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Investigations into the use of screen-printed carbon electrodes as templates for electrochemical sensors and sonochemically fabricated microelectrode arrays

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ABSTRACT

The paper critically evaluates the suitability of carbon inks as hosts for the fabrication and subsequent mass production of sonochemically produced microelectrode arrays. Two commercially available carbon inks (GEM and Dupont) were compared in terms of electroactivity towards standard redox couples, and their electroanalytical response was investigated in terms of reversibility, operational potential range, background currents and steady-state response characteristics. Following on from these findings, the inks were then subjected to simple activation and modification procedures (comprising of electrochemical, chemical and physical treatments), with a view to maximising the electrode response, in terms of how modifications to the carbon surface translate into changes in the performance characteristics of the electrodes. The results from these investigations are discussed in the context of the use of pre-treated carbon surfaces for the enhanced production of sonochemically fabricated microelectrode array sensors, for use as electrochemical sensors and biosensors.

1. Introduction

The mass production of disposable electrodes via thick-film (screen-printing) techniques presents the most promising route for inexpensive and yet highly reproducible chemical sensing devices [1]. Screen-printing methods and materials are already highly developed for the manufacture of capacitors, resistors and conductors used in hybrid electronic circuits, and resultantly, multilayer patterns deposited are repeatable in thickness and geometry. In addition, screen printing is a simple process and because screen-printable inks are now more developed, problems such as mutual compatibility, electrochemical activity, sealing at the interface and adhesion to substrates have to a large extent, been resolved.

It is not surprising then, that during recent years, the screen-printing technology applied to sensor and biosensor construction has been considerably improved, and a large number of papers and reviews have appeared in the literature [2,3]. Indeed, screen-printed sensors are expected to be widely used in numerous real-life applications of controlled-potential techniques, and are already being utilised for the commercialisation of ‘one-shot’ glucose [4] or metal [5] sensors.

A wide range of inks and substrate materials may be used to mass produce low cost sensor strips. Silver-based inks are usually employed for obtaining reference electrodes and dielectric plus metallic oxides, or some other binding material, are used for dielectric inks. Carbon or metal (such as platinum, gold or silver) ink formulations are commonly used for printing working electrodes. Such inks may also be utilised as bonding pads for electrical connections to the sensor instrumentation and/or as counter electrodes. In particular, carbon inks are attractive for sensing applications since they are relatively inexpensive and exhibit lower background currents over a wider potential window than metal electrodes, particularly in the cathodic region [6]. These attractive properties of carbon facilitate its use in various applications, in particular carbon (graphite) ink, which offers the advantage of a lower residual current leading to higher signal/noise responses and correspondingly lower detection limits [7,8]. Graphite based carbon ink electrodes also have the advantage of being robust and can also be produced in large numbers at low cost and since they are designed to be used once and then discarded, they are more convenient to use than solid electrodes (such as glassy carbon), which may need to be renewed or repolished.

Whilst the exact ink formulation is regarded by the manufacturer as proprietary information, in general carbon inks are composed of graphite particles, a polymer binder and other additives (for the dispersion, printing and adhesion tasks). Such differences in this heterogeneous surface and composition of inks (e.g. type, size or loading of graphite particles), and in the printing and curing conditions, may strongly affect the electron transfer reactivity and overall analytical performance of the resulting carbon sensors. It is important therefore, to study in detail the analytical performance of the base (planar) carbon ink electrodes to ascer-

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tain the electrochemical nature of the ink itself, before it is applied to analyte analysis. Indeed, previous studies by Wang et al. [9] have shown that different compositions and preparations of carbon electrodes have a profound effect upon their electrochemical behaviour and electroanalytical utility.

This paper will therefore focus towards investigations into the performance of two commercially available carbon inks, in the form of screen-printed carbon electrodes, with the intention of demonstrating the sensing utility of such electrodes for generic applications. The evaluation and comparison of the performance of two different commercially available carbon inks has been examined. These investigations have been undertaken via the use of benchmark redox couples with analysis in terms of reversibility, operational potential range, background current levels and steady-state response characteristics being reported. Recent work within this research group has shown that microelectrode array-based sensors can be produced via a novel sonochemical fabrication approach [10–12], using carbon ink as an underlying conductive substrate. Electropolymerisation of an insulating polymer upon the carbon ink, followed by a subsequent ultrasonic ablation process yields discreet microelectrode pores. These pores are all interconnected by the underlying carbon ink to form a microelectrode array. It is therefore important to assess the reproducibility and electrochemical activity of the carbon ink to ensure its suitability for use as the base, conductive layer.

The variation of the electrochemical properties of carbon ink, due to composition, has been the subject of previous investigations [9,13], the majority of which concluded that such electrodes may lend themselves to improvement in terms of electrochemical performance by modification and pre-treatment. It follows, therefore, that enhancement of the performance of carbon electrodes can be taken a step further, enabling specific pre-treatments to be applied for specific sensor applications or for the measurement of particular analytes. Various activation procedures have thus been shown to influence the electrochemical reactivity of these electrodes. This approach is more practical than formulating new and specific inks, partly due to the proprietary nature of carbon inks and the specialist knowledge required to develop ink compositions, but also because modification of the ink composition (for enhancing redox activity) may compromise the binding and adhesion properties of the ink. Therefore, three methods that may be applied *in situ* to either the sensor/instrument operation, or the fabrication procedure, are investigated; comprising electrochemical, chemical and physical treatments.

