



# Estimation of continuity of electroactive inorganic films based on apparent anti-Ohmic trend in their charge transfer resistance



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## ABSTRACT

We report on the microscopy-free, pure electrochemical approach for estimation of the continuity of electroactive inorganic films. Impedance spectra of the transition metal hexacyanoferrate films, electrochemically deposited under the optimized conditions, have been fitted to the Randles-type equivalent circuit, complicated by diffusion impedance with reflective boundary conditions, connected in series to the charge transfer resistance. An apparent anti-Ohmic trend is revealed in the sharp decrease of the latter with an increase in amount of the deposited inorganic film commonly presuming its thickness. Assigning charge transfer resistance to the resistance of the electrode|film interface, its observed decrease with subsequent saturation is explained in terms of an increase of the interface area until the entire electrode is covered with the inorganic film completely. Scanning electron microscopy (SEM) confirms the “anti-Ohmic” and saturation regions correspond to the partially covered and fully covered electrode surfaces, respectively. The dependence of charge transfer resistance on the amount of the deposited film thus provides an estimation of the continuity of inorganic films, which is highly important in a view of their practical applications. Except for cost efficiency, microscopy-free tools are attractive because in some cases, for instance for recessed electrodes, microscopy is hardly applicable.

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## 1. Introduction

Electroactive inorganic films immediately after discovery electroactivity of Prussian Blue [1–3] attracted a specific attention due to their unique properties. Among them transition metal hexacyanoferrates have already found wide use in analytical applications [4]. Of particular interest Prussian Blue is thought to be advanced electrocatalyst for hydrogen peroxide reduction: in neutral aqueous media, favorable for applications in life science as well as for biosensors, Prussian Blue is three orders of magnitude more active (in terms of 1000 times higher electrochemical rate constant) providing three orders of magnitude improved sensitivity of the corresponding sensors, and three orders of magnitude more selective compared to the commonly used platinum [4]. Nano-structuring the electrocatalyst onto an inert electrode supports results in elaboration of the electrochemical sensor with outstanding performance characteristics [5,6]. Despite non-iron

transition metal hexacyanoferrates being silent in the electrocatalysis of  $\text{H}_2\text{O}_2$  reduction [7], they serve as excellent matrixes for stabilization of Prussian Blue providing “super-stable” sensors [8].

Wide practical applications of transition metal hexacyanoferrates initiated an interest to study their fundamental properties, particularly charge transfer peculiarities. Prussian Blue is true redox film displaying at its redox potential (i) the highest conductance in terms of both maximum conductivity and the largest electron diffusion coefficient [9], (ii) the lowest charge transfer resistance at the electrode–film interface [10], as well as (iii) the maximum capacitance [11]. The latter was proposed to estimate the thickness of Prussian Blue film [12]. Impedance investigations were carried out also for cupric [13], cobalt [14] and nickel [15] hexacyanoferrates. We note that, transition metal hexacyanoferrates used in certain impedance studies [10,13,15,16] were, according to their cyclic voltammograms, of non-regular structure or even poor quality.

Accordingly, initial objective of the present study was to investigate charge transfer properties of electroactive inorganic films, synthesized under optimal conditions achieving their regular structure with the highest catalytic activity and/or stability.

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Indeed, in contrast to previous studies on charge transfer resistance reporting its independence of the amount of Prussian Blue deposited [10,16], we've found its sharp decrease with an increase in amount of inorganic film. We've found that the discovered apparent anti-Ohmic trend in charge transfer resistance with its subsequent saturation correlates with continuity of inorganic films thus providing a microscope-free approach for estimation of the latter.

## 2. Experimental

### 2.1. Materials

Experiments were carried out with Millipore Milli-Q water (resistivity 18.2 M $\Omega$  cm at a room temperature). Inorganic salts (FeCl<sub>3</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O and K<sub>3</sub>[Fe(CN)<sub>6</sub>]) were obtained at the highest purity from Reachim (Russia) and used as received. Glassy carbon disk electrodes (SU-2500, 2.0 mm in diameter) pressed in Teflon were used as working electrodes. Prior to use, the working electrodes were mechanically polished in a water suspension of alumina (Sigma-Aldrich) first with the particle size of 0.3  $\mu$ m up to a mirror finish observed, then with the particle size of 0.05  $\mu$ m until a stable voltammograms with minimum capacitance obtained.

