Impact of the energy landscape on the ionic transport of disordered rocksalt cathodes

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I. INTRODUCTION

Until recently, candidate materials studied for Li battery electrode applications have predominantly been ordered compounds [1]. A separation of sublattices on which Li and transition metal (TM) reside was considered essential for unhindered ionic transport in electrode materials. Commercialized layered cathodes—an example of such ordered materials—therefore use only a few TMs (e.g., Ni, Co, and Mn) which have the proper electronic structure to accommodate and retain the layered ordering for hundreds of cycles [2]. This constraint on the choice of metals has set the Li-ion battery industry on a path to consume a sizable fraction of the world’s annual Co/Ni production if energy storage goals of >1 TWh/yr are to be met [3,4].

The recent development of Li-excess cation-disordered rocksalt (DRX) cathodes [5–9], in which Li and other metals are disordered over the octahedrally coordinated sites in a rocksalt structure, lifts the restriction on a specific Li-TM ordering to enable the exploration of cathode materials in a much wider chemical space. In general, DRX cathodes are known to show high capacity [10,11] and good stability [12–14]. Some DRX compounds [15,16] as well as similar disordered materials with partial spinel-like features [17] have also shown exceptional rate capability. DRX compounds are also being studied as potential anode materials [18]. But this evolution of electrode materials towards disordered materials necessitates the development of new models [19] to understand the more complex ion transport through a disordered environment. While the basic transport theory in cation-disordered rocksalts has been developed through percolation models, we show in this paper that a more rigorous understanding requires consideration of the varying site energy landscape of the Li sites, and that in general this effect leads to a substantial reduction in Li-ion mobility.

In close-packed oxides, the Li ion resides in the oxygen octahedra (O₆) and migrates through intermediate face-sharing tetrahedral sites (T₄). In DRX cathodes, Li migration occurs through low-barrier Li-rich tetrahedral environments (0-TM channels, where the tetrahedral site does not face-share with any transition metal or TM) as this provides a low electrostatic repulsion pathway for migration [Fig. 1(a)]. Therefore, Li-excess compositions (x > 0.1 in Li₁₊ₓTi₁₋ₓO₂) in which all the 0-TM channels are connected as a percolating network [20] are expected to boost rate capability and maximize reversible capacity. Compared to 1-TM channels for diffusion, through which Li migration in layered cathodes occurs, the migration barriers for 0-TM channels in DRX compounds are generally much smaller and should lead to ionic diffusion at least two orders of magnitude faster [5]. Despite this, measured values of Li diffusivity in DRX compounds (10⁻¹⁵ cm² s⁻¹) [16,22,23] are often a few orders of magnitude smaller than that of layered compounds (10⁻¹⁸ – 10⁻¹⁹ cm² s⁻¹) with occasional measurements [24] reported in a comparable range. Barring a few exceptions, Li-excess...
FIG. 1. (a) Three-dimensional (3D) view of 0-TM and 1-TM tetrahedral diffusion channels between adjacent edge sharing Li sites in DRX compounds. The lower-barrier 0-TM channel (black arrow), with no face-sharing transition metals (TMs), forms the basis of the percolating Li pathway [20]. The other 1-TM channel consists of a tetrahedral site which has one face-sharing TM atom (purple). (b) Activation barrier $E_a$ associated with hopping out of an occupied octahedral ($O_h$) site in a DRX system vs a typical ordered compound. Even with the same kinetically resolved activation barrier ($E_{KRA}$), $E_a$ in DRX systems can be much larger due to a difference in the $O_h$ site energies [21].

DRX cathodes mostly show limited rate capability, which may be connected to poor Li-ion diffusion. Therefore, the current understanding of Li transport based entirely on 0-TM percolation is used largely only for qualitative comparisons of Li diffusion and rate capability between compounds [15,22].

The traditional percolation theory focuses on understanding Li-transport pathways by ensuring connectivity of the low-energy intermediate $T_d$ sites. However, the cation disorder in DRX compounds also lead to a varied TM environment, which influences the energies of Li $O_h$ sites. Li transport therefore will not depend only on the ($T_d$) site environments (0-TM, 1-TM, and 2-TM) but also on local variations in site energy. The sketch in Fig. 1(b) contrasts the migration barrier ($E_a$) associated with a Li hop in the DRX compounds with that in ordered compounds in the dilute carrier limit. While in ordered compounds the surrounding TM environments of the Li sites are mostly the same, the site energies of the $O_h$ Li sites in the DRX compounds vary, causing the migration barrier to change depending on the initial and final positions of the Li ion. As a result of such a varied energy landscape, the migration barrier of 0-TM channels in DRX compounds can vary significantly and a percolation analysis based on 0-TM connectivity alone—although applicable to ordered counterparts—may not be sufficient. For larger variations in site energy, some sites cannot be occupied, limiting the Li sites in the 0-TM percolating network that can participate in ionic transport.

