Electrochemical characterization of some commercial screen-printed electrodes in different redox substrates

Kalyan Kumar Mistry[1,2,*], **Sagarika Deepthy, T.**[1], **Chirasree Roy Chaudhuri**[2] **and Hiranmay Saha**[3]

[1]CSIR-Central Mechanical Engineering Research Institute, M.G. Avenue, Durgapur 713 209, India
[2]Department of Electronics and Telecommunication Engineering and
[3]Centre of Excellence for Green Energy and Sensor System, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711 103, India

Electrochemical sensors based on screen-printed electrodes (SPEs) are applied for the precise detection of an analyte concentration in a sample solution and is one of the thrust areas of research, especially in healthcare and environmental monitoring. In this article we report electrochemical characterization of some commercially available SPEs obtained from three different commercial manufacturers in three different redox probes such as potassium ferricyanide, ascorbic acid/vitamin-C and nicotinamide adenine dinucleotide. The main aim of this study is to compare the sensitivity, stability, ideality and reproducibility in the development of electrochemical sensors for specific detection of biological or chemical substances using SPEs.

Keywords: Electrochemical characterization, environmental monitoring, healthcare, redox probe, screen-printed electrode.

ELECTROCHEMICAL sensors based on screen-printed electrodes (SPEs) are convenient to use because of their ease of fabrication, ability to mass produce and low cost[1–3]. Surface of SPEs can be easily modified by immobilization of different biomolecules, enzymes and catalytic substances and thus can be tuned to enhance the sensitivity and selectivity of detection. The other important advantage of using SPEs is the requirement of minimal volume of analyte solutions which is cost effective and particularly useful when sample volume is minute[4].

SPE consists of three electrodes, namely working electrode (WE), reference electrode (RE) and auxiliary or counter electrode (AE) printed using conductive ink material on a solid substrate in planar form. WE is the main sensing platform mostly made of carbon and its composites. When a small volume of analyte sample solution is dispensed using a pipette on the electrode surface, it forms an electrochemical cell system and produces electrical signal at an applied control potential which corresponds to the analyte concentration. Commonly used electrochemical characterization technique is the current–voltage (CV) characteristics plot of the electrochemical cell system. When controlled potential is applied between RE and WE, current flows through AE and WE and it is measured by a potentiostat. Measurement of current amplitude at either reduction or oxidation potential, maintaining the current peak at a stable defined condition corresponds to detecting the precise concentration of the specific analyte, even ng/ml to a few fg/mL (femtograms/mL).

Electrode fabrication based on screen printing is based on thick film technology; it originated 3000 years ago and can be traced in the construction of the Great Wall of China as well as in ancient Egyptian cloth patterns[4,5]. SPE is an integrated electrically conducting layer and it is fabricated on a chemically inert insulating solid plate or film made of various materials such as ceramic[6–9], plastic[10–12], glass[13], flexible polyester film[14–16], etc. using the screen printing technique. SPEs are mostly disposable in nature. Several studies have been made on the development of electrochemical and biological sensing based on SPE using various methods of electrode surface functionalization and surface modification for specific applications[17–19]. Studies have reported that the electrode design parameters such as shape, geometric dimensions and spacing affect the performance of SPEs.

Studies also highlight the effect of electrode material, particularly WE on the electrochemical performance of SPEs. WE is typically made of carbon ink and many literature reports discuss various factors like carbon ink formulation, ink composition and particle size to affect the performance of these SPEs. But these being proprietary informations, the exact nature and composition of the electrode material cannot be deciphered[20,21]. The sensing platform of SPE not only depends upon the property of ink material, but also on the printing process, loading, curing temperature, etc. Carbon surface structure, morphology and surface orientation play an important role in electron transfer at the interface of the electrode surface and electrolyte solution.

---

*For correspondence. (e-mail: kalyan700@gmail.com)

Choudhary *et al.*[22] reported that the electrochemical behaviour of single-layer graphene-based electrodes, depends on the basal plane and edge plane of graphene. The graphene edge plane showed four orders of magnitude higher specific capacitance, much faster electron transfer rate and stronger electrocatalytic activity than those of graphene basal plane and hence graphene edge is an ideal electrode for electrocatalysis. Wang *et al.*[23] studied the effect of electrochemical response on edge plane and basal plane graphite layer in the NAD redox probe, where they observed that the edge plane had the highest peak current density and the basal plane exhibited high peak potential. Electrode surface area is the active site of an electrode and it can be improved by suitable formulation of carbon ink to make a larger edge plane site, by the formation of cracks and rough surface to facilitate faster electron transfer and thus increase the current response. The amount of organic binder used to make carbon ink also inhibits the cracks on the printed surface and indirectly enables increase in electron transfer rate. Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Ceramic which is used in the preparation of SPEs is a high-energy solid; high amount of energy is required to break these solids. Most molecular liquids achieve complete wetting with high-energy surfaces. The intrinsic hydrophobicity of a surface can be enhanced by texturing of solid surfaces with different scales of roughness because textured surfaces have high adhesive force compared to smooth surfaces. Therefore increase in hydrophobicity increases the adhesive force between the analyte and solid surface. These adhesive forces between liquid and solid cause a drop of analyte sample, when dropped on the electrode surface to spread over on it, which in turn enhances electron transfer capabilities at the time of electrochemical signal measurement. During curing of printed electrodes, high temperature creates unintentional cracks and defects of the electrode surface which also increase the edge plane effects. Edge plane of carbon surface increases electron transfer capabilities of the electrodes to enhance the sensitivity. Other than ink material and fabrication process, different parameters such as electrode geometry, dimensions, spacing and electrochemical signalling also play an important role.

Tan *et al.*[24] characterized an array of six micro-sized working electrodes surrounded by a common reference and counter electrode and observed that the magnitude of current peak in hexamine ruthenium (III) redox probe depends on the number of working electrodes in the array. Metters *et al.*[25,26] reported that micro band electrodes exhibit a greater current density and reproducibility over conventional screen-printed graphite electrode due to better mass transfer. Some studies have reported the characteristic performance of commercial SPEs and demonstrated deviation in electrochemical behaviour from theoretical values in FE-III solution.

One of the important factors which results in non-identical electrochemical activity of commercial SPEs is the different carbon compositions from different commercial inks[27,28]. Comparative electrochemical performance of SPEs fabricated by different commercial inks (such as Acheson, USA; Gwent, UK; Dupont, USA and Ercon, USA), have been analysed for their performance[1].

Electrochemical responses of some commercial SPEs – C110 (Dropsens Ltd, Spain)[29], KS540 (Kanichi Research Service Ltd, UK)[30] and (TE100 Zensor Ltd, Taiwan)[31], have been investigated and a large variation in CV characterization for a known analyte concentration has been observed[32]. This hinders their commercial application for the precise detection of bioanalytes of unknown concentration. The electrochemical performance of commercial SPEs does not rely on the specified geometrical surface area; it largely depends on the actual active surface and roughness factor. Determination of the real active surface area of SPE is difficult due to inherent physical properties and non-uniformity of material composition and fabrication process[33]. Yet no clear relation has been established regarding the difference in sensitivity due to the chemical composition of carbon ink and the surface roughness factor.