### 2.2. Instrumentation

Deposition of transition metal hexacyanoferrates, as well as their characterization by cyclic voltammetry, was carried out in a three-compartment electrochemical cell with Ag|AgCl |1 M KCl reference. PalmSens potentiostat/galvanostat (PalmSens Instruments BV, Netherlands) interfaced to PC was used.

Impedance spectra were recorded with Solartron 1255 frequency response analyzer (Solartron, UK). Impedance measurements were carried out in electrochemical cell with the common space of working and platinum cylinder auxiliary electrode, the latter encircling working electrode, and Ag|AgCl |1 M KCl reference, connected through Luggin capillary.

Scanning electron microscope Carl Zeiss NVision 40 (Carl Zeiss, Germany) was used to observe the surface morphology.

### 2.3. Methods

Electrodeposition of Prussian Blue was carried out by cycling the applied potential from 0.4 V to 0.75 V at a sweep rate of 0.02 V s<sup>-1</sup> during from 1 to 4 cycles. The growing solution contained 4 mM of K<sub>3</sub>[Fe(CN)<sub>6</sub>], 4 mM FeCl<sub>3</sub>·6H<sub>2</sub>O and 0.1 M KCl in 0.1 M HCl [5]. For deposition of Ni hexacyanoferrate the solution containing 0.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>], 1 mM NiCl<sub>2</sub>·6H<sub>2</sub>O and 0.5 M KCl in 0.1 M HCl was used. Solution pH of 0.1 M KCl with 0.1 M HCl supporting electrolyte was approximately 1.2. The deposition was carried out by cycling the applied potential from 0.0 V to 0.75 V at a sweep rate of 0.1 V s<sup>-1</sup> during from 1 to 15 cycles [8]. After deposition the transition metals hexacyanoferrate films were activated electrochemically by cycling in the background electrolyte until a stable voltammogram was obtained and then annealed at 100 °C during 1 h to improve operational stability removing weakly bounded water.

An amount of the deposited Prussian Blue was calculated integrating current peaks in cyclic voltammograms and assuming a transfer of 4 electrons per unit cell [17].

Impedance spectra were recorded at a room temperature applying sine-wave voltage amplitude of 5 mV at the redox potential of transition metal hexacyanoferrate found from its cyclic voltammograms in the same solution.

All experiments were carried out in air saturated solutions. Current values were recalculated to geometric electrode area.

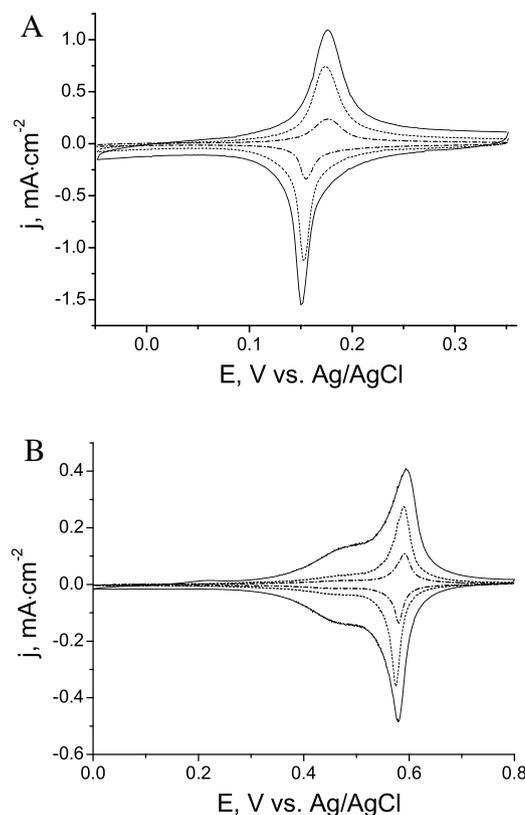
The micrographs were recorded with the scanning electron microscope operating at 7.00 kV accelerating voltage and from 4.6 to 5.1 mm working distance with InLens detector. The specimens were coated with 2 nm chromium film.

