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A sensitive reagentless pH probe with a ca. 120 mV/pH unit response

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Abstract The use of a basal plane pyrolytic graphite electrode immobilised with two redox active species each capable of undergoing a two-electron, two-proton redox process has allowed the development of a sensitive pH probe over a wide pH and temperature range. When the values of the peak potentials of the two processes are combined they shift by ca. 120 mV/pH unit at 25 °C, as measured against two independent, defined reference electrodes.

Keywords pH · Anthraquinone · *N,N'*-Diphenyl-*p*-phenylenediamine · Nickel (II) hexacyanoferrate (II) · Copper (II) hexacyanoferrate (II)

Introduction

The sensing of pH in solution is one of the most common analytical measurements performed within both academic and industrial applications. The most abundant systems for pH-sensing are based upon either potentiometric or amperometric devices [1]. The former

usually utilises the glass electrode [2, 3] due to its simplicity of handling and low sensitivity to the many potential interferents within the solution to be measured. Other devices include ion selective membranes [4, 5], ion-selective field effect transistors [3, 6], two terminal micro-sensors [7] as well as optical [8] and conductometric [9] pH sensing devices. However, these types of devices can often suffer from instability and/or drift and therefore require constant recalibration [10].

The majority of amperometric sensors are based upon the pH-switchable permselectivity of membranes or films on the electrode surface [11, 12, 13, 14, 15]. For example, recent work by Stred'ansky et al. has focused on the use of various pH-sensitive redox-active compounds as a means of designing suitable amperometric probes for biosensors, which are based upon pH-sensitive enzymes. In these cases the probe is held at a set potential and the current is measured such that the pH local to the electrode surface can be monitored [10].

The following report examines the possibility of developing a sensitive pH probe based on the redox chemistry of both anthraquinone (AQ) and *N,N'*-diphenyl-*p*-phenylenediamine (DPPD). It has been shown previously that AQ can be attached to carbon powder by the direct chemical, as opposed to electrochemical, reduction of anthraquinone-1-diazonium chloride in the presence of carbon (to form AQcarbon) to produce a reagentless pH sensor [16, 17]. In the present case the redox behaviour of the AQcarbon is measured along with that of the insoluble DPPD solid [18] in a single voltammetric sweep embracing the reduction of the former and the oxidation of the latter. The redox chemistry of each species is such that both undergo two-electron, two-proton redox processes over a wide pH range [17, 18].

Dedicated to Zbigniew Galus on the occasion of his 70th birthday

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Materials and methods

Unless stated otherwise all reagents were obtained from Aldrich and were of the highest grade available and used

without further purification. All solutions and subsequent dilutions were carried out using deionised water from an Elgastat (Elga, UK) UHQ grade water system with a resistivity of not less than 18 M Ω cm. All results were obtained at a temperature of 20 ± 2 °C unless stated otherwise.

Electrochemical measurements were recorded using a PalmSens potentiostat (Houten, Netherlands) controlled by an iPAQ H3760 pocket PC (Compaq, US) with a standard three-electrode configuration. A basal plane pyrolytic graphite (bppg, 0.20 cm²) electrode acted as the working electrode (see above). A platinum wire acted as the counter electrode and a saturated calomel as the reference electrode (SCE, Radiometer, Copenhagen) completed the cell assembly.

High-temperature voltammetry was undertaken using a double-walled glass cell thermostatted at the appropriate temperature via the circulation of water from a heated bath.

Results and discussion

In this report we immobilised both the solid DPPD and the derivatised AQcarbon particles simultaneously on the surface of a basal plane pyrolytic graphite (bppg) electrode [19, 20]. The voltammetric behaviour of each species is such that the redox waves are clearly resolved and do not overlap. Therefore, by monitoring the peak potential of each wave as a function of pH with respect to two suitable independent reference electrodes a new and very sensitive pH electrode can be developed whereby the combined change in peak potential will be ca 120 mV/pH unit at 25 °C.

