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Electrochemical Characterization of Commercial and Home-Made Screen-Printed Carbon Electrodes

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ABSTRACT

Screen-printing technology is widely used for the mass-production of disposable electrochemical sensors. The practical utility of carbon screen-printed electrodes has been exploited, despite the fact that little is known about the nature of the electrode reactions. (Wang, J.; Pedrero, M.; Sakslund, H.; Hammerich, O.; Pingarron, J. Electrochemical activation of screenprinted carbon strips. *The Analyst* **1996**, *121* (3), 345–350). Given the complexity of carbon electrodes in general, and differences in the composition of commercial carbon inks, the question arises as to how such differences and complexity affect their electrochemical reactivity. The aim of this

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work was to compare the electroactivity of both commercial electrodes and electrodes fabricated in-house from various commercial inks, in order to find the electrode most suited to amperometric sensor work. Methods of analysis include cyclic voltammetry, amperometry and linear sweep voltammetry. It was found that the commercial working electrodes were not suited to the high current work of interest, due to their poor charge transfer properties. The in-house electrode had less resistive properties, and was more suited for high current amperometric sensing. Utilizing this electrode configuration, an optimal carbon paste was chosen for the working electrode.

Key Words: Screen-printed electrode; Cyclic voltammetry; Linear sweep voltammetry; Amperometry; Charge transfer.

INTRODUCTION

Carbon electrodes are particularly attractive for sensing applications. These materials have a high chemical inertness and provide a wide range of anodic working potentials with low electrical resistivity. They also have a very pure crystalline structure that provides low residual currents and a high signal to noise ratio.^[2] Many of the devices reported rely on the use of carbon materials such as glassy carbon,^[3] and carbon pastes.^[4] Screen printing of the carbon ink for the fabrication of electrodes has realized commercial success in the glucose sensing field.^[5] Developed for the printing industry, this thick-film technology has been adapted for the electronics industries and biosensor research. Screen-printed electrodes have low unit costs and are capable of undergoing mass production, while still maintaining adequate levels of reproducibility. They also have the advantages of miniaturization and versatility.

Carbon ink used for working electrodes must contain a binder, solvent, and graphite particles. What is still of some concern with screen-printing, is the level of reproducibility in electrode production. This is mainly due to the nature of the carbon inks—the composition of which are proprietary—and the lack of control of the microscopic structure of individual electrodes. Grennan et al.^[6] investigated the effects of the curing temperature on the physical and electrochemical characteristics of carbon paste C10903D14 (Gwent Electronic Materials). Improved sensor performance and decreased variability was demonstrated at elevated curing temperatures and this was associated with morphological changes to the carbon electrode surface. Wang et al.^[7] compared the electrochemical

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behavior and electroanalytical performance of thick film carbon sensors on ceramic substrates fabricated from four different commercially available carbon inks. They found that C10903D14 (Gwent Electronic Materials) was optimal for amperometric sensing. This ink possessed an attractive electrochemical reactivity but was found to have high residual currents. This would render it most suited to amperometric work as this method is not dependent on background contributions. It would be less suited, however, to voltammetric or stripping voltammetry work.

It is not just the interfacial region between solution and electrode that is important in determining the electrode's characteristics, but also the rest of the electrode, including the properties of the conducting path. Carbon inks may have higher resistivities than other types of conducting inks and so may not be suitable as a conductive layer, e.g., for high current work. Cui et al.^[8] characterized a screen-printed strip comprising working, reference, and auxiliary electrodes. Silver acted as the conducting path. Erlenkotter et al.^[9] used a similar format with on-board reference and auxiliary electrodes. However, the difference was that carbon acted as the conducting path for the working and auxiliary electrodes. Both strips described potentially have different charge transfer properties due to their very different compositions, and although both strips were successful for their respective applications, they may not necessarily be suited to other applications. It is important when designing any type of screen-printed electrode that the charge transfer properties are suited to the end-use application.

EXPERIMENTAL

Materials

Horseradish peroxidase (HRP, 1100 U/mg and 1310 U/mg, P8672) was purchased from Sigma-Aldrich (Poole, Dorset, UK). Aniline was purchased from Aldrich (13,293-4), vacuum distilled and stored frozen under nitrogen. Thirty percent (v/v) hydrogen peroxide solution was purchased from Merck. Polyvinylsulphonate (PVS, 27,842-4), potassium hexacyanoferrate(II) (22,768-4) (potassium ferrocyanide trihydrate) and potassium hexacyanoferrate(III) (20,801-9) (potassium ferricyanide) were purchased from Aldrich. EuroflashTM and UltraTM electrode strips were donated from Inverness Medical Ltd. EuroflashTM, UltraTM, Ercon (661901), and LRH (C2010201R15) carbon paste inks were donated by Inverness Medical Ltd. (Inverness, Scotland). LifescanTM silver conductive ink was donated by Inverness Medical

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Ltd. Seriwash universal screen wash (ZT639) was obtained from Sericol Ltd. (Kent, UK). Glassy carbon and silver/silver chloride (Ag/AgCl) electrodes were purchased from Bioanalytical Systems Ltd. (Cheshire, UK). The platinum mesh (29,809-3) was purchased from Aldrich.

