

*Dedicated to the memory of
Professor Petru Spacu (1906–1995)*

IN-SITU COMBINED ELECTROCHEMICAL SURFACE PLASMON RESONANCE STUDY OF ULTRA-THIN PRUSSIAN BLUE FILMS DEPOSITED ON GOLD ELECTRODES

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This paper reports on the characterisation of ultra-thin Prussian Blue films using *in-situ* combined Electrochemical Surface Plasmon Resonance technique. Prussian Blue films were prepared, by potentiostatic method, on a gold-coated glass Surface Plasmon Resonance sensor. The electrochemical redox processes of Prussian Blue, *i.e.*, the reduction of Prussian Blue to Prussian White and the oxidation to Berlin Green, are accompanied by a change of the refractive index. The changes in the Surface Plasmon Resonance signal, during potential cycling on Prussian Blue films, are more pronounced for the Prussian Blue/Prussian White system than for the Prussian Blue/Berlin Green system. Due to the strong absorbance of Prussian Blue film in the sensing region of the instrument, only a qualitative characterization has been achieved. The *in-situ* combined Electrochemical Surface Plasmon Resonance technique is capable of evidencing minute changes of the oxidation state of the film and adsorption processes on electrode surface.

INTRODUCTION

The elaboration of new strategies for electrode surface modification in view of preparing new chemical sensors is a growing area. Over the last decades, many analytical techniques, such as electrochemical techniques, electrochemical impedance measurements, electrochemical quartz crystal microbalance,¹ and spectroelectrochemical techniques, have been used to investigate the electrochemical processes on which these devices are based. In recent years, Surface Plasmon Resonance (SPR)^{2, 3} has proved to be a highly sensitivity technique for characterizing ultra-thin films and for monitoring minute changes at the electrode | electrolyte solution interface.⁴⁻⁷ Among the different modifiers of the electrode surface, metal hexacyanoferrates have attracted much interest.^{8, 9} Prussian Blue (PB), *i.e.*, iron(III) hexacyanoferrate (II), layers deposited onto electrode surfaces are of interest because of their electrochromic, ion-exchange, ion-sensing and electrocatalytic properties.¹⁰⁻¹⁴ Furthermore, the electrochemical properties and electrocatalytic activity of new hybrid modifying layers containing PB is of high interest when considering bilayer electrode coatings.¹⁵⁻¹⁹

This paper presents the *in situ* monitoring of the redox behaviour of ultra-thin PB films using Electrochemical SPR (ESPR) technique. This new technique allows electrochemical and optical data to be simultaneously collected providing useful information on diffusion and adsorption/desorption processes on electrode surfaces and electrochemical doping/dedoping processes of electroactive layers. Ultra-thin PB films have been prepared on gold-coated glass sensors by the potentiostatic method. The thickness of the films was controlled by the amount of charge consumed during the deposition. The ESPR characterisation has been performed in aqueous media in order to check the stability of these ultra-thin films.

EXPERIMENTAL

All chemicals: FeCl₃ · 6H₂O (Carlo Erba, RPE), K₃[Fe(CN)₆] (Aldrich), KCl (Acros), toluidine blue (Merck), K₂SO₄ (Carlo Erba, RPE), and H₂SO₄ (Riedel de Hæn) were used as received. Doubly distilled water was always used to prepare aqueous solutions for electrochemical use.

The electrochemical experiments were carried out with an Autolab PGSTAT 12 potentiostat-function generator electrochemical instrument (Eco Chemie, Utrecht, The Netherlands). SPR measurements were performed with an Autolab SPR instrument, ESPRIT (Eco Chemie). The surface plasmon resonance effect is based on the interaction between electromagnetic waves of incident light and free electrons in a conducting surface layer.^{2,3} When light is reflected at the interface of two dielectric media, total internal reflection will take place above the so-called critical angle. At the same time, the light will generate an evanescent field.

This electromagnetic field has maximum intensity at the surface of the dielectricum. In case a metal layer is present in the evanescent field, the field can be enhanced and the free electrons on the outer surface (also called: surface plasmons) can resonate with the field. This is called surface plasmon resonance. In cases where this resonance effect takes place, light will be transferred to surface plasmon waves and one will thus see a decrease in the amount of reflected light. The angle at which this decrease takes place is called the resonance angle. Because the wave vector of light in air is always smaller than the wave vector in the noble metal surface, a prism is needed between the sample and air to make sure that the wave vectors in both media can be the same (Kretschmann configuration). The SPR effect is useful because any change in the dielectric constant or the refractive index, will result in a change in the resonance angle. In the Autolab ESPRIT instrument the reflection is measured as a function of the incident angle of the light beam. The incident angle is changed by using a vibrating mirror. The advantage of this system is that within a short time a broad range of incident angle can be measured. In the vibrating mirror set-up, the angular shift is measured for a non-coated gold sensor surface with a resolution of approximately 0.5 millidegrees, corresponding to a refractive index resolution of approximately 1×10^{-5} . For a coated gold sensor surface, the angular shift is measured with a resolution of approximately 1 millidegree.

