X-ray-Based Structural Analysis of Prussian Blue Compounds for Metal-Ion Batteries

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Prussian Blue (PB) and its analogues (PBAs) constitute a large family of transition-metal hexacyanoferrates with the general formula $A_xM[Fe(CN)_6]_y\square_{1-y}\cdot zH_2O$. They possess an open-framework structure, redox-active sites, and strong structural stability, which make them promising electrode materials. In particular, PBAs enable rapid ion insertion and extraction with minimal lattice strain.

This contribution firstly summarizes the investigation of battery materials using synchrotron radiation techniques trough CERIC facilities, highlighting X-ray absorption spectroscopy, X-ray diffraction, and X-ray fluorescence applied to several PBAs, with a focus on electronic, structural, and microscopic information trough 2D mapping.

Among simple PBAs, manganese hexacyanoferrate (MnHCF) exhibits high specific capacity and well-defined redox plateaus at high voltages versus lithium and sodium in lithium-ion (LIBs) and sodium-ion batteries (SIBs) as well as aqueous zinc systems (AZIBs). in this last system, the analysis revealed that electrochemical cycling transforms the Mn–NC–Fe framework into a Zn–NC–Fe while cycling with in ZnSO4, with Mn sites undergoing significant rearrangements, including Mn–N bond cleavage and MnO_2 formation. Although MnO_2 was not detected by XRD, its redox activity was clearly observed in electrochemical measurements. Zn-Mn substitution was also visible in 2D XRF images, as Zn entered the electrode from the corners, which, at the same time, experienced Mn depletion.

References

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Short bio:

Giorgetti Marco is an Full Professor of Analytical Chemistry at the University of Camerino, and he leads the group of Spectroscopy Electrochemistry and Energy (S2E) in Bologna and Camerino. His research interest covers the field of the structural and electronic characterization of battery materials, solid and solutions by core level spectroscopies (XAS, XRPD, XTM, XPS, XRF), the applied

electrochemistry, sensors, the synthesis and characterization of materials for advanced batteries. Marco has coordinated about 35 projects in synchrotron radiation facilities including LURE, SRS-Daresbury, ESRF, Brookhaven National Laboratory, SOLEIL, SOLARIS, ELETTRA and CERIC proposals.