Buffers and Solutions

Unless otherwise stated, all electrochemical measurements were carried out in phosphate buffered saline (PBS), (0.1 M phosphate, 0.137 M NaCl, and 2.7 mM KCl), pH 6.8.

Instrumentation

Screen-printing of in-house (noncommercial) electrodes was performed with a semi-automated DEK 248 printing machine (Weymouth, UK). Nylon screens with varying mesh thickness were used, and mounted at 45° to the print stroke. Blade rubber squeegees were employed, and a flood blade was utilized. All inks were cured in a conventional oven.

All electrochemical protocols were performed either on a BAS100/W electrochemical analyzer with BAS100/W software, or a CHI1000 potentiostat with CHI1000 software, using either cyclic voltammetry or time-based amperometric modes. An Ag/AgCl reference electrode and a platinum mesh auxiliary electrode were used for bulk electrochemical experiments.

Scanning electron microscopy (SEM) was performed with a Hitachi S 3000N scanning electron microscope. An acceleration voltage of 20 kV was employed.

Screen-Printed Electrode Fabrication

Five electrode types were fabricated for this study. Two were manufactured commercially (EuroflashTM and UltraTM) and three by in-house screen-printing (designated Ultra-inH, Ercon-inH, and LRH-inH, according to the working electrode carbon used). The structural characteristics of each of the electrodes are summarized in Table 1. The curing conditions for all inks are summarized in Table 2.

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Table 1. Summary of the composition of all electrodes used.

Electrode type	Conducting layer	Working electrode layer	Working electrode area	Insulation layer	Name
Euroflash™	Lifescan silver and Euroflash™ carbon	Euroflash™ carbon	8 mm ²	Ercon	Euroflash™
Ultra™	Ultra™ carbon	Ultra™ carbon	10 mm ²	”	Ultra™
Ultra in-house	Lifescan silver	Ultra™ carbon	9 mm ²	”	Ultra-inH
Ercon in-house	Lifescan silver	Ercon 661901	”	”	Ercon-inH
LRH in-house	Lifescan silver	LRH C2010201R15	”	”	LRH-inH

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Table 2. Curing conditions for all screen-printing inks used.

Ink type	Curing conditions
Lifescan silver ink	Conventional oven @70°C for 6 min
Carbon inks donated by Inverness Medical Ltd:	Conventional oven @70°C for 13 min
Euroflash TM	
Ultra TM	
Ercon 661901	
LRH C2010201R15	
Ercon insulation ink	Conventional oven @70°C for 15 min

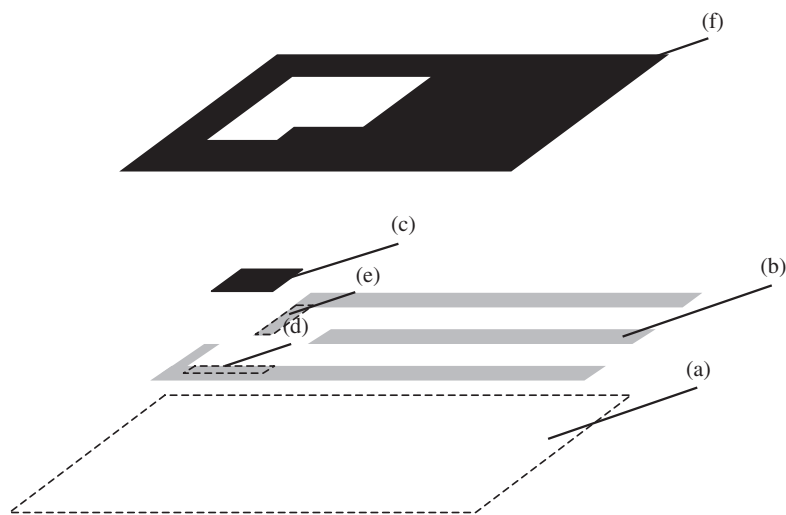


Figure 1. Components of the in-house screen-printed electrode: (a) substrate, (b) Ag/AgCl conducting paths, (c) carbon working electrode, (d) Ag/AgCl auxiliary electrode, (e) Ag/AgCl reference electrode, and (f) insulation layer. (Working electrode area: 9 mm²).

