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Random Walk Analysis of the Effect of Mechanical Degradation on All-Solid-State Battery Power

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Mechanical and electrochemical phenomena are coupled in defining the battery reliability, particularly for solid-state batteries. Micro-cracks act as barriers to Li-ion diffusion in the electrolyte, increasing the average electrode's tortuosity. In our previous work, we showed that solid electrolytes are likely to suffer from mechanical degradation if their fracture energy is lower than 4 J m^{-2} [G. Bucci, T. Swamy, Y.-M. Chiang, and W. C. Carter, *J. Mater. Chem. A* (2017)]. Here we study the effect of electrolyte micro-cracking on the effective conductivity of composite electrodes. Via random analyzes, we predict the average diffusivity of lithium in a solid-state electrode to decrease linearly with the extension of mechanical degradation. Furthermore, the statistical distribution of first passage times indicates that the microstructure becomes more and more heterogeneous as damage progresses. In addition to power and capacity loss, a non-uniform increase of the electrode tortuosity can lead to heterogeneous lithiation and further stress localization. The understanding of these phenomena at the mesoscale is essential to the implementation of safe high-energy solid-state batteries.

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In all-solid-state batteries (ASSBs), fracture may occur in the solid electrolyte (SE) phase. Therefore, mechanical damage produces additional battery degradation modes in ASSBs that do not exist in traditional liquid electrolyte batteries. Micro-cracks in the solid ionic conductor act as local barriers to Li-diffusion. SE materials with conductivity approaching that of liquid electrolytes have recently been discovered,²⁻⁸ and solid-state batteries are being pursued as potentially safe high-energy storage systems. However, the conductivity of highly performing solid electrolytes may degrade during battery operation due to mechanical damage. Via mesoscale modeling we predict the extension of SE micro-cracking during electrochemical cycling.¹ In particular, brittle electrolytes are prone to fracture in response to intercalation-induced stresses.^{1,9}

In this manuscript we seek to answer the question: what is the effect of damage on the rate performance of ASSBs? We will show two pertinent results below: 1) the effective diffusivity appears to fall approximately linearly with the extent of damage; 2) anomalous diffusion arises from meso-scale proximity effects: the characteristic diffusive length scale scales with $t^{\delta/2}$ where $\delta < 1$. With these results, it is possible to estimate the maximum possible mechanical damage that permits a given power performance.

The homogeneous porous-electrode model employs averaging methods to relate electrical conductivity and ion transport properties to the electrode porosity (i.e., volume filled by the electrolyte) or loading percent of active material. Cells are typically designed with about 50–60% volume of active material, in the attempt to maximize energy density while retaining sufficient rate capability to power critical applications. Ion transport in the electrolyte phase is typically several orders of magnitude faster than in the solid phase. Therefore, the effective diffusivity of lithium through a battery electrode microstructure D_{eff} is typically assumed to be a fraction of the diffusion coefficient of lithium in the electrolyte D_0 . Below, we assume that ion transport through the active particles has a negligible influence on the effective diffusivity.

A simple widely used model considers the scaling factor to be a function of the electrode porosity and tortuosity. Tortuosity characterizes the effective transport length through the electrolyte.¹⁰⁻¹⁴ Tortuosity is also interpreted as the ratio between the diffusion length and the geometric length (i.e., the electrode thickness). The tortuosity τ is often related to the electrode porosity ϵ according to the Bruggeman model $\tau = \epsilon^{1-\alpha}$.¹⁵ The exponent α is called the Bruggeman exponent, and it is usually assumed to be around 1.5. The approximation of

lithium effective diffusivity by means of the Bruggeman model leads to the following expression for the effective diffusivity

$$D_{\text{eff}} = \frac{\epsilon}{\tau} D_0 = \epsilon^\alpha D_0 \quad [1]$$

The simple form of Eq. 1 is often adopted independently of the specific geometry of the microstructure.

The effect of particle size distribution and particles' relative proximity appears in Eq. 1 and is empirically contained in the value of the Bruggeman exponent. Eq. 1, with $\alpha = 1.5$, is also equivalent to Archie's law (used to describe water percolation in rocks) and it is close to the Hashin-Shtrikman upper bound (calculated assuming zero conductivity for the solid phase).¹⁶ The Bruggeman relationship and Archie's law are empirical observations of related phenomena and may not apply to microstructure where damage correlates to inhomogeneous packing. These relationships include only single point correlations: they depend only on volume ratio but do not contain explicit information about the microstructure.

