



Towards electrochromic ammonium ion sensors

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ABSTRACT

The optical properties of electrochemically deposited Prussian blue (PB) on an indium tin oxide (ITO)-coated glass electrode (glass/ITO) were investigated at different ammonium ion concentrations (0.01 M to 0.1 M) in order to use this electrode to design an electrochromic sensor sensitive to ammonium ions. The glass/ITO/PB-based structure exhibited a fast optical-absorbance-based response towards ammonium ions. A protocol for simple regeneration of the glass/ITO/PB structure after the determination of ammonium ion concentration has been developed.

1. Introduction

Electrochromism is a unique feature of some materials, which is still relatively rarely exploited in the design of chemical sensors [1]. Prussian blue (PB) is an electrochromic material which exhibits specific electrochemical and optical properties [2]. The electrochemical properties of PB have been widely exploited in the design of various electrochemical sensors [3–5] and biosensors [6–12]. PB-based electrochemical sensors are widely used for various purposes including biomedical investigations such as glucose determination in blood samples [13,14]. It is also known that some interactions and/or redox reactions occurring on PB layers cause changes in the optical properties of PB layers [15]. During electrochemical reduction of PB, some cations (e.g. NH_4^+ , K^+ , Cs^+ , Rb^+) are able to exchange with Fe^{3+} ions in the outer sphere of the PB structure [16,17]. The trapping of these cations in the crystal lattice of PB causes a change in PB oxidation and reduction potentials, which depends on the concentration of cations in the solution [18]. This feature enables Prussian blue to be used in voltammetric sensors for the determination of H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} cations [18,19].

Depending on the amount of Fe^{3+} in the PB crystal lattice, Prussian blue can be obtained in two forms: the ferric (Fe^{3+})-ion-based form $\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3$ (regular PB) and a form of PB in which Fe^{3+} ions are partially replaced by potassium (K^+) ions $\text{K}^+\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]$ (K^+ -PB) [20]. During deposition, Prussian blue film is produced in the regular PB form [21]. Regular PB can be irreversibly converted into K^+ -PB by the insertion of K^+ into the PB crystal lattice during cycling in the potential range between 0 V and +0.45 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ in solution

containing KCl [22]. K^+ -PB is electrochemically stable and can be reversibly cycled between colourless Prussian white (PW) and the blue-colored PB forms [16]. This makes K^+ -PB a promising material in analysis where reversible oxidation–reduction cycles are used.

Electrochromic sensors based on oxides of transition metals for the determination of ammonium ions have been the subject of intensive research [23]. However, to the best of our knowledge, an electrochromic sensor based on Prussian blue for the detection of ammonium ions has not been reported yet.

In this work, a glass/ITO electrode covered with a PB layer (glass/ITO/PB) has been evaluated as an ammonium-ion-sensitive system, which is potentially suitable for the development of an electrochromic analytical sensor. The influence of ammonium concentration on the PB optical absorbance spectrum was investigated and calibration curves of changes in optical absorbance intensities and the shift of optical absorbance peaks (dependent on ammonium concentration) were recorded. The stability of the glass/ITO/PB-based electrode, its reusability and the regeneration of the electrode after the determination of ammonium ion concentration have been investigated.

2. Experimental

2.1. Materials

All inorganic salts ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, NH_4Cl , KCl) of ‘highest purity’ and acetone (purity $\geq 99.8\%$) were purchased from ROTH (Karlsruhe, Germany). MICRO®-90 concentrated cleaning solution was purchased from SIGMA-ALDRICH (Munich, Germany). Ultrafiltered

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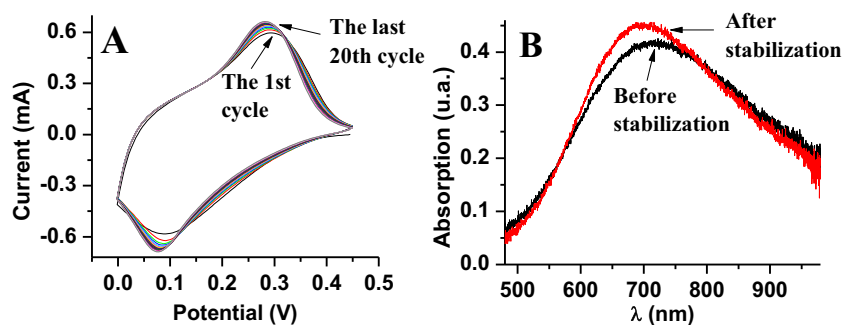


Fig. 1. A. Cyclic voltammograms of the glass/ITO/PB electrode recorded in 0.1 M KCl solution during electrochemical stabilization of the PB layer; B. Optical absorbance spectra of the glass/ITO/PB electrode (at equilibrium potential) measured in 0.1 M solution of KCl before and after the stabilization procedure.

water was used for the preparation of all solutions.