Figure 1 depicts a schematic of the in-house screen-printed electrode with onboard reference and auxiliary electrodes (Ultra-inH, Ercon-inH, and LRH-inH). Electrodes were screen-printed onto a preshrunk PET substrate (a). Initially, a layer of three Ag/AgCl tracks were deposited as the conducting paths from electrodes to contacts for the reference, auxiliary, and working electrodes (b). A layer of carbon was deposited as the working electrode (c). The Ag/AgCl acted as both reference (d) and

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auxiliary (e) electrodes. Finally, an insulation layer was deposited to eliminate cross-talk and to define the working electrode area (9 mm²) (f).

Cyclic Voltammetry

Glassy carbon or screen-printed electrodes were cycled in equimolar amounts of potassium ferrocyanide and potassium ferricyanide (1 × 10⁻³ M) using 1 M KCl as supporting electrolyte. Voltammograms were obtained using scan rates ranging from 10 to 100 mV s⁻¹ and at a sensitivity of 1 × 10⁻³ A V⁻¹ vs. Ag/AgCl under diffusion limited conditions.

Determination of Heterogeneous Electron Transfer Rate Constants

Heterogeneous electron transfer rate constants (k^0) were calculated using the method of Nicholson^[10] according to Eq. (1):

$$k^0 = \Phi \left(D_0 \pi \nu \left(\frac{nF}{RT} \right) \right)^{1/2} \left(\frac{D_R}{D_0} \right)^{\alpha/2} \quad (1)$$

where Φ refers to a kinetic parameter, D_0 is the diffusion coefficient for the ferricyanide (7.6 × 10⁻⁶ cm² s⁻¹), D_R is the diffusion coefficient for the ferrocyanide (6.3 × 10⁻⁶ cm² s⁻¹), and α is the transfer coefficient (0.5), R is the universal gas constant (8.314 JK mol⁻¹), T is the absolute temperature (K), n is the number of electrons transferred, and F is Faraday's constant (96,485 C). Φ values for the electrode systems were calculated with the aid of a solver program that generated the sixth polynomial plot of ΔE_p vs. log(Φ).

Electrode Pretreatment Procedure

Glassy carbon electrodes were cleaned by successive polishing on aqueous slurries of 1, 0.3, and 0.05 μm alumina powder, followed by ultrasonic cleaning in Milli-Q water for 10 min. The electrodes were then placed in a solution of 0.2 M H₂SO₄. A single voltammetric cycle was carried out between -1200 mV and 1500 mV at 100 mV s⁻¹ vs. Ag/AgCl. The same voltammetric procedure was employed for cleaning the screen-printed electrodes.

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Amperometric Electroanalytical Procedure

The electroanalytical procedure was carried out according to Killard et al.^[11]

RESULTS AND DISCUSSION

Two commercially manufactured screen-printed working electrodes (WE) were examined; EuroflashTM and One Touch UltraTM. These electrodes were manufactured by Inverness Medical Ltd., for glucose testing. The WE of the EuroflashTM strip were composed of a silver and carbon conducting path, a carbon working electrode and an insulation layer to define the electrode area. The UltraTM WE electrode, contained only carbon and insulation layers, relying on only carbon to act as the conductor and the electrode. The advantage of using less silver, or none at all, is to allow for reduced cost manufacturing. Electrochemical analyses were initially carried out on the commercial electrodes. However, subsequently the in-house artwork was designed as a result of finding that the commercial electrodes suffered from severe charge transfer problems and were not suitable to this amperometric sensor work. This in-house electrode design (Fig. 1) did not encounter charge transfer difficulties as the conducting tracks were composed solely of silver. It was used for the analysis of UltraTM, Ercon, and LRH inks and these electrodes are referred to in this section as Ultra-inH, Ercon-inH, and LRH-inH, respectively. Summaries of all inks used for fabrication and their respective curing conditions are given in Tables 1 and 2.

Voltammetric Performance of Screen-Printed Electrodes

The ferri/ferrocyanide redox couple was the redox system used for comparing the voltammetric behavior of screen-printed electrodes. Figure 2 displays the cyclic voltammograms of the redox couple at a glassy carbon electrode for comparison purposes, the commercial carbon strip electrodes (EuroflashTM and UltraTM) and the commercial inks printed in-house (Ercon-inH, LRH-inH, and Ultra-inH). The mean peak separations and anodic ($j_{p,a}$) and cathodic ($j_{p,c}$) peak current densities are also illustrated in Fig. 3 ($n = 3$). The commercial electrodes, EuroflashTM and UltraTM, yielded very poor reversibility with ΔE_p values of 471 (± 56) mV and 416 (± 37) mV, respectively and $j_{p,a}$ values of $-12.313 (\pm 2.025) \mu\text{A cm}^{-2}$ and $-15.107 (\pm 2.638) \mu\text{A cm}^{-2}$, respectively.

