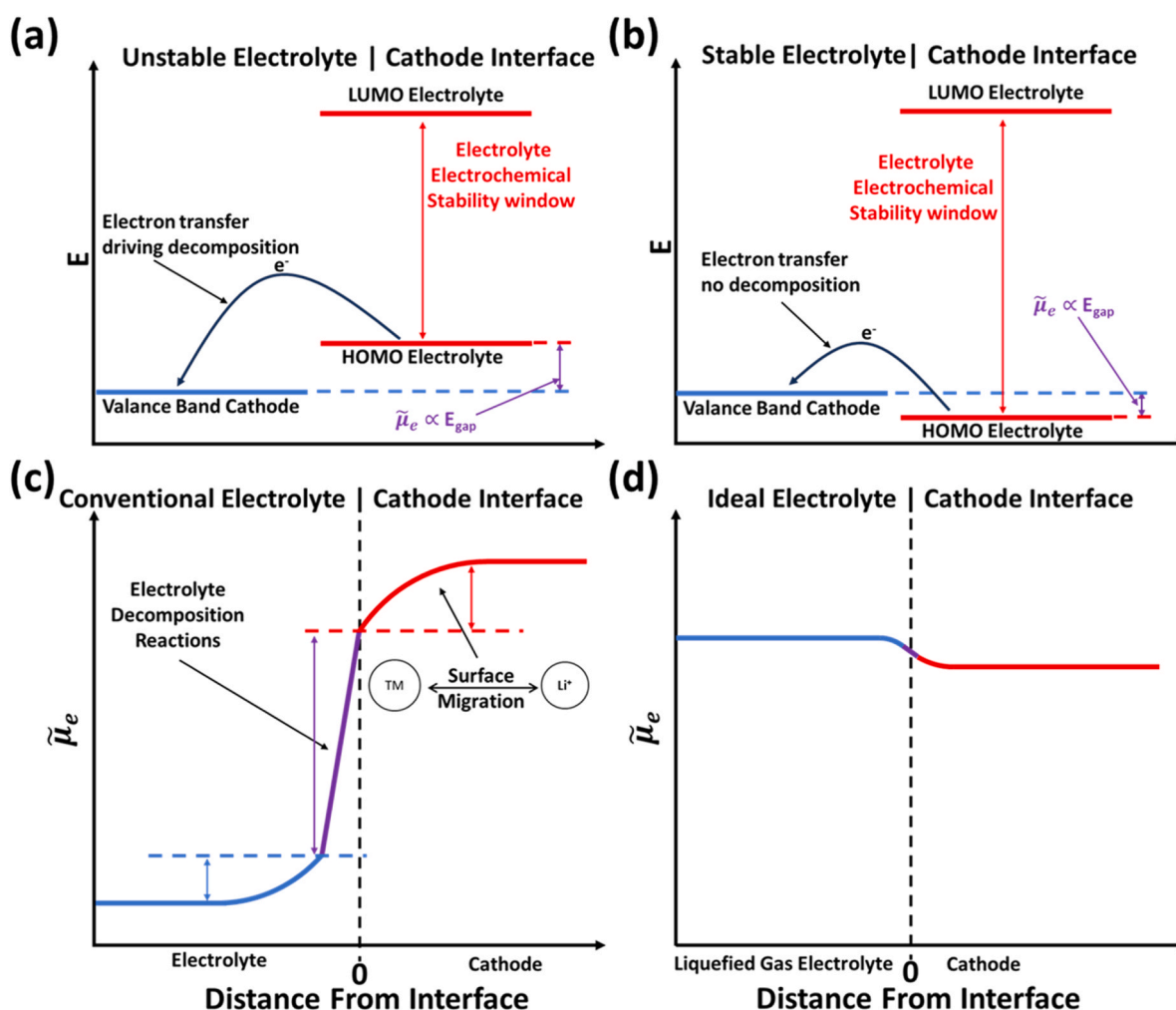

Fig. 9. – The interface between the LRLO cathode and the electrolyte is critical for stabilization of LRLO cathodes, possible interface interactions are shown in the following diagrams: (a) An unstable electrolyte interaction with a cathode, highlighting how the valance band of the cathode is lower than the HOMO of the electrolyte causing decomposition, also note that the energy gap is proportional to the electrochemical potential of this process. (b) A stable electrolyte interaction with the same cathode, where the lower HOMO of the electrolyte does not spark the decomposition during electron transfer. (c) An electrochemical potential plot representation of the case shown in (a) as a function of distance from the interface. (d) An electrochemical potential plot representing an ideal electrolyte/cathode interfaces, as a function of distance from that interface.

result in either smaller potential gaps, or situations similar to Fig. 9(b) [84,85]. Both cases would resemble the potential diagram seen in Fig. 9 (b), where the reduced gap mitigates and prevents the damaging reactions. The ultimate expression of a stable electrolyte would therefore be one with a well-matched potential. Since chemistry is difficult to adapt to every situation, the ability to externally tune potential would be ideal, this could be accomplished with the use of liquified gas electrolytes, where the potential window of the electrolyte would have both chemical and pressure contributions, as provided by the Gibbs-Duhem equation, see *Equation 4* [86]. These surface stabilizing techniques can mitigate the formation of undesirable surface defects in ES-LRLOs allowing them to maintain their phase entropy for great periods of time and therefore will be essential in the optimization of ES-LRLO cathodes.

