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

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

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## INTRODUCTION

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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.<sup>[2]</sup> Many of the devices reported rely on the use of carbon materials such as glassy carbon,<sup>[3]</sup> and carbon pastes.<sup>[4]</sup> Screen printing of the carbon ink for the fabrication of electrodes has realized commercial success in the glucose sensing field.<sup>[5]</sup> 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.<sup>[6]</sup> 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.<sup>[7]</sup> compared the electrochemical

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

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

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## 112 EXPERIMENTAL

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### 114 Materials

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116 Horseradish peroxidase (HRP, 1100 U/mg and 1310 U/mg, P8672)  
117 was purchased from Sigma–Aldrich (Poole, Dorset, UK). Aniline was  
118 purchased from Aldrich (13,293-4), vacuum distilled and stored frozen  
119 under nitrogen. Thirty percent (v/v) hydrogen peroxide solution was  
120 purchased from Merck. Polyvinylsulphonate (PVS, 27,842-4), potassium  
121 hexacyanoferrate(II) (22,768-4) (potassium ferrocyanide trihydrate) and  
122 potassium hexacyanoferrate(III) (20,801-9) (potassium ferricyanide)  
123 were purchased from Aldrich. Euroflash<sup>TM</sup> and Ultra<sup>TM</sup> electrode  
124 strips were donated from Inverness Medical Ltd. Euroflash<sup>TM</sup>,  
125 Ultra<sup>TM</sup>, Ercon (661901), and LRH (C2010201R15) carbon paste inks  
126 were donated by Inverness Medical Ltd. (Inverness, Scotland).  
Lifescan<sup>TM</sup> silver conductive ink was donated by Inverness Medical

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

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### Buffers and Solutions

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### Instrumentation

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### Screen-Printed Electrode Fabrication

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Five electrode types were fabricated for this study. Two were man-  
ufactured commercially (Euroflash<sup>TM</sup> and Ultra<sup>TM</sup>) and three by in-  
house screen-printing (designated Ultra-inH, Ercon-inH, and LRH-inH,  
according to the working electrode carbon used). The structural charac-  
teristics 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 <sup>2</sup>	Ercon	Euroflash™
Ultra™	Ultra™ carbon	Ultra™ carbon	10 mm <sup>2</sup>	”	Ultra™
Ultra in-house	Lifescan silver	Ultra™ carbon	9 mm <sup>2</sup>	”	Ultra-inH
Ercon in-house	Lifescan silver	Ercon 661901	”	”	Ercon-inH
LRH in-house	Lifescan silver	LRH C201020IR15	”	”	LRH-inH

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

170	Ink type	Curing conditions
171		
172	Lifescan silver ink	Conventional oven @70°C for 6 min
173	Carbon inks donated by	Conventional oven @70°C for 13 min
174	Inverness Medical Ltd:	
175	Euroflash™	
176	Ultra™	
177	Ercon 661901	
178	LRH C2010201R15	
179	Ercon insulation ink	Conventional oven @70°C for 15 min

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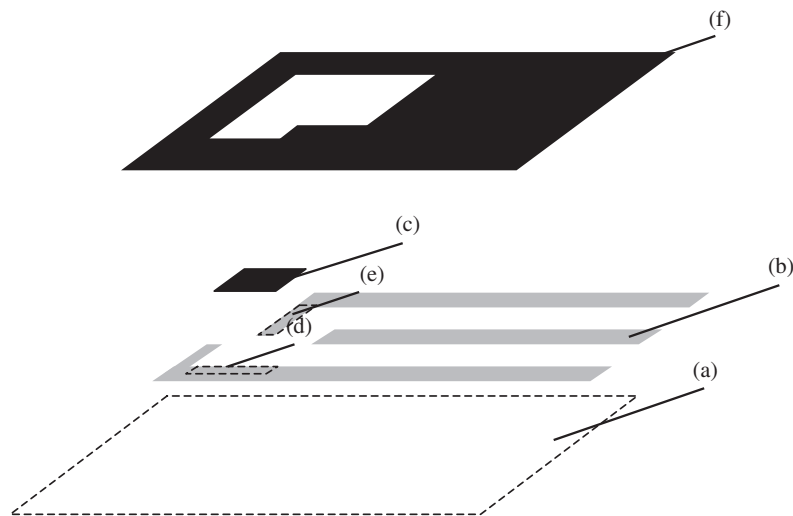
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**Figure 1.** Components of the in-house screen-printed electrode: (a) substrate, (b) Ag/AgCl conducting paths, (c) carbon working electrode, (d) Ag/AgCl auxiliary electrode, (e) Ag/AgCl reference electrode, and (f) insulation layer. (Working electrode area: 9 mm<sup>2</sup>).