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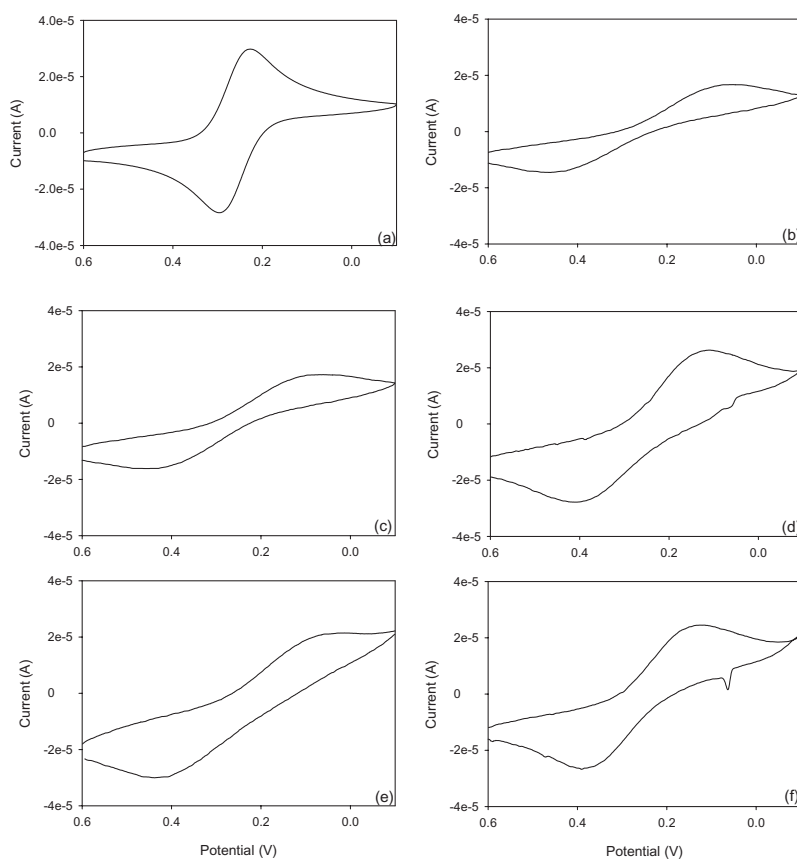


Figure 2. Cyclic voltammograms for different electrodes in 1×10^{-3} M ferri/ferrocyanide and 1 M KCl supporting electrolyte. (a) Glassy carbon, (b) Euroflash™, (c) Ultra™, (d) Ercon-inH, (e) LRH-inH, and (f) Ultra-inH. The commercial electrodes ((b), (c)) showed very poor reversibility. Using the in-house design, ((d), (e), (f)) reversibility improved, with the Ultra-inH exhibiting the best behavior.

This behavior was attributed to the poor charge transfer of the electrodes. The conducting paths (composed of segments of silver and carbon for Euroflash™ and fully carbon for Ultra™ electrodes) from WEs to contacts had resistive properties that may have become a significant limiting factor in charge transfer. It resulted in the poor reversibility of the redox couple and low $j_{p,a}$ values. This initial work motivated the in-house electrode artwork to be designed where the conducting tracks were

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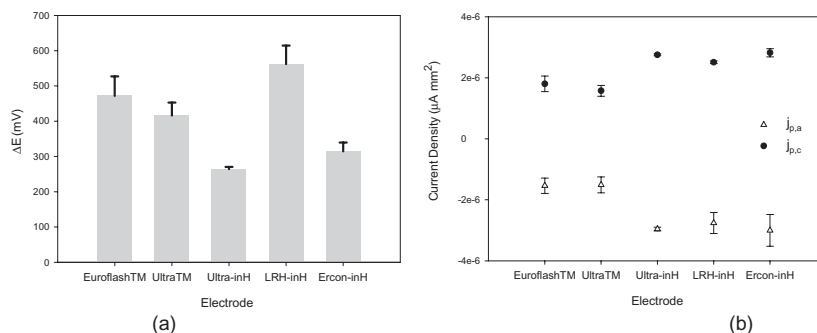


Figure 3. (a) Cyclic voltammetric peak separations (ΔE_p) and (b) anodic and cathodic peak current densities for 1×10^{-3} M ferri/ferrocyanide and 1 M KCl for each of the screen-printed electrodes ($n=3$).

composed solely of silver. Each in-house thick-film carbon electrode exhibited different electron-transfer reactivities towards ferri/ferro, with the Ultra-inH electrode yielding the most reversible behavior. For example, the redox couple gave a ΔE_p value of 264 (± 7) mV for Ultra-inH, as compared to 314 (± 25) mV and 562 (± 52) mV for Ercon-inH and LRH-inH, respectively. The Ultra-inH also offered the highest j_p values and lowest overvoltage of all the in-house electrodes (i.e., anodic peak potentials for ferrocyanide of 392 mV, compared to 452, 460, 410, and 439 mV for UltraTM, EuroflashTM, Ercon-inH, and LRH-inH, respectively).