Conclusions

For years research on lithium rich transition metal oxide has been focused on finding methods to synthesize, stabilize, and settle the structure of LRLO cathodes. Numerous studies were conducted to study the relationships between order and disorder in LRLO cathodes, their thermodynamic stability, and their electrochemical performance. In this perspective we extend the arguments centering around disorder through using the principles of entropic stabilization. We argue that LRLO cathodes are an ideal set of materials for entropic stabilization, due to their existence in a two-phase region, existing compositional flexibility, and metastability after electrochemical activation.

Since the electrochemical properties of LRLO are highly synthesis depend on the scaled consistent synthesis of LRLO cathodes is difficult. Here we argue this synthesis can be made more facile through synthesizing LRLO materials with high chemical entropy and through using synthesis methods that have a high degree of mixing. These increases in chemical entropy of the materials system would increase the single-phase stability window for the LRLO materials. With a larger single-phase stability window the number of synthetic pathways on the LRLO TTT diagram that result in phase pure material increases and these pathways can also possibly be conducted at lower temperatures, and or quicker time scales, both of which would reduce the cost of synthesis. Additionally, through focusing on maximizing chemical entropy and phase entropy of LRLO materials obtaining a phase pure material will be simplified due to the increase thermodynamic stability. Its is significant that increasing chemical and phase entropy for synthesis of LRLO materials would not require re-tooling of contemporary industrial synthesis methods and therefore once optimal compositions are found scaled synthesis would be able to leverage existing infrastructure.

This paper also introduces the idea that these principles are not unique to the relationships between time, temperature, and phase transformation, but that the principle of entropic stabilization can be applied to the relationships seen in electrochemical systems: voltage, time, and phase transformation. In this section we discuss how the electrochemical activation of LRLO materials results in a metastable material which undergoes phase decay over the course of repeated cycling. We discuss how these phase reactions can be mitigated or possibility eliminated through maximizing the initial entropy and therefore stability of the pristine material. We discuss how the use of the VTT diagram to explore the single-phase stability region of LRLO materials could be used to design optimized cycling protocol. We also review how in order to design pareto-optimal LRLO cathodes for performance and cycle stability *in operando* investigation of the LRLO system's entropy during cycling is needed.

Finally, we discuss the other consideration one must have when designing entropically stabilized cathode materials. The other sources of entropy in the LRLO system such as magnetic, vibrational, and electronic, must also be considered as their contributions to material stability, while more difficult to predict, can be more significant than the more commonly discussed chemical and phase entropy. The stabilizing effects of increased entropy also allow for the inclusion of a plethora of possible new consistent or dopant elements that have the potential to add in new and beneficial properties. Designing entropically stabilized systems also needs to consider surface stabilization so that the bulk stability offered through entropic stabilization can be maintained.

LRLO cathodes have seemingly always been 5 years away from commercial adoption, but as their complex history demonstrates, these exciting materials are as full of promise, as they are of unanswered questions. We hope that by exploring the role of entropy in the stabilization of these cathodes more of these questions can be answered.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nxmate.2024.100332.

References

[1] M. Rossouw, M. Thackeray, Lithium manganese oxides from Li2MnO3 for rechargeable lithium battery applications, Mater. Res. Bull. *26* (1991) 463–473, https://doi.org/10.1016/0025-5408(91)90186-P.

[2] K. Numata, C. Sakaki, S. Yamanaka, Synthesis of Solid Solutions in a System of LiCoO2-Li2MnO3 for Cathode Materials of Secondary Lithium Batteries, Chem. Lett. *26* (1997) 725–726, https://doi.org/10.1246/cl.1997.725.

[3] Lu, Z., and Dahn, J.R. (2005). Cathode compositions for lithium-ion batteries. Patent Number: US09845178.

[4] Thackeray, M.M., Johnson, C.S., Amine, K., and Kim, J. (2002). Lithium metal oxide electrodes for lithium cells and batteries. Patent Number: US20020136954A1.