## 3. Results and discussion

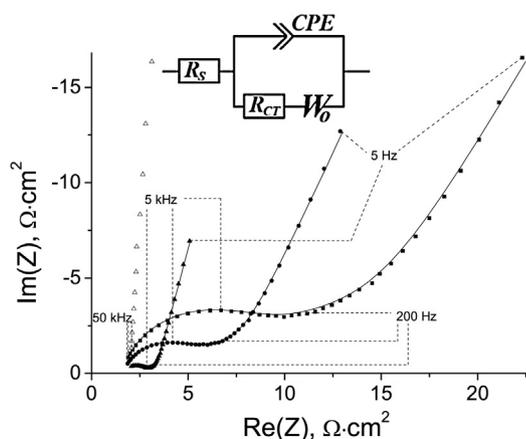
Since, as mentioned, a significant part of impedance studies was carried out with irregular or even poor quality transition metal hexacyanoferrate films, special attention has been paid to deposit them under the optimized conditions [4,5,8]. Fig. 1 a displays cyclic voltammograms of Prussian Blue modified electrodes in the supporting electrolyte. Sharp current peaks with separation less than 30 mV point to regular structure of inorganic film; the conclusion is made on the basis of spectroelectrochemical investigations carried out already 35 years ago [2]. Similar conclusion can be made for the deposited Nickel hexacyanoferrate from its cyclic voltammograms shown in Fig. 1 b.

Impedance spectra of Prussian Blue modified electrodes recorded at different dc potentials have shown that the lowest impedance values are recorded at the Prussian Blue|Prussian White redox potential confirming its property as a true redox film (above). All subsequent impedance spectra have been taken at the film redox potential.

Fig. 2 displays impedance spectra of Prussian Blue modified electrodes with different amount of inorganic film. As seen, the impedance spectra are successfully fitted to the simplest equivalent circuit valid for conducting polymers (Fig. 2, inset) [18]. Here R<sub>s</sub> is solution resistance, R<sub>ct</sub> is charge transfer resistance, CPE



**Fig. 1.** Cyclic voltammograms of (a) Prussian Blue: 0.90 nmol cm<sup>-2</sup> (dash-dot line), 2.45 nmol cm<sup>-2</sup> (short dash line), 4.05 nmol cm<sup>-2</sup> (solid line) and (b) nickel hexacyanoferrate: 0.40 nmol cm<sup>-2</sup> (dash-dot line), 1.15 nmol cm<sup>-2</sup> (short dash line), 4.10 nmol cm<sup>-2</sup> (solid line); in 0.1 M KCl and 0.1 M HCl, sweep rate 40 mV s<sup>-1</sup>.

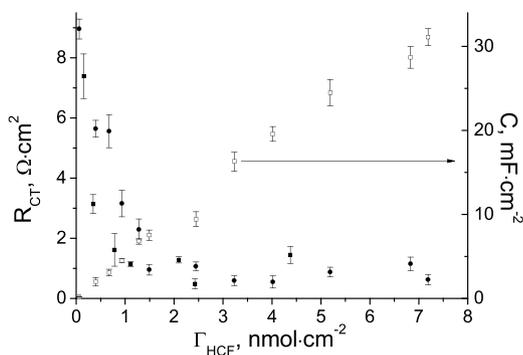


**Fig. 2.** Impedance spectra in Nyquist's plots of blank ( $\Delta$ ) and Prussian Blue modified electrodes:  $0.70 \text{ nmol cm}^{-2}$  ( $\blacksquare$ ),  $0.95 \text{ nmol cm}^{-2}$  ( $\bullet$ ),  $1.30 \text{ nmol cm}^{-2}$  ( $\blacktriangle$ );  $0.1 \text{ M KCl}$  in  $0.1 \text{ M HCl}$ ,  $\Delta E = 5 \text{ mV}$ ,  $E_{DC} = 155 \text{ mV}$  vs.  $\text{Ag|AgCl|1 M KCl}$  (Prussian Blue|Prussian White redox potential). Solid lines represent fitting to the equivalent circuit shown in the inset.

reflects double layer and film capacitance,  $W_0$  is the diffusion impedance with reflective boundary conditions [19]. Variation of the exponent in  $W_0$  is possible for fitting of real conductive polymer spectra [18].

