

Short communication

# A new electrode consisting of Prussian blue/Dibenzo-18-crown-6 ion-pair complex for electrochemical capacitor applications

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## Abstract

A new electrode consisting of iron(III) hexacyanoferrate(II) known as Prussian blue and Dibenzo-18-crown-6 macrocycle ion-pair complex formed in presence of chloroform was studied for its electrochemical behavior in 0.1 M KCl solutions. The ion-pair complex exhibited cyclic voltammetric response combining the Faradic redox characteristics of Prussian blue and the non-Faradic capacitance behavior of crown ether. Pseudo-capacitance values from the cyclic voltammetric measurements of the ion-pair complex showed a nine-fold increase as against the crown ether and a 1.5 times increase compared to Prussian blue. The ion-pair complex was chemically and electrochemically stable up to the cycled 1000 runs. Double potential step chronocoulometric measurements done at the lowest time scale of 10 s showed specific capacitance value of  $28.95 \times 10^3 \text{ F g}^{-1}$  for the reduction step and  $52.92 \times 10^3 \text{ F g}^{-1}$  for the oxidation step. Such pseudo-capacitive values are the requisite of electrochemical capacitors that can provide huge power pulse within a very short time.

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**Keywords:** New electrode; Prussian blue/crown ether ion-pair complex; Pseudo-capacitance; Electrochemical capacitors

## 1. Introduction

The need to identify new materials to be used as electrochemical capacitor (EC) electrodes has increased in recent times as the beneficial role of ECs in combining the energy storage capability of a battery and power storage behavior of normal capacitor has been recognized. The ideal applications for ECs are all those demanding energy for duration in the time range  $10^{-2}$  to  $10^2$  s. No phase changes are involved in the electrochemical processes of ECs and therefore they can be charged and discharged many times [1]. One such compound which has electrochemical stability over  $10^7$  cycles on a  $\text{SnO}_2$  electrode and  $10^5$  cycles on a ITO electrode and whose redox reactions are chemically reversible with no chemical and structural changes is iron(III) hexacyanoferrate or Prussian blue (PB). It has the molecular formula  $\{\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\}$  and it is a well-known inorganic blue colored pigment stable in acid and neutral solutions. It is a non-toxic compound having zeolitic channels and known to intercalate cations in its lat-

tice for charge compensation. It has been widely investigated in view of its applications in electrochromic displays, electrocatalysis, ion-selective electrodes and solid state reversible batteries [2].

In the present work, the most striking characteristic of crown compounds to form stable complexes with inorganic compounds was exploited. After the discovery of crown ethers by Pedersen [3], these macrocyclic systems have been extensively studied during the last three decades as complexing agents for alkali and alkaline earth metal ions. Researchers continue in their efforts to understand why inorganic salts dissolve in organic solvents in the presence of crown ether. Though the mechanism behind this observation is not yet clarified, nevertheless it has been proved that the ion-dipole interaction between the crown ether and the cation of the inorganic moieties was responsible for the stability of the complex. In a very recent work, it was proved that  $\text{K}^+$  interacts strongly with Dibenzo-30-crown-10 (DB30C10) in the presence of picrate as a counter ion, leading to a high value ( $2.9 \times 10^6$ ) of the extraction equilibrium constant. The crystal structure of  $[\text{K-DB30C10}][\text{picrate}]$  reported provides evidence of strong ion-pair interactions. The crystal structure of  $[\text{K-DB30C10}][\text{picrate}]$  shows evidence of such interactions ( $\text{C-H}\cdots\pi$ ,  $\pi\cdots\pi$  and  $\text{C-H}\cdots\text{O}$ ) between  $[\text{K-DB30C10}]^+$  and

