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Uncovering the interplay of competing distortions in the Prussian blue analogue $K_2Cu[Fe(CN)_6]$

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Abstract

We report the synthesis, crystal structure, thermal response, and electrochemical behaviour of the Prussian blue analogue (PBA) $K_2Cu[Fe(CN)_6]$. From a structural perspective, this is the most complex PBA yet characterised: its triclinic crystal structure results from an interplay of cooperative Jahn-Teller order, octahedral tilts, and a collective 'slide' distortion involving K-ion displacements. These different distortions give rise to two crystallographically-distinct K-ion channels with different mobilities. The crystal structure was solved by Rietveld refinement of synchrotron X-ray powder diffraction (XRD) pattern using ISODISTORT and TOPAS. The low symmetry can be explained in theory by the combination of the aforementioned distortion modes, and is justified from good fit to data in the diffraction pattern ($R_{wp} = 1.95\%$).

Variable-temperature X-ray powder diffraction measurements show that K-ion slides are the lowest-energy distortion mechanism at play, as they are the only distortion to be switched off with increasing temperature. At higher temperatures we propose a decomposition pathway to form a different Prussian blue material from exsolving the copper ions in the framework.

Electrochemically, the material operates as a K-ion cathode with a high operating voltage, and an improved initial capacity relative to higher-vacancy PBA alternatives. On charging, K^+ ions are selectively removed from a single K-ion channel type and the slide distortions are again switched on and off accordingly. We discuss the functional importance of various aspects of structural complexity in this system, placing our discussion in the context of other related PBAs.

Figure: Schematic representation of the structural transformations in $K_2Cu[Fe(CN)_6]$ that take place as a function of temperature and electrochemical cycling.

References

J. Cattermull, K. Sada, K. Hurlbutt, S. J. Cassidy, M. Pasta and A. L. Goodwin, (2022), 10.26434/ChemRxiv-2022-zr5nn

Schematic of structural changes