Of all the electrodes examined, the Ultra-inH electrode exhibited the best behavior towards the redox couple. It was observed immediately that the commercial electrodes, manufactured by Inverness Medical Ltd., were not suited to present purposes because of poor charge transfer properties. The in-house design had more optimal charge transfer properties, and in conjunction with the UltraTM commercial ink as the WE, behaved as the best screen-printed electrode. This work demonstrates the importance of optimizing *both* the conducting path and the carbon of the WE when designing a new screen-printed electrode. Both parameters have profound effects on the behavior of the electrode.

All k^0 values are given in Table 3. Recalling that for all the screen-printed electrodes the ΔE_p values were considerably greater than the 59 mV value expected for Nernstian one-electron reactions, k^0 values were then also inevitably low compared to glassy carbon. Commercial electrodes (EuroflashTM and UltraTM) exhibited k^0 values 2000-fold and 1250-fold lower than that obtained for glassy carbon, respectively. The LRH-inH electrode proved the poorest with regard to k^0 , being

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Table 3. Table of heterogeneous electron transfer rate constant (k^0) for glassy carbon and each of the screen-printed electrodes.

Electrode	k^0 (cm s ⁻¹)
Glassy carbon	5.9×10^{-2}
Euroflash TM	2.83×10^{-5}
Ultra TM	4.7×10^{-5}
Ercon-inH	1.74×10^{-4}
LRH-inH	1.67×10^{-5}
Ultra-inH	3.09×10^{-4}

3500-fold lower than glassy carbon. Ercon-inH and Ultra-inH both had the best k^0 values of the screen-printed electrodes, yielding k^0 values only 300-fold and 200-fold lower than glassy carbon, respectively. Thus, Ultra-inH exhibited the best k^0 value, even if this was still two orders of magnitude lower than glassy carbon. Such decreases in the electron-transfer reactivity may be consistent with the composition of the ink, being composed only partly of conductive carbon particles. In view of the proprietary composition of all the inks, it is difficult to explain why the Ultra-inH electrode displayed the most favorable redox behavior. Observed changes in redox behavior may be dictated by varying graphite content (good redox behavior suggests a high graphite loading), the nature of the graphite particles, and the presence or absence of an adherent (inhibitory) organic layer. Further studies employing energy dispersive x-ray analysis (EDX), and scanning electrochemical microscopy (SECM) may help to establish the relationship between carbon content and electrode performance.

Although Ultra-inH was shown to have the best behavior of all the screen-printed electrodes to ferri/ferrocyanide, its behavior was still far from ideal. Attempts to improve its behavior (by electrochemical pretreatment and optimization of curing conditions) were carried out and discussed in a later section.

Amperometric Performance of Screen-Printed Electrodes

The electrochemical performance of the screen-printed electrodes was investigated by incorporating them into a batch cell set-up.^[9] Previous work by this group had used these types of screen-printed carbon electrodes as the basis of a biosensor using electrodeposited

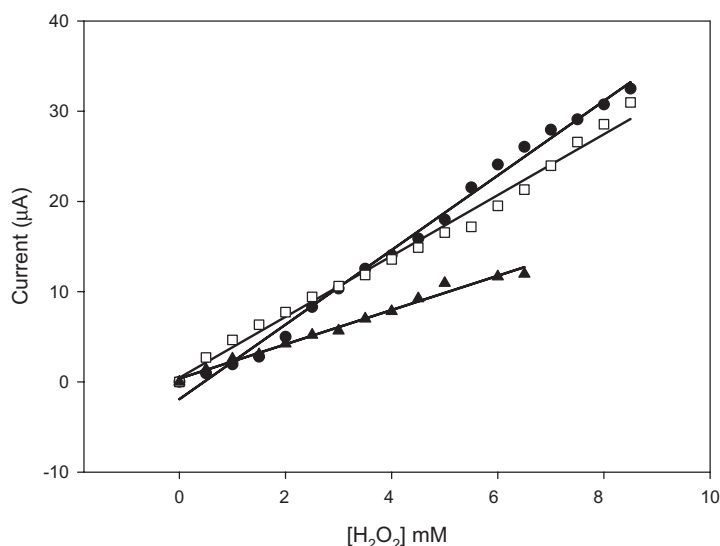


Figure 4. Amperometric sensor responses for successive additions of 0.5 mM hydrogen peroxide to a solution containing 2 mg/mL horseradish peroxidase. Electrodes used were (●) Ultra-inH, (□) Ercon-inH, and (▲) LRH-inH. Electrodes held at -100 mV vs. Ag/AgCl wire electrode.