In dense undamaged microstructures, conductivity is controlled by the narrow regions (throats) connecting the bulk of the electrolyte phase. Therefore, microstructures with the same average porosity may have very different pore structure and therefore conductivity. One way to approach this problem is by studying the conduction through a network of resistances representing microstructural constrictions.¹⁷⁻²⁰ Each resistor's value is assumed to be inversely proportional to the throat section area. Fracture tends to develop in narrow throats and further increase the local resistance. Therefore fracture should have a disproportionate effect on average diffusivity. In the literature on percolation theory, this type of model has been employed to study transport in porous media. This class is called random void continuum model, or 'Swiss-cheese' model and consists of uniform media in which spherical holes are randomly placed. The holes represent a material with nearly zero conductivity. When the concentration of inclusions is close to the threshold value, current has to flow through constrictions formed by the nonconducting inclusions. Therefore, the local resistance is a function of the throat's geometry.⁴

In this manuscript we assume a more fundamental point of view by simulating random walks through the electrode and using the Einstein relation²¹ to compute the average diffusivity as

$$D_{\text{eff}} = \frac{\Gamma \langle x(t)^2 + y(t)^2 + z(t)^2 \rangle}{6t} \Big|_{t \rightarrow \infty} \simeq \frac{(\Gamma/3) \langle z(t)^2 \rangle}{2t} \Big|_{t \rightarrow \infty} \quad [2]$$

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^aConversely, in discrete-lattice-percolation models each void occupies one lattice site and all bonds have the same conductivity.

(Γ is the rate of random steps.) In Eq. 2, the 3D form of the Einstein relation is reduced to a 1D form by assuming diffusion to be isotropic. We will focus on the transport in the direction z orthogonal to the current collector and the separator.

The linear time dependence of the mean-squared displacement is the characteristic continuum limit behavior of Brownian motion. In the results on transport in dense electrode compacts below, we show that a sub-linear relationship between mean-squared displacement—anomalous diffusion—is observed and D_{eff} depends on measurement time.

We quantify the battery's mechanical degradation in terms of relative fracture surface, i.e., the total fracture surface area normalized with respect to the squared electrode thickness. We find a linear relationship between effective diffusivity and crack surface area.

The method presented here is amenable to the study of various solid composite-electrodes. Understanding the role of microstructural heterogeneities and discontinuities on the impedance growth should be of interest to battery manufacturers and consumers.

In the next section we discuss the implementation and results of the random walk analyses.

Random Walk Analysis of Solid-State Electrode's Transport Properties

Method and results.—To study lithium transport in a composite solid-state electrode, a spatially periodic representative volume was generated. (For first passage times discussed below, the dimension normal to the separator will be equal to the electrode thickness). The cubic volume contains 200 randomly positioned (non-overlapping) particles of the same size. The particle radius is about 9% of the electrode's thickness. We did not vary the particle-size distribution, as this work's main focus is to study the effect of fracture and not the role of particle-size dispersity. The left image in Fig. 1 shows the particle ensemble; it also illustrates an example of red triangular cracks arranged within the microstructure. The triangles are generated by constructing a Delaunay triangulation on the particles' centers and selecting a subset of the triangular facets. The random choice of facets is biased with the reciprocal of the facets' surface area (i.e., it is more likely that a small facet will be selected for fracture which is consistent with our fracture simulations¹). The first level of damage is modeled by 250 cracks with a total fracture area equivalent to 75%

of the electrode thickness squared. Further mechanical degradation is modeled by raising the number of cracks to 500 and 750 respectively. The total fracture surface reaches respectively to about 150% and 210% of the electrode thickness squared. The distribution of cracks is intended to represent an isotropic uncorrelated damage state. The microstructure sketched in Fig. 1 is characterized by a 54% volume ratio of active material (AM)—a typical value for commercial Li-ion batteries—and by an ensemble of cracks.

The representative volume is discretized with $400 \times 400 \times 400$ voxels; they compose the regular cubic grid on which the random walk is performed. (Finer meshes did not produce appreciably different results and we consider $400 \times 400 \times 400$ to be sufficiently resolved.) We can use repeated trials random walks to characterize transport of Li-ions within a composite microstructure. Because Li mobility is much higher in the electrolyte than in the electrode material, diffusivity is set to zero within the particles: they are treated as obstacles in the random walk of Li ions. An element of the grid (i.e., a voxel) associated with the electrolyte material is generally marked as accessible. If the elements intersect a crack surface, it is also treated as an obstacle.