The effect of varying site energies on Li transport can be isolated by defining a kinetically resolved activation (KRA) barrier $E_{KRA}$ [21,25], which represents the contribution from the $T_d$ site environment ($E_{0-TM}^{KRA}$ for 0-TM channels) to the overall magnitude of the migration barrier $E_a$. As shown in Fig. 1(b), $E_{0-TM}^{KRA}$ is obtained by subtracting the average of the energies for the end points of the hop from the energy at the activated state $T_d$. Here, we study Li transport in a model DRX system keeping $E_{0-TM}^{KRA}$ constant and varying the extent of variance in the Li site energies.

In this paper, we perform kinetic Monte Carlo (KMC) simulations to calculate Li diffusion within a simplified model which includes varying site energies, mimicking the Li-TM site disorder as well as nearest-neighbor Li-Li interactions. We show that in disordered cathodes where the standard deviation in Li-site energy distribution ($w_{SE}$) is much larger than the thermal energy ($k_BT$), traditional percolation theory is not sufficient for understanding Li transport. Due to the larger migration barriers associated with the escape from lower-energy sites, only a fraction of the Li sites within the 0-TM percolating network actually participate in ionic transport at a given voltage (which sets the Li content and average energy of Li ions). In real DRX materials we find that the magnitude of $w_{SE}$ can be comparable to $E_{0-TM}^{KRA}$ itself, and the impact of cation disorder in limiting Li percolation is sufficient to suppress the room-temperature diffusion coefficient by over two orders of magnitude.

II. METHODOLOGY

To investigate the effect of a disordered energy landscape on cation diffusion, we construct a model system with a single fcc lattice on which Li and vacancies (Vac) are the only two species allowed. The transport properties in this model system are calculated with varying Li occupancies ($x_{Li}$) in the range [0,1]. To mimic the interactions between Li and TM atoms in a system, the Li-site energy is varied according to a Gaussian distribution with standard deviation $w_{SE}$. The Li-site energy landscape is kept static during Li diffusion to simulate a fixed TM environment (topotactic process). The interaction between Li sites is limited in the model to nearest neighbors and is accounted for using the effective cluster interaction $J_{Li-Vac}^{NN}$ [26]. Kinetic Monte Carlo simulations [21,27] were
performed using a rejection-free algorithm [28,29] to determine the tracer diffusion coefficient (D) and the correlation factor \( f \). Li-site energy distribution for \( \text{Li}_{1.3}\text{Mn}_{0.4}\text{Ti}_{0.3}\text{O}_{1.7}\text{F}_{0.3} \) (LMTOF) were performed using first-principles density functional theory (DFT) calculations. See Supplemental Material [30] (see also Refs. [31–33] therein) for details on the cluster expansion model and DFT calculations.

### III. RESULTS

To understand the impact of cation disorder on Li-site percolation, we compare in Fig. 3 the site energy distribution of all Li sites (blue histogram, left y axis) against the energy distribution of those sites that actually participate in diffusion (yellow, orange, and green histograms, right y axis) at room temperature (\( T = 300 \) K) is shaded in salmon.

![Fig. 2](image_url)

**FIG. 2.** (a) Impact of varying \( O_h \) site energy distribution (standard deviation \( w_{SE} \)) on the calculated Li-diffusion coefficient (\( T = 300 \) K) at different occupancies of the \( O_h \) sites. The magnitude of \( w_{SE} \), represented by the shade of the data points, is varied over 11 values in the range [0 eV, 1 eV]. (b) Contour plot of calculated correlation factor (\( f \)) at \( x_L = 0.3 \) in the two-dimensional parameter space (\( w_{SE}, J_{\text{Li-Vac}}^{\text{NN}} \)) of the model system. The parameters which best fit the experimentally measured voltage profile of \( \text{Li}_{1.17-},\text{Mn}_{0.343}\text{V}_{0.486}\text{O}_{1.8}\text{F}_{0.2} \) are given by the solid black line. The region in which the model system becomes ordered at room temperature (\( T = 300 \) K) is shaded in salmon.