conducting PANI/PVS films onto which was deposited HRP or antibodies. The nature of these biosensors has been described elsewhere.^[11,12] Briefly, PANI/PVS was deposited on the surface of the electrode and the potential was cycled the required number of times. No protein was immobilized onto the surface of the polymer. Ultra-inH, Ercon-inH, and LRH-inH electrodes were subjected to successive additions of 0.5 mM hydrogen peroxide added freshly to a solution of 2 mg mL^{-1} horseradish peroxidase and the amperometric response monitored. All three sensors responded to the changes in peroxide concentration (Fig. 4). Similar response times and noise levels were observed (data not shown). Ultra-inH offered the highest sensitivity ($4 \mu\text{A mM}^{-1}$ peroxide), with Ercon-inH exhibiting a slightly lower sensitivity ($3.2 \mu\text{A mM}^{-1}$ peroxide). LRH-inH showed the poorest sensitivity ($1.8 \mu\text{A mM}^{-1}$ peroxide). This correlates with the voltammetric behavior. Ultra-inH exhibited the highest sensitivity in terms of j_p values while LRH-inH exhibited the lowest values.

Amperometric experiments could not be carried out on either of the commercial electrodes as the charge transfer properties of the electrodes hindered deposition of adequate polymer. For example, the in-house

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strips required seven cycles to immobilize polymer to the required thickness, whereas the commercial electrodes needed 20 cycles in order to reach only one fifth the required thickness. The experiments on these strips were abandoned at this point.

Linear Sweep Voltammetric Performance of Screen-Printed Electrodes

The background current of thick-film carbon electrodes is strongly affected by the carbon ink employed.^[7] Figure 5 compares the background voltammograms for the different carbon electrodes in degassed phosphate buffer (pH 6.8). Several electrodes of each type were analyzed and Fig. 5 shows data representative of all analyses. LRH-inH exhibited the widest potential window particularly with respect to the cathodic potential limit (i.e., high hydrogen overvoltage). Its potential window had a range of 1150 to -300 mV, where the nonfaradaic current remained constant ($\approx 5.2 \mu\text{A}$) in this electrolyte solution. The background current of Ercon-inH was narrow and poor, exhibiting a lot of interference. Ultra-inH also had a narrow potential window (1097 to 60 mV) but

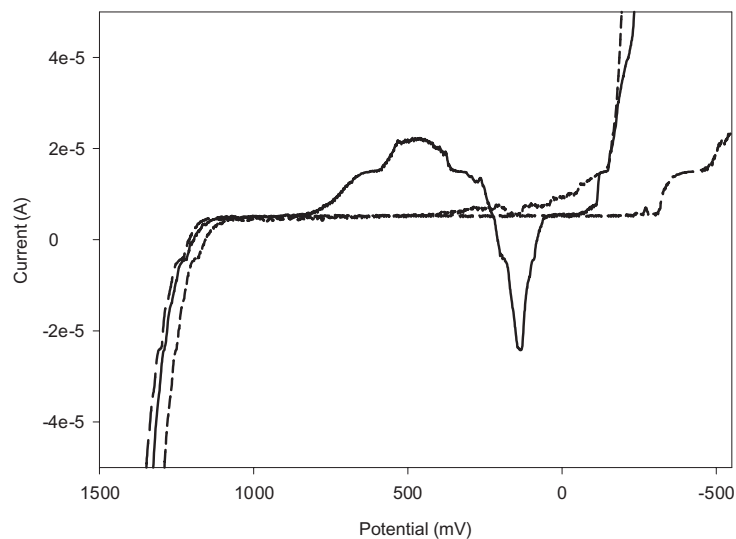
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Figure 5. Linear sweep voltammograms in degassed PBS buffer (pH 6.8). Electrodes used were (solid line) LRH-inH, (long dash) Ultra-inH, and (short dash) Ercon-inH.

was not affected by major interferences. The non-faradaic current was of the same magnitude as for LRH-inH. The anodic potential limits (i.e., oxygen overvoltage) were approximately the same for each of the inks.

A carbon ink possessing a narrow potential is not necessarily a negative property for amperometric sensing. It should be noted that an electrode of choice for fixed potential amperometric biosensors need not necessarily have the widest potential window as amperometric measurements are less affected by differences in the background contributions, as they are usually performed after the decay of transient currents to steady state values.^[7] However, the nonfaradaic background current measured in linear sweep voltammetry, could potentially have an effect on the sensitivity of the electrode. The background current can limit the lowest current that can be measured, and so could affect the detection limits of an assay.