2.2. Modification of glass/ITO electrode with PB

An ITO-coated glass (glass/ITO) plate 1 mm thick was used as an electrode, which was electrochemically modified with a PB layer. Before this modification the surface of the glass/ITO plate was treated by ultrasound (i) in a 2% laboratory dish cleaning solution of “micro 90”, (ii) in acetone, (iii) in deionized water for 8, 16 and 16 min, respectively. After these cleaning procedures the glass/ITO plate was modified in the following sequence: the glass/ITO plate was placed in an electrochemical cell filled with solution containing 1 mM of FeCl_3 and 1 mM of $\text{K}_3[\text{Fe}(\text{CN})_6]$, and electrochemical deposition of PB was carried out by potential cycling in the range between +0.4 V and +0.8 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ at a scan rate of 40.0 mV s^{-1} . Forty potential cycles were applied. During this potential-cycling-based modification, cyclic voltammograms (CVs) were recorded. After this procedure, the regular PB-based coating was converted into the K^+ -PB form by a stabilization procedure based on potential cycling between 0 and +0.45 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ at a scan rate of 40.0 mV s^{-1} for 20 cycles in a 0.1 M solution of KCl.

2.3. Electrochemical and optical equipment used for electrochemical deposition of PB and registration of optical signals

A $\mu\text{AUTOLAB}$ potentiostat/galvanostat from ECO-Chemie (Utrecht, The Netherlands) was used for the electrochemical deposition of PB and for all electrochromic investigations. A USB4000 spectrometer from Ocean Optics (Largo, USA) was used for optical absorbance measurements. All experiments were performed in the electrochemical cell in a three-electrode mode, where: (i) the glass/ITO plate of 1 cm^2 geometric area was used as the working electrode; (ii) a platinum wire served as the auxiliary electrode; (iii) $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ was used as the reference electrode. The reference electrode was placed as close as possible to the working glass/ITO electrode using a ‘Luggin capillary’-based connector. In order to investigate the influence of ammonium cations on the optical properties of the glass/ITO/PB plate, absorbance spectra were recorded in an electrochemical cell with transparent windows for the connection of optical fibres. An optical/electrochemical cell with a light pathway of total length 10 mm was used for all optical/electrochemical investigations. The thickness of the glass/ITO plate was 1 mm and the Prussian-blue-modified side of the electrode was facing the light source. During the investigation the cell was filled with $\text{NH}_4\text{Cl}_{(\text{aq})}$ solutions of various concentrations ranging from 0.01 M up to 0.1 M. In order to get the required ammonium ion concentration, an appropriate amount of 1 M solution of $\text{NH}_4\text{Cl}_{(\text{aq})}$ was added to the deionized water and stirred for about 1 min with a magnetic stirrer. To ensure the incorporation of ammonium ions within the crystal lattice of PB, a potentiostatic pulse of 0 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ was applied for 5 s before each optical measurement of absorbance. The optical absorbance spectra were recorded at a

potential of +0.2 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$. The dependence of the maximum absorbance and the corresponding wavelengths (λ_{max}) on ammonium concentration were represented as linear curves.

All optical measurements in KCl solution were performed at +0.2 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ in the cell described previously for measurement of ammonium ion concentration. After the optical measurement in NH_4Cl solution, the glass/ITO/PB plate was regenerated by immersing it in 0.1 M KCl solution and applying a potential of +0.2 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ for 5 s.

3. Results and discussion

Electrochemical cycling in 1 mM of FeCl_3 and 1 mM of $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution in the potential range between +0.4 V and +0.8 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$ produces a blue-colored PB film on the surface of the glass/ITO/PB electrode. According to reference [16], the regular form of PB ($\text{Fe}_4^{3+}[\text{Fe}^{2+}(\text{CN})_6]_3$) should be converted into $\text{K}^+\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]$ (K^+ -PB), achieving electrochemical stability of PB and enabling reversible oxidation/reduction cycles for possible application in analytical sensors. For this purpose, the glass/ITO/PB electrode was electrochemically stabilized by cycling in 0.1 M KCl solution (Fig. 1A). Cyclic voltammograms recorded during potential cycling achieved steady-state values after approximately the sixth potential cycle. The redox potential of PB calculated from the voltammograms in Fig. 1A was +0.18 V vs $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$. Therefore, a potential of +0.2 V, which is very close to the redox potential of PB, has been used in further optical-absorbance-based investigations of the behavior of the glass/ITO/PB electrode in ammonium-ion-containing solutions. The optical absorbance spectra of the glass/ITO/PB electrode immediately after PB deposition and after electrochemical stabilization in 0.1 M KCl solution were recorded and analyzed (Fig. 1B) in order to compare their optical properties. The experimental data showed that after electrochemical stabilization by cycling in 0.1 M KCl solution, the intensity of optical absorbance of the glass/ITO/PB electrode increased from 0.418 (before stabilization) to 0.449 (after stabilization) and the wavelength of maximum absorbance shifted from 720 to 707 nm, indicating the positive influence of the stabilization procedure.

The optical absorbance spectra of the glass/ITO/PB electrode (Fig. 2A) showed significant changes in optical absorbance depending on the concentration of the NH_4Cl solution. Increasing the ammonium ion concentration in the electrochemical cell caused a decrease in the intensity of maximum absorbance and a shift of λ_{max} to longer wavelengths. Plotting the maximum absorbance at a given wavelength of 730 nm (Fig. 2B) and/or λ_{max} against the concentration of ammonium ions (Fig. 2C) yields linear calibration curves in both cases, suggesting that this electrode is very promising for the development of an electrochromic ammonium-ion sensor based on the variation of optical properties of PB.

We consider that the change in the optical properties of PB is caused by variation of the PB redox potential. During the electrochemical

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