Defects, graphs and route-finding: Probing ion transport using time-based centrality

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Introduction

Ion conduction through a material can be represented as movement through a graph where each vertex corresponds to an ion-binding site and the edges correspond to single, bidirectional transitions between sites. Site probabilities indicate the likelihood of propagating conduction from a particular site while the rate constant for transition between sites ($k_{i,j}$) indicates the speed of motion between sites. While our research group has developed time-based centrality measures[1] which highlight traps and conduction highways in a single picture, an ion graph. Until now, we have only applied these to fully ergodic complete graphs (Figure 1(a)) where all vertices are available and reachable from any vertex. This poster considers time-based centrality measures in systems where a site is blocked by another conducting ion as in Fig. 1(b) and where several sites are blocked leading to a disconnection within the graph as in Fig 1(c). These scenarios are typical when there are multiple conduction ions and correlation between ion motions are expected.

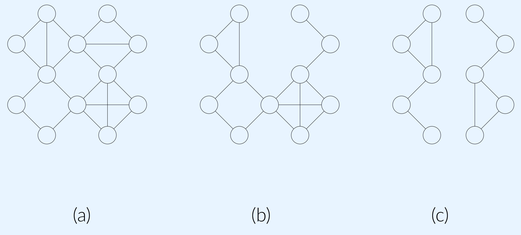

Figure 1. Removing one vertex from the ergodic graph (a) yields the ergodic graph (b). However, removing two vertices yields the disconnected graph (c).

Methodology

Calculation site probabilities and rate constants

Our research group[1, 2, 3, 4, 5] has typically used *ab initio* energies and vibrational frequencies of binding and transition states to find site probabilities and rate constants using the Boltzmann distribution and harmonic transition state theory respectively. In this poster, we consider scenarios using *ab initio* derived graph parameters, and parameters found from molecular dynamics trajectories which have inherent statistical noise. Probabilities to move between sites can be found by $p_{ij} = \frac{k_{ij}}{\sum_n k_{in}}$.

Finding the centrality of a site i

Both trapped ions and ions on periodic highways return to sites quickly. At trapped sites ions never go far from the site, while on periodic highways ion are moving at high speeds. The centrality at site i, C_i ,is defined as the inverse of the average time to first returns to i or $C_i = \frac{1}{R_i}$. The average time to first returns to i, R_i, is the average of the time to first return to i after visiting any other site j or $R_i = \frac{1}{N}\sum_j R_{ij}$. Krueger et al.[1] show that

$$R_{ij} = \left(\frac{Z_{jj} - Z_{ij}}{\pi_j} + \frac{Z_{ii} - Z_{ji}}{\pi_i}\right) \sum_n \pi_n c_n$$

$$Z = (I - P + W)^{-1}$$

Z is the fundamental matrix for ergodic chains. I is the identity matrix. P is the matrix of probabilities of going from site i to site j. W is a matrix whose rows are π, the vector of site probabilities.

The highest centrality measure for each system type is used to scale centralities between 0 and 1 and set the greyscale for the site centrality image.

Kinetic Monte Carlo (KMC)

1. Consider all possible moves from i.
2. A random number between 0 and 1 chooses the next move.

$p_{i,2}$	$p_{i,38}$	$p_{i,52}$	$p_{i,79}$

3. The system clock is advanced by a time step drawn from the first escape time distribution.
4. Process is repeated until the desired simulation time is reached.

The desired simulation time was increased until a long-range pathway was observed. This method is described in more detail by Voter[6].

Removing one vertex from the graph

Using the site probabilities and rate constants found in [4] for a probe proton in the presence of a proton at the lowest energy site in yttrium doped barium zirconate, binding site centralities and most probable pathways for the probe proton were found. Figure 2 shows that the most probable pathways for the probe proton (right) follow the most central or darkest sites (left). The centrality images show how the probe proton's motion is correlated to the fixed proton's position. Surprisingly, centrality predicts a preference for pathways in the neighborhood of the fixed proton. Recent experiments and calculations[7] observe positively correlated motion with direct indications that lattice relaxation by one proton prepares the lattice for the next one.