The plot of the intensity of the reflected beam vs. the reflectance angle shows a minimum in correspondence of resonance conditions. The presence of a thin layer of adsorbed molecules on the surface of gold leads to a change in the resonance conditions; in particular, the position of the minimum depends on the thickness and on the optical properties, in particular on the refractive index and the dielectric constant, of the adsorbed species on the gold surface.

In the Autolab ESPRIT instrument the light source is a laser (670 nm) and the radiation is p-polarized; the light beam is focused on a thin layer of gold (*ca.* 50 nm) deposited on BK-7 glass by means of a thin layer of Ti (*ca.* 1.5 nm). The Ti layer improves the adhesion of Au film. The instrument can measure the intensity of the reflected light over reflectance angle or over time at a fixed angle. In the present article the results are expressed in terms of shift of the SPR resonance angle, at varying the electrode potential. The SPR resonance angle shift is measured in millidegrees (m°) and represented on the right ordinate axis.

The gold-coated glass surface SPR probe was the working electrode, a platinum ring was used as pseudo-reference electrode, and a platinum rod was the auxiliary electrode. Before each electrochemical test the surface of the working electrode was washed with ethanol (96%) and then allowed to dry at room temperature. Films were removed from the working electrode surface by dipping it into 3 M KOH solution, then washing it carefully with distilled water, acetone, and finally with ethanol (96%).

Deposition procedure of PB films

PB was deposited onto the electrode by potentiostatic method at a potential value of -0.20 V, from freshly prepared aqueous solution containing 1 mM FeCl₃, 1 mM K₃Fe(CN)₆, 0.08 M K₂SO₄, and 0.008 M H₂SO₄

The thickness (*d*) of the PB film was estimated using equation (1):

$$d = \frac{Q \cdot l^2 \cdot N_A}{4nFA} \quad (1)$$

where *Q* is the charge consumed for deposition, *l* the length of the PB unit cell, in centimeters ($l = 10.28 \cdot 10^{-8}$ cm), *N_A* the Avogadro's number, *n* the number of electrons (*n* = 1 in our case), *F* the Faraday's constant, and *A* the area of the SPR gold sensor surface coated with the PB film, in square centimeters (*A* = 0.071 cm² in this case).²⁰ The thickness of freshly deposited films was 4.3 nm. After deposition, the modified electrode was rinsed with fresh electrolyte solution flowing through the SPR cuvette. The characterisation of the films was performed in aqueous solutions containing 0.1 M K₂SO₄ and 0.01 M H₂SO₄ as supporting electrolytes.

RESULTS AND DISCUSSION

PB has been described by two formulations, *i.e.* the soluble form, KFe^{III}[Fe^{II}(CN)₆], and the insoluble form, *i.e.* Fe₄^{III}[Fe^{II}(CN)₆]₃. Both compounds are actually insoluble (*K_{sp}* = 10⁻⁴⁰) and the denomination soluble and insoluble refers to the ease of the peptisation of the potassium compound. It has been suggested that freshly deposited films are under the insoluble form and during the initial electrochemical cycling in K⁺-containing solutions a portion of the film is converted into the soluble one.^{21, 22} Furthermore, PB is converted into Prussian White (PW) by reduction to Fe^{II}-Fe^{II} system and oxidised to Berlin Green (BG), *i.e.*, to the corresponding Fe^{III}-Fe^{III} compound.

PB was deposited onto the gold-coated glass sensor by potentiostatic method from an aqueous solution containing 1×10^{-3} M K₃[Fe(CN)₆], 1×10^{-3} M FeCl₃, 0.08 M K₂SO₄, and 0.008 M H₂SO₄. After deposition, the modified electrode was rinsed with aqueous solution containing 0.1 M K₂SO₄ and 0.01 M H₂SO₄. Then, the modified electrode was characterised in an aqueous solution containing 0.1 M K₂SO₄ and 0.01 M H₂SO₄, at room temperature, by *in-situ* combined SPR and cyclic voltammetry. The electrode potential was first cycled between 0.20 and -0.30 V at different scan rates, in order to monitor the PB/PW redox system by cyclic voltammetry and by simultaneous recording of the SPR signal. All the potential scans, at any scan

rates, have started from the open circuit potential, where no current flows. Cyclic voltammograms and corresponding SPR resonance angle shift signals are presented in Fig. 1.

