

# Flow injection analysis of hydrogen peroxide on copper-plated screen-printed carbon electrodes

Jyh-Myng Zen,\* Hsieh-Hsun Chung and Annamalai Senthil Kumar

Department of Chemistry, National Chung-Hsing University, Taichung 402, Taiwan.  
E-mail: jmzen@dragon.nchu.edu.tw

Received 22nd May 2000, Accepted 20th July 2000

Published on the Web 17th August 2000

A disposable copper-plated screen-printed carbon electrode (CuSPE) was developed for the determination of hydrogen peroxide by flow injection analysis (FIA) at ambient temperature without deoxygenation. Cyclic voltammetry on the CuSPE in pH 7.4 phosphate buffer solution showed the growth of CuO and Cu<sub>2</sub>O. A well-defined reduction signal corresponding to the mediation of CuO and Cu<sub>2</sub>O occurred in the presence of hydrogen peroxide. The mechanistic study revealed that the reduction is a coupled-chemical reaction mechanism with the operation of pseudo-first order kinetics with respect to the concentration of Cu<sub>2</sub>O. The calculated electrochemical rate constant ( $k_e$ ) from Laviron's model is 13.7 s<sup>-1</sup>. Systematic investigations were made to optimize the experimental parameters for hydrogen peroxide detection by FIA. With a poised potential of -0.3 V versus Ag/AgCl and a flow rate of 2 ml min<sup>-1</sup>, the calibration curve was found to be linear up to 200 μM hydrogen peroxide with a detection limit of 0.97 μM (S/N = 3). The CuSPE is fairly stable for repetitive measurements.

## Introduction

The detection and determination of hydrogen peroxide are of practical importance in chemical, biological, clinical, environmental and many other fields. The conventional analytical technique for the detection of hydrogen peroxide was developed using horseradish peroxidase (HRP).<sup>1-8</sup> To increase the robustness and durability, a variety of electrode materials and configurations, such as graphite carbon paste,<sup>9</sup> polypyrrole,<sup>10</sup> sol-gel tetramethyl orthosilicate<sup>11</sup> and ferrocene-immobilized polyion complex,<sup>12</sup> and a diversity of mediators suitable for peroxidase-based electrodes, *e.g.*, Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>,<sup>13</sup> methylviologen,<sup>14</sup> Prussian Blue,<sup>15,16</sup> phosphomolybdic anion,<sup>17</sup> iron(III) tetramethoxyphenylporphyrin chloride<sup>18</sup> and cobalt(II) octaethoxyphthalocyanine,<sup>19</sup> have been reported. Nevertheless, a serious problem in using these electrodes is the stability and fouling of the mediators by the working matrix.<sup>20</sup> For example, Prussian Blue-modified electrodes were unstable and lost portions of charge upon strong mechanical stress during measurements with a rotating disc electrode or in gas evolution reactions.<sup>21</sup> Moreover, most of the mediators and complexes are unstable at high pH and hence have a limited working pH range.

From the viewpoint of chemical sensors, several metal electrodes, *e.g.*, Ag, Pt, Pd and Cu, as their oxides, have been reported to be promising for hydrogen peroxide reduction reactions.<sup>20,22-24</sup> Among these, considering the operability, commercial availability and cost, copper electrodes are of particular interest. Electrochemical investigations with copper electrodes have been documented and the basic hydrogen peroxide reduction mechanism on copper electrodes involves a major contribution from its surface oxides such as Cu<sub>2</sub>O and CuO.<sup>25-29</sup> However, so far this property has rarely been used for analytical applications, even though it has potential and an enhanced effect towards the hydrogen peroxide reduction reaction.

The purpose of this work was to construct a high precision but inexpensive analytical method. A working copper electrode was prepared using screen-printing technology, *i.e.*, a copper-plated screen-printed carbon electrode (CuSPE). Screen-printing technology is inexpensive, simple, rapid and versatile and it also

allows the mass production of reproducible, low-cost electrochemical sensors.<sup>30,31</sup> On the other hand, flow injection analysis (FIA) coupled with a wall-jet type electrode offers advantages such as high speed, precision, simplicity and working with a large dead volume.<sup>32,33</sup> The radial flow of the working solution on the wall-jet electrode system minimizes the diffusion layer thickness of the analyte during the electron transfer reaction on the electrode-electrolyte interface. In turn, the current signals are effectively amplified compared with the normal thin layer flow cell systems. In the present method, we combined the wall-jet system with SPE technology and the experimental parameters were optimized. We expect that this non-enzymatic method will meet the new challenge and demand for hydrogen peroxide assays.