[5] W.S. Yoon, S. Iannopollo, C.P. Grey, D. Carlier, J. Gorman, J. Reed, G. Ceder, Local structure and cation ordering in O3 lithium nickel manganese oxides with stoichiometry Li[NixMn(2-x)/3Li(1-2x)/3] O2 NMR studies and first principles calculations, Electrochem. Solid-State Lett. *7* (2004) A167, https://doi.org/10.1149/1.1737711/XML.

[6] Y.-J. Kang, J.-H. Kim, S.-W. Lee, Y.-K. Sun, The effect of Al(OH)3 coating on the Li [Li0.2Ni0.2Mn0.6]O2 cathode material for lithium secondary battery, Electrochim. Acta *50* (2005) 4784–4791, https://doi.org/10.1016/j.electacta.2005.02.032.

[7] A.R. Armstrong, M. Holzapfel, P. Novk, S. Christopher, S.-H. Kang, M. M. Thackeray, P.G. Bruce, L. Ni, L. Mn, P. Nova, et al., Demonstrating Oxygen Loss and Associated Structural Reorganization in the Lithium Battery Cathode Li[Ni 0.2 Li 0.2 Mn 0.6]O 2, J. Am. Chem. Soc. *2006* (2006) 8694–8698, https://doi.org/10.1021/ja062027.

[8] J. Hong, J.-H. Seo, S.-W. Kim, S. Hwon, S.-T. Oh, K. Kang, Structural evolution of layered Li1.2Ni0.2Mn0.6O2 upon electrochemical cycling in a Li rechargeable battery, J. Mater. Chem. *20* (2010) 10179, https://doi.org/10.1039/c0jm01971b.

[9] M. Sathiya, G. Rousse, K. Ramesha, C.P. Laisa, H. Vezin, M.T. Sougrati, M.-L. Doublet, D. Foix, D. Gonbeau, W. Walker, et al., Revers. anionic Redox Chem. High. -Capacit. Layer. -oxide Electrodes (2013) https://doi.org/10.1038/NMAT3699.

[10] H. Koga, L. Croguennec, M. Ménétrier, K. Douhil, S. Belin, L. Bourgeois, E. Suard, F. Weill, C. Delmas, Reversible oxygen participation to the redox processes revealed for Li1.20Mn0.54Co0.13Ni0.13O2, J. Electrochem. Soc. *160* (2013) A786, https://doi.org/10.1149/2.038306jes.

[11] H. Koga, L. Croguennec, M. Ménétrier, P. Mannessiez, F. Weill, C. Delmas, Different oxygen redox participation for bulk and surface: a possible global explanation for

the cycling mechanism of Li1.20Mn0.54Co0.13Ni0.13O2, J. Power Sources *236* (2013) 250–258, https://doi.org/10.1016/j.jpowsour.2013.02.075.

[12] E. Mccalla, A.W. Rowe, R. Shunmugasundaram, J.R. Dahn, Structural Study of the Li−Mn−Ni oxide pseudoternary system of interest for positive electrodes of Li-ion batteries, Chem. Mater. *25* (2013) 989–999, https://doi.org/10.1021/cm4001619.

[13] E. McCalla, C.M. Lowartz, C.R. Brown, J.R. Dahn, Formation of layered-layered composites in the Li-co-mn oxide pseudoternary system during slow cooling, Chem. Mater. *25* (2013) 912–918, https://doi.org/10.1021/cm304002b.

[14] K.G. Gallagher, J.R. Croy, M. Balasubramanian, M. Bettge, D.P. Abraham, A. K. Burrell, M.M. Thackeray, Correlating hysteresis and voltage fade in lithium- and manganese-rich layered transition-metal oxide electrodes, Electrochem. Commun. *33* (2013) 96–98, https://doi.org/10.1016/j.elecom.2013.04.022.

[15] H.Z. Zhang, Q.Q. Qiao, G.R. Li, X.P. Gao, PO4- polyanion-doping for stabilizing Li-rich layered oxides as cathode materials for advanced lithium-ion batteries, J. Mater. Chem. A *2* (2014) 7454–7460, https://doi.org/10.1039/c4ta00699b.

[16] D. Qian, B. Xu, M. Chi, Y.S. Meng, Uncovering the roles of oxygen vacancies in cation migration in lithium excess layered oxides, Phys. Chem. Chem. Phys. *16* (2014) 14665–14668, https://doi.org/10.1039/C4CP01799D.

[17] J.W. Min, A.K. Kalathil, C.J. Yim, W.B. Im, Morphological effects on the electrochemical performance of lithium-rich layered oxide cathodes, prepared by electrospinning technique, for lithium-ion battery applications, Mater. Charact. *92* (2014) 118–126, https://doi.org/10.1016/j.matchar.2014.03.008.

[18] K. Luo, M.R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D.M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, et al., Anion Redox Chemistry in the Cobalt Free 3d Transition Metal Oxide Intercalation Electrode Li[Li0.2Ni0.2Mn0.6]O2, J. Am. Chem. Soc. *138* (2016) 11211–11218, https://doi.org/10.1021/jacs.6b05111.