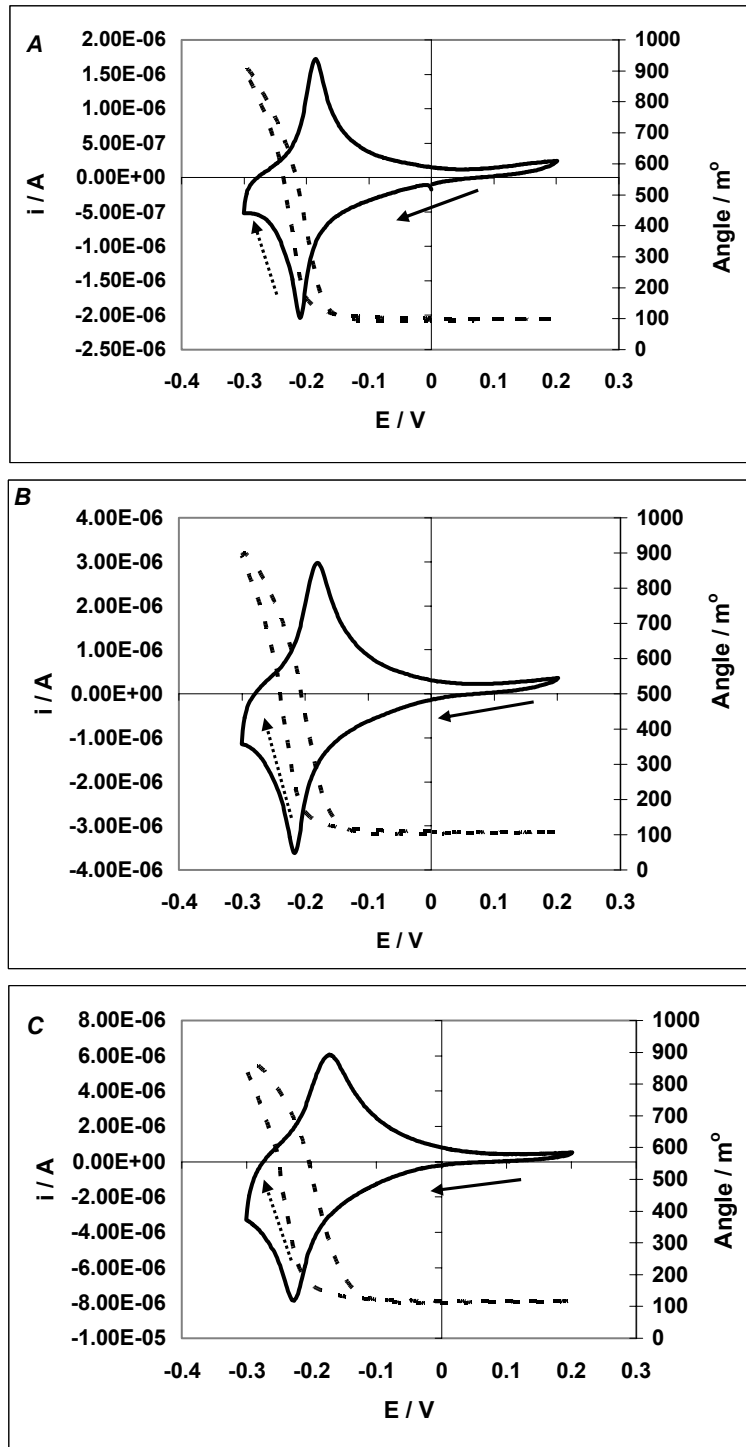


Fig. 1 – Cyclic voltammograms on a PB film ($d = 4.3$ nm) gold-coated glass electrode in aqueous solution containing $0.1 M K_2SO_4 + 0.01 M H_2SO_4$, in the range from $+0.10$ to -0.30 V and reversed to $+0.20$ V. The ordinate axis on the right reports the changes in the SPR resonance angle during potential cycling. A) $0.01 V \cdot s^{-1}$; B) $0.02 V \cdot s^{-1}$; C) $0.05 V \cdot s^{-1}$ potential scan rate.

