Adsorption effects during the analysis of caffeic acid at PEDOT electrodes

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Abstract: Polyphenol compounds, such as caffeic acid, are important substrates of oxidation in beverages such as wine, and more rapid and sensitive methods of analysis are being sought. The conducting polymer poly-3,4-ethylenedioxythiophene (PEDOT) provides good separation of caffeic acid from antioxidant additives in wines, and produces a clear anodic peak that can be used to quantify caffeic acid and related hydroxycinnamic acids. Various adsorption effects are examined in this report, as shown through electrochemical tests such as sweep rate dependence of the anodic peak current and voltammetric shape. The importance of a controlled holding time prior to measurement is seen, owing to the gradual increase in anodic peak current over a period of 10–20 min, with implications for the design of a measurement system involving PEDOT electrodes.

Keywords: poly-3,4-ethylenedioxythiophene; PEDOT; sensor; antioxidants; cyclic voltammetry; conducting polymer; adsorption.


Biographical notes: Qiang Zhang obtained a BSc in Chemistry at the Ocean University of China. At the same time, he took part in research into the photocompition of nitrite in water and the protective function of nitric oxide on marine phytoplankton, and completed a dissertation on acrylic acid in Jiaozhou Bay. Since March 2014, he has been working on the PEDOT-based sensor for analysing antioxidants in white wine as his BSc (hons.) project at the University of Auckland.

Paul A. Kilmartin is a Professor in the School of Chemical Sciences at the University of Auckland. He completed a PhD in the Electrochemistry of Polyanilines at the same university in 1997 and joined the academic staff soon after. He has undertaken research projects involving electrodes modified by conducting polymers in selective electrochemical sensors, with applications in the wine industry. The conducting polymers and natural tannin extracts are also being developed as solid antioxidant and antimicrobial materials, including
blends with conventional plastics. His research projects within Paul Kilmartin’s

group have engaged over 60 postgraduate students and have been reported in

more than 150 refereed publications.

1 Introduction

Electrodes modified with conducting polymers have been developed for various

applications as chemical sensing elements [1,2]. Among the conducting polymers,

poly-3,4-ethylenedioxythiophene (PEDOT) [3–5] has proved to be of particular interest

for the analysis of reducing agents, including antioxidants, owing to improved sensitivity

and the ability to resolve oxidation peaks for different analytes in voltammograms [3].

PEDOT has attracted wider interest in materials science owing to its high optical

transparency in the conducting state, along with good stability and low band gap, leading

to applications in optoelectronics and photolithography [6].

Among the analytical targets for beverage industries, small molecule antioxidants,

including polyphenols, are of particular interest. Many polyphenols contain easily

oxidisable groups, such as the ortho-diphenol (catechol) moiety, which make them both

important in beverage oxidation processes, and amenable to detection using voltammetric

methods at inert electrodes [7,8]. The major family of polyphenols in white wines is the

hydroxycinnamic acids, represented by the parent compound caffeic acid (Figure 1).

During wine oxidation, catechol-containing polyphenols such as caffeic acid are oxidised

through processes catalysed by iron and copper, leading to quinones and hydrogen

peroxide, which can react further to form brown-coloured polyphenol oxidation products,

and remove certain desirable aroma compounds [9]. While wine oxygenation can be

beneficial for the maturation of red wines, it usually leads to a lower quality wine in the

case of white wine varieties, hence the interest in monitoring the hydroxycinnamic acid

content of white wines and how this changes with time.

Figure 1  Structure of the hydroxycinnamic acid caffeic acid

The quantification of caffeic acid and its derivatives in white grape juices and wines

provides a quality parameter that could be used more widely by winemakers, should a

rapid and easy-to-use analytical method become available, particularly compared to lengthy

HPLC procedures. The oxidation of caffeic acid at inert electrodes has been previously

described and oxidation potentials established in relation to other hydroxycinnamic acids [10,11]. More recently, newer electrode materials such as reduced

graphene oxide have been used to investigate the electrochemistry of caffeic acid, where

an improved current response was obtained relative to glassy carbon electrodes [12].
PEDOT based electrodes have also been applied in recent times to study the oxidation of caffeic acid [13]. Using PEDOT electrodes it was possible to separate the signal for caffeic acid from other antioxidants present in wines, such as ascorbic acid and sulphites [5]. In this work, certain effects related to analyte adsorption of caffeic acid at PEDOT electrodes are investigated using electrochemical techniques. The implications for the analysis of polyphenols at PEDOT electrodes are then considered.