Analyses are carried out with the assumption of periodic boundary conditions in all three directions (reference system marked on Fig. 1). This assumption neglects any effect associated with the shape and the size of the representative volume and is accurate when the periodic domain is large compared to the mesoscale. (Condamine et al. analyzed the effect of boundary and domain size on the random walk in confined geometries²² and Torquato & Kim calculated the mean first passage time for square and cubic domains). At the beginning of the analysis, the walkers occupy all the available sites on a plane parallel to the current collector and the separator, and located halfway between them (plane $z = 0$, in the reference system drawn in Fig. 1). The total number of walkers is 400^2 . The images on the right of Fig. 1 represents the intersection of such a median plane with the four microstructures, one pristine and three damaged ones. Pixels marked in black correspond to impermeable points of the lattice whether they particles or cracks. Particles and cracks tend to form clusters and behave as collective obstacles. The 2D projections shown in Fig. 1 overly emphasize the system's tortuosity (obstacles in 2D may be bypassed in 3D). The random walk on a 3D lattice is less constrained than in 2D.

The average square distance covered in the z direction (orthogonal to the separator) is plotted versus time in Fig. 2a. Time and space are discrete variables in the random walk: the actual time is the number of steps divided by the successful jump-attempt frequency, and the distance is determined by the length-scale of a voxel in the representative microstructure. Below we will refer time as "steps" and total length as "pixels". The analyses were carried out for ten million steps. A subset of the data is plotted in Fig. 2a, as no change can be perceived in this plot over the full data-set. Trends emerging at different stages of the random walk are presented in the discussion of Fig. 4.

The reference case (black curve in Fig. 2a) represents the diffusion in a homogeneous electrolyte material. This is characterized by a diffusivity D_0 . The average diffusivities calculated for the other cases are expressed as a fraction of D_0 . The heterogeneous medium's effective diffusivity can be obtained from the asymptotic value of mean-square displacement (Eq. 2). Therefore, the slope of each curve in Fig. 2a is proportional to the average diffusivity.

The evolution of D_{eff}/D_0 over the number of steps is represented in Fig. 2b. A clear convergence is achieved after a few thousand steps. In a dense microstructure, the presence of the particles (occupying 54% of the volume) decreases the effective diffusivity by 23%. This value of effective diffusivity is below the Hashin-Shtrikman (H-S) upper bound (calculated as $D_U = D_0/(1 + 0.5 \times (1 - \epsilon)) = 0.79$), with $1 - \epsilon = 0.54$ for packing of impermeable spheres²³—the lower bound is zero in this case. Eq. 1 leads to a much lower diffusivity ($D_{\text{eff}} = 0.46D_0$) even in the limit of tortuosity $\tau = 1$. Eq. 1 may capture the behavior of microstructures with heterogeneous particles distributions (including binder and carbon particles).

The random walk analysis shows that the system's ionic diffusivity decreases as the mechanical damage increases; therefore the rate performance will also decrease. Intuitively, cracks obstruct the direct

Figure 1. The geometry of an electrode microstructure generated to study the electrode's percolation as a function of its mechanical degradation. The representative volume includes 200 electrode particles of the same size and cracks forming triangular surfaces (red triangles in the left image). Transport in the direction orthogonal to the separator is studied, considering particles and cracks as obstacles along Li-diffusion path. The intersection of the pristine microstructure with the plane $z = 0$ is plotted on the right side. Black pixels are assumed to be impenetrable to the walkers. The same section at $z = 0$ is illustrated for the microstructure with increasing levels of damage. The increase in tortuosity associated with fracture arises from the formation of larger clusters of non-conductive material.

Figure 2. The discrete mean-square distance covered in the direction orthogonal to the separator is plotted vs. the number of time steps in Fig. 2a. The slopes relative to the base case indicate the “effective tortuosity”. The average diffusivity, derived from the continuum limit behavior according to Eq. 2, is plotted in Fig. 2b. A clear convergence is reached after a few thousand steps. Values on the vertical axis of Fig. 2b are normalized with respect to the reference case of diffusion in homogeneous solid electrolyte material (black curve). Four tests were performed with various levels of electrolyte integrity. As fracture extends, the slope of the representative curve (and the overall diffusivity) decreases. The pristine microstructure with 54% of active material is characterized by an effective diffusivity 23% lower than the reference case. Mechanical degradation of the solid electrolyte material is modeled as impenetrable surfaces (representing cracks) randomly arranged within the electrolyte matrix.