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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**Screen-Printed Carbon Electrodes**

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211 auxiliary (e) electrodes. Finally, an insulation layer was deposited to  
 212 eliminate cross-talk and to define the working electrode area (9 mm<sup>2</sup>) (f).  
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**Cyclic Voltammetry**

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217 Glassy carbon or screen-printed electrodes were cycled in equimolar  
 218 amounts of potassium ferrocyanide and potassium ferricyanide  
 219 ( $1 \times 10^{-3}$  M) using 1 M KCl as supporting electrolyte. Voltammograms  
 220 were obtained using scan rates ranging from 10 to 100 mV s<sup>-1</sup> and  
 221 at a sensitivity of  $1 \times 10^{-3}$  A V<sup>-1</sup> vs. Ag/AgCl under diffusion limited  
 222 conditions.  
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**Determination of Heterogeneous  
Electron Transfer Rate Constants**

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

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

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**Electrode Pretreatment Procedure**

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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 H<sub>2</sub>SO<sub>4</sub>. A single voltammetric  
 cycle was carried out between -1200 mV and 1500 mV at 100 mVs<sup>-1</sup> vs.  
 Ag/AgCl. The same voltammetric procedure was employed for cleaning  
 the screen-printed electrodes.

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**Amperometric Electroanalytical Procedure**

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The electroanalytical procedure was carried out according to Killard et al.<sup>[11]</sup>

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**RESULTS AND DISCUSSION**

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**Voltammetric Performance of Screen-Printed Electrodes**

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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 (Euroflash<sup>TM</sup> and Ultra<sup>TM</sup>) 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, Euroflash<sup>TM</sup> and Ultra<sup>TM</sup>, yielded very poor reversibility with  $\Delta E_p$  values of 471 ( $\pm 56$ ) mV and 416 ( $\pm 37$ ) 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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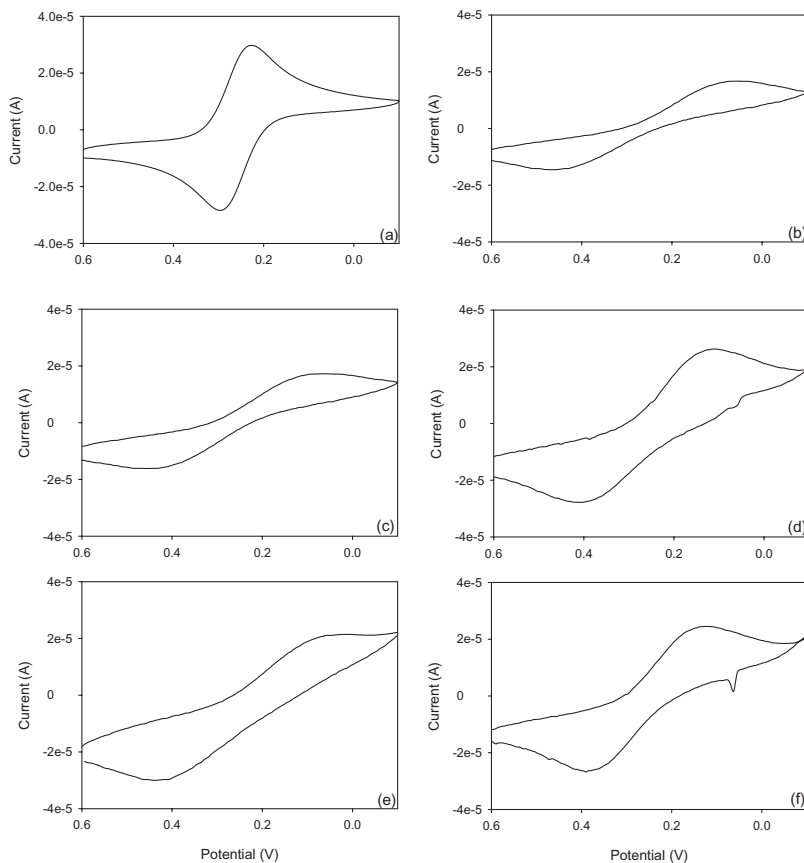
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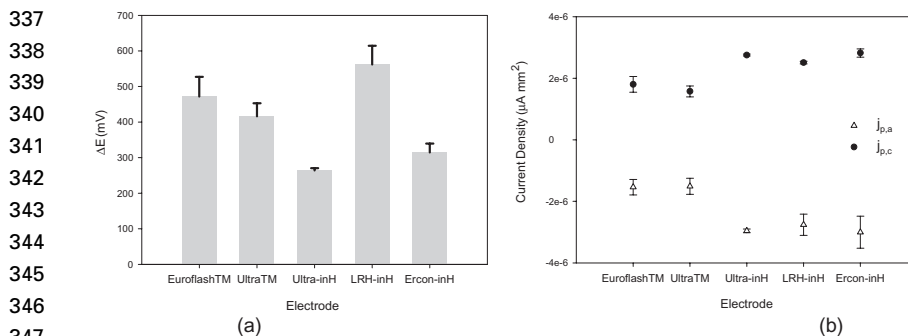
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**Figure 2.** Cyclic voltammograms for different electrodes in  $1 \times 10^{-3}$  M ferri/ferrocyanide and 1 M KCl supporting electrolyte. (a) Glassy carbon, (b) Euroflash<sup>TM</sup>, (c) Ultra<sup>TM</sup>, (d) Ercon-inH, (e) LRH-inH, and (f) 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<sup>TM</sup> and fully carbon for Ultra<sup>TM</sup> 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



