

## Protective Properties of Hybrid Polypyrrole Based Films Containing Hexacyanoferrate Ions

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There has been growing interest in application of conducting polymers for corrosion protection. Our approach concerns fabrication of composite materials of conducting polymers (e.g. polyaniline, polypyrrole) and polynuclear inorganic compounds (e.g. hexacyanoferrates, Prussian blue). In the present, we explore protective properties of polypyrrole containing hexacyanoferrate anions. The composite coatings were electrodeposited galvanostatically on mild and stainless steels in the aqueous solutions of pyrrole and potassium hexacyanoferrate(II) at concentrations 0.1 mol dm<sup>-3</sup> and 0.5 mol dm<sup>-3</sup>, respectively. The protective properties of the resulting coatings were investigated in highly aggressive medium of 0.1 mol dm<sup>-3</sup> HCl and 0.4 mol dm<sup>-3</sup> NaCl. Diagnostic experiments included potentiodynamic measurements and chronoamperometric (current-time) monitoring at constant potential. To get insight into dynamics of the steel dissolution, changes of concentrations of iron and chromium were determined using atomic absorption spectrometry. Morphology of the composite film was examined using scanning electron microscopy. It has been established that incorporation of hexacyanoferrate anions into polypyrrole significantly decreases pitting corrosion of steels. We believe that protective mechanism originates from blocking the access of chloride anions to the metal surface due to the presence of negatively charged hexacyanoferrates (electrostatic repulsion) within polypyrrole film. In addition, the Prussian blue (iron hexacyanoferrate) film, that is formed on steel surface, seems to act as barrier layer for chloride ions. From structural point of view, the inner portion of the film, that is adjacent to the steel surface, seems to be dominated by polynuclear Prussian blue whereas the outermost portions of the film are likely to contain hexacyanoferrate anions. Another important feature is the stability and very low solubility of Prussian blue in acid and chloride media. The formation of robust Prussian blue leads to stabilization of passive state of the steel. Hexacyanoferrate ions (present in the conducting polymer based composite film) strongly inhibit transfer of iron and/or chromium cations into the solution even in chloride containing aggressive media. Semi-conducting Prussian blue does not prevent further electrochemical processes, namely deposition of the outer layer of polypyrrole containing hexacyanoferrates. By neutralizing the positive charge of polypyrrole matrix with inorganic anions, its anion exchange properties are reversed or minimized, and the access of pitting causing chlorides is blocked. Even if some chlorides reach the steel surface and the breakdown of passive film occurs, any iron and chromium ions appearing in the pits would immediately

form Prussian blue. In other words, formation of stable pits in the presence of hexacyanoferrate anions (present in the composite film) is largely suppressed. Composite films have been found to be stable and robust on stainless steel surfaces. This work has much in common with recent concepts of both forming initial stable precursor layers and changing the permselectivity of a conducting polymer by introducing such large size organic counterions as polystyrenesulfonate.