Optimization of Ultra-inH

Although Ultra-inH did exhibit the best properties of all electrodes, for the purpose of designing an electrode suited towards amperometric sensing, there were major concerns that the UltraTM ink for the WE was still not ideal. This was highlighted in the cyclic voltammetric study of ferrocyanide. Attempts to decrease the ΔE_p values were done by varying the curing temperature and length of curing time of the carbon ink, and also the effect of electrochemical pretreatment was studied.

Curing Parameters

Due to the composition of carbon inks, the parameters of curing can have a profound effect on their performance.^[6] ΔE_p values and i_p values for the ferri/ferrocyanide redox couple were monitored over a range of curing temperatures and it was found that above a temperature of 70°C, ΔE_p values increased greatly and the $i_{p,a}$ decreased (Fig. 6).

Carbon inks may be composed of three basic constituents: graphite, vinyl, or epoxy-based polymeric binders and solvent to enhance the ink's affinity for the substrate in terms of adhesion, and to improve viscosity for the screen-printing process. It has been suggested that increases in curing temperature may result in evaporation of the solvent and decomposition of the polymeric binder to give a greater definition of the graphite or carbon particles. This would mean that the increases in

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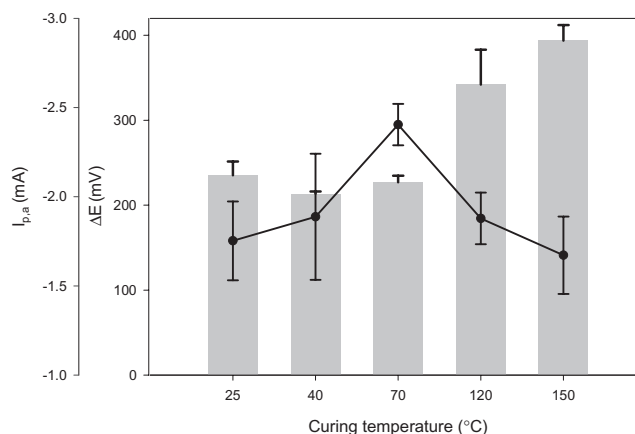


Figure 6. Mean cyclic voltammetric peak separations ($n=4$) (bar) and mean anodic peak currents ($n=4$) (line) for 1×10^{-3} M ferrocyanide and 1 M KCl for varying curing temperatures of the Ultra™ ink on the Ultra-inH electrode. A curing temperature of 70°C showed optimal voltammetric performance for ΔE_p and $i_{p,a}$ values.

temperature should result in an increase in the microparticulate nature of the carbon and greater definition of the graphite particle surface area.^[6] According to this theory, electron transfer rates should increase as the graphite particle surface area becomes increasingly defined (i.e., with increasing temperature). This behavior was not observed for the Ultra ink. Increases in temperature above 70°C resulted in reduced reaction kinetics. This demonstrates that that the individual nature of the ink and its unknown constituents can have a profound effect on its characteristics. The Ultra ink seemed to maintain a very defined microparticulate character (Fig. 7), which was quite different from the Gwent electrode.^[6] This difference in behavior could be attributed to different solvents with different evaporation rates, different graphite particles or binders or other additives, and their relative concentrations/solubilities etc. If the viscosity of inks differ, the film thickness after a single print will most likely also differ and may cause a difference in the electrochemical and physical characteristics. Below 70°C, ΔE_p values were relatively constant. There were no resistive effects observed that one might expect if there was excess polymeric binder present at the electrode surface due to curing at lower temperatures. $i_{p,a}$ values peaked at 70°C, and this temperature was chosen as optimum, as greatest sensitivity was exhibited at this curing temperature.

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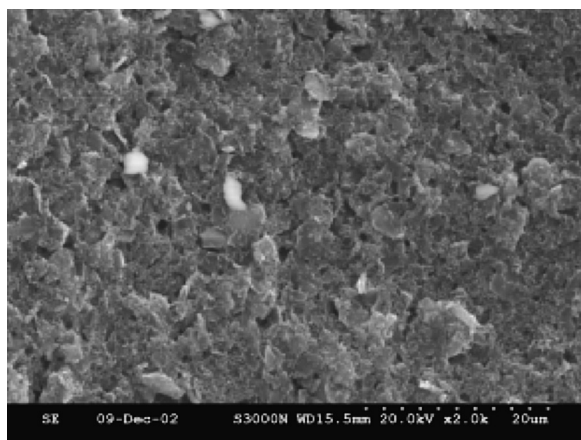


Figure 7. Typical scanning electron micrograph of the Ultra ink cured at 70°C for 13 min (2500 X magnification). The surface topography shows good definition of graphite particles.

