

# The effect of cations on the Electrochemistry of Prussian blue

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Prussian blue (PB) has been deposited over carbon electrode by a novel procedure reported earlier [5]. Presently cyclic voltammetric studies have revealed that various supporting electrolyte cations such as  $K^+$ ,  $Li^+$ ,  $NH_4^+$ ,  $Rb^+$ ,  $Na^+$  etc. have preferential entry or blocking effect on the lattice of PB.

**Key words:** Modified electrodes, Prussian blue film, cation effects

## INTRODUCTION

**M**odification of solid electrodes like GC, Pt, Au,  $SnO_2$  etc with Prussian blue (PB) or its analogs attained importance in very recent years. Though the effect of supporting electrolyte cations on the redox behaviour of PB was studied by a few workers [1-4], these reports are not uniform with respect to the cation effects. In this communication, we examine the above with Prussian blue prepared by a method reported from this laboratory [5].

## EXPERIMENTAL

The wax impregnated graphite electrode (WIGE) was modified in neutral medium of 0.5M KCl containing equimolar mixture of ferro/ferricyanide by a cyclic polarization method [5]. All the potentials reported are with respect to 1N calomel electrode. All the chemicals were of reagent grade and used without any purification. The cyclic voltammograms were recorded using potentiostatic Wenking POS 73 coupled with X-Y recorder (Rikadenki).

## RESULTS AND DISCUSSION

### Effect of $K^+$ ions

The WIGE after the modification showed two sets of sharp and narrow redox peaks one at 200mV(I) and the other at 850mV(II) in 0.5M KCl with  $\Delta E_p(E_{pa} - E_{pc})$  tending to zero at slowest scan rate (5mV/sec). Such narrow waves unambiguously signal the presence of attractive interactions [6]. These peak characteristics (Fig. 1) in KCl together with their potentials are taken as reference for the comparisons for data obtained with other supporting electrolyte cations. It is found that  $i_p$  vs  $V$  plot is linear upto 50mV/sec (Fig. 2) indicating that the redox species is attached to the surface of WIGE. As noted by us earlier [5] the carbon electrode is covered with PB during the cyclic polarization and is responsible for the noted redox peaks at 200mV and 850mV. The electrode processes may be

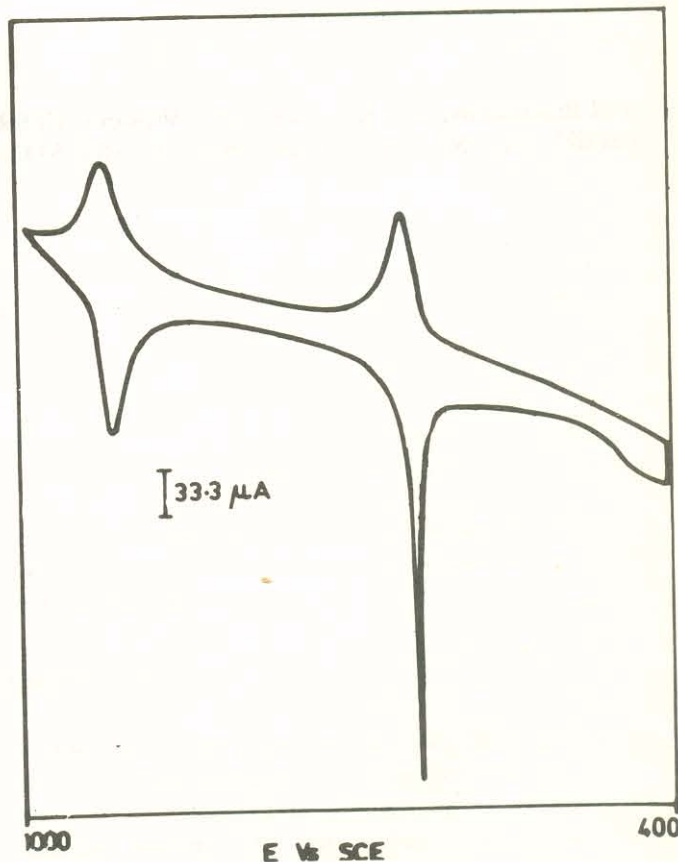
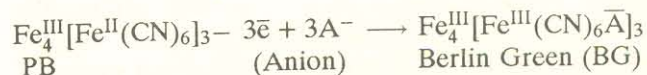
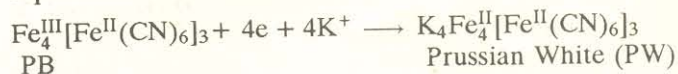


Fig. 1: Cyclic voltammetric response of Pb modified electrode in 0.5 M KCl. Scan rate 50 mV/s

represented as follows:



From the above equation it is clear that  $K^+$  ion gets into and out of the film during  $PB \rightleftharpoons PW$  transition. The