## Experimental

### Chemicals and reagents

All chemicals were of analytical-reagent grade from Merck (Darmstadt, Germany). Stock standard solutions of hydrogen peroxide were prepared daily in the working buffer and stored in the dark at < 4 °C. A 1000 ppm Cu<sup>II</sup> solution in 0.1 M nitric acid was used for the plating experiments. The other standard solutions used in interference studies were also obtained from Merck. Unless stated otherwise, the buffer used was 0.1 M phosphate buffer solution (pH 7.4) (PBS). All aqueous solutions were prepared with de-ionized water. When anaerobic conditions were chosen, purified argon gas was used to expel the dissolved oxygen.

### Apparatus

Cyclic voltammetric (CV) measurements and FIA experiments were carried out with a Model 660 electrochemical workstation (CH Instruments, Austin, TX, USA). The three-electrode system consists of the CuSPE working electrode, an Ag/AgCl reference electrode and a platinum auxiliary electrode. The flow injection system consisted of a Cole-Parmer (Vernon Hills, IN,

USA) microprocessor pump drive, a Rheodyne (Cotati, CA, USA) Model 7125 sample injection valve (20  $\mu\text{L}$  loop) with an interconnecting Teflon tube and a BAS (West Lafayette, IN, USA) electrochemical detector. The BAS wall-jet system consists of the working CuSPE between the gasket and the closing holder. This assembly with CuSPE is new to FIA. In the base set-up, a circular path of 3 mm diameter was left for fixing the working electrode. The working part of the CuSPE was suitably designed to fix exactly in the circular path of the base.

### Design and fabrication on SPE and CuSPE

A semi-automatic screen printer was used to prepare disposable SPEs. A stencil with a structure of five continuous electrodes was used in printing the conducting carbon on a flexible polypropylene film (50  $\times$  70 mm). A silver layer (not in the working portion) was first printed before coating the carbon ink

(Acheron, Tokyo, Japan) to make the SPE effectively conducting. The unit was then cured by UV irradiation at an intensity of 1.85  $\text{mW cm}^{-2}$  for 2 h. After drying, an insulator layer was finally printed over the SPE, leaving a working area of 0.196  $\text{cm}^2$  with a conductive track radius of 2.5 mm. The measured average resistance for the five strips is  $85.64 \pm 2.10 \Omega \text{ cm}^{-1}$ , which is  $\sim 10$  times lower than that in a recent SPE report.<sup>34</sup> For the preparation of the CuSPE, a Cu layer was electrochemically plated on an SPE in 200  $\text{mg l}^{-1}$   $\text{Cu}(\text{NO}_3)_2$  aqueous solution at  $-0.7 \text{ V}$  versus  $\text{Ag}/\text{AgCl}$  for 300 s. The optimized plating time was chosen based on experiments ranging from 100 to 400 s in the presence of 100 or 200  $\text{ppm Cu}^{\text{II}}$  solution.