To gain insights into the origin of the large drop in \( D \) with \( w_{SE} \), we inspect the corresponding calculated correlation factor (\( f \)), which is a measure of the degree to which successive hops of the diffusing species are correlated (\( f = 1 \) for noninteracting particles performing a random walk) [34,35]. In variants of the rocksalt compounds with layered cation ordering such as \( \text{Li}_x\text{CoO}_2 \), \( f \) is typically \( >10^{-3} \), except at values of \( x \) approaching 1 [21]. Calculated \( f \approx 1 \) for \( w_{SE} = 0 \) eV and \( J_{\text{Li-Vac}}^{\text{NN}} = 0 \) meV in the model signify an unhindered random walk because successive Li hops have no correlation between them. Figure 2(b) shows the correlation factor as a function of \( w_{SE} \) and \( J_{\text{Li-Vac}}^{\text{NN}} \) at \( x_L = 0.3 \) and \( T = 300 \) K using a color scale. The region corresponding to ordered Li-Vac configurations in the model is shaded in salmon color (see Supplemental Material [30]) and is not relevant here. The solid line, obtained by comparing the calculated voltage profile for the model with the experimentally measured voltage profile for \( \text{Li}_{1.17-},\text{Mn}_{0.343}\text{V}_{0.486}\text{O}_{1.8}\text{F}_{0.2} \), can be expected to almost be an upper limit for \( w_{SE} \) and \( J_{\text{Li-Vac}}^{\text{NN}} \) in DRX compounds (see discussion below). We find that by increasing \( w_{SE} \) alone, as in Fig. 2(a), \( f \) is suppressed by three orders of magnitude, suggesting a strong correlation between successive hops. Although \( f \) is suppressed with increasing \( J_{\text{Li-Vac}}^{\text{NN}} \) as well, its effect on \( f \) appears much weaker than that of \( w_{SE} \). For \( w_{SE} \sim 0.2 \) eV, \( f \) is of the same order of magnitude as \( \text{Li}_x\text{CoO}_2 \) at similar Li concentration (\( x \approx 0.3 \)), suggesting that this extent of site energy variation does not have a very adverse impact on Li diffusion.

To understand the impact of cation disorder on Li-site percolation, we compare in Fig. 3 the site energy distribution of all Li sites (blue histogram, left y axis) against the energy distribution of those sites that actually participate in diffusion (yellow, orange, and green histograms, right y axis) at room temperature (\( T = 300 \) K) is shaded in salmon.

![Fig. 3](image_url)

**FIG. 3.** Li-site energy distribution (blue histogram) with standard deviation \( w_{SE} = 0.8 \) eV. Distribution of Li sites involved in Li diffusion at \( x_L = 0.2, 0.5, 0.8 \) are shown in yellow, orange and green respectively.
temperature for different values of $x_{Li}$. The solid red curve represents the Gaussian distribution curve with the same standard deviation as the $w_{SE}$ ($=0.8$ eV) used in the model. We find that most of the transport occurs predominantly through Li sites with site energies falling within a few $k_B T$ of the highest-energy occupied Li site. All vacant sites above this range and occupied sites below it are effectively immobile due to the prohibitively large migration barriers connecting nearest neighbors with relatively larger site energy differences. For the model system with $w_{SE} = 0.8$ eV, the sites participating in transport for $x_{Li} = 0.2$, 0.5, and 0.8 are almost entirely different from each other. These results show that as the applied voltage is varied during delithiation of DRX compounds, the sites available for ionic transport may differ drastically and can be severely limited when $w_{SE} \gg k_B T$. As a result, the fraction of Li sites available for percolation can effectively be much smaller than that expected from the 0-TM channel connectivity [20].

An Arrhenius plot of $D$ for multiple $w_{SE}$ is shown in Fig. 4 (for $x_{Li} = 0.3$). Note that values of $D$ are normalized by $\text{exp}(\frac{E_{SE}}{k_BT})$ to isolate the effect of the site energy distribution on the activation energy. Consistent with the calculations for room temperature in Fig. 2, $D$ is suppressed at all temperatures with increasing $w_{SE}$. In the high-temperature limit, $D$ displays an Arrhenius behavior varying as $D \propto \text{exp}(\frac{E_{SE}}{k_BT})$ and suggests that the transport through 0-TM channels can still be modeled with a single effective activation barrier ($E_a^{\text{eff}}$), which approximately behaves as $E_a^{\text{eff}} \sim E_{KRA} + 0.45w_{SE}$. At lower temperatures, the diffusion coefficient gradually deviates from this behavior, signifying a smaller effective activation barrier caused by the participation of sites lying in a narrower energy window. Importantly, Fig. 4 shows that, unlike in ordered compounds, $E_a \neq E_{KRA}$ in disordered materials even when nearest-neighbor Li-Vac interactions are absent ($J_{Li-Vac}^{NN} = 0$ eV). Furthermore, results in Fig. 4 suggest that $E_a^{\text{eff}} > E_{KRA}^{0-\text{TM}}$ and $E_a^{\text{eff}}$ lies quite close in range to $E_{KRA}^{1-\text{TM}}$ (typically $E_{KRA}^{1-\text{TM}} - E_{KRA}^{0-\text{TM}} \sim 0.2$ eV [14]), and 1-TM channels could therefore also participate in ionic transport.

