An Overview on the Facile and Reversible Cations Intercalation in Nickel-Hexacyanoferrate Open Framework

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doi: 10.20964/2018.06.37

Received: 14 February 2018 / Accepted: 23 March 2018 / Published: 10 May 2018

The paper reports a detailed study about the influence of the electrolyte composition in nickel-hexacyanoferrate (NiHCF) electrochemical behavior. Shapes and positions of the CV waves are strongly related to the cation of the supporting electrolyte, which undergoes intercalation/de-intercalation during the redox process. The electrochemical behavior of NiHCF has been characterized in different electrolyte solutions containing either pure monovalent or trivalent metal nitrates. Nickel-hexacyanoferrate permits the reversible insertion of a wide variety of monovalent, divalent and trivalent ions in aqueous solution; the characteristic potential E_p of the cathodic process depends upon the nature of the intercalated cation. Electrochemical measurements demonstrate the unprecedented fast kinetics of trivalent ion insertion associated with this material. The reported findings represent the first systematic step toward understanding the principles of multivalent charge screening and provide a novel cation intercalation mechanism in NiHCF, assisted by both water molecules and ferrocyanide vacancies. The synergistic mechanism can reduce the electrostatic repulsion and provide a preferential path for the rapid cation intercalation.

Keywords: alkali cations, cation exchange, ion sensing, nickel-hexacyanoferrate, trivalent cations.

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