**Figure 3.** (a) Cyclic voltammetric peak separations ( $\Delta E_p$ ) and (b) anodic and cathodic peak current densities for  $1 \times 10^{-3}$  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  $\Delta E_p$  value of 264 ( $\pm 7$ ) mV for Ultra-inH, as compared to 314 ( $\pm 25$ ) mV and 562 ( $\pm 52$ ) 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 Ultra<sup>TM</sup>, Euroflash<sup>TM</sup>, 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 Ultra<sup>TM</sup> 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  $\Delta E_p$  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 (Euroflash<sup>TM</sup> and Ultra<sup>TM</sup>) 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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379 **Table 3.** Table of heterogeneous electron transfer rate  
 380 constant ( $k^0$ ) for glassy carbon and each of the screen-  
 381 printed electrodes.

382 Electrode	$k^0$ (cm s <sup>-1</sup> )
383 Glassy carbon	$5.9 \times 10^{-2}$
384 Euroflash <sup>TM</sup>	$2.83 \times 10^{-5}$
385 Ultra <sup>TM</sup>	$4.7 \times 10^{-5}$
386 Ercon-inH	$1.74 \times 10^{-4}$
387 LRH-inH	$1.67 \times 10^{-5}$
388 Ultra-inH	$3.09 \times 10^{-4}$

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392 3500-fold lower than glassy carbon. Ercon-inH and Ultra-inH both had  
 393 the best  $k^0$  values of the screen-printed electrodes, yielding  $k^0$  values only  
 394 300-fold and 200-fold lower than glassy carbon, respectively. Thus,  
 395 Ultra-inH exhibited the best  $k^0$  value, even if this was still two orders  
 396 of magnitude lower than glassy carbon. Such decreases in the electron-  
 397 transfer reactivity may be consistent with the composition of the ink,  
 398 being composed only partly of conductive carbon particles. In view of  
 399 the proprietary composition of all the inks, it is difficult to explain why  
 400 the Ultra-inH electrode displayed the most favorable redox behavior.  
 401 Observed changes in redox behavior may be dictated by varying graphite  
 402 content (good redox behavior suggests a high graphite loading),  
 403 the nature of the graphite particles, and the presence or absence of an  
 404 adherent (inhibitory) organic layer. Further studies employing energy  
 405 dispersive x-ray analysis (EDX), and scanning electrochemical micros-  
 406 copy (SECM) may help to establish the relationship between carbon  
 407 content and electrode performance.

