

**ANION CATALYZED INNERSPHERE
ELECTRON TRANSFER IN SURFACE
IMMOBILIZED INNER IRON HEXACYANO-
FERRATE THIN FILM**

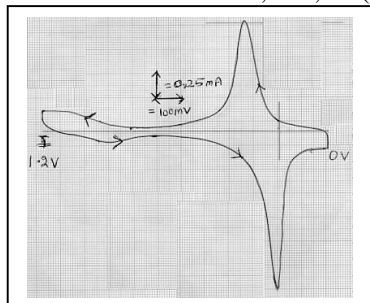
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Abstract

In the surface modification of electrodes with metal hexacyanoferrate thin films new strategies are introduced from time to time and the interesting observations are reported. In one such strategic approach higher homologues of quaternary ammonium halides for example, cetyl trimethyl ammonium bromide (CTAB) showed marked influence on the response characteristics of metal hexacyanoferrate and their oxide derivative species modified electrode surfaces in presence of alkali metal cation containing supporting electrolytes [1-3]. In a new turn of event it has been noticed that the quaternary ammonium halides behave in a different fashion among chloride, bromide and iodide salts studied. Chloride when present as quaternary salt or as simple KCl does not have any effect (Fig.1). The influence of quaternary ammonium bromide or simple KBr, on the innersphere electron transfer of PB molecule is indistinguishable owing to Br_2 evolution reaction at the same potential (Fig.2). Tetrabutyl ammonium iodide has marked influence on the innersphere ferri/ferrocyanide electron transfer of the prussian blue molecule. Subsequently the innersphere electron transfer was also found to be markedly influenced by the addition of KI (Fig. 3) to the KCl solution in which prussian blue modified electrode is normally cycled to check the response and demonstrate the K^+ ion insertion/excursion by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox centre. In the present communication it is highlighted that iodide when present as quaternary ammonium salt or as simple KI in solution leads to the acceleration of the innersphere electron transfer of the PB molecule. The interaction between surface bound PB molecule and solution generated I/I⁻ species in enhancing the innersphere electron transfer of PB molecule is a novel and interesting observation, which can be usefully exploited, in the catalytic applications of chemically modified electrodes of metal hexacyanoferrates.

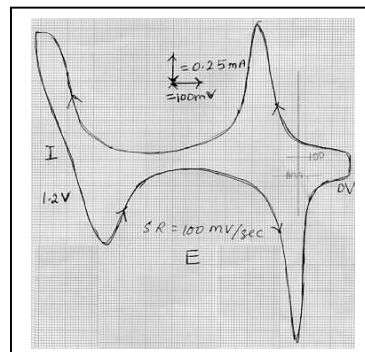
References:

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2. R. Vittal, H. Gomathi, G. Prabhakara Rao, Electrochim. Acta, 45, 2083 (2000)
3. R. Vittal, H. Gomathi, G. Prabhakara Rao, J. Electroanal. Chem., 497, 47 (2001).



Potential V (vs SCE)

Fig.1. CV response of Pt electrode modified with PB in presence of TBA Cl (5 mM) Scan rate = 100 mVs^{-1}



Potential V (vs SCE)

Fig.1. CV response of Pt electrode modified with PB in 5 mM TBA Br Scan rate = 100 mVs^{-1}

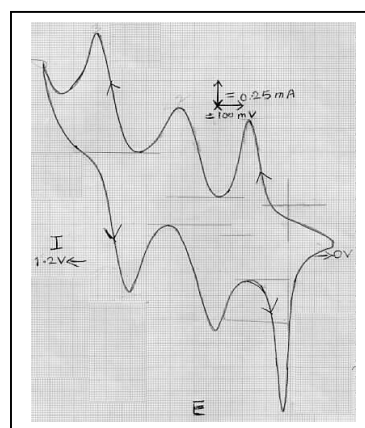


Fig.1. CV response of Pt electrode modified with PB in 5 mM KI. Scan rate = 100 mVs^{-1}