Making the Most of Neutron-Diffraction Data Lithium Diffusion Pathways in Ramsdellite-Like $Li_2Ti_3O_7$

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Ramsdellite-like $Li_2Ti_3O_7$ exhibits fast and strongly anisotropic lithium-ion conduction. Although proposed applications range from energy storage to lithium processing, the crucial diffusion pathways in this material have not yet been studied in depth; even aspects of its crystal structure are still under discussion [1].

In our studies, we have examined $Li_2Ti_3O_7$ using variable-temperature neutron diffraction to probe its nontrivial lithium-ion distribution. At 24 °C, a Rietveld-refined structural model with anharmonic-anisotropic displacement parameters shows a statically disordered snapshot of the dynamic behavior during synthesis. We found no significant occupation of the framework cation positions by lithium ions and agree with the recently favored formulation as $[Li_{2\square 5}]_i[(Ti_{3\square 0.5})O_7]_f$ (□: vacancy, i: interstitial, f: framework). Reconstruction of the scattering-length density via maximum-entropy methods (MEM) indicates successive partial relaxation and activation of lithium movement with increasing temperature in the metastability range.

Using topological analyses of procrystal voids and Voronoi-Dirichlet partitioning (VDP), we have identified two pathways of lithium diffusion: interstitial migration along ribbons as the major, framework migration through vacancies as the most probable minor mechanism. Thusly, we explain former empirical results and shed light on this paradigmatic lithium-ion conductor [2].

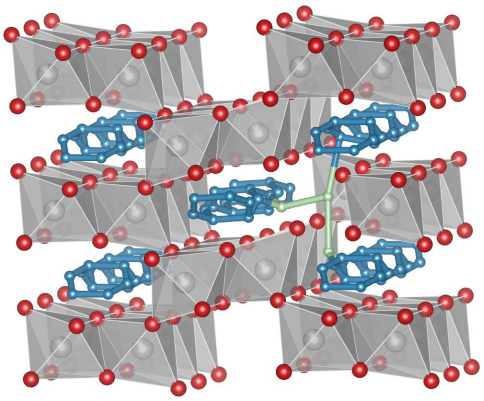

Figure 1: Void structure of the $Ti_3O_7^{2-}$ framework at 422 °C (gray: titanium, red: oxide ions, blue: preferred, green: probabilistic voids/channels).

[1] Pseudo-weak-phase-object Approximation in High-resolution Electron Microscopy. II. Feasibility of Directly Observing Li^+, D. Tang, C. M. Teng, J. Zou, F. H. Li, Acta Cryt. B 42 (1986) 340.

[2] Lithium Diffusion Pathways in Metastable Ramsdellite-like $Li_2Ti_3O_7$ from High-temperature Neutron Diffraction, D. Wiedemann, S. Nakhal, A. Franz, M. Lerch, Solid State Ion. 293 (2016) 37.