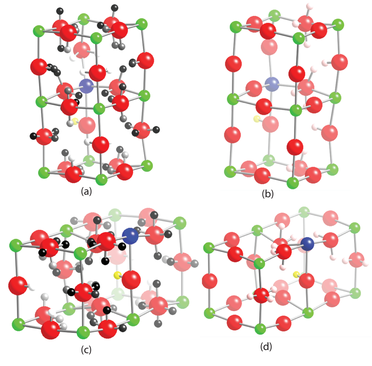

Figure 2. Two sections of yttrium doped barium zirconate are shown with centrality shading for proton binding sites on the left. The highest centrality sites are black while the lowest centrality sites are white. The most probable trajectories through the system sections are shown on the right. The fixed proton is shown in yellow.

What to expect from noisy graph parameters

To assess the effect of error from sampling when sampling $k_{i,j}$ from MD trajectories, normally distributed noise was added to *ab initio* calculated graph parameters from earlier work[5] prior to calculating the centrality. As seen in Table 1, errors of 1% maintain centrality minima, maxima, and range. However, 10% and higher errors significantly affect the centrality range. Surprisingly, Figure 3 shows very similar centrality topology for up to 10% errors though at 20% error the measure sees very little difference between sites.

SD	Min	Max	Range
0.00	0.000151	0.000507	0.000356
0.01	0.000148(4)	0.00050(1)	0.000356(7)
0.1	0.0000(6)	0.0009(3)	0.0009(7)
0.2	-0.04(9)	0.01(2)	0.05(9)

Table 1. The minimum, maximum, and range of the centralities are shown as a function of the standard deviation (SD) of the normally distributed noise added to rate constants and transfer probabilities.

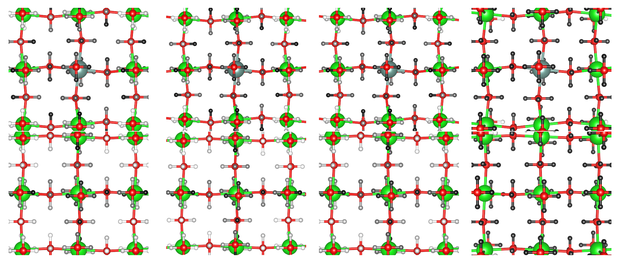

Figure 3. Centrality in the dopant plane and away from the dopant is shown in the top and bottom rows, respectively. From left to right, centrality is calculated with normally distributed noise with standard deviation of 0.0(no noise), 0.01, 0.1, and 0.2 for all probabilities and rates. White and black are set to the minimum and maximum centrality values.

Disconnecting the graph

LLZO ($Li_7La_3Zr_2O_{12}$) system is a fast lithium ion conductor which often exhibits oxide depleted amorphous phases. These can disconnect the conduction graph. With $k_{i,j}$ obtained from analysis of molecular dynamics (MD) trajectories by Heo *et. al.*[8], the centrality and kMC trajectories were found. Some of these cases had disconnected graphs and removing rows and columns of problematic sites from the fundamental matrix was critical to finding the centrality.

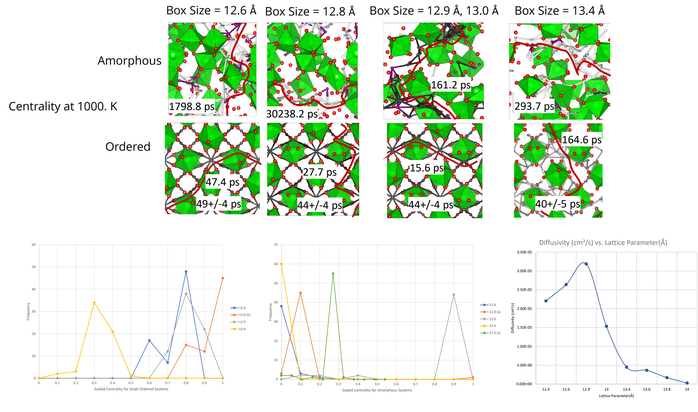

Figure 4. The structures with distributions shifted towards the highest centrality values show the highest conduction. Further, kMC conduction paths move through the higher centrality sites. The bottom two plots indicate with a (s) the system with the highest individual centrality which was used to set the gray scale range.

Conclusion

With some care to maintain small errors in graph measures and removing of problematic sites from the Fundamental matrix, time based centrality measures highlight likely paths and traps in conduction graphs with some sites removed.

References

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