2 Materials and methods

2.1 PEDOT electropolymerisation

PEDOT electrodes were prepared by electrochemical polymerisation of 0.1 M 3,4-ethylenedioxythiophene in propylene carbonate with 0.1 M LiClO₄, after the removal of oxygen by purging with nitrogen, typically using four potential sweeps between -300 and 1200 mV (Ag/AgCl; BAS MF-2052, +207 mV vs. SHE) at 100 mV s⁻¹ on a 3 mm glassy carbon electrode (BAS MF-2012). The electrochemical experiments were undertaken at a bioanalytical systems electrochemical analyser (BAS100A), and included a platinum wire as counter electrode. Before each polymerisation, the surface of the electrode was polished using 0.05 µm alumina powder (BAS CF-1050) on a cloth pad [4,5].

The PEDOT electrodes were then transferred to a model wine solution prepared by dissolving 0.033 M L-tartaric acid in a 12% (v/v) ethanol-water mixture and adjusting the pH to 3.6 ± 0.2 with 1 M NaOH. To obtain reproducible results, 10 voltammetric cycles were first undertaken in the model wine solution containing 0.1 M NaClO₄ from –200 mV and 800 mV (Ag/AgCl) at 100 mV s⁻¹, in order to reach a steady response as the PEDOT adjusted to the aqueous ethanolic conditions, before recording the background curve [3].

2.2 Caffeic acid analysis

The PEDOT electrodes were then transferred to the test solution containing caffeic acid dissolved in the model wine solution, and the first voltammetric cycle was recorded. In each of the experiments, the background curve for PEDOT in the model wine solution in the absence of caffeic acid, was subtracted away to obtain the voltammetric response for caffeic acid. Where repeat runs were undertaken (n = 3), the average with standard deviation is presented.

For the initial experiments, the voltammetry was performed as soon as possible after inserting the working electrode into the caffeic acid solution. The initial tests involved a comparison of PEDOT electrodes with a different number of preparative cycles, and thus of a different thickness, using 0.05 mM caffeic acid solution, to obtain the optimum voltammetric response on the anodic scan. Comparisons were also made of the sweep rate dependence of the anodic peak current for caffeic acid oxidation, between PEDOT and glassy carbon electrodes.

In later experiments a certain holding time was introduced, being a period of up to 20 min in which the PEDOT working electrode was left still in the caffeic acid solution prior to running a voltammogram. These experiments were undertaken with three
Results and discussion

3.1 Caffeic acid oxidation at PEDOT electrodes

An anodic peak for caffeic acid oxidation was seen at around 435–440 mV at the PEDOT electrodes in the model wine solution (Figure 2). This peak corresponds to the oxidation of the diphenol group of caffeic acid to a quinone, which is readily reversed on the return cathodic scan at around 380 mV. The thickness of the PEDOT films was varied by the number of preparative cycles, for up to six cycles. A larger current peak was produced as the number of preparative cycles was increased to four, but remained steady with further preparative cycles (Figure 2). On the basis of these results, PEDOT electrodes formed using four preparative cycles were chosen for further work.

![Figure 2](image)

The current response for different concentrations of caffeic acid was linear in the range from 0.005 mM to 0.2 mM ($r^2 = 0.9995$), at which point an anodic peak current of around 37 µA was obtained (Figure 3). For each caffeic acid concentration, the standard deviation of the anodic peak current for triplicate runs was less than 0.2 µA in each case. These results can be compared to a peak current of 10 µA at an unmodified glassy carbon electrode, which also showed a linear response for concentrations of caffeic acid up to 0.2 mM.
3.2 Caffeic acid adsorption at PEDOT

To further characterise the electrochemical response, the variation of the anodic peak current for caffeic acid oxidation with sweep rate \( (\nu) \) was tested, for both the PEDOT electrodes and the bare glassy carbon electrode. It is well known that for processes under diffusion control at macroelectrodes, the peak current scales with the square root of the sweep rate \([14]\). By contrast for adsorbed species or surface-confined processes, the peak current scales directly with the sweep rate.

The slope for plots of the log of the anodic peak current against the log of the sweep rate was obtained (Figure 4). For a process under purely diffusion control, a slope of 0.5 is expected for the peak current varying with the square root of the sweep rate. For a process controlled by adsorption effects and for thin films of electroactive materials, a slope of 1.0 is expected. For example, the oxidation of the PEDOT itself owing to internal redox process, produced a slope of 1.01 for the anodic current at 450 mV in the model wine solution, pointing to capacitive-like effects with little diffusional limitation. With caffeic acid present, the log/log slope at the bare glassy carbon electrode, for an anodic peak at about 415 mV, was 0.59, indicating diffusion control as main mechanism with slight adsorption effects (Figure 4). With the PEDOT coated electrode, the log/log slope for the larger caffeic acid oxidation peak was 0.83, demonstrating that adsorption effects were dominating.