Scanning electron microscopy (SEM) was carried out on all of these electrodes, and no discernible differences were noted at the different curing temperatures. Therefore, any changes in charge transfer effects by varying the curing temperature cannot be attributed to physical changes in the morphology of the surfaces. Figure 7 shows a typical UltraTM ink carbon surface cured at 70°C.

The effect of curing time on electrode performances was monitored at a curing temperature of 70°C. Over a range of 0–20 min, there did not appear to be any significant effect on electrode performance. ΔE_p values for ferrocyanide did not vary significantly (data not shown). This data appears to suggest that curing had very little impact on the performance of the ink at all. Even at 0 min (no curing), ΔE_p was only marginally higher. This correlates with the curing temperature data in that up to about 70°C, there is very little gain in electrochemical performance. Heat may serve only to physically dry the constituents of the ink. This may also suggest that any solvents present are extremely volatile or extremely non-volatile and ink-drying may be brought about by polymerization processes rather than evaporative processes. It certainly suggests a very different composition for the Ultra ink, as opposed to the Gwent ink previously characterized.^[6]

Since curing temperature and time were not found to be such important factors, it was decided not to deviate from the standard

using conditions of 70°C for 13 min. For all future work, these curing parameters would be used for the Ultra™ ink.

Electrochemical Pretreatment

Pre-treatment of working electrodes is a method employed by many researchers in order to enhance the electrochemical activity of their screen-printed electrodes.^[1,8,13] It is generally agreed that pretreatment effectively removes organic binders and contamination that occur at electrode surfaces such as carbon and gold and may bring about an increase in the numbers of chemically reactive sites on the electrode surface. Wang et al.^[1] employed an electrochemical pretreatment method involving short preanodization (30 s to 3 min in the 1.5 to 2.0 V range) of screen-printed electrodes in phosphate buffer solution (0.05 M). This pretreatment method appeared to increase the surface functionalities and roughness or to remove surface contaminants and resulted in enhanced electrochemical activity. Electrochemical pretreatment of electrodes can also be carried out by cycling the potential in acidic media. Gue et al.^[13] simply used a chemical cleaning step with sulphuric acid and hydrogen peroxide solution for gold microelectrodes. This step was critical for sensor sensitivity.

The electrochemical pretreatment method of Killard et al.^[11] has been employed in this work. Cycling the screen-printed electrode in sulphuric acid (0.2 M) is believed to have the effect of stripping the surface of the carbon electrode. Any insulative materials present at the surface may be removed. The procedure may even have the effect of renewing the surface by removing the whole outer layer of the ink. To assess the effect of electrode pretreatment on the Ultra™ ink, the electrodes were subjected to varying numbers of cycles in 0.2 M H₂SO₄, and the effect of this on electrode behavior was examined by looking at the ferri/ferro couple. By electrochemically pretreating the Ultra electrode, its behavior towards the ferri/ferrocyanide redox couple improved dramatically. ΔE_p values decreased by 50%. Before pretreatment, electrodes were exhibiting an average ΔE_p value of 222 mV (RSD = 2.0%, $n=9$). After pretreatment, this was reduced to 112 mV (RSD = 3.5%, $n=9$). i_p current values also increased as a result. One pretreatment cycle was sufficient to observe this behavior. Increasing the number of pretreatment cycles did not have a significant effect. k^0 values increased from $3.09 \times 10^{-4} \text{ cm s}^{-1}$ (no pretreatment) to $3.97 \times 10^{-3} \text{ cm s}^{-1}$ (pretreated); a 10-fold improvement. These figures suggest that the electrochemical pretreatment of the screen-printed

electrode greatly improved their electrochemical performance. After pretreatment, the kinetics and charge transfer rates at the UltraTM electrode were enhanced greatly.

CONCLUSION

Initially, commercial screen-printed electrodes were examined with a view to using them for amperometric immunosensing. It was found however, that although the working electrodes of the strips may have been suitable, the charge transfer properties of the strips were not high enough for the high current work of interest. This was due to the fact that the electrode surfaces and conducting paths were too resistive and hindered the required current flow from the working electrode to the potentiostat. A new in-house electrode was designed with a silver conducting path. The charge transfer properties of the electrode were not limiting, and this design was used for the electrochemical analysis of various working electrode carbon inks. The inks were analyzed using voltammetry, linear sweep voltammetry, and amperometry and it was found that the Ultra-inH electrode had the most preferable electrochemical properties (i.e., a k^0 value of $3.09 \times 10^{-4} \text{ cm s}^{-1}$, and a high sensitivity in the amperometric experiments). These properties were further enhanced by electrochemical pretreatment rendering it the most suitable for amperometric sensing.

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