In this article we study the electrochemical response of some commercially available SPEs by cyclic voltammogram in different redox probes such as potassium ferricyanide Fe(III), ascorbic acid (AA) and nicotinamide adenine dinucleotide (NAD) solution. The electrode surface is characterized through field emission scanning electron microscopy (FESEM) and energy dispersion spectroscopy (EDS). Several critical issues regarding the performance of SPEs in order to make a reliable electrochemical sensor have been identified, which need to be overcome for practical applications of biosensors based on SPE.

Principle of electrochemical sensing

A typical definition of electrochemical sensing is the conversion of chemical or biological response of a substance into an electrically measurable signal; the signal magnitude corresponds to the species concentration. When the unknown sample solution is dispensed on the surface of a SPE, it forms a three-electrode electrochemical cell system. At an applied sweep potential current flows in between WE and AE due to electron transformation between the electrolyte and electrode interface. The CV characteristic plot indicates the rate of electrochemical reaction that takes place at the surface of WE. The main aim is to obtain the desirable change in the current response to the change of concentration of specific analyte in the sample solution and determine the sensitivity of the commercial electrodes at a stable equilibrium condition.

Practical recording of electrochemical response using SPEs has various noise factors which have to be optimized in such a way that unknown species contribute dominantly to the reaction rate as well as electron transfer. There are three common modes of electrochemical transduction: (i) potentiometric, (ii) conductometric and (iii) amperometric. Potentiometric and conductometric measurements require equilibrium state of reaction which takes a large time to achieve stable electrochemical response. Amperommetry type of transduction is a subclass of voltametric measurement. Ideal voltametric measurement is measurement of current at a known constant applied potential to the system. By measuring the peak current magnitude of either the anodic or cathodic side corresponds to the unknown species concentration. Randles–Sevcik equation describes the effect of scan rate on the peak current (I_p).

For simple redox events such as the ferrocene/ferrocenium couple, I_p depends not only on the concentration and diffusional properties of the electroactive species but also on scan rate.

$$I_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{1/2}, \tag{1}$$

or if the solution is at room temperature:

$$I_p = 268600n^{3/2}AD^{1/2}Cv^{1/2}, \tag{2}$$

where I_p is current peat at redox potential, n the number of electrons transferred in the redox event (usually), A is the electrode surface area (cm^2), F the Faraday constant in (C mol^{-1}), D the diffusion coefficient (cm^2 s^{-1}), C the concentration (mol cm^{-3}), and v is the potential scan rate (Vs^{-1}).

Reagents and apparatus used

Three commercial SPEs, C110, KS-540 and TE100, were obtained as mentioned before. Standard Ag/AgCl reference electrode CHI111 was obtained from CH Instrument Inc. (USA). Electrochemical workbench of CH Instrument Inc, USA (model CHE600E) with potentiostat driven by electro analytical control and measuring software was interfaced to a desktop PC in order to perform cyclic voltammetry.

Chemicals: potassium ferricyanide (FE-III), was obtained from Sigma Aldrich Inc, USA; AA, potassium chloride (KCl), sodium chloride (NaCl) were obtained from Merck, Specialities Pvt Ltd, Germany; NAD and phosphate buffer saline (PBS) were obtained from Sisco Research Lab Pvt Ltd, India. Electrode surface morphology and surface material properties are characterized by Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS, ZEISS, Germany). pH meter CL-51B was obtained from Utech Instrument Inc, India.

Experimental method

Current–voltage characteristics of commercial SPEs

The electrochemical response of SPEs was recorded with a redox probe FE-III (ref. 34). A sample solution of FE-III was prepared in 0.5 M KCl aqueous solution. SPE leads were connected according to the WE, RE and AE configuration, through coaxial shielded cable and connector clip. A 50 μl volume of prepared sample solution was dispensed on the active surface of the electrode and cyclic voltammogram was recorded at a scan rate of 50 mV/s.

The cyclic voltammogram (CV) response at a single concentration showed good anodic and cathodic peaks for all the electrodes, but the peaks magnitude and nature of the response were different for different electrodes (Figure 1). The electrochemical response of SPEs was recorded with redox probe 1 mM FE-III in 0.5 M KCl using

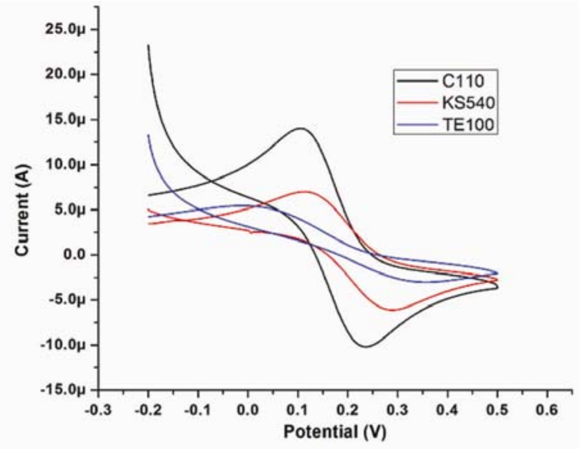

Figure 1. CV response of C110, KS540 and TE100 SPEs in 1 mM potassium ferricyanide solution prepared in 0.5 M KCl aqueous solution. Applied potential scan rate is 50 mV/s.

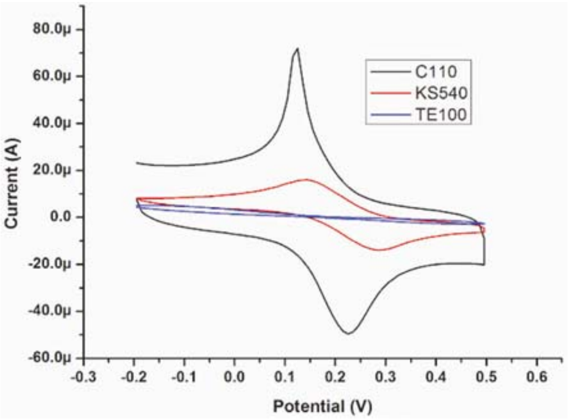

Figure 2. CV response of C110, KS540 and TE100 SPEs in 1 mM potassium ferricyanide solution prepared in 0.5 M KCl aqueous solution. Standard Ag/AgCl is used as RE. Applied potential scan rate is 50 mV/s.

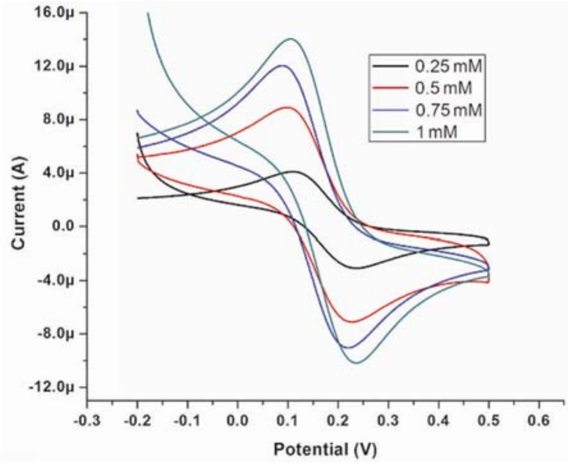

Figure 3. CV response of C110 in 0.25, 0.5, 0.75 and 1 mM potassium ferricyanide solution respectively, prepared in 0.5 M KCl aqueous solution. Applied potential scan rate is 50 mV/s.

