



22nd International Conference on
Diffusion in Solids and Liquids
22 TO 26 JUNE 2026 | RHODES, GREECE

ABSTRACT:

Applying Point Defect Thermodynamics to Prussian Blue – Experiments and Modelling

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Prussian Blue, $\text{Na}_{1+\xi}\text{Fe}[\text{Fe}(\text{CN})_6]$, is a promising low-cost cathode material for sodium-ion batteries. Despite the importance, the point defect structure and the range of stoichiometry ξ of this mixed ionic and electronic conducting phase are not known in detail. An electrochemical cell using a Na electrode, NASICON and Prussian Blue is assembled. The course of the cell potential U_{cell} vs. ξ is measured by galvanostatic intermittent coulometric titration, the chemical diffusion coefficient \mathcal{D}_{Na} is determined by evaluation of the cell potential transients.

Point defect thermodynamics is used to model relations between ξ , chemical potential μ_{Na} , U_{cell} and \mathcal{D}_{Na} . [1] The thermal equilibrium between high-spin Fe^{3+} , low-spin Fe^{2+} , low-spin Fe^{3+} and high-spin Fe^{2+} , i.e. “electrons” and “holes”, is decisive for the electro-chemical properties. U_{cell} vs. ξ and \mathcal{D}_{Na} vs. ξ exhibit characteristic sigmoidal courses, the equilibrium constant K_{el} for electron-hole formation and the charge carrier mobilities $u_{e'}$ and $u_{h\cdot}$ are obtained by fitting. The free enthalpy $\Delta G_{\text{el}0}$ has a value of 0.3 eV, that is significantly lower than the energy E_g of the optical charge transfer process of 1.7 eV. [2] \mathcal{D}_{Na} is in the order of 10^{-8} to 10^{-9} $\text{cm}^2 \text{s}^{-1}$, $u_{e'}$ and $u_{h\cdot}$ in the order of 10^{-7} and 10^{-6} $\text{cm}^2 (\text{V s})^{-1}$, indicating strongly localised small polarons. A full sodiation results in a Prussian White phase with a nominal composition $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$, a full desodiation seems to be impossible. It ends up at a limiting composition of about $\text{Na}_{0.2}\text{Fe}[\text{Fe}(\text{CN})_6]$. [3] The results offer valuable insights for a better understanding the electrochemical (cycling) behaviour.

[1] C. Wagner, Prog. Solid State Chem. 6, 1–15 (1971)

[2] N. S. Hush, Progr. Inorg. Chem. 8, 391–444 (1967)

[3] F. De Wet, R. Rolle, Z. Anorg. Allg. Chem. 336, 96–103 (1965)