

Structural dynamics in prussian blue-based cathodes for ion batteries

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The development of novel electrode materials for more sustainable battery systems has become increasingly important. Among these materials, Prussian Blue and its analogues (PBAs) have garnered significant attention as potential cathode materials for both Li-ion and post-Li-ion devices, due to their open-framework structures consisting of bimetallic cyanides arranged in three-dimensional lattices. These lattices can reversibly host ions due to their large interstices and channels.

Among PBAs, Manganese hexacyanoferrate (MnHCF) has attracted particular interest as a promising cathode material, not only for Li and Na-ion batteries—due to its high specific capacity (>130 mAh g⁻¹), high discharge potential, and sustainability—but also for Zn-ion batteries. However, capacity fading during cycling remains a key challenge for these systems. This could be caused by various factors, including structural transformations upon cycling [1-3], inhomogeneous oxidation states of metal sites, or Mn dissolution [4]. To address these challenges, several X-ray techniques have been employed together [5].

This study focuses on the structural changes observed through scattering technique studies, particularly operando and ex-situ analyses of electrodes based on PBAs. The research utilizes various experimental setups and modalities, including both transmission and fluorescence modes.

Results for Li- and Na-ion cells indicated that the electrochemical reaction of MnHCF is accompanied by phase and structural transformations, as well as Jahn-Teller (JT) distortions of the Mn sites during the charge process [1]. On the other hand, phase and crystal structure evolution in aqueous zinc-ion batteries (AZIBs) [3] revealed that structural changes primarily occurred during the first cycle, with the original monoclinic peaks disappearing and new peaks forming after the first charge. Operando XRD (X-ray diffraction) revealed new peaks during Mn oxidation (>1.8 V), which became dominant upon discharge. By the 10th cycle, the XRD pattern stabilized, indicating minimal further changes. High-resolution capillary XRD initially showed a two-phase mixture, but by the 10th and 50th cycles, only a newly formed stable phase remained, differing from prior reports.

The full interpretation of structural dynamics, both locally and on a long-range scale, was achieved by adopting a multi-technique X-ray approach. XAS (X-ray absorption spectroscopy) and XRF (X-ray fluorescence) showed that cycling transformed the Mn–NC–Fe framework into a Zn–NC–Fe framework, with Mn sites undergoing significant rearrangement, including Mn–N bond cleavage and MnO₂ formation. Although MnO₂ wasn't detected by XRD, its redox behavior was evident in electrochemical tests. Phase transformation occurred primarily during the first cycle, forming a stable cubic ZnHCF phase. A refined cubic ZnHCF structure was proposed, linking structural evolution to electrochemical performance and providing insights for future battery design.

[1] Mullaliu, A., Gaboardi, M., Plaisier, J.R., Passerini, S., Giorgetti, M. (2020) *ACS Appl. Energ. Mater.*, 3, 5728–5733.

[2] Li, M., Maisuradze, M., Mullaliu, A., Carlomagno, I., Aquilanti, G., Plaisier, J.R., Giorgetti, M. (2024) *Small*, 20, 240458.

[3] Li, M., Gaboardi, M., Mullaliu, A., Maisuradze, M., Xue, X., Aquilanti, G.; Plaisier, J.R., Passerini, S., Giorgetti, M. (2023) *ChemSusChem* 16, e202300291.

[4] Maisuradze, M., Li, M., Carlomagno, I., Gaboardi, M., Aquilanti, G., Plaisier, J.R., Giorgetti, M., *Batteries* (2024), 10, 123.

[5] Li, M., Maisuradze, M., Paputungan, Z., Denecke, R., Plaisier, J.R., Aquilanti, G., Agostini, G., Giorgetti, M. (2025) *J. Mater. Chem. A*, 13, 11314.

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