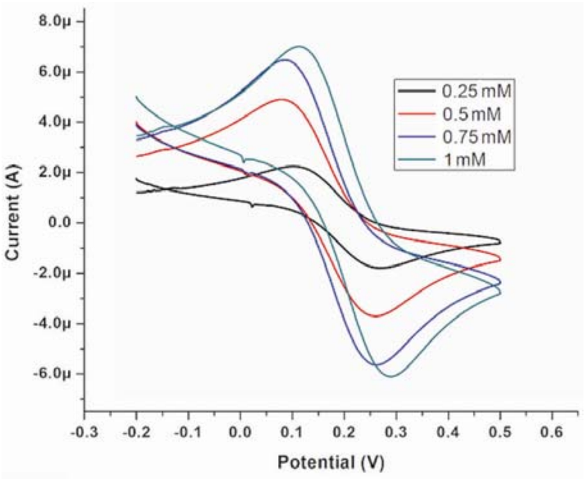

Figure 4. CV response of KS540 in 0.25, 0.5, 0.75 and 1 mM potassium ferricyanide solution respectively, prepared in 0.5 M KCl aqueous solution. Applied potential scan rate is 50 mV/s.

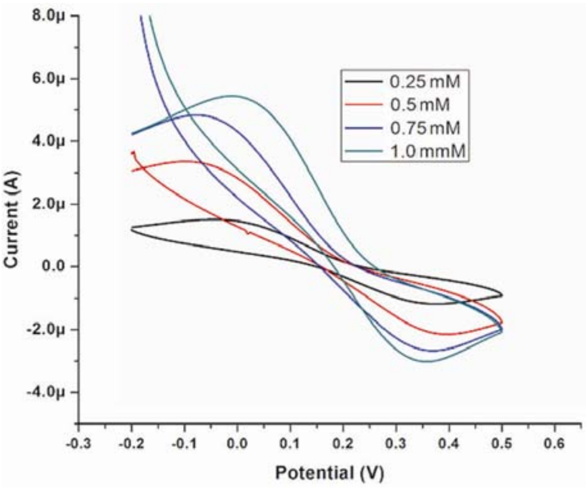

Figure 5. CV response of TE 100 in 0.25, 0.5, 0.75 and 1 mM potassium ferricyanide solution respectively, prepared in 0.5 M KCl aqueous solution. Applied potential scan rate is 50 mV/s.

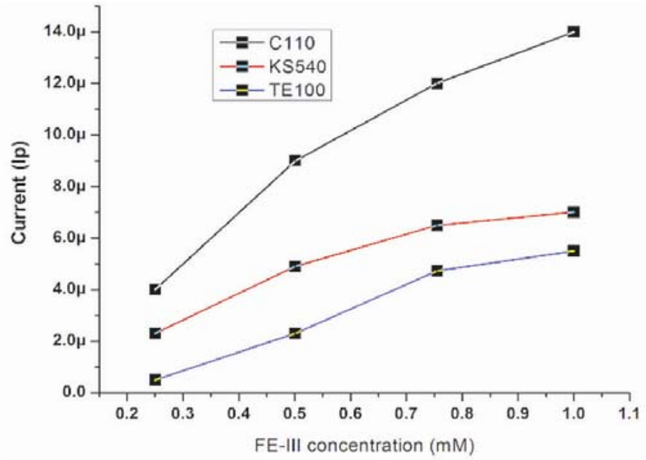

Figure 6. Plot of current peak (I_p) versus concentration of potassium ferricyanide solutions prepared in 0.5 M aqueous KCl for different SPEs. Applied potential scan rate is 50 mV/s.

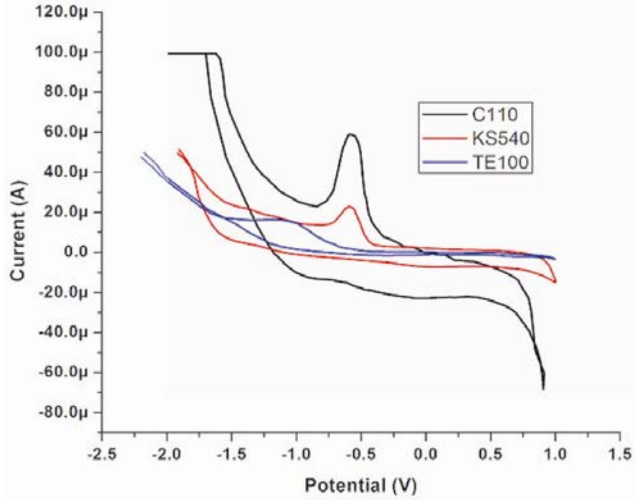

Figure 7. CV response of C110, KS540 and TE100 SPEs in 1 mM NAD solution prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

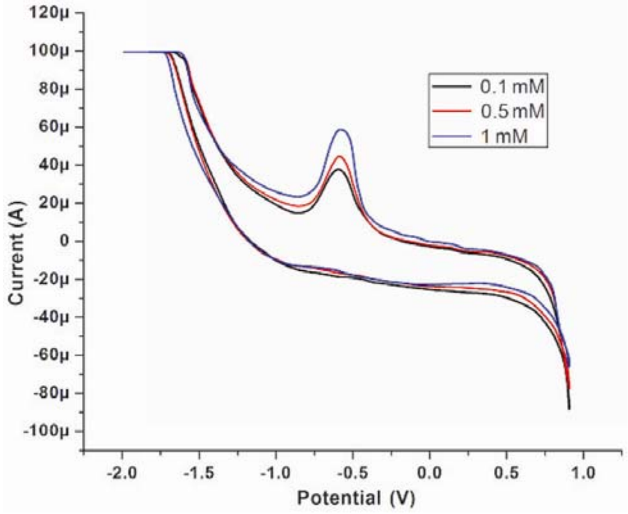

Figure 8. CV response of C110 in 0.1, 0.5 and 1 mM NAD solution prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

standard reference electrode and corresponding CV recorded at a scan rate 50 mV/s. SPE leads were connected accordingly to the WE and AE of commercial electrode and standard reference electrode. The current amplitude of all three commercial SPEs using standard reference electrode showed good anodic and cathodic peaks with higher peak amplitude (Figure 2).