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the counter ion [4]. Ferrocene-based multiple-decker sandwich complexes with lithium ion as counter cation and it was found that the lithium ions are coordinated by solvent molecules (THF), the pyrazolyl side-arm, cyclopentadienyl ring and the crown ether [5]. Earlier works on the electrochemical behavior of crown ether are rather limited though the remarkable complexing ability of crown ether with alkali metal cations enables them to be used in isotope separation, analysis and ion-selective electrodes [6]. Solid-state light-emitting devices have been fabricated from blends of lithium salt/18-crown-6 ether complex with a ruthenium(II) binuclear complex containing 1,6-bis[4-(4'-methyl-2,2'-bipyridyl)]hexane and regular 2,2'-bipyridine ligands and the role of Li/crown ether complexes is of solid electrolyte to increase ionic conductivity [7]. A new supported liquid membranes (SLM) system containing different crown ethers dissolved in a mixture of chloroform/ethanol immobilized in a thin polypropylene film for the transport of silver and copper as complex cyanide anions has been reported [8]. The application of KI complex with 18-crown-6 (18-C-6) macrocycle in dye sensitized solar cells was investigated by cyclic voltammetry and electrochemical impedance spectroscopy [9].

Unlike iron oxide whose complex with this crown ether was soluble in aqueous solutions, the ion-pair of Prussian blue with Dibenzo-18-crown-6 (designated as DB18C6) was highly stable in aqueous solutions. In this communication, the PB/DB18C6 ion-pair complex formed in presence of chloroform is electrochemically investigated for its use as electrode in super capacitor applications.

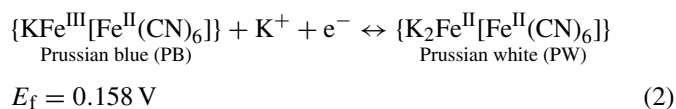
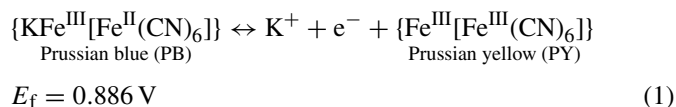
## 2. Experimental

A three electrode cell assembly consisting of PB/DB18C6 ion-pair complex immobilized on paraffin impregnated graphite electrodes (PIGE) as working electrode, a platinum foil as counter electrode and Ag/AgCl (3 M KCl) electrode as reference electrode was used. 0.1 M KCl solution was used as electrolyte for all the galvanostatic and potentiostatic control of the experiments. The Paraffin impregnated graphite electrodes were made by impregnating graphite rods with melted paraffin (mp 65 °C) under vacuum. All electrochemical experiments were conducted with a PGSTAT 30 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES software. GPES software was used for all electrochemical data analysis. The working electrode was PB/DB18C6/PIGE prepared as described in earlier works [10].

Prussian blue was prepared chemically, by the well established procedure of mixing equimolar (1.0 mM) solutions of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and 0.1 M KCl for precipitation and the final blue colored pigment was filtered, washed thoroughly and dried in a hot air oven. Dibenzo-18-crown-6 (DB18C6) was used as received from Merck, Germany. To a mixture of DB18C6 and PB (1:1) placed on a clean glass plate, few drops of chloroform were added and mixed thoroughly to make a paste. After a few seconds, the solvent evaporates leaving behind a PB/DB18C6 ion-pair complex.

## 3. Results and discussion

Fig. 1 shows the cyclic voltammograms of blank PIGE (curve A), pure Prussian blue (curve B), DB18C6 (curve C) and PB/DB18C6 (curve D) immobilized on PIGE. Prussian blue undergoes two consecutive redox transitions as denoted by the peaks I–IV in curve B. In the forward anodic scan, peak I appears due to the oxidation of PW to PB and subsequent oxidation of PB to PY is represented by peak II. In the reverse reduction scan, peak III denotes the reduction of PY to PB and peak IV appears due to further reduction of PB to PW. The electrochemical reversible reactions can be written as [11]:



Curve C shows the electrochemical response of DB18C6 macrocycle which was purely capacitive and the CV response was found to be stable for 500 cycles. DB18C6 with its oxygen atoms consisting of lone pair of electrons would interact electrostatically with potassium ions from the solutions forming a layer at the interface. The most interesting cyclic voltammetric response was given by PB/DB18C6 ion-pair complex as shown in curve D. The cyclic voltammogram reflects both salient features of PB and DB18C6 though the peaks were broadened and the peak potentials shifted towards positive direction in the oxidation scan and towards negative direction in the reduction scan, tending to decrease the reversibility of the redox reactions. The peak potentials of PB from curve B were: peak I, 0.24 V; peak II, 0.979 V; peak III, 0.794 V; peak IV, 0.078 V, and those of PB/DB18C6 ion-pair complex from curve D were: peak I, 0.335 V; peak II, 1.078 V; peak III, 0.753 V; peak IV, -0.065 V.

