Graph theory ideas reveal long range conduction pathways

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Long range proton conduction pathways can be have a dominant limiting barrier
Ways of investigating proton conduction pathways

- Energetics
- Ab initio Molecular Dynamics
- Ensemble of pathways

- Kinetic Monte Carlo trajectories
- Centrality measures


Proton conduction at different temperatures

\[ \lambda = \frac{h}{mv} \]
\[ \left\langle \frac{1}{2} mv^2 \right\rangle = \frac{3}{2} k_B T \]


PROTON-CONDUCTING OXIDES

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Figure 1  Proton conductivities of various oxides as calculated from data on proton concentrations and mobilities, according to Norby & Larring [type of dopant is not indicated, for source data, see (21)]. Conductivities of oxides with perovskite-type structure are shown by bold lines.
Protonic conduction in SrZrO$_3$-based oxides

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Fig. 3. Conductivity of SrZr$_{0.95}$M$_{0.05}$O$_3$--$_\alpha$ in hydrogen atmosphere.

Fig. 4. Dependence of proton conductivity on ionic radii of dopant cations.
Perovskite Geometry

Ionic size:  \( \text{Al}^{3+} < \text{Ga}^{3+} < \text{Zr}^{4+} < \text{Sc}^{3+} < \text{In}^{3+} < \text{Er}^{3+} < \text{Y}^{3+} \)
The environment can make the pathways

\[ \text{BaZr}_{0.875}\text{Y}_{0.125}\text{O}_3 \]
The environment can make the pathways

M. A. Gomez, Fan-Jean Liu “Protons in Al doped BaZrO$_3$ escape dopant traps to access long range conduction highways,” Solid State Ionics, 252, 40 (2013);
Map to graph: Each binding site is a vertex and are connected by an edge when there is a single transition state between them.

\[ \text{probability} = \rho(x_{i_1})P_{i_1i_2}P_{i_2i_3} \cdots P_{i_{N-1}i_N} \]

Rate constant between sites

\[ k_{HTST}^{i \rightarrow j} = \frac{N_{\text{min}}}{\prod_{k=1}^{N_{\text{ne}}}} \exp(-\beta E_{\text{barrier}}^{i \rightarrow j}) \]

Probability between sites

\[ p_{i \rightarrow j} = \frac{k_{HTST}^{i \rightarrow j}}{\sum_{m=1}^{N_{\text{neighbors}}} k_{HTST}^{i \rightarrow m}} \]

Weight of an edge

\[ w_{i \rightarrow j} = -\ln(p_{i \rightarrow j}) \]

Weight of a path

\[ -\ln(\rho_n) + \sum_{n=1}^{N} w_{i_n \rightarrow j_{n+1}} \]
Some paths are loops while others are longer range pathways.

Most probable periodic paths in Al/SrZrO$_3$ avoid dopant while those in Y/SrZrO$_3$ hug dopant.


kMC suggests that individual proton motion is characterized by trapping and escape to fast conduction barriers.

Showing the whole trajectory site probabilities yields the Boltzmann distribution

\[ \text{Y/BaZrO}_3 \quad \text{Al/BaZrO}_3 \]
Towards centrality measures based on time

Mean first passage number of steps to go from i to j. (Grinstead and Snell)

\[ m_{ij} = p_{ij} + \sum_{l \neq j} p_{il} \left( 1 + m_{lj} \right) \]

Mean first passage time to go from i to j.
Towards centrality measures based on time

Round trip time to go from i to j and back to i

\[ R_{ij} = m_{ij} + m_{ji} \]

Average round trip time to go from i to any j and back

\[ R_i = \frac{1}{N} \sum_j R_{ij} \]

Centrality of i

\[ \frac{1}{R_i} \]
Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories

## Barriers to proton conduction

<table>
<thead>
<tr>
<th></th>
<th>Limiting Barrier in Long range paths (graph theory) (eV)</th>
<th>Barrier Range to Escape dopant Trap (eV)</th>
<th>Long Range Limiting Barrier to Kinetic Monte Carlo 1 proton (eV)</th>
<th>Long Range Kinetic Monte Carlo 4 protons (eV)</th>
<th>Experiment (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y/BaZrO$_3$</td>
<td>0.32</td>
<td>same</td>
<td>0.39</td>
<td>0.43</td>
<td>0.43 for 10% doping</td>
</tr>
<tr>
<td>Al/BaZrO$_3$</td>
<td>0.40</td>
<td>0.7-0.9</td>
<td>0.81</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>

In Y/BaZrO$_3$, the percent of limiting barriers that are intra-octahedral transfers, rotations, and inter-octahedral transfers changes from 87%, 11%, and 2% in the single proton case to 90%, 0%, and 10% in the four proton case.
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<tr>
<td><strong>Y/SrZrO₃</strong></td>
<td>0.43</td>
<td>same</td>
<td>0.57</td>
<td>0.69</td>
<td>0.43 for 5% doping</td>
</tr>
<tr>
<td><strong>Al/SrZrO₃</strong></td>
<td>0.60</td>
<td>0.7-0.8</td>
<td>0.73</td>
<td>0.84</td>
<td>0.97 for 5% doping</td>
</tr>
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</table>

Lattice distortions stabilize a second proton binding near the first proton.

Maria A. Gomez, Dana L. Fry, Marie E. Sweet, “Effects of the proton conduction limiting barriers and trajectories in BaZr0.875Y0.125O3 due to the presence of other protons,” J. of the Korean Ceramic Society. 53, 1, 2016.
Second proton pathways move along regions of high centrality.
Conclusions

- Traditional graph theory ideas can help find long range conduction highways.

- Centrality measures using mean time to first returns rather than mean number of steps to first returns can highlight traps, access points to fast long range pathways, and long range pathways.

- Kinetic Monte Carlo both verifies the path information seen using centrality measures and also allows us to calculate limiting barriers which compare well with experiment.

- Proton conduction pathways in yttrium doped barium zirconate tend to be in regions with the dopant which include the yttrium trap. In contrast, protons moving in the aluminum doped system escape traps to fast highways away from the dopant to do long range conduction.
Collaborators and Funding

- Maria A. Gomez*, Dana L. Fry, Marie E. Sweet, “Effects of the proton conduction limiting barriers and trajectories in BaZr0.875Y0.125O3 due to the presence of other protons,” J. of the Korean Ceramic Society. 53, 1, (2016).
- Megha Patel, Jiayun Zhong, Konrad Gomez-Haibach, Maria A Gomez*, and Graham King, “Low energy Sr2MSbO5.5 (M=Ca and Sr) show significant distortions near oxygen vacancies,” Accepted by International Journal of Quantum Chemistry (2020).
- Peng Du, Qianli Chen*, Zhijun Fan, Huizhu Pan, Frederick G. Haibach, Maria A Gomez, and Artur Bruan, “Cooperative origin of proton pair diffusivity in yttrium substituted barium zirconate,” In review with Communications Physics.

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