The redox chemistry of AQcarbon is shown in Scheme 1, where E_p^a (vs nickel (II) hexacyanoferrate) = $X - 0.059$ pH at 25 °C and X is an arbitrary constant. Likewise for DPPD (Scheme 2) E_p^b (vs cupric hexacyanoferrate) = $A - 0.059$ pH where A is an arbitrary constant and E_p is the peak potential for the redox couple in question measured relative to suitable reference electrodes, which are also immobilised along with both AQ and DPPD onto a bppg electrode. In the case of AQ, the shift in peak potential was measured relative to a reference electrode consisting of insoluble nickel (II) hexacyanoferrate, which has a E_p of 0.55 V [21]. For

DPPD, the shift in peak potential was measured relative to a reference electrode consisting of cupric hexacyanoferrate, which has a E_p of 0.69 V [22]. It follows that if the peak potential for both systems are measured and summed then at 25 °C:

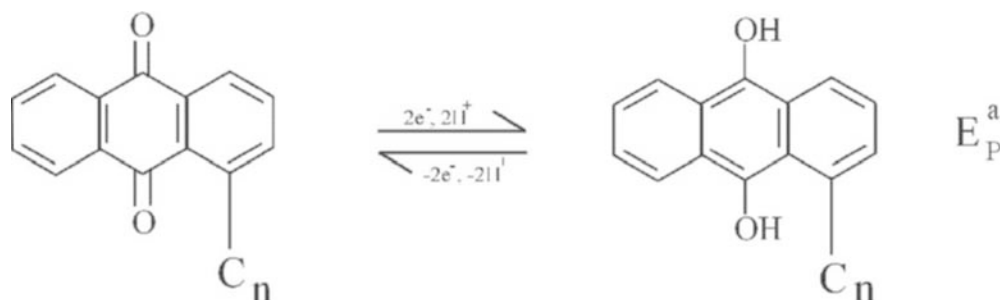
$$E_p^b + E_p^a = A + X - 0.118\text{pH} \quad (1)$$

In all studies square wave voltammetry [23] was utilised as the electrochemical probe of the system. This has significant advantages to conventional cyclic voltammetry as it provides a means of carrying out a single sweep that produces a well-defined voltammetric peak due to the reversibility of both anthraquinone [16, 17] and DPPD systems [18]. Furthermore, at higher pH the electrochemically irreversible reduction of oxygen might mask the electrochemically reversible AQ reduction wave. The use of square wave voltammetry helps remove this possible interference as, under square wave conditions, electrochemically irreversible reactions give broad undefined signals [23].

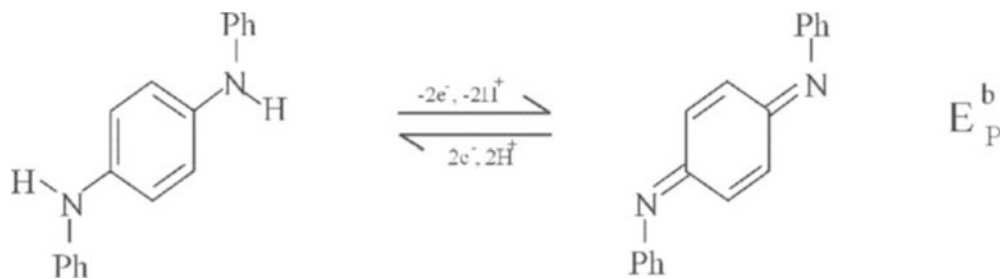
The doubly modified electrode consisted of both AQcarbon and solid DPPD particles abrasively immobilised [19, 20] onto a bppg electrode. Initially the electrode was polished on glass polishing paper (H00/240) and then on silicon carbide paper (P1000C) for smoothness. The two solids were then mixed and immobilised onto the bppg by gently rubbing the electrode surface on a fine qualitative filter paper (Whatman) containing the two materials [16, 17, 18].