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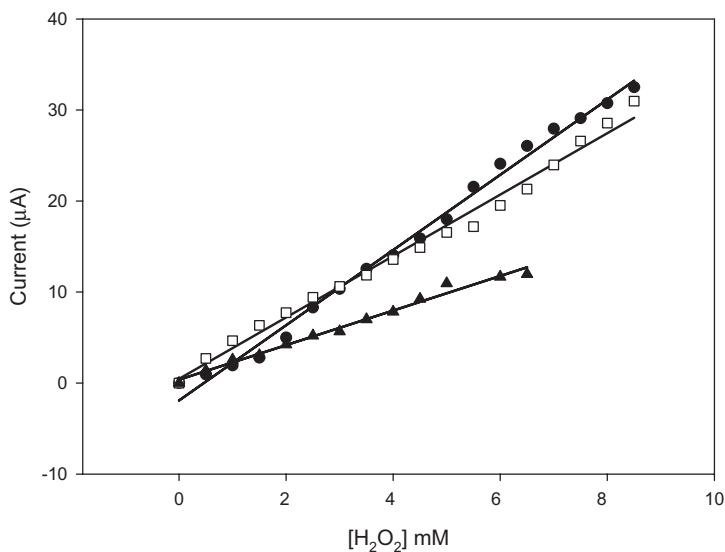
Although Ultra-inH was shown to have the best behavior of all the  
 screen-printed electrodes to ferri/ferrocyanide, its behavior was still  
 far from ideal. Attempts to improve its behavior (by electrochemical  
 pretreatment and optimization of curing conditions) were carried out  
 and discussed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

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#### 415 Amperometric Performance of Screen-Printed Electrodes

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The electrochemical performance of the screen-printed electrodes  
 was investigated by incorporating them into a batch cell set-up.<sup>[9]</sup>  
 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.<sup>[11,12]</sup> 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  $2 \text{ mg mL}^{-1}$  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

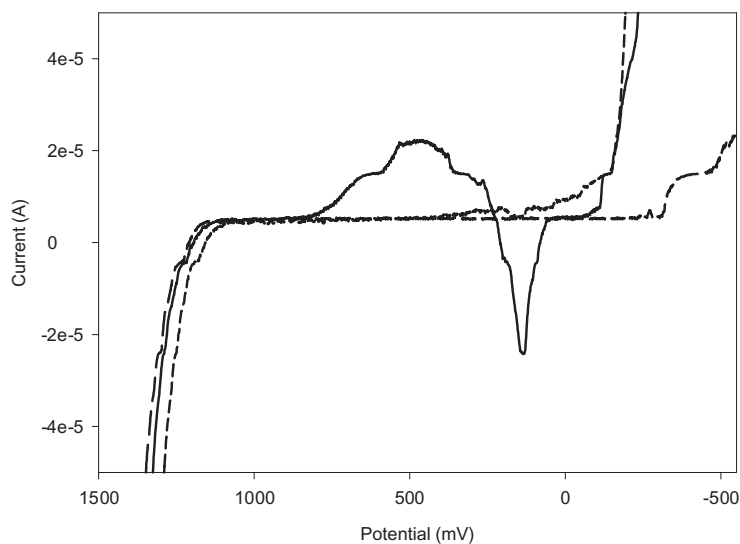
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463 strips required seven cycles to immobilize polymer to the required thick-  
 464 ness, whereas the commercial electrodes needed 20 cycles in order to  
 465 reach only one fifth the required thickness. The experiments on these  
 466 strips were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

### 469 Linear Sweep Voltammetric Performance of 470 Screen-Printed Electrodes

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

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

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

508 A carbon ink possessing a narrow potential is not necessarily a  
509 negative property for amperometric sensing. It should be noted that an  
510 electrode of choice for fixed potential amperometric biosensors need not  
511 necessarily have the widest potential window as amperometric measure-  
512 ments are less affected by differences in the background contributions, as  
513 they are usually performed after the decay of transient currents to steady  
514 state values.<sup>[7]</sup> However, the nonfaradaic background current measured  
515 in linear sweep voltammetry, could potentially have an effect on the  
516 sensitivity of the electrode. The background current can limit the  
517 lowest current that can be measured, and so could affect the detection  
518 limits of an assay.

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### Optimization of Ultra-inH

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### Curing Parameters

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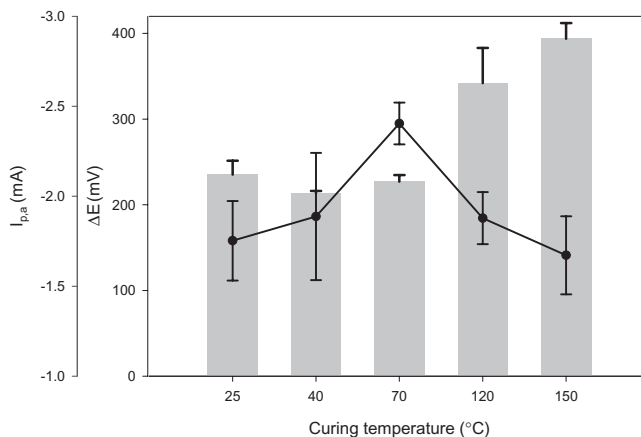
Although Ultra-inH did exhibit the best properties of all electrodes,  
for the purpose of designing an electrode suited towards amperometric  
sensing, there were major concerns that the Ultra<sup>TM</sup> ink for the WE was  
still not ideal. This was highlighted in the cyclic voltammetric study of  
ferrocyanide. Attempts to decrease the  $\Delta E_p$  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.