The shape of the voltammetric response is also indicative of the electrochemistry of a species largely adsorbed onto the electrode surface, rather than relying on ongoing diffusion of the analyte from the bulk solution. In Figures 2 and 5, the return of the anodic current close to zero after the completion of the anodic peak, is typical of a surface-based process, and differs from the larger ongoing current seen with a process under diffusion-control.
Figure 4 Logarithm of anodic peak current ($I_{pa}$) vs. logarithm of sweep rate ($v$) for 0.02 mM caffeic acid in the model wine solution, at bare glassy carbon and PEDOT electrodes, taken immediately after the electrodes were inserted into the test solution ($n = 3$).

Figure 5 Voltammograms (background subtracted) taken at 100 mV s$^{-1}$ of 0.02 mM caffeic acid in a pH 3.6 model wine solution at a PEDOT covered glassy carbon electrode, after inserting a fresh PEDOT electrode into the sample solution for different holding times.

3.3 Effect of PEDOT electrode holding time

Adsorption of analytes onto a conducting polymer such as PEDOT can provide a pre-concentration step that provides an enhanced analytical signal, as seen above. At the same time the kinetics of the adsorption event need to be considered to gain an understanding of the time required for a saturated signal to be obtained. It is also important to know how fast the response will change with electrode holding time, which has implications for sensor reproducibility. In the experiments described above, the
voltammograms were obtained shortly after inserting the PEDOT electrode into the sample solution, using a consistent test procedure. To examine the effect of holding time, freshly prepared PEDOT electrodes were placed into 0.02 mM caffeic acid in the model wine solution, and held for times up to 20 min before recording the voltammogram.

**Figure 6** Anodic peak current \( (I_{pa}) \) at PEDOT electrodes in the model wine solution, for (a) different concentrations of caffeic acid using a PEDOT electrode prepared by four cycles, and (b) for 0.02 mM caffeic acid for different PEDOT preparative cycles \( (n = 3) \)

The anodic peak for 0.02 mM caffeic acid was around 5.3 µA when the voltammogram was taken as soon as possible after insertion of the PEDOT electrode into the solution (time = '0 min', Figure 5). As the holding time was increased by several minutes,
the anodic peak increased progressively, reaching 15 µA for a 20 min holding time. We can also note from Figure 4, that the ratio of the cathodic peak current \( I_{p,c} \) to the anodic peak current \( I_{p,a} \) was in the range of 0.7 to 0.75. For a fully reversible redox couple, this value would be 1.0, so a small degree of irreversibility in the response is indicated in the present case, perhaps brought on by subsequent chemical reactions of the caffeic acid quinone. A similar peak current ratio was seen previously for caffeic acid at a glassy carbon electrode [7].

The effect of holding time on the anodic peak current for three different concentrations of caffeic acid are show in Figure 6(a). It is apparent that a holding time of 15–20 min was required to obtain a value approaching a maximum. Larger current responses for lower concentrations of caffeic acid are also an advantage of employing a longer holding time. These results would indicate that an analytical procedure utilising the PEDOT electrodes should employ a holding period of this duration. However, it was also found with a longer holding time that the current response was no longer linear for concentrations of caffeic acid greater than 0.05 mM, unlike the more immediate measurement. Should a rapid measurement be sought, a carefully controlled insertion time could be employed, in which case the reproducibility needs to be carefully monitored. As shown in Figure 6, the standard deviations for triplicate measurements were not excessive, but were most problematic for the time zero measurements.

Given that the adsorption process is likely to take longer to complete with thicker films, a comparison of holding times was made with PEDOT films of three different thicknesses, obtained by PEDOT electropolymerised for 2, 3 and 4 preparative cycles (Figure 6(b)). In the case of the thinner 2-cycle PEDOT preparation, a near-maximum anodic peak response was obtained earlier after 8–10 min, despite having a lower analytical signal compared to the thicker PEDOT films. By contrast, with the 3 and 4-cycle preparations, the anodic peak current was still rising past the 10 min hold-time point, and reached a maximum closer to 20 min.

4 Conclusions

Caffeic acid adsorption onto PEDOT electrodes was evident through a number of features of the subsequent electrochemistry. Pre-adsorption at the PEDOT electrodes helped to enhance the analytical signal and give a more sensitive response to lower concentrations of caffeic acid. The need for holding times of the order of 10–20 min, depending upon the thickness of the PEDOT layer, means that attention needs to be given to the timing of the measurement procedure, to either allow adequate time for near-full saturation of the PEDOT surface, or else to employ a very precise measurement protocol. Through the miniaturisation of PEDOT electrodes, pre-adsorption of analytes could be used to obtain enhanced analytical signals with micro and nanoscale electrodes.

References