Four sets of sample solution with different molar concentrations of FE-III, i.e. 0.25, 0.5, 0.75 and 1 mM were prepared in aqueous solution of 0.5 M KCl. Each of prepared FE-III concentrated sample solutions of 50 μl volume was dispensed on the four identical SPEs of all three commercial electrodes and allowed for stabilization. Cyclic voltammogram was carried out for different concentrations of the analyte for the SPEs with an applied potential scan rate of 50 mV/s and the current-voltage characteristics were recorded. The current peak amplitude increases with increasing FE-III concentration for all the three SPEs, but the nature of response is different for three different commercial SPEs (Figures 3–5).

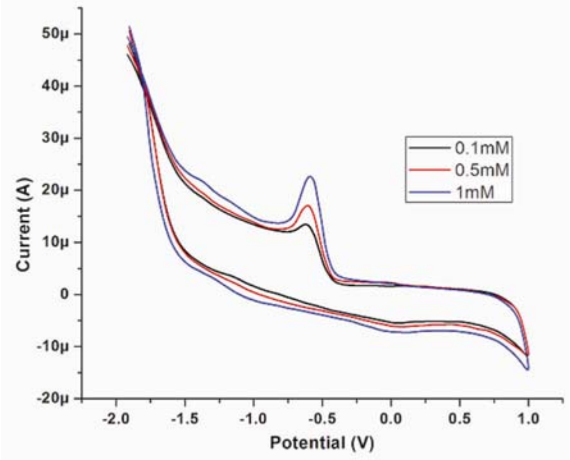

Figure 9. CV response of KS 540 in 0.1, 0.5 and 1 mM NAD solution prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

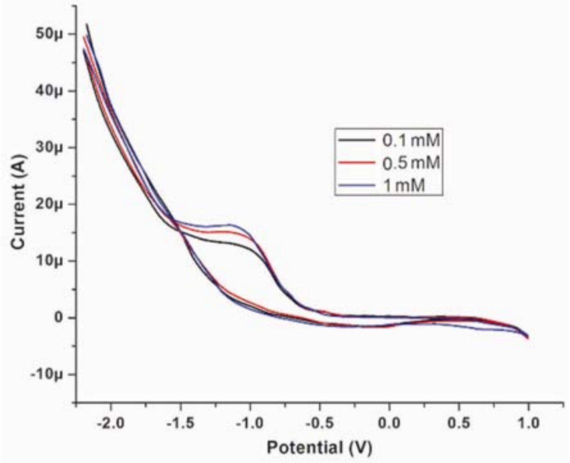

Figure 10. CV response of TE 100 in 0.1, 0.5 and 1 mM NAD solution prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

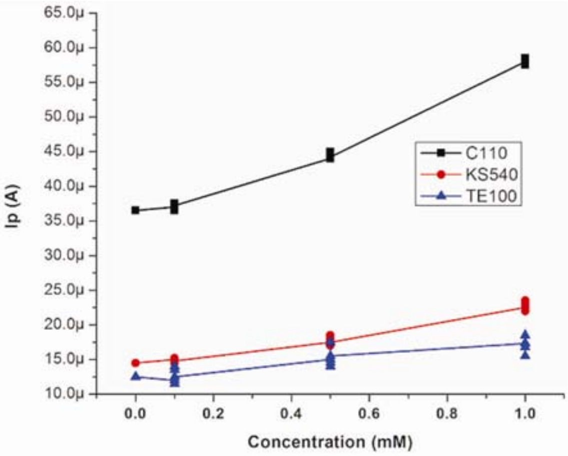

Figure 11. Plot of current peak (I_p) versus concentration of NAD solutions prepared in PBS. pH = 7. Applied potential scan rate is 50 mV/s.

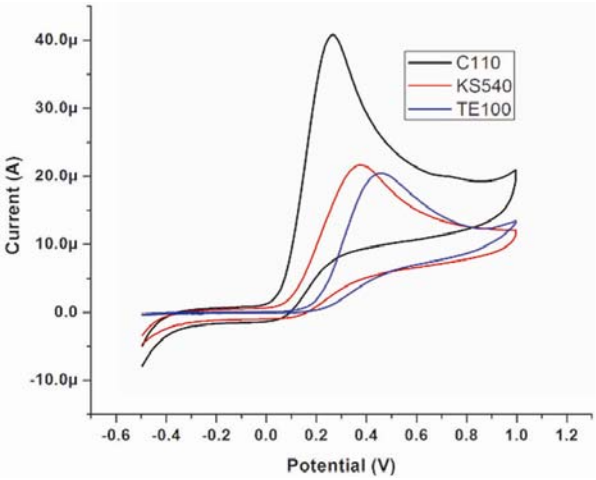

Figure 12. CV response of C110, KS540 and TE100 SPEs in 1 mM AA solution prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

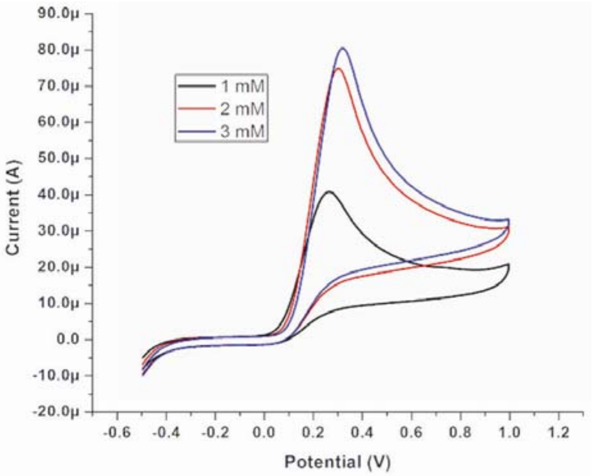

Figure 13. CV response of C110 in 1, 2 and 3 mM AA solutions prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

The current response of C110 is highly sensitive and percentage deviation is better than KS540 and TE100. The slope of sensitivity plot is better for C110 than KS540 and TE100, with a linear range 0–0.75 mM and slope of sensitivity is recorded lowest for TE100 and highest for C110 (Figure 6).

The electrochemical response was also recorded in other two redox probes NAD[35] and AA. In each experiment the sample volume was 50 μl and same procedure was followed as that of FE-III. Sample solutions of NAD and AA were prepared in PBS of pH 7. Three different concentrations, i.e. 0.1, 0.5 and 1 mM of NAD, and 1, 2 and 3 mM of AA sample solution were prepared in PBS solution, pH 7.

Interestingly, CV response of NAD gives only the oxidation peak and peak magnitude is different for different NAD concentrations. The current response of C110 in NAD is very high compared to KS540 and TE100. The oxidation potential of both C110 and KS540 is in the same position of about –0.5 V, but no reduction peak is observed (Figure 7). The current oxidation peak amplitude increases with increasing NAD concentration and a comparatively sharp peak current is observed for C110 and KS540 (Figures 8 and 9). The current response of TE100 is different for different concentrations, but does not correlate with the other two commercial SPEs; and the oxidation potential is about –1 V (Figure 10). The poorer electrochemical performance of TE100 may be due to differences in the composition of this SPE compared with the other two commercial SPEs. Current peak values are directly proportional to NAD concentration and slope of sensitivity is large for C110 and least for TE100 (Figure 11).