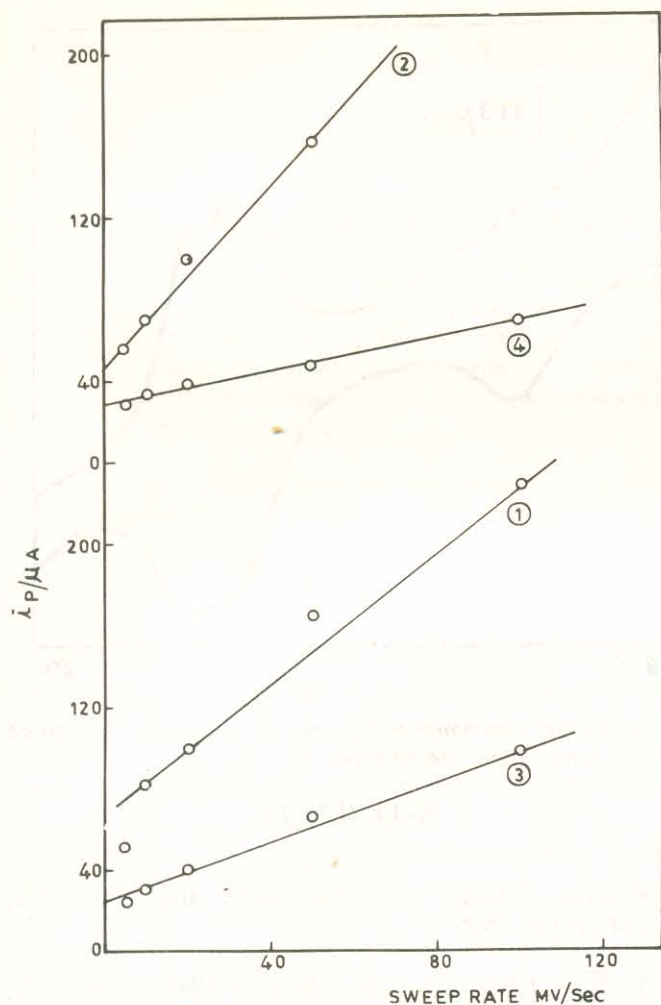


Fig. 2:  $i_p$  vs  $v$  plot for Pb modified electrode response in 0.5 M KCl

cathodic peak corresponding to  $PB \rightleftharpoons PW$  is very sharp.

#### Effect of lithium ions

In 0.5M LiCl, CV response of modified WIGE is stable. CV showed reduced peak currents with shift in the redox potentials to more negative potentials viz. 50mV and +650 for PB/PW and PB/BG waves respectively (Fig. 3). The small peak currents in 0.5M KCl after treatment in LiCl indicate that either the bigger hydrated  $Li^+$  cations block the faradaic reaction due to its slow entry into and out of the film or the PB got removed from the surface.

#### Effect of ammonium ions

In the case of 0.5M  $NH_4Cl$  the cyclic voltammograms were very stable but less reversible. Peak broadening was observed for both the redox couples as observed from Fig. 4. In the case of polymer films on electrodes, peak

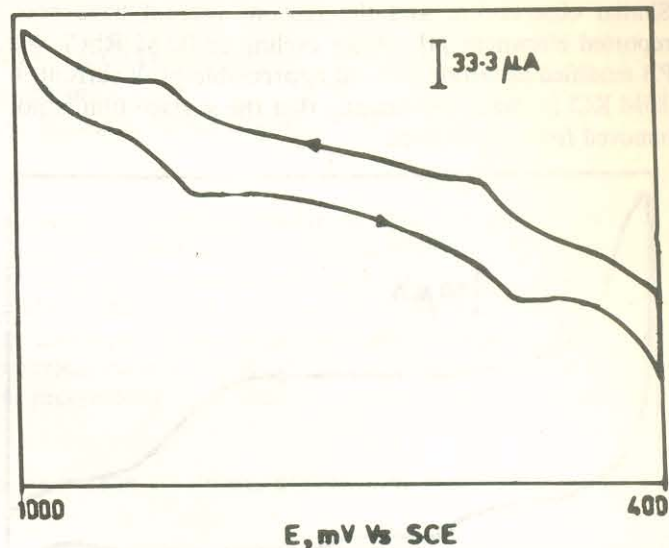


Fig. 3: Cyclic voltammetric response of Pb modified electrode in 0.5M LiCl. Scan rate 50 mV/s

broadening is proposed [6] to occur either due to repulsive interactions or, if all the redox sites in the film are not characterised by the same value of  $E^\circ$ . However, in the case of ammonium ions no peak splitting was observed. The redox wave (I) shifts more anodically ( $\Delta E_p = 100mV$ ) and wave II occurred at 200mV less anodic when compared to the response in KCl medium. The response of the electrode can be reverted back to the original KCl response after treatment in  $NH_4Cl$  by cycling the electrode again in 0.5M KCl. This clearly shows that PB film has got strong attractive interactions for potassium ions selectively.