[19] D.-H.H. Seo, J. Lee, A. Urban, R. Malik, S. Kang, G. Ceder, The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials, Nat. Chem. *8* (2016) 692–697, https://doi.org/10.1038/nchem.2524.

[20] M.D. Radin, J. Vinckeviciute, R. Seshadri, A. Van der Ven, Manganese oxidation as the origin of the anomalous capacity of Mn-containing Li-excess cathode materials, Nat. Energy *4* (2019) 639–646, https://doi.org/10.1038/s41560-019-0439-6.

[21] N. Li, S. Hwang, M. Sun, Y. Fu, V.S. Battaglia, D. Su, W. Tong, Unraveling the Voltage Decay Phenomenon in Li-Rich Layered Oxide Cathode of No Oxygen Activity, Adv. Energy Mater. *9* (2019) 1902258, https://doi.org/10.1002/aenm.201902258.

[22] B. Qiu, M. Zhang, S.-Y. Lee, H. Liu, T.A. Wynn, L. Wu, Y. Zhu, W. Wen, C.M. Brown, D. Zhou, et al., Metastability and Reversibility of Anionic Redox-Based Cathode for High-Energy Rechargeable Batteries, Cell Rep. Phys. Sci. *1* (2020) 100028, https://doi.org/10.1016/j.xcrp.2020.100028.

[23] Y.J. Park, Y.-S. Hong, X. Wu, K.S. Ryu, S.H. Chang, Structural investigation and electrochemical behaviour of Li[NixLi(1/3−2x/3)Mn(2/3−x/3)]O2 compounds by a simple combustion method, J. Power Sources *129* (2004) 288–295, https://doi.org/10.1016/j.jpowsour.2003.11.024.

[24] Z. Lu, D.D. MacNeil, J.R. Dahn, Layered Cathode Materials Li [Ni x Li(1/3 - 2x/3) Mn (2/3 - x/3)]O2 for Lithium-Ion Batteries, Electrochem. Solid-State Lett. *4* (2001) A191–A194, https://doi.org/10.1149/1.1407994.

[25] Y. Wu, A. Manthiram, High Capacity, Surface-Modified Layered Li†Li„1−x…/3Mn „2−x…/3Nix/3Cox/3‡O2 Cathodes with Low Irreversible Capacity Loss, Electrochem. Solid-State Lett. *9* (2006) A221–A224, https://doi.org/10.1149/1.2180528.

[26] Z. Lu, L.Y. Beaulieu, R.A. Donaberger, C.L. Thomas, J.R. Dahn, Synthesis, Structure, and Electrochemical Behavior of Li [Ni x Li(1/2-2x/3) Mn(2/3-x/3)]O2, J. Electrochem. Soc. *149* (2002) A778–A791, https://doi.org/10.1149/1.1471541.

[27] J. Wang, L. Wang, X. He, J. Li, Z. Dai, J. Wang, One-step Hydrothermal Synthesis of Li 1.24 Mn 0.66 Ni 0.1 O 2 Cathode for Lithium-ion Batteries, Int. J. Electrochem. Sci. *11* (2016) 333–342.

[28] M. Jiang, B. Key, Y.S. Meng, C.P. Grey, Electrochemical and Structural Study of the Layered, "Li-Excess"; Lithium-Ion Battery Electrode Material Li[Li 1/9 Ni 1/3 Mn 5/9]O 2, Chem. Mater. *21* (2009) 2733–2745, https://doi.org/10.1021/cm900279u.

[29] C.R. Fell, D. Qian, K.J. Carroll, M. Chi, J.L. Jones, Y.S. Meng, Correlation Between Oxygen Vacancy, Microstrain, and Cation Distribution in Lithium-Excess Layered Oxides During the First Electrochemical Cycle, Chem. Mater. (2013) 1621–1629, https://doi.org/10.1021/cm4000119.

[30] N. Dupré, M. Cuisinier, E. Legall, D. War, D. Guyomard, Contribution of the oxygen extracted from overlithiated layered oxides at high potential to the formation of the interphase, J. Power Sources *299* (2015) 231–240, https://doi.org/10.1016/J.JPOWSOUR.2015.08.006.

[31] Hiemenz, P.C., and Rajagopalan, R. (1997). Principles of Colloid and Surface Chemistry (Marcel Dekker, Inc.). ISBN: 978-0-8247-9397-5.

[32] J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, S.-Y. Chang, Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes, Adv. Eng. Mater. *6* (2004) 299–303, https://doi.org/10.1002/adem.200300567.

[33] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent, Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng.: A *375–377* (2004) 213–218, https://doi.org/10.1016/j.msea.2003.10.257.