As seen in Fig. 2, fitting lines perfectly match the experimental data confirming the chosen equivalent circuit is valid for impedance spectra of transition metal hexacyanoferrates. The use of CPE instead of pure capacitance is possible due to distribution in film thickness caused by the polycrystalline nature of Prussian Blue films noticed from their AFM pictures [6]. Fractional exponent in CPE is approximately of 0.9 indicating the CPE behavior close to pure capacitance.

According to the equivalent circuit used (Fig. 2, inset) charge transfer resistance ( $R_{ct}$ ) can be evaluated from the diameter of the high frequency semicircle in Nyquist plots (Fig. 2). As seen, it is decreased with an increase in amount of the deposited Prussian Blue ( $\Gamma_{PB}$ ). The charge transfer resistance evaluated after fitting the experimental impedance spectra to the equivalent circuit used (Fig. 2, inset) is plotted as a function of  $\Gamma_{PB}$  in Fig. 3. Indeed, at vanishing  $\Gamma_{PB}$  charge transfer resistance is sharply decreased as amount of the deposited Prussian Blue is increased (Fig. 3). Similar dependence is observed for nickel hexacyanoferrate (Fig. 3). This can be referred to as an apparent anti-Ohmic trend since the amount of the deposited film usually presumes film thickness and an increase of the latter means an increase of a resistor length.



**Fig. 3.** Charge transfer resistance as a function of iron- ( $\bullet$ ) and nickel ( $\blacksquare$ ) hexacyanoferrate (HCF) amount electrodeposited; total Prussian Blue film capacitance calculated from a plot of the imaginary part of impedance vs.  $1/\omega$  in the low frequency range as the inverse of the slope ( $\square$ ). Error bars indicate the 95% confidence intervals based on the Student's T distribution.

As seen in Fig. 3, after the sharp decrease at low  $\Gamma_{PB}$  values charge transfer resistance reaches its limiting value and becomes independent of the hexacyanoferrate amount. The constant phase element (CPE), on the contrary, sharply increases with an increase in Prussian Blue amount and reaches its saturation in similar range of  $\Gamma_{PB}$  (Supplementary Information). However, the use of CPE instead of charge transfer resistance for further study is less convenient. As mentioned, its fractional exponent deviates from the unity due to polycrystalline nature of inorganic film. Accordingly, CPE is determined with much less precision compared to charge transfer resistance.

No monotonic evolution of exponents for both  $W_0$  and CPE with the amount of deposited Prussian Blue has been registered (Supplementary Information).

Since peak currents in Prussian Blue cyclic voltammograms are increased as the hexacyanoferrate amount is increased, it is essential to evaluate the total capacitance  $C$ . We note that the value of constant phase element (CPE) evaluated through fitting the impedance spectra is attributed to the capacitance of the electrode|film interface. To evaluate the total capacitance it is necessary to plot the imaginary part of the impedance against reciprocal angular velocity in the low frequency range [10]. The total film capacitance is expected to reflect film electroactivity. Indeed, as seen in Fig. 3, the total Prussian Blue film capacitance evaluated from its impedance spectra is gradually increased with the raise of  $\Gamma_{PB}$ .

The apparent anti-Ohmic trend in charge transfer resistance of inorganic films can be explained as follows. Such films are known to grow forming nucleation centers which expand afterwards occupying the entire electrode area. Accordingly, at low amount of the inorganic film deposited, the electrode is only partially covered with the film. Hence, if the charge transfer resistance is attributed to the electrode|film interface, its behavior in Fig. 3 matches the Ohm's law. Indeed, when the electrode is only partially covered, the area of the electrode|film interface is increased as the amount of the deposited inorganic film is increased. An increase of the interface area obviously causes the decrease of the total resistance. After the film covers the entire electrode completely the resistance of the electrode|film interface has to become independent of the amount of the deposited film, what is indeed observed experimentally (Fig. 3).

A confirmation that charge transfer resistance evaluated from impedance spectra of electroactive inorganic film, represents the degree of surface coverage has been found from the SEM images of the corresponding modified electrodes (Fig. 4). Whereas Fig. 4A represents blank electrode, Fig. 4B is taken for  $\Gamma_{PB} = 0.5 \text{ nmol cm}^{-2}$ , which corresponds to the area of the sharp decrease in  $R_{ct}$  (Fig. 3). As seen, in Fig. 4B electrode surface is only partially covered with Prussian Blue film. Fig. 4C displaying the almost completely covered surface, is taken at surface amount of  $1.1 \text{ nmol cm}^{-2}$ .