The reduction of PB to PW occurs in the potential region from -0.10 V to -0.20 V. The electrochemical reduction process is accompanied by a change of both refractive index and colour, from deep blue to colourless. The PB films are very stable at different applied potentials and the observed changes in the electronic spectrum are reversible, as reported in Refs. 23-25. It is obvious that the electrochemical changes of PB films are observed as an optical response of these films. From Figure 1A it can be seen that at the start of the cycle the SPR signal is almost constant showing a minimum change followed by a sharp increase for potential values near to the reduction peak potential of PB. When the electrode potential is swept back toward +0.20 V, when the oxidation of PW to PB takes place, a sharp change, showing a decrease of the SPR signal, is observed in the region of the oxidation peak potential of PW. A similar behaviour was observed in the case of a higher scan rate, which is 0.02 V/s (see figure 1B). A difference in the shape of the SPR response is the higher separation between the forward and backward scan. Regarding the change of the SPR signal during prolonged potential cycling, there is only a small decrease of the response after the first scan. This behaviour is clearly due to the fact that the changes of the SPR signal of the PB films are more reversible at low scan rate, similar to the electrochemically induced changes during potential cycling. At higher scan rate as 0.05 V/s (see Fig. 1C), the SPR response shows a similar shape as for lower scan rates. However, the maximum values of the SPR signal is lower than in the above situations, *i.e.*, with 5.4 % and 3.8% than at 0.01 V/s and 0.02 V/s potential scan rates, respectively. It is well known that PB films show a reversible behaviour for scan rates up to 0.1 V/s. The SPR response suggests that when the electrode potential is scanned slowly, some changes of the optical properties of the PB film occur. Because these changes are due in fact to the electrochemical changes of the species present into the film it is obvious that both forms, *i.e.*, PB and PW, are present simultaneously in the film.

For the sake of comparison, the behaviour of toluidine blue at an Au coated SPR sensor in 0.1 M H₂SO₄ solution is described in Fig. 2. The Au coated SPR sensor was the working electrode, a Pt wire was used as counter electrode and a miniature Ag/AgCl electrode was the reference electrode. The SPR signal has a sigmoidal shape which is different from that observed for ultrathin PB films deposited onto Au coated SPR sensor. The negative change in the SPR angle during the potential scan toward negative values shows desorption of the oxidised toluidine blue from the Au coated SPR surface sensor, therefore the SPR signal shape indicates a soluble solution species behaviour. During the reverse scan, the adsorption of the oxidised toluidine blue takes place and a positive change in the SPR signal is observed. Therefore, the ESPR technique is able to monitor adsorption processes, even if these processes are not displayed in the cyclic voltammograms by specific peaks. For instance, SPR measurements have been also used for the detection of the initial adsorption of the hexacyanoferrate complexes in the submonolayer region and to monitor their transformation to PW/PB film.²⁶ Therefore, ESPR technique proves to be a valuable tool for discriminating the behaviour of immobilised electroactive species against soluble solution species as well as to monitor minute changes at the electrode/film/electrolyte solution interface.

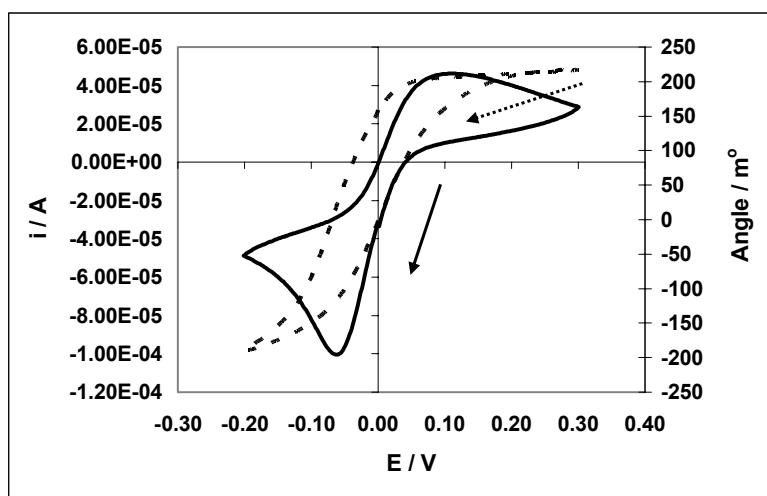


Fig. 2 – Cyclic voltammogram of 0.01 M toluidine blue at a gold coated glass electrode in aqueous solution containing 0.1 M H₂SO₄ in the range from +0.029 to -0.20 V and reversed at +0.30 V. The right ordinate axis shows the changes in the SPR resonance angle during potential cycling at 0.05 V · s⁻¹ potential scan rate.