[34] C.M. Rost, E. Sachet, T. Borman, A. Moballegh, E.C. Dickey, D. Hou, J.L. Jones, S. Curtarolo, J.-P. Maria, Entropy-stabilized oxides, Nat. Commun. *6* (2015) 8485, https://doi.org/10.1038/ncomms9485.

[35] P. Sharma, V.K. Dwivedi, S.P. Dwivedi, Development of high entropy alloys: A review, Mater. Today.: Proc. *43* (2021) 502–509, https://doi.org/10.1016/j.matpr.2020.12.023.

[36] S.S. Aamlid, M. Oudah, J. Rottler, A.M. Hallas, Understanding the Role of Entropy in High Entropy Oxides, J. Am. Chem. Soc. *145* (2023) 5991–6006, https://doi.org/10.1021/jacs.2c11608.

[37] Y. Ma, Y. Ma, Q. Wang, S. Schweidler, M. Botros, T. Fu, H. Hahn, T. Brezesinski, B. Breitung, High-entropy energy materials: challenges and new opportunities, Energy Environ. Sci. (2021). https://doi.org/10.1039/D1EE00505G.

[38] J.R. Croy, K.G. Gallagher, M. Balasubramanian, B.R. Long, M.M. Thackeray, Quantifying Hysteresis and Voltage Fade in xLi2MnO3●(1-x)LiMn0.5Ni0.5O2 Electrodes as a Function of Li2MnO3 Content, J. Electrochem. Soc. *161* (2013) A318, https://doi.org/10.1149/2.049403jes.

[39] J. Zheng, M. Gu, A. Genc, J. Xiao, P. Xu, X. Chen, Z. Zhu, W. Zhao, L. Pullan, C. Wang, et al., Mitigating voltage fade in cathode materials by improving the atomic level uniformity of elemental distribution, Nano Lett. *14* (2014) 2628–2635, https://doi.org/10.1021/nl500486y.

[40] J. Bréger, N. Dupré, P.J. Chupas, P.L. Lee, T. Proffen, J.B. Parise, C.P. Grey, Short-and Long-Range Order in the Positive Electrode Material, Li(NiMn) 0.5 O 2: A Joint X-ray and Neutron Diffraction, Pair Distribution Function Analysis and NMR Study, J. Am. Chem. Soc. *127* (2005) 7529–7537, https://doi.org/10.1021/ja050697u.

[41] H. Koga, L. Croguennec, P. Mannessiez, M. Ménétrier, F. Weill, L. Bourgeois, M. Duttine, E. Suard, C. Delmas, Li1.20Mn0.54Co0.13Ni0.13O2 with Different Particle Sizes as Attractive Positive Electrode Materials for Lithium-Ion Batteries: Insights into Their Structure, J. Phys. Chem. C *116* (2012) 13497–13506, https://doi.org/10.1021/jp301879x.

[42] S.J. McCormack, A. Navrotsky, Thermodynamics of high entropy oxides, Acta Mater. *202* (2021) 1–21, https://doi.org/10.1016/j.actamat.2020.10.043.

[43] T. Liu, J. Liu, L. Li, L. Yu, J. Diao, T. Zhou, S. Li, A. Dai, W. Zhao, S. Xu, et al., Origin of structural degradation in Li-rich layered oxide cathode, 606:7913, Nature 2022 *606* (2022) 305–312, https://doi.org/10.1038/s41586-022-04689-y.

[44] F. Amalraj, D. Kovacheva, M. Talianker, L. Zeiri, J. Grinblat, N. Leifer, G. Goobes, B. Markovsky, D. Aurbach, Synthesis of Integrated Cathode Materials xLi2MnO3· (1 − x) LiMn1 / 3Ni1 / 3Co1 / 3O2 (x = 0.3, 0.5, 0.7) and Studies of Their Electrochemical Behavior - IOPscience, J. Electrochem. Soc. *157* (2010) A1121–A1130, https://doi.org/10.1149/1.3463782.

[45] C. Liu, Z.G. Neale, G. Cao, Understanding electrochemical potentials of cathode materials in rechargeable batteries, Biochem. Pharmacol. *19* (2016) 109–123, https://doi.org/10.1016/j.mattod.2015.10.009.

[46] Z. Lun, B. Ouyang, D.-H. Kwon, Y. Ha, E.E. Foley, T.-Y. Huang, Z. Cai, H. Kim, M. Balasubramanian, Y. Sun, et al., Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries, Nat. Mater. *20* (2021) 214–221, https://doi.org/10.1038/s41563-020-00816-0.