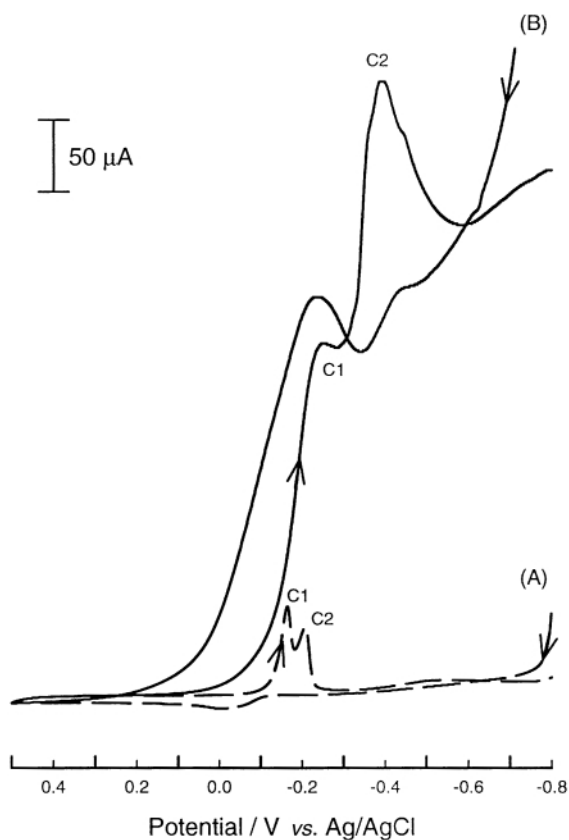
### Procedure

The CuSPE was first washed thoroughly with de-ionized water, then dipped into a working hydrogen peroxide solution containing PBS for subsequent static experiments. For FIA, the CuSPE was equilibrated in blank PBS at an optimized potential until the current became constant. The quantification of hydrogen peroxide was achieved by measuring the reduction current from chronoamperometric signals. All experiments were performed at room temperature (25  $^\circ\text{C}$ ).

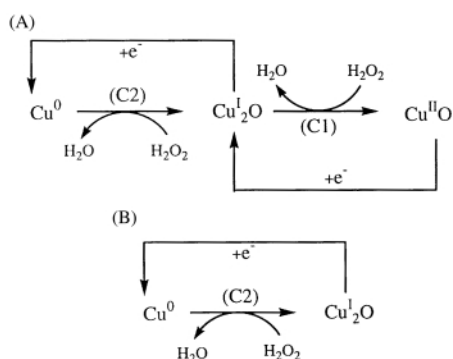
### Results and discussion

#### Electrochemical reduction behavior of hydrogen peroxide on the CuSPE

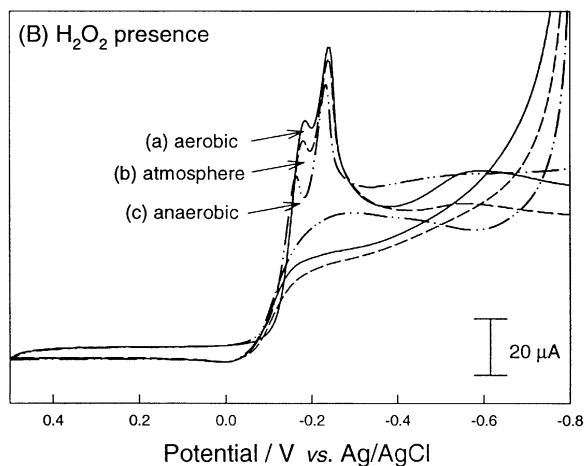
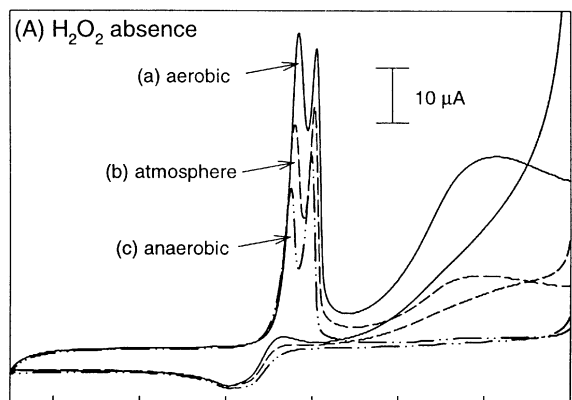
Cyclic voltammograms of the CuSPE under quasi-steady condition (*i.e.*, at  $v = 5 \text{ mV s}^{-1}$ ) in an oxygen free PBS (pH 7.4)



**Fig. 1** Cyclic voltammograms in the absence (A) and presence (B) of 3.2 mM hydrogen peroxide in pH 7.4 PBS at the CuSPE. Scan rate =  $5 \text{ mV s}^{-1}$ ; starting potential =  $-0.8 \text{ V}$ .



**Scheme 1** Mechanism of the mediated reduction of hydrogen peroxide at the CuSPE. (A) Overall  $\text{H}_2\text{O}_2$  reduction reaction under static conditions. (B) FIA at an applied potential of  $-0.3 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  (*i.e.*, on C2).