The $w_{SE}$ values used in the model can be estimated using density functional theory (DFT). Figure 5 shows the calculated site energy distribution for Li$_{1.17}$Mn$_{0.34}$V$_{0.486}$O$_{1.8}F_{0.2}$ (LMTOF) with short-range order (SRO) annealed at $T = 1273$ K as well as the fully disordered limit. The site energies largely show a Gaussian distribution with $w_{SE}$ values for the fully disordered (∼0.6 eV) and SRO (∼0.2 eV) structures in agreement with the values used in the transport model [Fig. 2(b)]. For delithiated compositions, $w_{SE}$ values can be expected to be somewhat larger due to reduced screening of Coulombic interactions resulting from a smaller effective charge on O ions [36] and a wider distribution of charge in the Li environment (Li$^{1+} \rightarrow$ Vac, Mn$^{3+} \rightarrow$ Mn$^{4+}$).

IV. DISCUSSION

Because the oxygen framework is the same and cation-anion distances are similar, one can expect a typical value for $J_{Li-Vac}^{NN}$ to be used in our model to be similar to that of the layered oxides, where $J_{Li-Vac}^{NN} \sim 15$–35 meV [36,37]. The value of $w_{SE}$ and $J_{Li-Vac}^{NN}$ in DRX compounds can also be gauged by comparing the model’s calculated voltage profile to experimentally measured voltage profiles. Because both Li-TM and Li-Vac interactions contribute to increasing the slope of the voltage profile ($\frac{dV}{dx}$) in DRX compounds [38], the upper limit for $J_{Li-Vac}^{NN}$ and $w_{SE}$ can be gauged by comparing with an experimentally measured voltage profile for systems which show a large $\frac{dV}{dx}$. The inset in Fig. 5 compares the calculated and measured profiles of Li$_{1.17}$Mn$_{0.34}$V$_{0.486}$O$_{1.8}F_{0.2}$ [39], which has the largest voltage profile slopes among experimentally measured DRX compounds. The series of $J_{Li-Vac}^{NN}$ and $w_{SE}$ values which lead to the same voltage slope as Li$_{1.17}$Mn$_{0.34}$V$_{0.486}$O$_{1.8}F_{0.2}$ is used as the upper limit in Fig. 2(b) (solid line).
Our analysis can be used to develop general guidelines for correlating the rate capability of disordered cathode materials to their voltage profile. Since increasing either $I_{\text{NN}}^{\text{Li-Vac}}$ or $I_{\text{SE}}^{\text{Li-Vac}}$ suppresses Li diffusion and increases the slope of the voltage profile, one can expect the rate capability to be better for materials with a flatter voltage profile. An example of this behavior can be found in partially disordered Li-excess spinel materials $\text{Li}_{1+x+y}\text{Mn}_{2-x-y}\text{O}_4$, for which the rate capability improved in compounds with relatively flat voltage profiles [40].

Previous works have focused on improving the rate performance of DRX compounds by minimizing cation short-range ordering (SRO) to increase the connectivity of low-barrier 0-TM pathways for Li transport [22]. While this design principle mostly relies on increasing cation disorder, we demonstrate that the increased variance in Li-site energy distribution associated with the disorder might also negatively influence its rate performance. Contrastingly, SRO also decreases the variance in Li-site energy distribution (Fig. 5) and in some cases might therefore be beneficial for rate performance. Hence, SRO that does not impact the 0-TM percolation but decreases the width of the site energy distribution would be most favorable.

The analysis presented here for DRX compounds could in principle also be extended to describe ionic transport in (i) systems with disorder on the anionic sublattice ($\text{F}^-$, $\text{O}^-$, and $\text{O}^{2-}$) due to the occurrence of an O redox mechanism [41–45] or fluorination [14,46,47], (ii) compounds containing mobile TM elements such as Cr which undergo reversible octahedral-to-tetrahedral (oct-tet) migration during electrochemical cycling [16], and (iii) partially disordered spinel compounds [48], where the $T_d$ and $O_h$ site energy distributions overlap to cause a rearrangement of Li occupancy.

V. CONCLUSION

In conclusion, we specifically identify the effect of the varied TM environment seen by Li sites in DRX compounds on ionic transport. This effect of Li-TM interactions is isolated by calculating diffusion coefficients for increasing variances in Li-site energy distributions and contrasted with that of Li-Vac interactions. We find that, for a DRX compound with a given voltage profile, the impact of Li-TM interactions on suppressing the diffusion coefficient can be much stronger than that of the Li-Vac interactions. Suppressed Li diffusion occurs despite the connectivity of Li sites through a network of 0-TM channels and results in part from effectively “immobile” Li ions, which reside in sites with significantly lower energy than the Li ions that participate in transport. Therefore, in comparison to simple ordered compounds, identifying ionic transport pathways in disordered compounds requires considering two additional levels of complexity, namely (a) connectivity through lowest-barrier channels between hopping sites and (b) the varied energy landscape of the hopping sites itself.

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