[47] Q. Wang, A. Sarkar, D. Wang, L. Velasco, R. Azmi, S. S. Bhattacharya, T. Bergfeldt, A. Düvel, P. Heitjans, T. Brezesinski, et al., Multi-anionic and -cationic compounds: new high entropy materials for advanced Li-ion batteries, Energy Environ. Sci. *12* (2019) 2433–2442, https://doi.org/10.1039/C9EE00368A.

[48] Q. Wang, L. Velasco, B. Breitung, V. Presser, High-Entropy Energy Materials in the Age of Big Data: ACritical Guide to Next-Generation Synthesis and Applications, Adv. Energy Mater. *11* (2021), https://doi.org/10.1002/aenm.202102355.

[49] M. Zhang, D.A. Kitchaev, Z. Lebens-Higgins, J. Vinckeviciute, M. Zuba, P.J. Reeves, C.P. Grey, M.S. Whittingham, L.F.J. Piper, A. Van der Ven, et al., Pushing the limit of 3d transition metal-based layered oxides that use both cation and anion redox for energy storage, 2022 7:7, Nat. Rev. Mater. *7* (2022) 522–540, https://doi.org/10.1038/s41578-022-00416-1.

[50] H. Guo, Z. Wei, K. Jia, B. Qiu, C. Yin, F. Meng, Q. Zhang, L. Gu, S. Han, Y. Liu, et al., Abundant nanoscale defects to eliminate voltage decay in Li-rich cathode materials, Energy Storage Mater. *16* (2019) 220–227, https://doi.org/10.1016/J.ENSM.2018.05.022.

[51] J. Zheng, Y. Ye, T. Liu, Y. Xiao, C. Wang, F. Wang, F. Pan, Ni/Li Disordering in Layered Transition Metal Oxide: Electrochemical Impact, Origin, and Control, Acc. Chem. Res. *52* (2019) 2201–2209, https://doi.org/10.1021/acs.accounts.9b00033.

[52] H.-Z. Zhang, G.-L. Pan, G.-R. Li, X.-P. Gao, The Effect of Polyanion-Doping on the Structure and Electrochemical Performance of Li-Rich Layered Oxides as Cathode for Lithium-Ion Batteries, J. Electrochem. Soc. *162* (2015) 1899–1904, https://doi.org/10.1149/2.1031509jes.

[53] A. Singer, M. Zhang, S. Hy, D. Cela, C. Fang, T.A. Wynn, B. Qiu, Y. Xia, Z. Liu, A. Ulvestad, et al., Nucleation of dislocations and their dynamics in layered oxide cathode materials during battery charging, 2018 3:8, Nat. Energy *3* (2018) 641–647, https://doi.org/10.1038/s41560-018-0184-2.

[54] L. Wang, T. Liu, A. Dai, V. De Andrade, Y. Ren, W. Xu, S. Lee, Q. Zhang, L. Gu, S. Wang, et al., Reaction inhomogeneity coupling with metal rearrangement triggers electrochemical degradation in lithium-rich layered cathode, Nat. Commun. *12* (2021) 5370, https://doi.org/10.1038/s41467-021-25686-1.

[55] B. Zhang, D. Deng, J. Chen, Y. Li, M. Yuan, W. Xiao, S. Wang, X. Wang, P. Zhang, Y. Shu, et al., Defect Engineering of High-Entropy Oxides for Superior Catalytic Oxidation Performance, ACS Appl. Mater. Interfaces 15, 52705–52715. (2023), https://doi.org/10.1021/acsami.3c15235.

[56] Z. Xie, N. Zhao, C. Wang, C. Yuan, M. Zhou, F. Li, F. Ma, Y. Chen, W. Yan, A simple and efficient strategy to construct Li-rich layered materials with surface layered/spinel heterostructures, J. Alloy. Compd. *937* (2023) 168293, https://doi.org/10.1016/j.jallcom.2022.168293.

[57] B. Zhao, Y. Du, Z. Yan, L. Rao, G. Chen, M. Yuan, L. Yang, J. Zhang, R. Che, Structural Defects in Phase-Regulated High-Entropy Oxides toward Superior Microwave Absorption Properties, Adv. Funct. Mater. *33* (2023) 2209924, https://doi.org/10.1002/adfm.202209924.

[58] Z. Grzesik, G. Smoła, M. Stygar, J. Dąbrowa, M. Zajusz, K. Mroczka, M. Danielewski, Defect structure and transport properties in (Co,Cu,Mg,Ni,Zn)O

high entropy oxide, J. Eur. Ceram. Soc. *39* (2019) 4292–4298, https://doi.org/10.1016/j.jeurceramsoc.2019.06.018.

[59] Y. Han, X. Liu, Q. Zhang, M. Huang, Y. Li, W. Pan, P. Zong, L. Li, Z. Yang, Y. Feng, et al., Ultra-dense dislocations stabilized in high entropy oxide ceramics, Nat. Commun. *13* (2022) 2871, https://doi.org/10.1038/s41467-022-30260-4.