In Figure 3A the first three scans and the SPR signal of a PB film with a thickness of 4.3 nm, recorded in acidic solution in the potential range from 0.10 to -0.30 and reversed to 0.60 V, are presented. The variation of the SPR resonance angle shift during the cyclic voltammetric measurements is illustrated in Fig. 3B. The shape and the values of the SPR signals in Fig. 3B reveal that the change of the refractive index of PB film in its oxidised form (BG) is smaller than that observed for the reduced form (PW). The SPR signal reveals small changes in the electro-optical properties of the film during prolonged potential cycling. A decrease of 1%, 3%, 6%, and 6% for anodic and cathodic PB/PW peak currents or for anodic and cathodic PB/BG peak currents, respectively, is observed after 3 potential scans, at the $0.050 \text{ V} \cdot \text{s}^{-1}$ potential scan rate. However, the corresponding changes of the SPR signal are more marked, as it is evident from Fig. 3B. In this case, a decrease for the SPR signal of 6% for the PB/PW system and 9% for the PB/BG system, respectively, is observed.

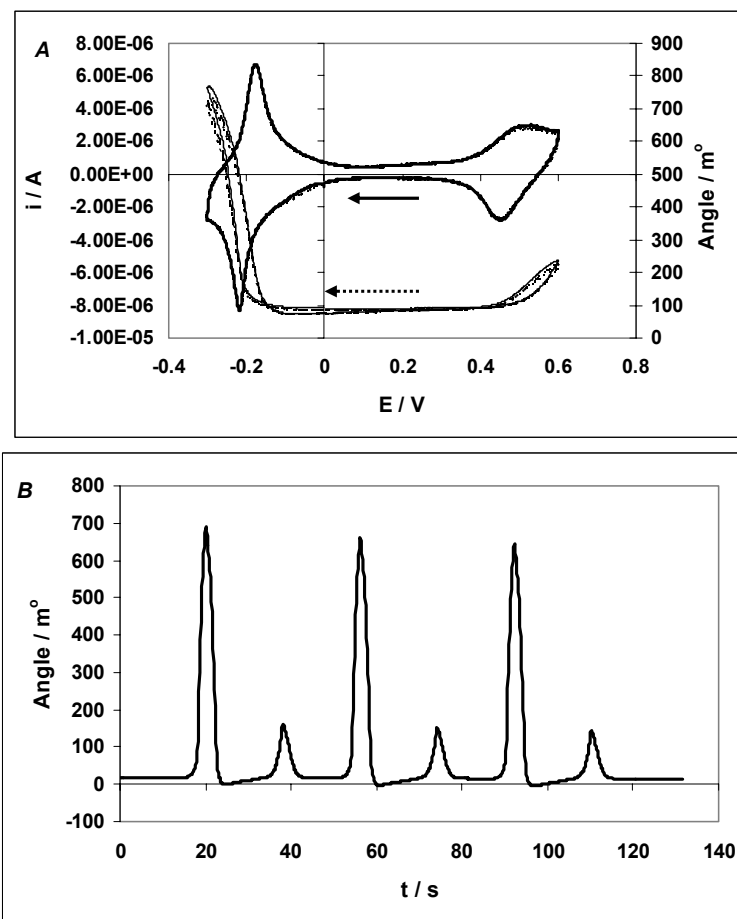


Fig. 3 – A) Cyclic voltammograms on a PB film ($d = 4.3 \text{ nm}$) gold-coated glass electrode in aqueous solution containing $0.1 \text{ M K}_2\text{SO}_4 + 0.01 \text{ M H}_2\text{SO}_4$, in the range from $+0.10$ to -0.30 V and reversed to $+0.60 \text{ V}$. The ordinate axis on the right reports the changes in the SPR resonance angle during potential cycling. $0.05 \text{ V} \cdot \text{s}^{-1}$ potential scan rate. B) SPR resonance angle variation during potential cycling displayed as a function of time t from the start of the experiment (the first 3 scans are presented).

These results attest once more that the ESPR technique is more sensitive than cyclic voltammetry to small changes of the electro-optical properties of PB films, although the information from the two techniques are qualitatively in accord with each other.

CONCLUSIONS

In this work, the reduction and oxidation of PB films have been studied using SPR technique combined with cyclic voltammetry. *In-situ* combined electrochemical SPR measurements have shown to be very

sensitive to small changes at the electrode/PB/electrolyte interfaces, which can not be detected when using electrochemical techniques. Furthermore, new information regarding the stability of PB films and the behaviour of soluble solution species under different experimental conditions has been obtained. The changes in the SPR signal during potential cycling on PB films are more pronounced for the PB/PW system than for the PB/BG system, which could be exploited for the construction of chemical sensors with optical transducers. Therefore, the PB coated SPR probe can be used as an optical transducer of electrochemical processes.

The results obtained are promising and prove that SPR is a valuable tool for in-situ monitoring of minute changes of optical properties of ultra-thin PB films deposited on the electrode surface.

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