The square wave voltammograms (frequency 12.5 Hz, step potential 2 mV, amplitude 5 mV) obtained for the doubly modified electrode were recorded in pH 1.0 (0.1 M HCl + 0.1 M KCl), pH 12 (0.1 M KOH + 0.1 M KCl), pH 4.6 (0.1 M acetic acid + 0.1 M sodium acetate), pH 6.8 (0.025 M Na₂HPO₄ + 0.025 M KH₂PO₄) and pH 9.2 (0.05 M disodium tetraborate). Figure 1a illustrates the corresponding voltammetric responses when the initial potential applied to the cell was sufficiently reducing such that both the anthraquinone and the DPPD species were in their reduced states. Analysis of each voltammetric response reveals that two oxidative waves are present. The first, at more oxidising potential, can be attributed to the oxidation of the parent DPPD species to the oxidised quinone-imine form (Scheme 2) and the second wave, at more negative

Scheme 1 Proposed reduction of the anthraquinonyl carbon species



Scheme 2 Electrochemical pathway for the oxidation of *N,N'*-diphenyl-*p*-phenylene diamine



potential, can be attributed to the oxidation of the reduced hydroquinone structure illustrated in Scheme 1 back to the parent anthraquinone species.

Further examination into the electrochemical properties of the doubly modified electrode was sought by analysing the corresponding reductive square wave sweep at each pH. The corresponding voltammograms obtained when the starting potential was sufficiently positive that both the anthraquinone and the DPPD

were in their oxidised forms (Schemes 1 and 2) are detailed in Fig. 1b. These once again reveal two voltammetric waves. The first, at more positive potentials, can be attributed to the two-electron reduction of the oxidised quinone-imine species to its parent DPPD species. The second voltammetric response, at more negative potentials, can be attributed to the reduction of the anthraquinone species to the reduced hydroquinone structure as illustrated in Scheme 1. A comparison of Figs. 1a and b reveal that the oxidative sweep produces well-defined waves and therefore will be used in further studies. The voltammetric responses for the reduction of the anthraquinone species reveal that for each pH study a slight shoulder is observed at a higher potential on each of the voltammetric waves. The presence of this shoulder can be tentatively attributed to the intermediate electrochemical reduction of the quinone to a semi-quinone species [17]. It can also be seen from Fig. 1 that as the pH increases the peak potential shifts towards more negative values, as predicted.

Analysis of the oxidative square wave voltammograms by means of a plot of peak potential for both the DPPD and AQ waves as a function of pH for the different pHs studied revealed a linear response from pH 1 to 9.2 at 20 °C with a corresponding gradient of ca. 57 mV/pH unit, which is consistent with literature values [17, 18]. It can be foreseen that an addition of the two redox potentials as a function of pH produces a slope of gradient 114 mV/pH unit consistent with that alluded to in Eq. 1. Note that both reference signals were stable and independent of pH within the range 1–9.2.

Next, the voltammetric response of the doubly modified electrode was examined at elevated temperatures to show the adaptability of this sensitive pH probe under these conditions. Analysis of the Nernst equation (Eq. 2) shows that as the temperature increases the gradient of the peak potential against pH plot should increase:

$$E_p = E^{\circ'} - \frac{2.3RTm}{nF} pH \quad (2)$$

where $n=2$ and $m=2$.

The theoretically calculated values for the gradient of the reductive peak potential against pH plot for a range of temperatures for a single species are shown in Table 1. A second factor to be noted whilst studying the effect of temperature on the AQ and DPPD waves is