[60] Z. Pei, An overview of modeling the stacking faults in lightweight and high-entropy alloys: Theory and application, Mater. Sci. Eng.: A *737* (2018) 132–150, https://doi.org/10.1016/j.msea.2018.09.028.

[61] Y. Sun, T. Wu, Z. Bao, J. Moon, Z. Huang, Z. Chen, H. Chen, M. Li, Z. Yang, M. Chi, et al., Defect Engineering of Ceria Nanocrystals for Enhanced Catalysis via a High-Entropy Oxide Strategy, ACS Cent. Sci. *8* (2022) 1081–1090, https://doi.org/10.1021/acscentsci.2c00340.

[62] C. Toher, C. Oses, D. Hicks, S. Curtarolo, Unavoidable disorder and entropy in multi-component systems, npj Comput. Mater. *5* (2019) 69, https://doi.org/10.1038/s41524-019-0206-z.

[63] W. Shi, J. Zheng, J. Xiao, X. Chen, B.J. Polzin, J.-G. Zhang, The Effect of Entropy and Enthalpy Changes on the Thermal Behavior of Li-Mn-Rich Layered Composite Cathode Materials, J. Electrochem. Soc. *163* (2016) A571, https://doi.org/10.1149/2.0031605jes.

[64] G. Assat, S.L. Glazier, C. Delacourt, J.-M. Tarascon, Probing the thermal effects of voltage hysteresis in anionic redox-based lithium-rich cathodes using isothermal calorimetry, Nat. Energy *4* (2019) 647–656, https://doi.org/10.1038/s41560-019-0410-6.

[65] S. Burke, J.F. Whitacre, How Synthetic Quench Rate and Composition Affect the Performance of Lithium Nickel Manganese Oxide Cathode Materials, J. Electrochem. Soc. *167* (2020) 160518, https://doi.org/10.1149/1945-7111/abcd4b.

[66] B.R. Long, J.R. Croy, F. Dogan, M.R. Suchomel, B. Key, J. Wen, D.J. Miller, M.M. Thackeray, M. Balasubramanian, Effect of Cooling Rates on Phase Separation in 0.5Li 2 MnO 3 ·0.5LiCoO 2 Electrode Materials for Li-Ion Batteries, Chem. Mater. *26* (2014) 3565–3572, https://doi.org/10.1021/cm501229t.

[67] S. Burke, J.F. Whitacre, The Importance of Structural Uniformity and Chemical Homogeneity in Cobalt-Free Lithium Excess Nickel Manganese Oxide Cathodes, Adv. Sci. *N./a* (2023) 2300068, https://doi.org/10.1002/advs.202300068.

[68] A. Sarkar, Q. Wang, A. Schiele, M.R. Chellali, S.S. Bhattacharya, D. Wang, T. Brezesinski, H. Hahn, L. Velasco, B. Breitung, High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties, Adv. Mater. *31* (2019) 1806236, https://doi.org/10.1002/adma.201806236.

[69] T. A. Wynn, C. Fang, M. Zhang, H. Liu, D. M. Davies, X. Wang, D. Lau, J. Z. Lee, B.-Y. Huang, K.-Z. Fung, et al., Mitigating oxygen release in anionic-redox-active cathode materials by cationic substitution through rational design, J. Mater. Chem. A *6* (2018) 24651–24659, https://doi.org/10.1039/C8TA06296J.

[70] J. Zheng, P. Xu, M. Gu, J. Xiao, N.D. Browning, P. Yan, C. Wang, J.-G. Zhang, Structural and Chemical Evolution of Li- and Mn-Rich Layered Cathode Material, Chem. Mater. *27* (2015) 1381–1390, https://doi.org/10.1021/cm5045978.

[71] C. Oses, C. Toher, S. Curtarolo, High-entropy ceramics, Nat. Rev. Mater. *5* (2020) 295–309, https://doi.org/10.1038/s41578-019-0170-8.

[72] L. Yao, P. Zou, C. Wang, J. Jiang, L. Ma, S. Tan, K.A. Beyer, F. Xu, E. Hu, H.L. Xin, High-Entropy and Superstructure-Stabilized Layered Oxide Cathodes for Sodium-Ion Batteries, Adv. Energy Mater. *12* (2022) 2201989, https://doi.org/10.1002/aenm.202201989.

[73] J. Wang, Y. Cui, Q. Wang, K. Wang, X. Huang, D. Stenzel, A. Sarkar, R. Azmi, T. Bergfeldt, S.S. Bhattacharya, et al., Lithium containing layered high entropy oxide structures, Sci. Rep. *10* (2020) 18430, https://doi.org/10.1038/s41598-020-75134-1.