Electrochemical response of three electrodes with AA followed the same pattern, but the signal intensity of both anodic and cathodic peak current was different. Among the three electrodes, C110 gives the best and comparatively stable electrochemical response for AA (Figure 12).

Single peak is observed and the peak potential increases with increase in concentration of AA. The current response of C110 is highly sensitive and percentage deviation is better than KS540 and TE100 (Figures 13–15) Slope of sensitivity for C110 is high and is quasi linear in nature (Figure 16).

The nature and amplitude of voltammetric responses of three commercial electrodes in three different redox probes differ from each other due to several reasons like amount and nature of graphite material used in the formulation of the ink, functionalization of the electrode surface, curing temperature, binder materials, wettability of the electrode surface, etc. Among the three commercial electrodes, the electrochemical response of C110 is better than the other two. The relationship between roughness factor and electrochemical response shows that increased roughness causes the formation of a large number of edge plane sites which improves the electrochemical reversibility of the SPE.

Sensitivity analysis

We analysed the nature of electrochemical responses of the three commercial SPEs in three different redox probes and

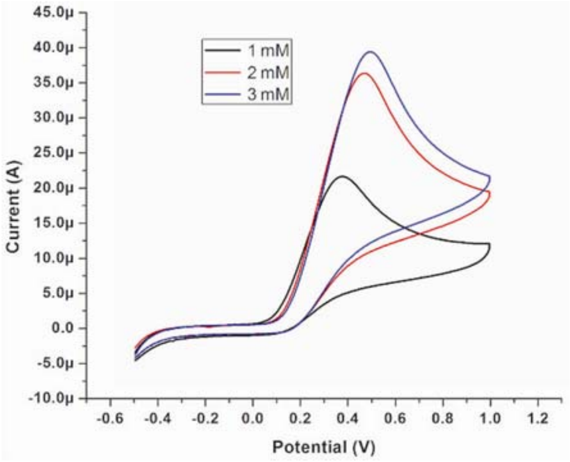

Figure 14. CV response of KS 540 in 1, 2 and 3 mM AA solutions prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

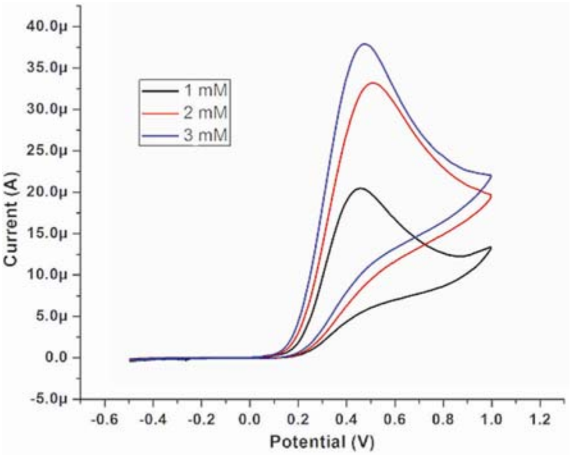

Figure 15. CV response of TE 100 in 1, 2 and 3 mM AA solutions prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

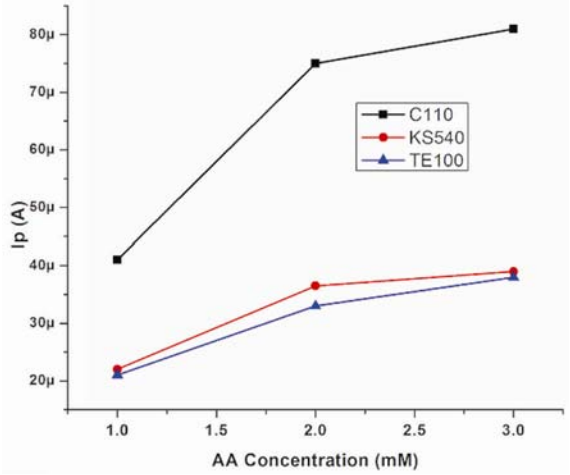

Figure 16. Plot of current peak (I_p) versus concentration of AA solutions prepared in PBS, pH = 7. Applied potential scan rate is 50 mV/s.

Table 1. Electrochemical experimental results in 1 mM potassium ferricyanide prepared in 0.5 M aqueous solution of KCl

Electrode type	Area of WE (mm^2)	I_{pa} (μA)	I_{pc} (μA)	I_{pa}/I_{pc}	δ (μA/mm^2)	E_{pa} (V)	E_{pc} (V)	ΔE (mV)
C110	12.566	14.2	10.3	1.36	1.114	0.105	0.235	130
KS540	7.068	6.9	6.2	1.13	0.976	0.115	0.287	172
TE100	7.068	5.5	3.0	2.5	0.778	0.0	0.35	350

WE, Working electrode geometric surface area; I_{pa}, anodic peak current; I_{pc}, Cathodic peak current; δ, current density; E_{pa}, Anodic peak potential; E_{pc}, Cathodic peak potential; ΔE, Peak to peak separation.

Table 2. Electrochemical experimental results in 1 mM ascorbic acid prepared in 0.1 M of PBS

Electrode type	Area of WE (mm^2)	I_{pa} (μA)	I_{pc} (μA)	I_{pa}/I_{pc}	δ (μA/mm^2)	E_{pa} (V)	E_{pc} (V)	ΔE (mV)
C110	12.566	41.2	–	–	3.270	0.26	–	–
KS540	7.068	21.5	–	–	3.041	0.38	–	–
TE100	7.068	20.5	–	–	2.900	0.46	–	–

Table 3. Electrochemical experimental results in 1 mM nicotinamide adenine dinucleotide prepared in 0.1 M of PBS

Electrode type	Area of WE (mm^2)	I_{pa} (μA)	I_{pc} (μA)	I_{pa}/I_{pc}	δ (μA/mm^2)	E_{pa} (V)	E_{pc} (V)	ΔE (mV)
C110	12.566	58	–	–	4.615	–0.55	–	–
KS540	7.068	24	–	–	3.395	–0.55	–	–
TE100	7.068	16	–	–	2.263	–1.0	–	–

Table 4. Characterization of three commercial electrodes using different redox probes

Redox sample	SPE type	Geometric surface area (S_g) (mm^2)	I_{pa} (μA)	Active surface area (S_a; mm^2)	S_a/S_g	% Activity
1 mM FE-III IN 0.5 M KCl	C110	12.56	14	24.32	1.94	93.63
	KS540	7.07	6.9	13.5	1.91	90.95
	TE100	7.07	5.5	12.4	1.75	75.39
1 mM AA in 0.1 M PBS	C110	12.56	41.2	23.4	1.86	86.31
	KS540	7.07	21.5	12.24	1.73	73.13
	TE100	7.07	20.5	11.67	1.65	65.06
1 mM NAD in 0.1 M PBS	C110	12.56	58	23.01	1.83	83.20
	KS540	7.07	24	12.6	1.78	78.22
	TE100	7.07	16	10.8	1.53	52.76

compared the sensitivity by measuring current peak amplitude with the variation of specific redox concentration.