Due to the composition of carbon inks, the parameters of curing can  
have a profound effect on their performance.<sup>[6]</sup>  $\Delta E_p$  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,  
 $\Delta E_p$  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 decom-  
position 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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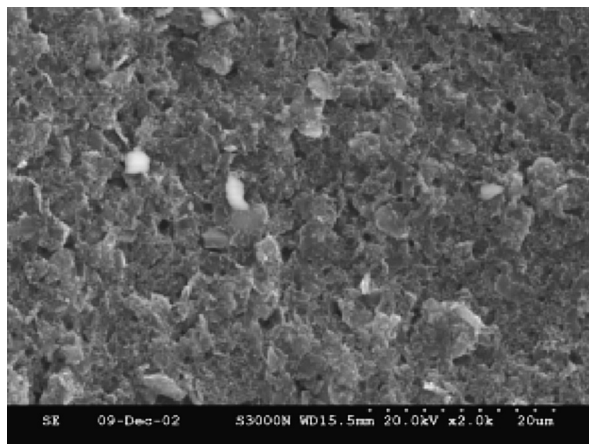
**Figure 6.** Mean cyclic voltammetric peak separations ( $n=4$ ) (bar) and mean anodic peak currents ( $n=4$ ) (line) for  $1 \times 10^{-3}$  M ferrocyanide and 1M KCl for varying curing temperatures of the Ultra™ ink on the Ultra-inH electrode. A curing temperature of 70°C showed optimal voltammetric performance for  $\Delta E_p$  and  $i_{p,a}$  values.

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temperature should result in an increase in the microparticulate nature of the carbon and greater definition of the graphite particle surface area.<sup>[6]</sup> 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.<sup>[6]</sup> 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,  $\Delta E_p$  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.

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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 Ultra™ 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.  $\Delta E_p$  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),  $\Delta E_p$  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.<sup>[6]</sup>

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



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

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

653 The electrochemical pretreatment method of Killard et al.<sup>[11]</sup> has  
654 been employed in this work. Cycling the screen-printed electrode in  
655 sulphuric acid (0.2 M) is believed to have the effect of stripping the  
656 surface of the carbon electrode. Any insulative materials present at the  
657 surface may be removed. The procedure may even have the effect of  
658 renewing the surface by removing the whole outer layer of the ink. To  
659 assess the effect of electrode pretreatment on the Ultra™ ink, the  
660 electrodes were subjected to varying numbers of cycles in 0.2 M H<sub>2</sub>SO<sub>4</sub>,  
661 and the effect of this on electrode behavior was examined by looking at  
662 the ferri/ferro couple. By electrochemically pretreating the Ultra  
663 electrode, its behavior towards the ferri/ferrocyanide redox couple  
664 improved dramatically.  $\Delta E_p$  values decreased by 50%. Before  
665 pretreatment, electrodes were exhibiting an average  $\Delta E_p$  value of  
666 222 mV (RSD = 2.0%,  $n=9$ ). After pretreatment, this was reduced to  
667 112 mV (RSD = 3.5%,  $n=9$ ).  $i_p$  current values also increased as a  
668 result. One pretreatment cycle was sufficient to observe this behavior.  
669 Increasing the number of pretreatment cycles did not have a significant  
670 effect.  $k^0$  values increased from  $3.09 \times 10^{-4} \text{ cm s}^{-1}$  (no pretreatment) to  
671  $3.97 \times 10^{-3} \text{ cm s}^{-1}$  (pretreated); a 10-fold improvement. These figures  
672 suggest that the electrochemical pretreatment of the screen-printed

673 electrode greatly improved their electrochemical performance. After pre-  
674 treatment, the kinetics and charge transfer rates at the Ultra<sup>TM</sup> electrode  
675 were enhanced greatly.

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### 679 CONCLUSION

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

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