[74] F. Ding, C. Zhao, D. Xiao, X. Rong, H. Wang, Y. Li, Y. Yang, Y. Lu, Y.-S. Hu, Using High-Entropy Configuration Strategy to Design Na-Ion Layered Oxide Cathodes with Superior Electrochemical Performance and Thermal Stability, J. Am. Chem. Soc. *144* (2022) 8286–8295, https://doi.org/10.1021/jacs.2c02353.

[75] A. Eldesoky, N. Kowalski, J.R. Dahn, Highlighting the Advantages of Operating NMC811 Cells to Voltages below 4.20 V Compared to NMC Grades with Lower Ni Content, J. Electrochem. Soc. (2023), https://doi.org/10.1149/1945-7111/aceffd.

[76] J. Huang, C. Delacourt, P. Desai, C. Gervillié-Mouravieff, L.A. Blanquer, R. Tan, J.-M. Tarascon, Unravelling Thermal and Enthalpy Evolutions of Commercial Sodium-Ion Cells upon Cycling Ageing via Fiber Optic Sensors, J. Electrochem. Soc. *170* (2023) 090510, https://doi.org/10.1149/1945-7111/acf625.

[77] F. Friedrich, S. Pieper, H.A. Gasteiger, Entropy Measurements of Li-Ion Battery Cells with Li- and Mn-Rich Layered Transition Metal Oxides via Linear Temperature Variation, J. Electrochem. Soc. *168* (2021) 120502, https://doi.org/10.1149/1945-7111/ac3938.

[78] F. Friedrich, A. Kunz, A. Jossen, H.A. Gasteiger, Heat Generation during the First Activation Cycle of Li-Ion Batteries with Li- and Mn-Rich Layered Oxides Measured by Isothermal Micro-Calorimetry, J. Electrochem. Soc. *170* (2023) 050506, https://doi.org/10.1149/1945-7111/accf38.

[79] S. Hy, H. Liu, M. Zhang, D. Qian, B.J. Hwang, Y.S. Meng, Performance and design considerations for lithium excess layered oxide positive electrode materials for lithium ion batteries, Energy Environ. Sci. *9* (2016) 1931–1954, https://doi.org/10.1039/c5ee03573b.

[80] J. Song, H. Wang, Y. Zuo, K. Zhang, T. Yang, Y. Yang, C. Gao, T. Chen, G. Feng, Z. Jiang, et al., Building Better Full Manganese-Based Cathode Materials for Next-Generation Lithium-Ion Batteries, Electrochem. Energy Rev. *6* (2023) 20, https://doi.org/10.1007/s41918-023-00184-8.

[81] B. Li, H. Yan, J. Ma, P. Yu, D. Xia, W. Huang, W. Chu, Z. Wu, Manipulating the Electronic Structure of Li-Rich Manganese-Based Oxide Using Polyanions: Towards Better Electrochemical Performance, Adv. Funct. Mater. *24* (2014) 5112–5118, https://doi.org/10.1002/adfm.201400436.

[82] C. Zhu, Y. Hu, N. Jiang, D. Pan, C. Li, Promoting reversible reaction of oxygen anions in cobalt-free lithium-rich layered oxides to improve their electrochemical performance, Appl. Surf. Sci. (2021) 150587, https://doi.org/10.1016/J.APSUSC.2021.150587.

[83] M.M. Quintano, M.X. Silva, J.C. Belchior, J.P. Braga, Electronic Entropy as a Periodic Property of the Elements: A Theoretical Chemistry Approach, J. Chem. Educ. *98* (2021) 2574–2577, https://doi.org/10.1021/acs.jchemed.1c00140.

[84] M.D. Radin, S. Hy, M. Sina, C. Fang, H. Liu, J. Vinckeviciute, M. Zhang, M.S. Whittingham, Y.S. Meng, A. Van Der Ven, Narrowing the Gap between Theoretical and Practical Capacities in Li-Ion Layered Oxide Cathode Materials, Adv. Energy Mater. *7* (2017) 1602888, https://doi.org/10.1002/aenm.201602888.

[85] J. Cabana, B.J. Kwon, L. Hu, Mechanisms of Degradation and Strategies for the Stabilization of Cathode–Electrolyte Interfaces in Li-Ion Batteries, Acc. Chem. Res. *51* (2018) 299–308, https://doi.org/10.1021/acs.accounts.7b00482.

[86] Y. Yin, Y. Yang, D. Cheng, M. Mayer, J. Holoubek, W. Li, G. Raghavendran, A. Liu, B. Lu, D.M. Davies, et al., Fire-extinguishing, recyclable liquefied gas electrolytes for temperature-resilient lithium-metal batteries, Nat. Energy *7* (2022) 548–559, https://doi.org/10.1038/s41560-022-01051-4.