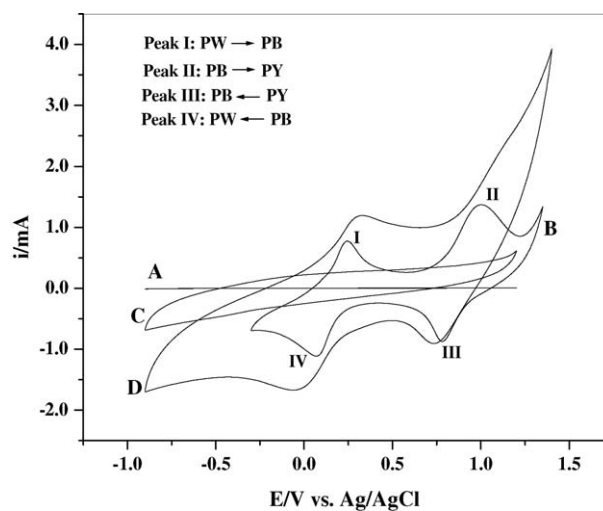
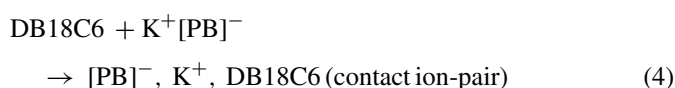
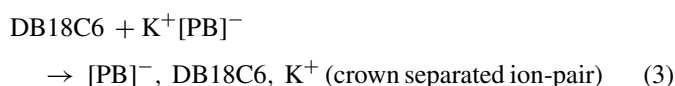


Fig. 1. Cyclic voltammograms of blank PIGE (curve A); Prussian blue (curve B); DB18C6 (curve C); PB/DB18C6 (curve D) recorded in 0.1 M KCl solution at the scan rate of  $20 \text{ mV s}^{-1}$ .

The similarity in the shape of the cyclic voltammograms indicates that the redox characteristics did not get affected by the formation of ion pair with crown ether via ion–dipole interaction but the broadened peaks indicate a diffusion limitation imposed to the potassium ion movements by the presence of crown ether. It was reported that from the entropic point of view alone, the cation–crown ether formation is unfavorable, but the entropic loss arising from the cation–crown ether association is often compensated by the gain from the extensive desolvation of cation and ligand. Under such circumstances, the complexation of cation with crown ether, which is essentially a molecular association process, is driven mainly through the ion–dipole interaction, although accompanying extensive desolving, giving the larger enthalpy changes and highly negative entropy values [12]. The PB–K<sup>+</sup>–(DB18C6) combination in chloroform would be accompanied by entropic loss from the structural freezing of the resulting complex and unfavorable desolvation, but it is compensated by the enthalpic changes increased through the interaction among PB, crown, cation and solvent molecules.

The nature of ion pair to be formed also depends on the concentration of crown ether. If it is low, it forms a complex with contact pair at the outside of the ion pair, tending to separate the ion pair; when the crown concentration is higher, a 2:1 complex (PB<sup>-</sup>, DB18C6, K<sup>+</sup>, DB18C6) of crown separated ion pair is formed by co-ordination of one more molecule of crown. In the case of equal concentrations, 1:1 complex and crown separated ion pair as shown in Eq. (3) were formed. Such a formation has been established in earlier works and proved in the case of ferrocene/crown complexes [5,13].



Since in the present study, equal weights of DB18C6 and PB were taken, the crown separated ion-pair was the most plausible permutation to be considered and in such a situation, the crown ether molecule is sandwiched between the potassium ion and Prussian blue.