In Table 1, shows that the current density with respect to geometric surface area of WE is higher for C110 than KS540 and TE100 in a stable concentration of FE-III, whereas the ratio of anodic and cathodic peak current is better for KS540. It is also observed from Table 1 that there is a narrow peak-to-peak potential separation for C110.

From Table 2 which gives a comparison of electrode performance using 1 mM AA, only anodic peak is observed for all the three electrodes. The current density is almost double for C110 compared to KS540 and TE100 and redox reaction occurs comparatively at lower potential of about 260 mV for C110.

In Table 3, the electrochemical performance of the three electrodes in a sample solution of 1 mM NAD concentration is compared and highest current density is observed for C110; the same redox potential is observed for both C110 and KS540. No traceable anodic peak is observed in the NAD redox probe for all the three electrodes.

Though it is difficult to calculate the active surface area of an electrode exactly, efforts have been taken to estimate the active surface area (S_a) of WE from the current peak amplitude obtained from nonlinear CV characteristics in a redox analyte using Randels–Sevcik equation (eq. (2))[36,37]. The active surface area (S_a) of WE of the three different commercial SPEs is estimated by measuring the anodic current peak (I_{pa}) for three different redox probes at its fixed 1mM concentration. The activity of the electrode surface w.r.t. geometric surface area (S_g) is numerically calculated with the help of electrochemical measurement (Table 4). The effective active surface area of SPEs were estimated using eq. (2). For 1mM potassium ferricyanide solution, the active surface area was found to increase by 94%, 91% and 75% for C110, KS 540 and TE 100 SPE respectively. Similarly, the active surface area again maximum increased of about 86% for

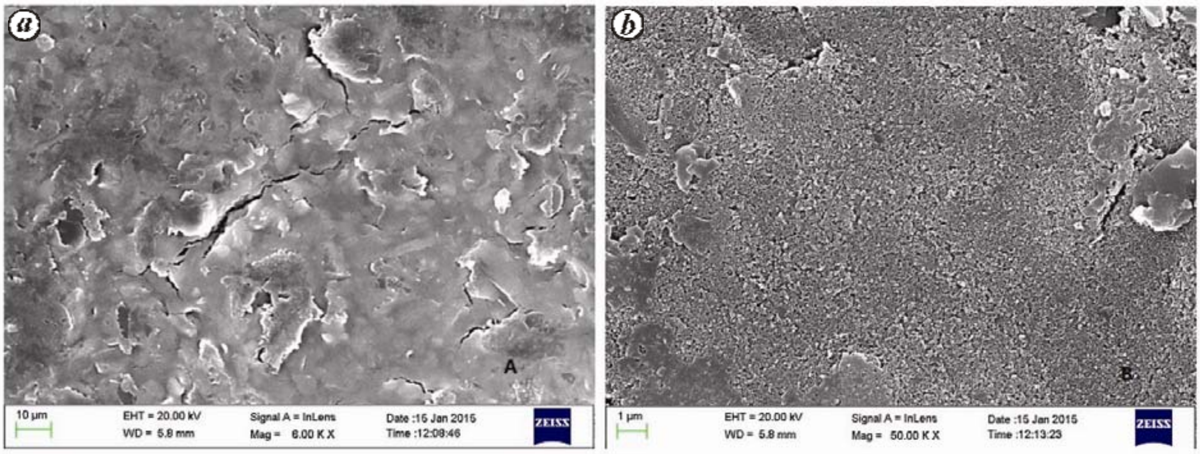

Figure 17. SEM image of WE surface of C110 by FESEM at magnification (***a***) 6.00 KX and (***b***) 50.00 KX.

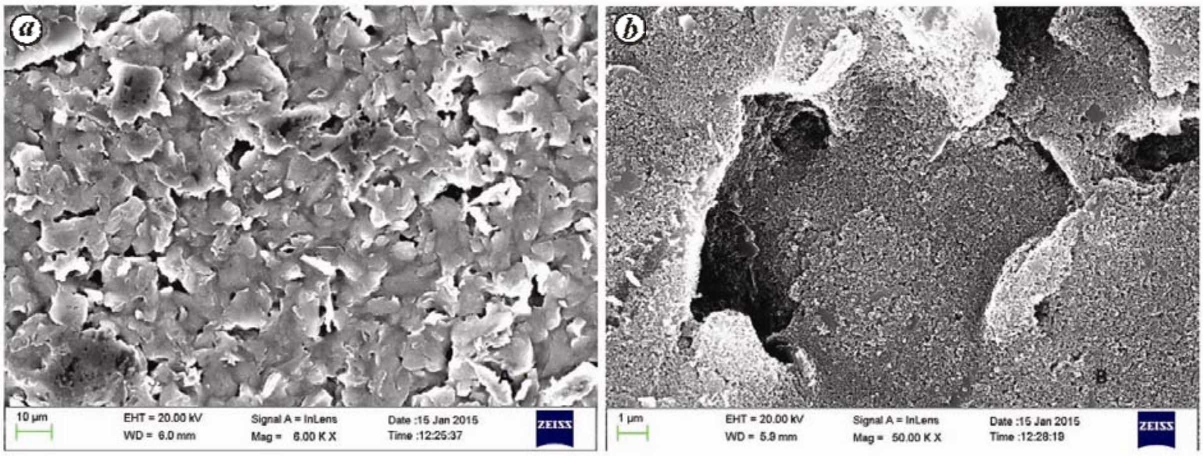

Figure 18. SEM image of WE surface of KS540 by FESEM at magnification (***a***) 6.00 KX and (***b***) 50.00 KX.

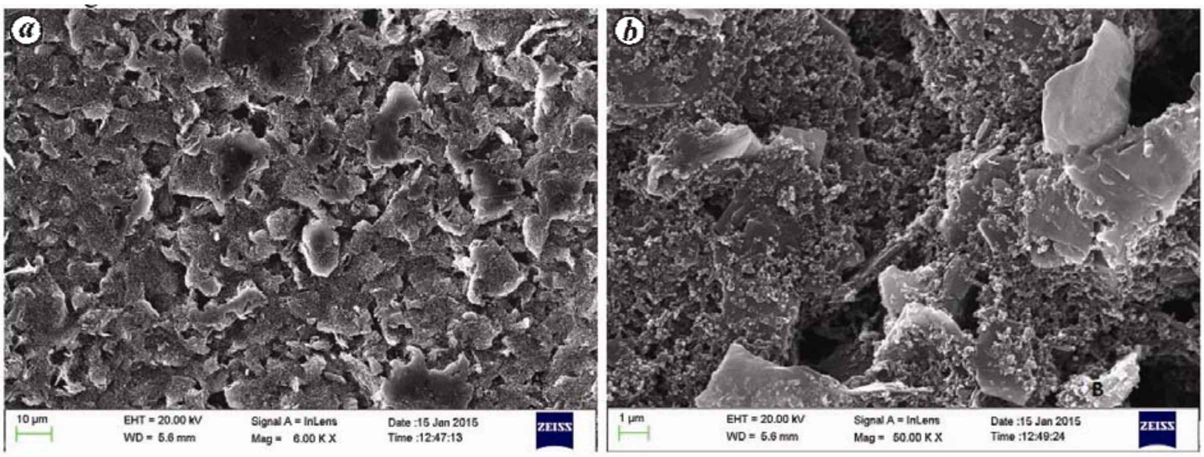

Figure 19. SEM image of WE surface of TE100 by FESEM at magnification (***a***) 6.00 KX and (***b***) 50.00 KX.