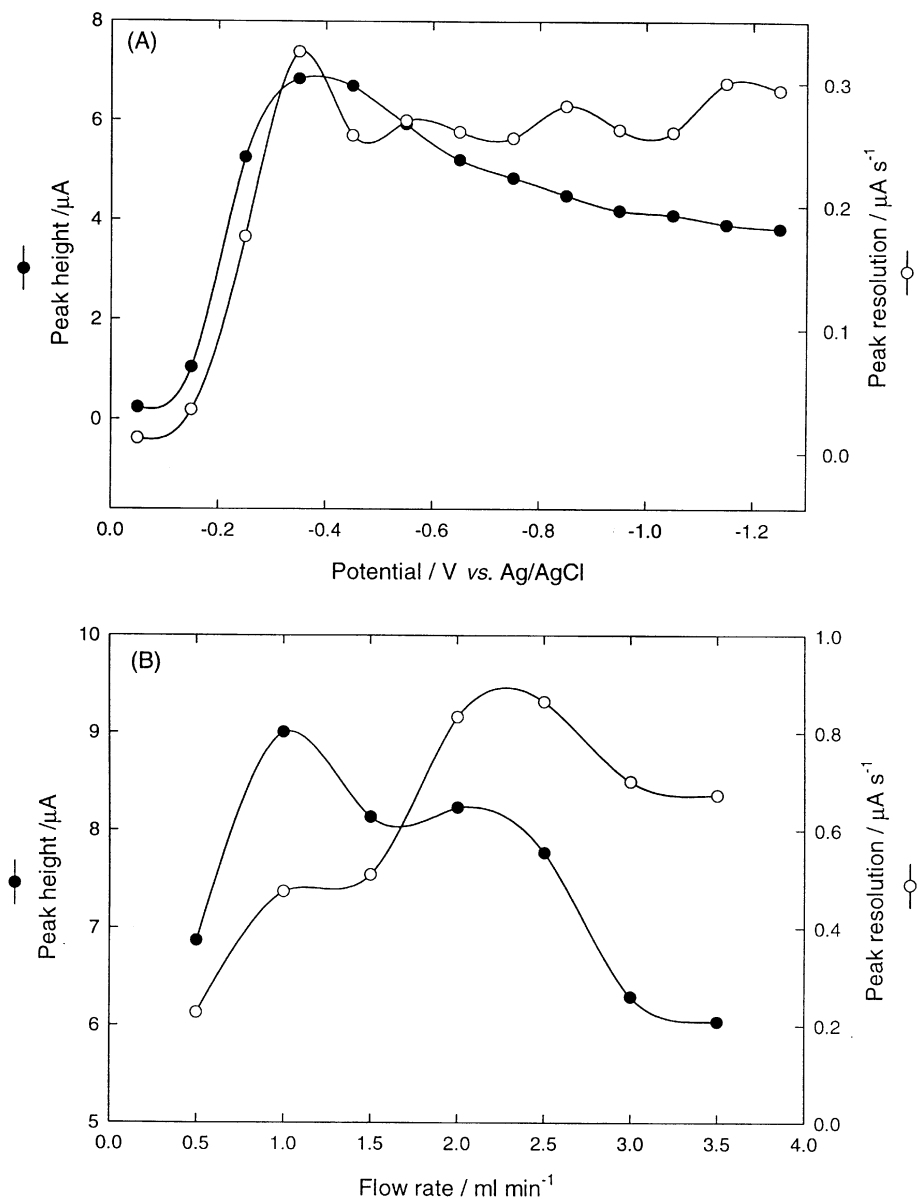
**Fig. 2** CV response of the CuSPE in the absence (A) and presence (B) of hydrogen peroxide under atmospheric, aerobic and anaerobic conditions in pH 7.4 PBS.  $[\text{H}_2\text{O}_2] = 1.62 \text{ mM}$ .

is shown in Fig. 1(A). Two distinct peaks at  $-0.164$  V (C1) and  $-0.205$  V (C2) in a cathodic sweep with one anodic shoulder at  $E_{1/2} = -0.075$  V were observed. Note that only a single peak corresponding to the total redox transition of CuO/Cu could be obtained when the scan rate was higher than  $40$   $\text{mV s}^{-1}$ . Based on earlier reports, C1 and C2 correspond to  $\text{Cu}^{\text{II}}\text{O} \rightarrow \text{Cu}^{\text{I}}_2\text{O}$  and  $\text{Cu}^{\text{I}}_2\text{O} \rightarrow \text{Cu}^0$ , respectively, and the shoulder comes from the formation of  $\text{Cu}_2\text{O}$  and CuO multilayers.<sup>23,29,35</sup> In other words, C1 and C2 are the reduction peaks of the CuO/Cu<sub>2</sub>O and Cu<sub>2</sub>O/Cu redox couples, respectively. Since C1 and C2 have comparable peak magnitudes, CuO/Cu<sub>2</sub>O and Cu<sub>2</sub>O/Cu transformation rates are almost equal. Numerous investigations regarding the physical and electrochemical behavior of Cu<sub>2</sub>O and CuO have been reported.<sup>25–29</sup> It is worth noting that Cu<sub>2</sub>O is a semiconductor in nature because Cu<sup>I</sup> has a filled electronic configuration and is the key oxide of Cu in most electrocatalytic applications.<sup>29,36–39</sup>