It could be shown that the ion-pair formation would not occur in the absence of chloroform by the cyclic voltammetric responses shown in Fig. 2. Curve 'a' was that of pure PB, curve 'b' was that of homogeneous mixture of PB and DB18C6 while curve 'c' was that of bilayered one, i.e. the electrode could be depicted as: PIGE/PB/DB18C6. It was clear from these CVs that curve 'b' reflects the electrochemical behavior of PB rather than crown ether and the dominant double layer capacitance of crown ether was not evident. This was an indirect proof for the lack of ion-pair formation. In curve 'c' where the crown ether was preferably exposed to the KCl solution, the peak currents decreased considerably, though the peak positions remained intact; the response indicates that the DB18C6 sterically hinders the ionic diffusion to and from the PB and the solutions, thereby reducing the peaks currents. This observation was consistent with an earlier work [14]; the nature of the current–potential

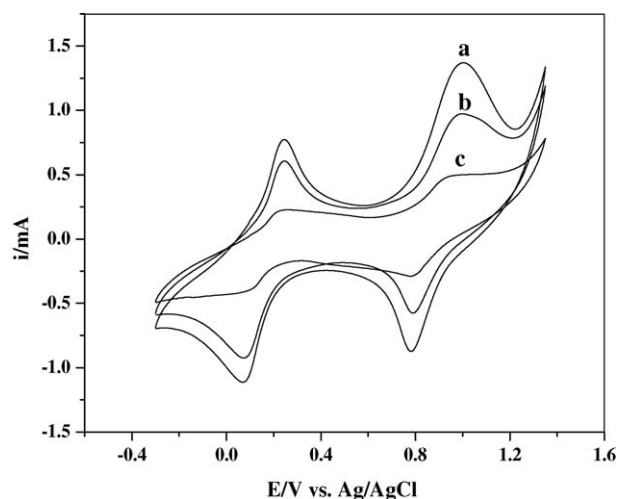


Fig. 2. Cyclic voltammograms of pure PB (curve a); homogeneous mixture of PB and DB18C6 (curve b); bilayered electrode—PIGE/PB/DB18C6 (curve c) recorded in 0.1 M KCl solution at the scan rate of 20 mV s<sup>-1</sup>.

responses was shown to be strongly dependent on the system's degree of hydration, the related potassium mobility and the possibility of coupling electron transfer with the K<sup>+</sup> counter ion transport. Transport of K<sup>+</sup> ion was the rate limiting factor. The ohmic effects may also appear in the hydrated systems, owing to migration, when the population or mobility of structural K<sup>+</sup> ions is decreased.

Table 1 shows the specific capacitance values evaluated from the CVs of PB, DB18C6 and PB/DB18C6 ion-pair complex. Capacitance is expressed as,

$$C = \frac{dq}{dE} \quad \text{or} \quad C = I \frac{dt}{dE} \quad (5)$$

For the calculation of specific capacitance (F g<sup>-1</sup>) from CV measurements, the average anodic ( $Q_a$ ) and cathodic ( $Q_c$ ) capacitances were calculated from the following expression:

$$C = \frac{i \text{ (A)} \times t \text{ (s)}}{w \text{ (g)} \times \Delta E \text{ (V)}} \quad (6)$$

where all the terms have the usual meaning. The difference in weight of the PIGE before and after immobilization gives the mass ( $w$ ) taken. The capacitive current for both anodic and cathodic scans was obtained from the CVs of slow scan rate (20 mV s<sup>-1</sup>). Since in the technique of cyclic voltammetry, there is a linear change of potential with time, this being excitation signal, the potential axis simultaneously represents a linear time axis. On integration of the current over time between two potential limits, the charge value, i.e. the numerator of the above

Table 1  
Specific capacitances evaluated from the cyclic voltammograms showed in Fig. 1

Electrode	Specific capacitance (F g <sup>-1</sup> )	
	Anodic scan	Cathodic scan
DB18C6	2.08	2.24
PB	12.27	10.31
PB/DB18C6	17.51	16.62