It has long been reported that *electrochemical* pre-treatments of carbon electrodes can improve their electrochemical behaviour. Studies have shown that exposure of carbon to short pre-anodisation periods (<2 min), at high overpotentials in differing buffer solutions, improved the electron transfer kinetics for a variety of irreversible and *quasi*-reversible redox systems [14,15]. The application of such high positive potentials seemed to lower the static barrier, increase the surface functionality and roughness, and/or remove surface contaminants.

It has previously been demonstrated that the use of polymer coatings to produce *chemically* modified surfaces offers advantages during analysis [16–18]. Polymer materials have been attached to substrates by covalent bonding, adsorption, physical mixing, or electrodeposition and it is the latter of these mechanisms of attachment that is utilised for this investigation. One group of monomers that can be electropolymerised and that display marked analytical utility are those based upon substituted aromatics, such as aniline. Polyaniline is the polymer of choice here due to its ease of polymerisation, low cost, high conductivity and particularly, its high chemical durability against oxygen and moisture. Furthermore, it is thermodynamically possible that dissolved redox species may be oxidised or reduced by the oxidised or reduced form of the polyaniline film. This means that the film may behave as an electron-transfer mediating catalyst [19].

Previous studies have shown that modification via sonication of glassy carbon electrodes (i.e. *physical* treatment) also exhibit enhanced heterogeneous electron-transfer rates for a variety of aqueous redox probes [20,21] and consequently, tremendous increases in current levels have been observed for a number of differing analytes [22]. In principle, these results may be attributed to any combination of increased rate of electron transfer, changes in electrode area or changes in the physical and chemical properties of the electrode surface. To determine the effect of extended sonication times on the activation as well as to determine whether a correlation between enhanced electron-transfer rates exists, screen-printed carbon electrodes were sonicated in water for varying time durations, prior to electrochemical analysis.

The modified and pre-treated electrodes were examined using electrochemical techniques and comparisons are made to the responses previously obtained for unmodified surfaces. The results drawn from all these investigations will aid the development of sonochemically fabricated microelectrode array sensors based upon substrates screen printed with easily available commercial carbon inks, in terms of carbon ink composition for the base sensor and most suitable pre-treatment procedures to facilitate an enhanced sensor response.

2. Materials and methods

2.1. Reagents and solutions

Aniline hydrochloride, disodium hydrogen orthophosphate 12-hydrate, sodium dihydrogen orthophosphate dehydrate and sodium chloride (all 'AnalaR' grade), were all purchased from BDH Ltd. (Lutterworth, UK). Ferrocenemonocarboxylic acid, hexaammineruthenium(III) chloride, *o*-phenylenediamine dihydrochloride and potassium ferricyanide(III) (all Analytical Grade) were purchased from Sigma–Aldrich Ltd. (Gillingham, UK). Maleic acid, potassium chloride, potassium hydroxide and sodium carbonate (all 'Analytical Reagent' grade) were purchased from Fisher Scientific (Loughborough, UK).

A 1.0×10^{-3} M ferrocenemonocarboxylic acid solution, a 1.0×10^{-3} M hexxaamineruthenium(III) chloride solution and a 1.0×10^{-3} M potassium ferricyanide(III) solution were all prepared in pH 7.4 phosphate buffer solution comprising 5.28×10^{-2} M Na_2HPO_4, 1.3×10^{-2} M NaH_2PO_4 and 5.1×10^{-3} M NaCl in distilled de-ionised water. A saturated solution of sodium carbonate in pH 7.4 phosphate buffer and separately, a pH 7.0 buffer comprising 2.01×10^{-2} M sodium dihydrogen orthophosphate 1-hydrate, 2.98×10^{-2} M disodium hydrogen orthophosphate 12-hydrate and 0.1 M sodium chloride, were used for investigations into the activation of bare carbon electrodes.

A 0.2 M aniline hydrochloride solution used for electrode modification studies was prepared in a pH 2.0 buffer comprising 4.6×10^{-3} M maleic acid, 5.3×10^{-3} M potassium hydroxide and 8.6×10^{-3} M potassium chloride.

2.2. Materials

Carbon ink screen-printed electrodes were obtained from Microarray Ltd. (Manchester, UK) following production at Polyflex Circuits Ltd. (Parlex Corporation, Newport, Isle of Wight, UK). Each sensor unit comprised a carbon-working electrode, in addition to a carbon counter electrode and a silver/silver chloride (Ag/AgCl) reference, all printed upon a polycarbonate substrate. They therefore act as generic disposable templates and may be easily adapted for a range of differing applications. The electrodes were received as