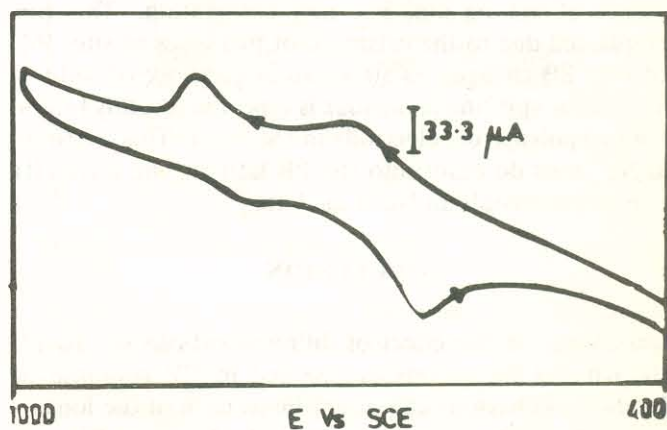


Fig. 4: Cyclic voltammetric response of Pb modified field electrode in 0.5 M  $NH_4Cl$ . Scan rate 50 mV/s

#### Effect of rubidium ions

In the case of 0.5M RbCl, no well defined peak currents for both redox centres were observed as seen from Fig. 5.



Similar observations and the reasons thereof have been reported elsewhere [4]. After cycling in 0.5M RbCl, the PB modified electrode showed appreciable peak current in 0.5M KCl for wave I indicating that the surface film is not removed from the surface.

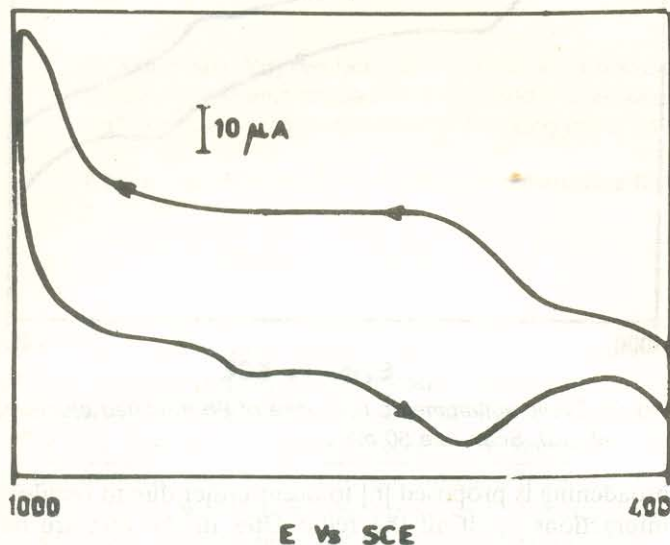


Fig. 5: Cyclic voltammetric response of Pb modified electrode in 0.5M RbCl. Scan rate 50 mV/s

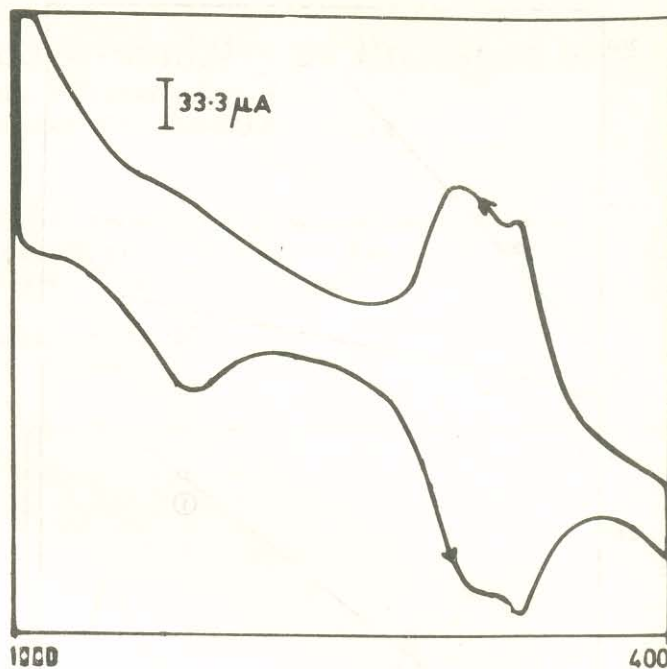


Fig. 6: Cyclic voltammetric response of Pb modified electrode in 0.5M NaCl. Scan rate 50 mV/s

### Effect of sodium ions

In the case of 0.5M NaCl the peak corresponding to PB splits into two resulting in shoulders on the waves as represented in Fig. 6. This type of peak splitting in the presence of sodium ions is a new observation. This can be explained due to the existence of two types of sites [6]. Probably, PB changes its structure in presence of sodium ions. Similar splitting behaviour is reported recently [4] for PB doped polypyrrole electrode in 1M NaCl. This confirms that  $\text{Na}^+$  ions do enter into the PB lattice. The wave (II) becomes irreversible in NaCl medium.

### CONCLUSION

Observations on the effect of different cations viz. K, Li,  $\text{NH}_4$ , Rb and Na cations as revealed in CV response of PB indicate behaviour characteristic to each of the ions in terms of its ability to enter or block the lattice of PB.

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