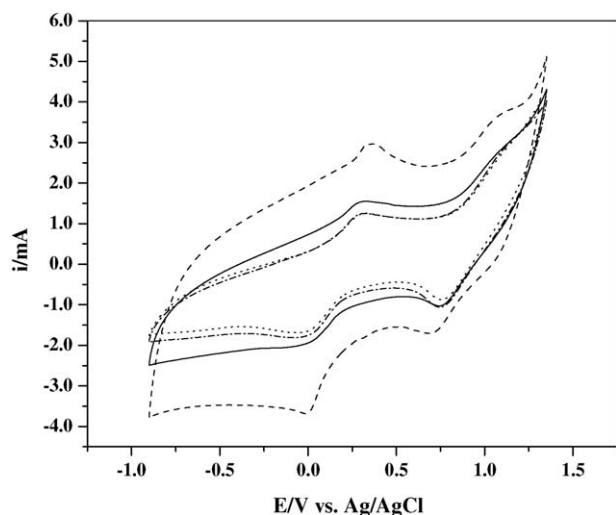


Fig. 3. Cyclic voltammograms of PB/DB18C6 ion-pair complex immobilized on PIGE electrode in 0.1 M KCl solutions; scan rate  $20 \text{ mV s}^{-1}$ ; progressive cycle recorded; ( $\cdots$ ) 1st cycle; ( $-\cdot-\cdot-$ ) 10th cycle; ( $\longrightarrow$ ) 100th cycle; ( $- - -$ ) 1000th cycle.

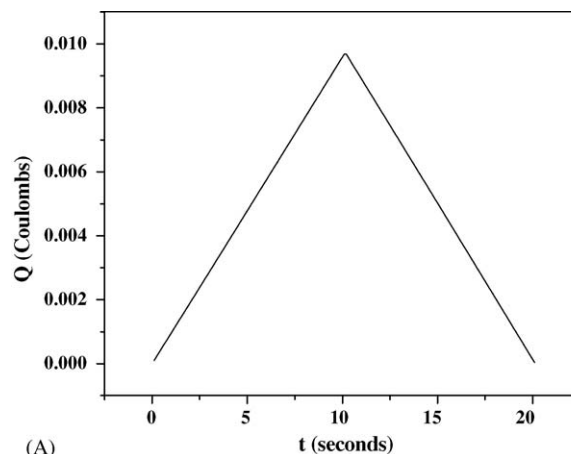
equation, can be evaluated. In this case, the capacitance values calculated include both Faradic and non-Faradic components and hence become the pseudo-capacitance as in the case of transition metal oxides. Fig. 3 shows the cyclic voltammograms recorded for the continuous 1000 cycles and Table 2 presents the specific capacitance values.

The increase in charges under the CV curves for the ion-pair complex could be due to the difference in electron transfer mechanism; analogous to electrodes covered by organic molecules, here, the electron can be transferred from the iron centers of PB to the potassium cation located outside a compact layer of the crown ether as a result of an elastic tunneling transition [15]. Also, an increase in potassium ion conductivity by the presence of space charge layer due to crown ether and PB is also a pointer to increase of charges. From conductivity measurements, it is well known that the conductivity of a KCl solution increases in the presence of dicyclohexyl-18-crown-6 due to complex formation [3].

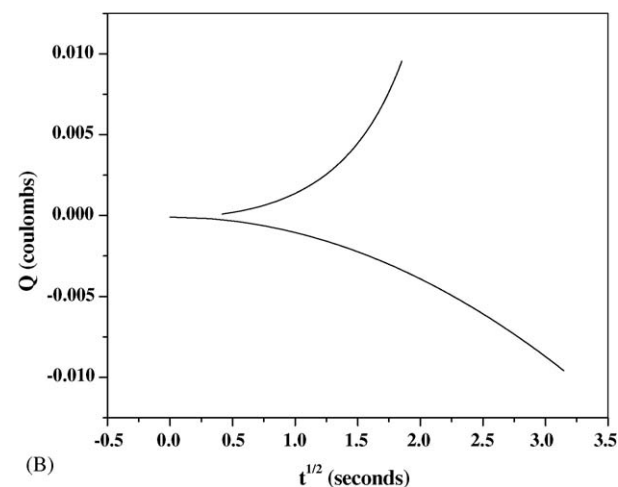
Fig. 4 shows the double potential step chronocouloumograms and the derived Anson plots obtained by stepping the potentials from 1.2 to  $-0.9 \text{ V}$  in the forward step and  $-0.9$  to  $1.2 \text{ V}$  in the reverse step. Chronocoulometry is a controlled potential technique, where the electrochemical response is to integrate the current, so that the charge passed as a function of time,  $Q(t)$ , is obtained. Double potential step chronocoulometry and chronoamperometry are two powerful techniques for the study