Surface coverage evaluated from SEM images as a function of the deposited amount of Prussian Blue is displayed in Fig. 5. Deviations from 100% at saturated hexacyanoferrate amounts are probably due to software constrains (recognizing inter-crystalline borders as uncovered surface). As seen, the degree of surface coverage is increased as the amount of the deposited Prussian Blue is increased, and the saturation region is reached at similar amounts of Prussian Blue as compared to the dependence of the charge transfer resistance (Fig. 3). Hence, the apparent anti-Ohmic trend in charge transfer resistance reaches its limiting saturation value when the inorganic film covers the entire electrode surface completely.

As seen in Fig. 4, the crystalline dimension of the film is below  $100 \text{ nm}$ . Since the film thickness is close to crystalline dimensions, the film can be referred to as nano-layer.

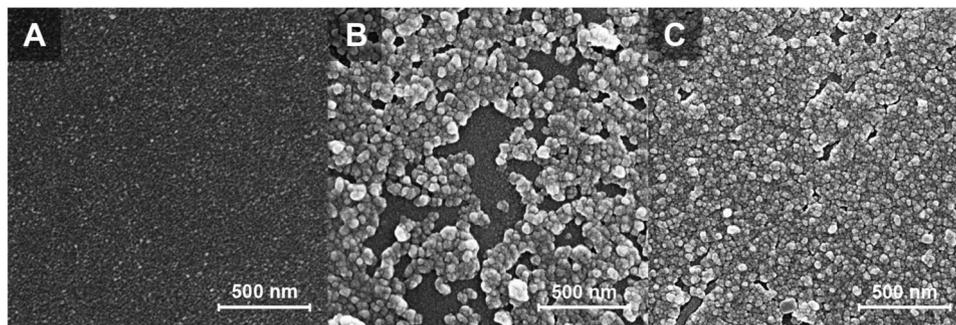


Fig. 4. SEM images of (A) 0 nmol cm<sup>-2</sup>, (B) 0.5 nmol cm<sup>-2</sup>, (C) 1.1 nmol cm<sup>-2</sup> Prussian Blue deposited.

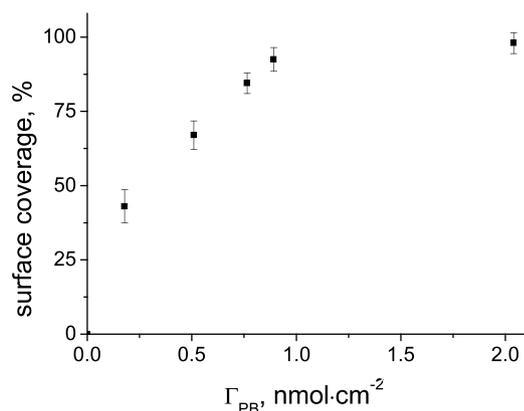


Fig. 5. Surface coverage evaluated from SEM images (software package ImageJ, version 1.48 v) as a function of the amount of Prussian Blue deposited.

Despite we've mostly discussed the properties of Prussian Blue (ferric hexacyanoferrate), similar behavior of charge transfer resistance is observed for nickel hexacyanoferrate (see, for example, Fig. 3). Hence, it is possible to extend the subject of our article to transition metal hexacyanoferrates or even to inorganic electroactive films.

#### 4. Conclusions

Morphology of inorganic films can significantly affect their applications. Particularly, the highest operational stability is usually observed for thin (with the thickness close to crystalline dimensions) films completely covered surface area. On the other hand, the deposition conditions depend not only on the electrode material, but also on its geometry. From this point of view it is hard to overestimate the microscopy-free pure electrochemical tool for the estimation of the continuity of inorganic electroactive films.

We show here that impedance investigation of transition metal hexacyanoferrate films provides an independent approach for evaluation of their continuity. Indeed, the apparent anti-Ohmic trend in charge transfer resistance reaches its limiting saturation value when the inorganic polycrystalline film covers the entire electrode surface completely. Except for cost effectivity, an avoiding microscopic investigations is important, because in some

cases, for instance, for recessed electrodes, microscopy tools are hardly applicable.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.09.145>.

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