paths of lithium ions between particle-agglomerates and deteriorate the electrode’s transport properties. The relationship between fracture surface and average diffusivity appears to be linear for the regime of damage investigated. This result is illustrated in Fig. 3 with the three red data-points obtained from the random walk analysis for the three increasingly damaged microstructures. The red data-points are also aligned with the average diffusivity for the intact microstructure (black point). In Fig. 3 the total fracture area is normalized with respect to the mean electrolyte cross-section area (calculated over 400 planes parallel to the separator). If all the cracks were oriented parallel to the separator transport would be blocked at the first damage level. Conversely, if all the cracks were orthogonal to the separator Li-transport would be unaffected. The mechanical degradation modeled here falls into regime of uncorrelated and isotropic damage. A linear decay is predicted in the limit of dilute cracks because the effectiveness of each cracks in blocking transport remains roughly the same as the number of cracks increases. Once cracks and electrode particles start clustering Li-ion motion is no longer uncorrelated. Linearity is expected to fail before the total fracture surface reaches the value of damage extrapolated from Fig. 3 at zero diffusivity.

The continuum-limit behavior of normal diffusion is characterized by the mean-square displacement being proportional to the time. When diffusion is hindered by the microstructure, anomalous dif-

fusion may arise. Anomalous diffusion is characterized by a mean-square displacement proportional to a power δ of time less than one. This phenomenon has been observed, for instance, in diffusion in cell membranes thwarted by proteins.^{24–26}

Depending on the concentration and size of the obstacles, diffusion can have a transient anomalous behavior and converge to normal diffusion over long distances. Different diffusion regimes are hard to observe in the linear plot of square distance vs. time of Fig. 2a, but they can be easily detected in Fig. 4a, where the quantity $\log \left(\frac{\langle z(t)^2 \rangle}{6D_0 t} \right)$ is plotted vs. $\log(t)$. Here time and space are discrete quantities. The slope of the curves in Fig. 4a represents the value $(\delta - 1)$. In a normal diffusion regime, the slope is zero. The black curve, referring to transport in a homogeneous medium tends to be horizontal. The remaining four curves in Fig. 4a have negative slope, indicating anomalous diffusion. The duration increases and the power-law exponent decreases with increasing damage. The value of δ is plotted in Fig. 4b. For the system with high level of damage, we calculate that initially $\langle z(t)^2 \rangle \sim t^{0.82}$. Normal diffusion is achieved as an asymptotic behavior for all the microstructures. The value of δ evolves toward unity in Fig. 4b. However, considering the time scales in Fig. 4b, the effective convergence distance is larger than the electrode thickness. Motion becomes more and more constrained as the fracture extends, because the number of available diffusion paths decreases.

The continuum limit approximation of the random walk in the form of Fick’s law has been used to study the tortuosity of electrode microstructures.^{10,12,27} However, such approximation may lead to inaccurate results in cases when diffusion is anomalous. We expect the microstructure chosen here, relatively homogeneous at the pristine state, to produce a lower bound for the value of δ . In addition to micro-cracking, inhomogeneous particle-packing can contribute to the formation of low-permeability clusters. Liasneuski et al.²³ have calculated that the average diffusivity decrease with the degree of heterogeneity of the microstructure. Their analyzes suggest that the influence of the packing microstructure on diffusion depends on the local environment of the individual spheres. In particular, pathways between adjacent pores, i.e., the pore throats, play an important role. Lower average diffusivity and non-uniform tortuosity have a negative impact on battery life and performance, as they can lead to local lithium plating, power and capacity loss. Other forms of heterogeneous microstructures will be treated in future studies.

Finally we calculate the first passage time (FPT) for a walker traveling from the current collector to the separator, as this time correlates to the charge/discharge time of a battery. The statistical distribution of first passage times is a direct indication of the battery power. The

Figure 3. Linear relationship between the extension of crack surface and the effective diffusivity within the electrode microstructure. The crack surface is normalized with respect to the electrolyte cross-section area averaged over 400 sections. The sections are taken along planes parallel to the separator. The effective diffusivity is normalized with respect to the average diffusivity in the pristine microstructure.

Figure 4. Diffusion hindering by particles and cracks is apparent in the emerging of anomalous diffusion regimes. We call diffusion anomalous when the average square distance is proportional to t^δ , with $\delta < 1$. In Fig. 4a, the slope of the curves corresponds to the value of $(\delta - 1)$. The black curve represents the simulation of random hopping in an homogeneous material and displays normal diffusion behavior. The other four curves have a negative slope at intermediate time ranges. They eventually converge to zero after approximately 10^5 steps. The anomalous diffusion regime is more extended in time and more pronounced, as the level of mechanical degradation increases. Fig. 4b shows the value of δ as it evolves over distances that are multiples of the electrode thickness.

mean of the FPTs (obtained for a large number of trials) scales with the reciprocal of the average diffusivity. The scattering of FPTs correlates with the degree of heterogeneity of the microstructure.

