

Stabilization process of Prussian blue: A revised mechanism

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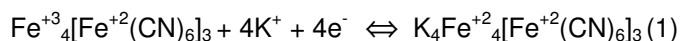
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Abstract – About 30 years ago, it was proposed a mechanism to explain the electrochemical processes that occur during the stabilization of iron (III) hexacyanoferrate electrodeposited films (FeHCF – called popularly Prussian blue). This electrochemical process is currently accepted, but some results obtained using *ac* electrogravimetry measurement complemented by structural analysis contradicts that model previously proposed leading to a new one that was recently presented [1]. Therefore, the main goal of the present work is to review the FeHCF stabilization process based on the new model for the electrochemical process.

The structural analysis in the FeHCF compound prepared electrochemically and stabilized after different voltammetric cycles indicates a $\text{Fe}^{+3}_4[\text{Fe}^{+2}(\text{CN})_6]_3 \cdot [\text{K}^+_{h_1} \text{OH}^-_{h_1} m\text{H}_2\text{O}]$ structure very similar to that obtained by traditional chemical methods, proposed as $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot m\text{H}_2\text{O}$. Based on this fact, the only type of structure that is *insoluble* is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot m\text{H}_2\text{O}$. When this structure is electrochemically synthesized, the K^+ ions are inserted into the water substructure during the stabilization process, leading to $\text{Fe}^{+3}_4[\text{Fe}^{+2}(\text{CN})_6]_3 \cdot [\text{K}^+_{h_1} \text{OH}^-_{h_1} (m\text{H}_2\text{O})]$. Thus, the entire redox process and intercalation mechanism depends on the water crystalline substructure. Based on this fact, the ionic interplay mechanism was reviewed in reference [1].

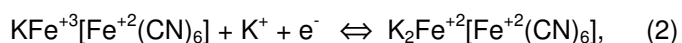
The general historical picture outlined in the literature must then be revised carefully. Therefore, the classical picture of the intercalation process in *insoluble* hexacyanometallate compounds, considered as a reversible intercalation reaction, is achieved by an electrochemical cycle, i.e.,



for K^+ cationic intercalation.

It is important to note that the above historical and classical statement does not take into account the water substructure of the PB compound. As a result, in the voltammetric cycling process, K^+ ion is considered to intercalate in the interstices or in the lattice of cubic PB. Furthermore, though always written in a reversible form, eq. (1) is considered to possess a parallel irreversible reaction that leads to the stabilization of a final compound called *soluble* FeHCF. At the end, the stabilization process is presumed to lead to a stable conversion of $\text{Fe}^{+3}_4[\text{Fe}^{+2}(\text{CN})_6]_3$ (*insoluble*) to $\text{KFe}^{+3}[\text{Fe}^{+2}(\text{CN})_6]$ (*soluble*) compound.

In other words, it is believed that after the newly deposited FeHCF, $\text{Fe}^{+2}_4[\text{Fe}^{+2}(\text{CN})_6]_3$, is cycled in a solution containing K^+ ions, and assuming that structural changes occur in the FeHCF material (stabilization process), the *insoluble* structure is converted into a *soluble* one. It is especially important to note that during the structural changes, FeHCF presumably loses approximately one quarter of the high spin Fe^{+3} atoms in the structure and K^+ ions occupy the interstitial 4a sites (intercalating in the place of lost Fe^{+3}) in the structure of the *insoluble* PB, leading to another structure, called a *soluble* structure. The reversible electrochemical process related to the *soluble* structure is proposed as



Eq. (2) is known as a reversible intercalation process between the *soluble* PB structure and Everitt's Salt (ES). In this work, the process of Eq. (1) and (2) were revised and justified based on the recent structural analysis and changeover overview of the process.

References

[1] Bueno, P. R., F. F. Ferreira, et al. (2008). Journal of the Physics Chemistry C **112**, 34 (2008) 13264-13271.