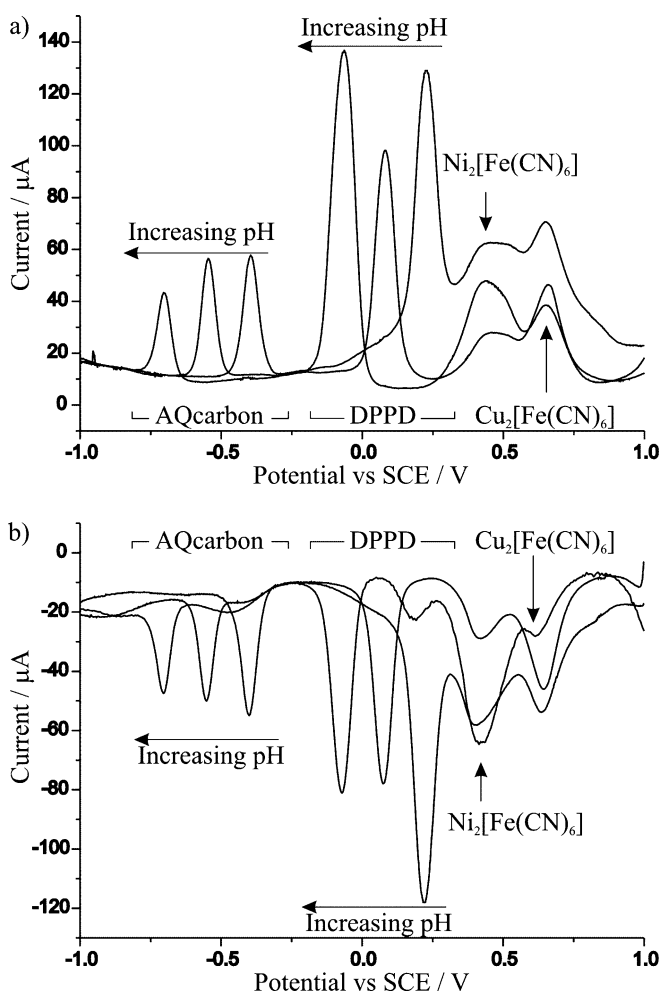


Fig. 1a, b Square wave voltammograms detailing the effect of pH 4.6 (0.1 M $\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^- \text{Na}^+$), pH 6.8 (0.025 M $\text{Na}_2\text{HPO}_4 + 0.025 \text{ M } \text{KH}_2\text{PO}_4$) and pH 9.2 (0.05 M disodium tetraborate buffer) on the doubly modified electrode at 20 °C for **a** the oxidative sweep and **b** the reductive scan

Table 1 A comparison of the theoretically predicted gradient and experimentally obtained gradient for the plot of peak potential against pH for a range of temperatures from 20 to 60 °C along with the combined shift in peak potentials of the two waves at each temperature, relative to two suitable reference electrodes

Temperature (°C)	Theoretical shift (mV/pH)	Experimental shift of AQ wave relative to nickel hexacyanoferrate \pm 5% (mV/pH)	Experimental shift of DPPD wave relative to copper hexacyanoferrate \pm 5% (mV/pH)	Combined shift of the two waves (mV/pH)
20	58.1	56.8	57.3	114.1
30	60.1	57.6	54.1	111.7
40	62.1	60.4	53.6	114.0
50	64.1	58.7	63.2	121.9
60	66.1	63.8	65.5	129.3

how the pH of the solution will vary with temperature, as the dissociation constants of the components of the buffer solutions vary as the temperature is changed. Therefore, three IUPAC standard buffers (pH 4.6, pH 6.8, pH 9.2), which have a known pH at a set of temperatures [24], were utilised in these studies.

The oxidative voltammetric response of the doubly modified electrode was examined at each pH from 20 to 60 °C. The corresponding square wave voltammograms (not shown) produced analogous behaviour to that observed at ambient temperature. However, an enhancement in the peak current was observed as the temperature was increased, as expected due to the increase in the rate of electron transfer as the temperature is raised.

Analysis of the peak potentials as a function of pH at each temperature are detailed in Table 1, which shows how the gradient of the pH against peak potential plot varies with the temperature for both the DPPD and anthraquinone waves. These are compared with those predicted theoretically from the Nernst equation for a two-electron, two-proton transfer. The data shows good agreement between the experimental and theoretically predicted values, thereby showing that the doubly modified electrode might easily be used as a basis for a simple, inexpensive pH probe which works over a wide range of temperatures. Also depicted in Table 1 is the combined potential shift with pH of the two waves. This illustrates the sensitivity of the doubly modified electrode as a pH probe when it is measured against two independent, defined reference electrodes.

These results reveal how an electrode modified with two redox-active species, which undergo a two-electron two-proton redox process, allows the development of a sensitive pH probe over a wide pH and temperature range. This produces a combined change in peak potential of ca. 114 mV/pH unit at 20 °C when measured with respect to two suitable reference electrodes, so offering considerable benefit in sensitivity for pH measurement.

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