ref. C110 at 1 mM but 73% and 65% increased for KS540 and TE100 respectively. The increase of active surface area of the working electrode surface which improves the electron transfer capabilities results in larger amplitude of I_p. The overall electrochemical performance of SPE TE100 is not as good as that of C110 and KS540. This may be due to difference in composition and construction of the SPEs. Performance deviation of KS540 and TE100 also observed due to the absence of silver track line beneath the printed electrodes in the construction of KS540 and

TE100 which offers resistance to deviate its sensitivity. S_a of SPE is also considered as aroughness factor which is high for C110, as larger the roughness of the electrode surface greater is the electron transfer rate.

From the performance characteristics we observed that commercial electrodes from different manufacturers are not comparable to each other in terms of amperometric current peak magnitude and shape of current voltage plots[38]. We also observed there is some deviation in ideality of a same batch of commercial SPEs due to the fact that the three different electrodes were fabricated by three different compositions of graphite. Also, till date, there are no reports available regarding the effects on substrate material. We observed that precise detection of species concentration using commercial SPEs is still difficult in practical applications. It is possible to overcome this by increasing the sensitivity by further modification of electrode surface[39].

C110 can be reused up to 5–7 times with proper washing using distilled water, after which the magnitude reduces abruptly. KS540 and TE100 can be reused up to 2–3 times; this is may be due to erosion of the carbon surface after each experiment which results in low electron transfer capability[40].

Electrode surface characterization by microscopy

Investigation of electrode surface texture was carried out using scanning electron microscopy (SEM) to evaluate the electrode surface effects on electrochemical response. WE surface of C110 is a uniform carbon layer with numerous cracks; this may be due to the application of high temperature at the time of curing the printed ink (Figure 17). Unintentional formation of defects and cracks increases edge plane effect on the graphite surface with faster electrochemical reaction rate, which results in larger electron transfer, i.e. large sensitivity. SEM image of WE surface of SPE (ref. C110) revealed the presence of microscopic features which increased the effective surface area and in turn resulted in comparatively larger current peaks at redox potential. WE surface of KS540 shows uneven carbon layer with some voids throughout the surface (Figure 18). This supports the reduction of electrode active surface area; as a result comparatively lesser current peaks were recorded. SEM image of TE100 (Figure 19) reveals a non-uniform and rough carbon surface with numerous voids which may have resulted in distorted CV responses obtained in various redox probes.

Table 5. Substrate material properties by energy-dispersive X-ray spectroscopy

SPE type	Element (weight%)	Atomic%
C110	O (41.47), Al (58.53)	O (54.44), Al (45.56)
KS540	C (72.82), O (27.18)	C (78.11), O (21.89)
TE100	C (69.58), O (30.42)	C (75.29), O (24.71)

EDS is an analytical technique used for elemental analysis of the SPE substrate. A high energy beam of X-rays is focused on the substrate to excite the electron in the inner shell leaving a hole; then the outer shell high-energy electrons fill the gap. The difference between the high-energy and low-energy shells is released in the form of an X-ray. This emission of characteristic X-rays from the substrate helps measure the elemental composition of the substrate. The EDX results of all the three commercial SPEs indicate that (Al, O), (C, N, O) and (C, N, O, Cl) are the major elements in C110, KS540 and TE100 respectively (Table 5).

Conclusions

In the present study, experimental characterization of available commercial SPEs by CV and electrode surface morphology using microscopy has been described. Variation of CV response has been investigated and compared with theoretical values. The performance characteristics of different commercial SPEs do not match with each other, which means it is difficult to replace commercial one SPE with another in electrochemical and biomedical sensing applications. Experimental results obtained in our studies have demonstrated that C110 SPE exhibited better electrochemical response and sensitivity when compared to the other two types of commercial SPEs. It was observed that electrochemical performances varied with the types of SPEs and thus reproducible results could not be obtained using different types of SPEs albeit using the same analyte species and concentration. This is a huge drawback and requires thorough characterization prior to use for any analytical applications.

1. Wang, J., Tian, B., Nascimento, V. B. and Angnes, L., Performance of screen-printed carbon electrodes fabricated from different carbon inks. *Electrochim. Acta*, 1998, **43**, 3459–3465.
2. Kadara, R. O., Jenkinson, N. and Banks, C. E., Characterization and fabrication of disposable screen printed microelectrodes. *Electrochemistry Commun*., 2009, **11**, 1377–1380.
3. Mistry, K. K., Layek, K., Mahapatra, A., RoyChaudhurib, C. and Saha, H., A review on amperometric type immunosensors based on screen-printed electrodes. *Analyst*, 2014, **139**, 2289–2311.
4. Freire, R. S., Duran, N., Wang, J. and Kubota, L. T., Laccase-based screen printed electrode for amperometric detection of phenolic compounds. *Anal. Lett.*, 2002, **35**(1), 29–38.
5. Horvath, E., Henap, G. and Harsany, G., Materials and technological development of screen printing in transportation, *Int. J. Traffic Trans. Eng.*, 2012, **2**, 133–141.
6. Hart, J. P., Crew, A., Crouch, E., Honeychurch, K. C. and Pemberton, R. M., Some recent designs and developments of screen-printed carbon electrochemical sensors/biosensors for biomedical, environmental, and industrial analyses. *Anal. Lett.*, 2004, **37**(5), 789–830.
7. Ping, J., Wang, Y., Ying, Y. and Wu, J., Application of electrochemically reduced graphene oxide on screen-printed ion-selective electrode. *Anal. Chem.*, 2012, **84**, 3473–3479.
8. Viswanathan, S., Rani, C., Anand, A. V. and Ho, J.-A., Disposable electrochemical immunosensor for carcinoembryonic antigen

using ferrocene liposomes and MWCNT screen-printed electrode. *Biosens. Bioelectron*., 2009, **24**, 1984–1989.