In these analyzes, the periodic boundary condition in the z direction is removed, and each random walk ends when the walker reaches the separator. The probability distribution function obtained for 400^2 walkers is plotted in Fig. 5 for the five different cases. On Fig. 5, the mean is marked by an arrow and the standard deviation is visualized by the length of the horizontal line. We annotate their values in the form of a sum, where the first term is the mean and the second is the standard deviation.

As the system becomes more tortuous, the mean FPT increases, but the data also becomes more scattered. Both the mean and the standard deviation scale with approximately the same factor with respect to the reference case (μ_H and σ_H are the mean and standard deviation calculated for the FPT in a homogeneous material). The black dashed line represents the probability distribution function $f(t, z = 400) = \sqrt{\frac{6}{\pi}} \frac{z}{t^{3/2}} \exp\left(-\frac{3z^2}{2t}\right)$ for the first passage through z at time step t ,

approximated for large z . Such a function is a generalization of the probability distribution function for first passage time in 1D,^{28,29} and it accounts for the fact that 4/6 of the random steps are within the plane and do not contribute to the displacement toward the separator. The analytic and numerical results for FPT in homogeneous media (dashed black and blue curves) are in excellent agreement. A slower decay of the blue curve for large first passage times can be explained by the finite number of sample points. We expect that increasing the number of walkers would make the prediction more accurate in the low probability range. Just as the effective diffusivities decrease, the mean FPTs tend to increase with increasing damage—the linear co-factor being the reciprocal of the one calculated for the average diffusivities. This indicates that effective diffusivity contains the same information as a first passage time which is intuitively a more relevant measure of rate capability. The standard deviation of FPTs contains additional information about the increasing heterogeneity of the microstructure caused by mechanical damage.

Figure 5. The probability distribution function (PDF) for the first passage time (FPT) calculated via random walk analysis is shown for five different configurations. Diffusion in a homogeneous solid electrolyte material is represented by the blue curve and is the reference case. Each PDF is annotated with the value of the mean and standard deviation normalized with respect to the reference (μ_H , σ_H) values. The yellow curve corresponds to the pristine microstructure with a 54% volume density of active material. The remaining three curves illustrate the effect of micro-cracking on the FPT. Mean and standard deviation increase with approximately the same scaling factor as diffusion becomes more hindered. Reflecting crack surfaces randomly located within the electrolyte are the cause for such increase in tortuosity. The analytic expression for the PDF of first passage time in a homogeneous material is plotted with a dashed black curve. It matches almost perfectly the numerical result, with the exception for the tail at large FPT values. We expect the fit to improve with the number of walkers.

Conclusions

Via random analyzes, we predict the average diffusivity of lithium in a solid-state battery electrode to decrease linearly with the extension of mechanical degradation. In particular, we studied the effect of micro-cracking of the solid electrolyte material on decreasing the electrode's effective conductivity.

The implementation of safe high-energy solid-state batteries depends on the discovery of highly conductive solid-electrolyte (SE) materials that retain their properties over a large number of cycles. In our previous work, we showed that SEs are likely to suffer from mechanical degradation if their fracture energy is lower than 4 J m^{-2} .¹ In this work we establish a direct link between mechanical reliability and rate performance of a battery.

Micro-cracks act as barriers to Li-ion diffusion in the electrolyte, increasing the average electrode's tortuosity. Furthermore, the statistical distribution of first passage times indicates that the microstructure becomes more and more heterogeneous as damage progresses. Cracks and particles form clusters that hinder Li diffusion, causing it to deviate from the continuum limit behavior described by Fick's law. The random walk analyzes capture anomalous diffusion regimes emerging in mechanically-degraded electrodes. Anomalous diffusion is characterized by a mean-square displacement proportional to a power δ of time less than one. The value of δ and the average diffusivity keep decreasing with the extension of fracture.

Mechanical and electrochemical phenomena are coupled in defining the battery reliability. In addition to power and capacity loss, a non-uniform increase of the electrode tortuosity can lead to heterogeneous lithiation and further stress localization. The understanding these phenomena at the mesoscale is essential to the prediction of failure in Li-ion batteries.

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