Table 2  
Specific capacitances evaluated from the cyclic voltammograms (Fig. 3) of PB/DB18C6

Cycle number	Specific capacitance ( $\text{F g}^{-1}$ )	
	Anodic scan	Cathodic scan
1	7.98	6.16
100	10.14	9.88
1000	19.29	18.88



(A)



(B)

Fig. 4. Double potential step chronocouloumograms of PB/DB18C6 ion-pair complex immobilized on PIGE electrode in 0.1 M KCl solutions at the time scale of 10 s (A) and derived Anson plot (B).

of chemical reactions following the electrode reaction, reactant and product adsorption. A major reason, characteristic of the methods, is that the Faradaic and charging currents are easily separated. The total forward chronocoulometric response in either step can be described by the integrated Cottrell equation [16],

$$Q = Q_d + Q_{dl} + nFAG\Gamma \quad (7)$$

$$Q_d = \frac{2nFACD^{1/2}t^{1/2}}{\pi^{1/2}} \quad (8)$$

All the terms in the equations have usual meaning. The linearization of the chronocoulometric response can be done (Anson plot) and the slope of the  $Q$  versus  $t^{1/2}$  plot gives  $Q_d$  (diffusional component) while the intercept is  $Q_{dl} + nFAG\Gamma$  (interfacial component).

Table 3 presents the parameters derived for different time scales of the potential step experiment. In the recorded 10–50 s time scale, the charge due to Faradic component was much higher than that of double layer component. It was clear that time plays a crucial role as seen by the increase in  $Q_{dl}$  and subsequent decrease in  $Q_d$  with increase in time. As one considers the time scale of a CV scan ( $\approx 100 \text{ s}$  at  $20 \text{ mV s}^{-1}$ ), the values from both

Table 3

Parameters derived from the Anson plot of the double potential step chronocoulomograms conducted at different time scales

Time (s)	Forward reduction step, +1.2 to -0.9 V		Net specific cathodic capacitance ( $\times 10^3 \text{ F g}^{-1}$ )	Reverse oxidation step, -0.9 to +1.2 V		Net specific anodic capacitance ( $\times 10^3 \text{ F g}^{-1}$ )
	$Q_d/C$	$Q_{dl}/C \times 10^{-2}$		$Q_d/C$	$Q_{dl}/C \times 10^{-3}$	
10	151.9	0.497	28.95	275.0	2.877	52.92
20	91.05	1.312	17.59	204.6	5.246	39.97
30	86.84	1.440	16.82	159.0	8.760	31.95
40	70.78	2.206	13.9	125.7	14.02	26.6
50	41.19	6.291	9.05	91.6	26.75	22.54

techniques were comparable. The charges were the highest at the lowest time scale. The specific capacitances were calculated using the above equation for cyclic voltammetric experiments. The numerator values were given by the software while the other factors remained the same.

#### 4. Conclusions

A new electrode consisting of Prussian blue/DB18C6 ion-pair complex was recognized and its electrochemical behavior in aqueous solutions was noted to reflect both the characteristics of Prussian blue and Dibenzo-18-crown-6. The chemical and electrochemical stability up to the cycled 1000 times was highly significant in view of super capacitor applications. The pseudo-capacitance values were very attractive, especially at very short times, making the electrode highly useful for applications that need high power pulses in the order of microseconds. The simplicity of the route by which the ion-pair complex could be prepared makes it hugely desirable for fabrication. Currently, this method is used in our laboratory, in combination with cholesterol to develop cholesterol sensors.

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