9. Honglan Q, C. Ling, Q. Ma, Q. Gao and Zhang, C., Sensitive electrochemical immunosensor array for the simultaneous detection of multiple tumor markers. *Analyst*, 2012, **137**, 393–399.
10. Rao, V. K., Sharma, M. K., Goel, A. K., Singh, L. and Sekhar, K., Sensitive electrochemical immunosensor array for the simultaneous detection of multiple tumor markers amperometric immunosensor for the detection of vibrio cholera O1 using disposable screen-printed electrodes. *Anal. Sci*., 2006, **21**, 1207–1211.
11. Darain, F., Park, D. S., Park, J.-S., Chang, S.-C. and Shim, Y.-B., A separation-free amperometric immunosensor for vitellogenin based on screen-printed carbon arrays modified with a conductive polymer, *Biosens. Bioelectron*., 2005, **20**, 1780–1787.
12. Piermarini, S., Micheli, L., Ammidaa, N. H. S., Palleschi, G. and Moscone, D., Electrochemical immunosensor array using a 96-well screen-printed microplate for aflatoxin B1 detection. *Biosens. Bioelectron.*, 2007, **22**, 1434–1440.
13. Grennan, K., Killard, A. J. and Smyth, M. R., Physical characterizations of a screen-printed electrode for use in an amperometric biosensor system, *Electroanalysis*, 2001, **13**, 745–750.
14. Mu, S., Wang, X., Li, Y.-T., Wang, Y., Li, D.-W. and Long, Y.-T., A novel screen-printed electrode array for rapid high-throughput detection. *Analyst*, 2012, **137**, 3220–3223.
15. Metters, J. P., Mingot, M. G., Iniesta, J., Kadara, R. O. and Banks, C. E., The fabrication of novel screen printed single-walled carbon nanotube electrodes: electroanalytical applications. *Sensors Actuat. B*, 2013, **177**, 1043–1052.
16. Foste, C. W., Metters, J. P., Kampouris, D. K. and Banks, C. E., Ultraflexible screen-printed graphitic electroanalytical sensing platforms. *Electroanalysis*, 2014, **26**, 262–274.
17. Wang, S., Qi, Z., Huang, H. and Ding, H., Electrochemical determination of methotrexate at a disposable screen-printed electrode and its application studies. *Anal. Lett.*, 2012, **45**, 1658–1669.
18. Mandil, A., Pauliukaite, R., Amine, A. and Brett, C. M. A., Electrochemical characterization of and stripping voltammetry at screen printed electrodes modified with different brands of multiwall carbon nanotubes and bismuth films. *Anal. Lett.*, 2012, **45**, 395–407.
19. Niu, X., Lan, M., Zhao, H., Chen, C., Li, Y. and Zhu, X., Review: electrochemical stripping analysis of trace heavy metals using screen-printed electrodes. *Anal. Lett.*, 2013, **46**, 2479–2502.
20. Saciloto, T. R., Cervini, P. and Cavalheiro, E. T., New screen printed electrode based on graphite and polyurethane composite for the determination of acetaminophen. *Anal. Lett.*, 2013, **46**, 312–322.
21. Metters, J. P., Kadara, R. O. and Banks, C. E., New directions in screen printed electroanalytical sensors: an overview of recent developments. *Analyst*, 2011, **136**, 1067–1076
22. Choudhry, N. A., Kampouris, D. K., Kadara, R. O. and Bank, C. E., Next generation screen printed electrochemical platforms: Non-enzymatic sensing of carbohydrates using copper(II) oxide screen printed electrodes. *Electrochem. Commun.*, 2010, **12(**1), 6–9.
23. Wang, T., Randviir, E. P. and Banks, C. E., Detection of theophylline utilising portable electrochemical sensors. *Analyst*, 2014, **139**, 2000–2003.
24. Tan, F., Metters, J. P. and Banks, C. E., Electroanalytical applications of screen printed microelectrode arrays. *Sensors Actuat. B*, 2013, **181**, 454–462.
25. Metters, J. P., Kadara, R. O. and Banks, C. E., Electroanalytical properties of screen printed graphite microband electrodes. *Sensors Actuat. B*, 2012, **169**, 136–143.
26. Metters, J. P., Kadara, R. O. and Banks, C. E., Fabrication of co-planar screen printed microband electrodes. *Analyst*, 2013, **138**, 2516–2521.
27. Morrin, A., Killard, A. J. and Smyth, M. R., Electrochemical characterization of commercial and home-made screen-printed carbon electrodes. *Anal. Lett*., 2003, **36**, 2021–2039.
28. Boladoa, P. F., Santosa, D. H., Ardisanaa, P. J. L., Perníab, A. M. and García, A. C., Electrochemical characterization of screen-printed and conventional carbon paste electrodes. *Electrochim. Acta*, 2008, **53**(10), 3635–3642.
29. http://www.dropsens.com/pdfs_productos/new_brochures/110-c110.pdf
30. http://www.kanichi-research.com/documents/Kanichi3mmElectrodesSpecification.pdf
31. http://www.zensor.com.tw/download/spe3_en.pdf
32. Kadara, R. O., Jenkinson, N. and Banks, C. E., Characterisation of commercially available electrochemical sensing platforms. *Sensors Actuat. B*, 2009, **138**, 556–562.
33. Fragkou, V., Ge, Y., Steiner, G., Freeman, D., Bartetzko, N. and Turner, A. P. F., Determination of the real surface area of a screen-printed electrode by chronocoulometry. *Int. J. Electrochem. Sci.*, 2012, **7**, 6214–6220.
34. Hart, J. P. and Honeychurch, K. C., The chronoamperometric and voltammetric behaviour of glutathione at screen-printed carbon micro-band electrodes modified with cobalt phthalocyanine. *Anal. Chem.*, 3012, **2**(5), 46–52.
35. Hart, J. P., Abass, A. K., Cowell, D. C., Chappell, A. and Pemberton, R. M., Development of a disposable amperometric ammonia (NH4+) biosensor based on a chemically modified screen-printed carbon electrode coated with glutamate dehydrogenase and NADH. *Electroanalysis*, 2009, **11**(6), 406–411.
36. Lee, S.-H., Fang, H.-Y. and Chen, W.-C., Electrochemical characterization of screen-printed carbon electrodes by modification with chitosan oligomers. *Electroanalysis*, 2005, **17**(23), 2170–2174.
37. Nicholson, R. S., Theory and application of cyclic voltammetry fm measurement of electrode reaction kinetics. *Anal. Chem.*, 1965, **37**(11), 1351.
38. Hart, J. P., Abass, A. K., Honeychurhc, K. C., Pemberton, R. M., Ryan, S. L. and Wedge, R., *Indian Jr. Chem. A*, 2003, **42**, 709–718.
39. Caygill, J. S., Collye, S. D., Holmes, J. L., Davis, F. and Higson, S. P. J., Electrochemical detection of TNT at cobalt phthalocyanine mediated screen-printed electrodes and application to detection of airborne vapours. *Electroanalysis*, 2013, **25(**11), 2445–2452.
40. Caygill, J. S., Collye, S. D., Holmes, J. L., Davis, F. and Higson, S. P. J., Disposable screen-printed sensors for the electrochemical detection of TNT and DNT. *Analyst*, 2013, **138**, 346–352.

ACKNOWLEDGEMENTS. K.K.M. and S.D.T. thank the Director, CSIR-CMERI, Durgapur and Dr S. Majumdar (Head, Surface Robotics Lab, CSIR-CMERI) for providing support and encouragement during this work. We thank CSIR, New Delhi for financial support (12th Five-Year Plan). The authors acknowledge Dr Himadri Roy for helping in FESEM-EPS analysis.

Received 9 February 2015; revised accepted 29 June 2015

doi: 10.18520/v109/i8/1427-1436