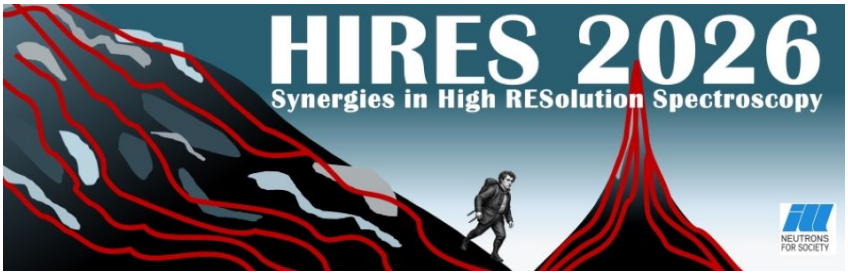

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The Role and Dynamics of Interstitial Water and Sodium in Hydrated Manganese Iron Prussian Blue Analogs: A Synergistic Study Combining NPD, QENS, and MLIP-MD

Manganese-iron Prussian blue analogs (MnFePBA) are promising cathode materials for sodium-ion batteries due to their high energy density, low cost, and facile synthesis. While most studies advocate dehydration to enhance cycling stability, recent findings suggest that hydration stabilizes a monoclinic phase with superior sodium diffusivity and greater capacity retention than the dehydrated rhombohedral phase.

However, the structure and reaction mechanisms of hydrated MnFePBA remain contested. Though the monoclinic unit cell is established, contradictions persist between computational predictions—placing interstitial water at body-center and sodium at face-center—and experimental observations from X-ray diffraction (XRD) and neutron powder diffraction (NPD). These discrepancies arise from the similar electron densities of oxygen and sodium in XRD analysis, while the inherent mobility of both species complicates site occupancy refinement even with NPD's superior scattering contrast.

We combine NPD, quasi-elastic neutron scattering (QENS), and machine learning interatomic potential molecular dynamics (MLIP-MD) to resolve these ambiguities. NPD on D_2O- and H_2O-hydrated samples confirms water at body-center sites and sodium at face-center sites. QENS experiments at IN16b and SHARPER (ILL) characterize sodium and water diffusion on nanosecond and picosecond timescales, respectively. Comparing dehydrated and hydrated samples, we extract sodium diffusivity and activation energy.

MLIP-MD simulations agree with experimental findings and reveal that the hydrated monoclinic structure enables significantly faster sodium diffusivity (10^{-12} m^2/s) than the dehydrated rhombohedral structure (10^{-18} m^2/s at 300 K), while elucidating distinct diffusion pathways for each species.

Session

Hard Condensed Matter

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