

Degradation mechanisms and thermal stability of of vacancy-free $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$: The impact of water and guest cations

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Prussian blue analogues (PBAs) with formula $A_xM[M'(\text{CN})_6]_{1-y}\cdot z\text{H}_2\text{O}$, show considerable promise as highly sustainable electrodes in sodium ion batteries. PBAs are formed of metal that are octahedrally coordinated by cyanide groups which act as bridges between the metal centers. This corner linked framework creates a highly porous structure into which either cations such as Na^+ or molecules such as H_2O can insert into. However, PBAs receive criticism on their thermal stability and moisture sensitivity, which can be detrimental to the electrochemical performance or compromise safety. However, existing pessimism towards the material is based on studies of traditional Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), whereas the vacancy-free compounds such as iron hexacyanoferrate (Fe-HCF), $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6]_{1-y}\cdot z\text{H}_2\text{O}$ ($x \approx 2$, $y \approx 0$, $z \approx 0$), do not show any similarity in terms of structural transitions or performance in a battery. In this contribution, our efforts at understanding the thermal and moisture stability of vacancy-free Fe-HCF are presented.

We have optimised a method of consistently producing Fe-HCF with <5% vacancies on the $\text{Fe}(\text{CN})_6$ site. Consequently, the effect of sodium content and moisture on structure and stability has been independently quantified. In the absence of vacancies, the moisture sensitivity of the material is determined by the Na^+ content, with a sodium-rich structure absorbing more water and binding with higher affinity. Interestingly, despite a higher moisture sensitivity, the Na^+ rich system features higher thermal stability. The interplay between the host framework, sodium and water also appears to influence the phase transitions of the material. The sodium-free material does not undergo any phase transitions, remaining cubic ($Fm-3m$) from 4K to 300K, whereas the sodium rich ($x > 1.5$) systems exhibit several phase transitions between $R-3$ and $P2_1/n$ as a function of temperature and water content. These are driven by octahedral tilting (cf. perovskites) and given that such transitions are generally rare in PBAs, their presence within a single system provides a platform for investigating driving factors. As described, the moisture sensitivity of PBAs is often understood as the tendency to absorb water into the bulk structure. However, water can negatively affect cation rich Fe-HCF via other mechanisms. We identified that contact with airborne moisture during storage can lead to a loss of capacity in FeHCF. The capacity fading mechanism proceeds via two steps, first by sodium from the bulk material reacting with moisture at the surface to form sodium hydroxide and partial oxidation of Fe^{2+} to Fe^{3+} . The sodium hydroxide creates a basic environment at the surface of the PW particles, leading to decomposition to $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and iron oxides. Although the first process leads to loss of capacity, which can be reversed, the second stage of degradation is irreversible. The combination of each process ultimately leads to a surface passivating layer which prevents further degradation.

Thus, the interaction of water with cation rich PBAs is complex and should not be overlooked. Gaining an understanding of the degradation mechanisms, including structural and chemical driving forces provides substantial insight into effective design strategies for increasing the performance.

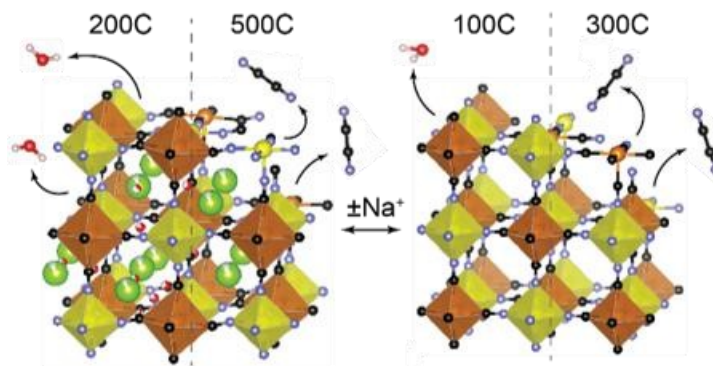


Figure 1: Pictorial representation of the differences in dehydration and decomposition temperatures for sodium rich and sodium poor iron hexacyanoferrate.

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