Fig. 1(B) shows the CV response of the CuSPE after the addition of  $3.2$  mM hydrogen peroxide. A considerable increase in the reduction peaks C1 and C2 was observed, which clearly indicates a mediated reaction through the hydrogen peroxide reduction on the CuSPE. The lack of a specific signal in the anodic direction indicates an irreversible reduction mechanism of hydrogen peroxide on the CuSPE. Most important, the

mediated reduction signals C1 and C2 obtained were not equal in magnitude, the mediated signal corresponding to Cu<sub>2</sub>O/Cu being much higher than that from CuO/Cu<sub>2</sub>O. A simple deconvolution fitting program based on a Gaussian model yields  $\sim 80\%$  of the peak area from the Cu<sub>2</sub>O/Cu mediated process, which strongly suggests the effective participation of Cu<sub>2</sub>O over CuO in the hydrogen peroxide reduction reaction. The exact hydrogen peroxide reduction processes on the CuSPE could be demonstrated with a coupled-chemical type reaction mechanism as shown in Scheme 1(A). C1 and C2 correspond to the chemical oxidation of Cu and Cu<sub>2</sub>O, respectively, by hydrogen peroxide together with the electrochemical reduction reaction on the CuSPE. The very small anodic peak suggests that both Cu and Cu<sub>2</sub>O are oxidized chemically by hydrogen peroxide. The rate of reduction of hydrogen peroxide can be expected as a first order dependence on the concentration of Cu<sub>2</sub>O. Indeed, later experiments based on steady state FIA confirmed this expectation. Most important, adaptation to a flow injection system can simplify the reaction mechanism to that shown in Scheme 1(B), and hence largely favors the analytical application.

Further CV experiments at various scan rates showed a slope of  $0.499$  in a double logarithmic plot of  $i_{\text{pa}}$  versus  $v^{1/2}$  for the hydrogen peroxide reduction revealing diffusion-controlled



**Fig. 3** Hydrodynamic voltammograms for FIA of hydrogen peroxide on the CuSPE with respect to (A) applied potential and (B) flow rate in pH 7.4 PBS.  $[\text{H}_2\text{O}_2] = 0.32$  mM.

operation of the system. The current function ( $i_t$ ) value obtained is  $1.145 \times 10^3 \text{ A V}^{-1/2} \text{ s}^{1/2} \text{ mol}^{-1} \text{ cm}^3$ . The mechanistic parameters cathodic transfer coefficient ( $\alpha_c$ ) and electrochemical rate constant ( $k_c$ ) were calculated based on Laviron's model.<sup>40</sup> The plot of  $E_{pc}$  versus  $\log v$  yielded a gradient of 85 mV per decade, which is equal to  $-2.303/\alpha_c n_c F$ . Thus,  $\alpha_c$  was calculated as 0.35 with a Tafel slope ( $b_a$ ) of 168.5 by assuming that the number of electron transfers in the rate-determining step,  $n_c$ , is one. Based on  $k_c = \alpha_c n F v / RT$ ,<sup>40</sup> the calculated value of  $k_c$  at  $1 \text{ V s}^{-1}$  is  $13.7 \text{ s}^{-1}$ . Compared with the reported values of  $k_c$ ,  $\alpha_c$  and  $b_a$  on copper wire electrodes of  $12.3 \text{ s}^{-1}$ , 0.16 and 368.8, respectively,<sup>23</sup> the CuSPE obviously shows a more efficient behavior towards the reduction of hydrogen peroxide. Further, the apparent diffusion coefficient ( $D$ ) was also calculated by potential step chronoamperometric experiments at a potential step of 0 to  $-0.25 \text{ V}$  with a pulse width of 300 s for 1.62, 3.24, 4.86 and 6.48 mM hydrogen peroxide. Based on the Cottrell equation,  $i(t) = nFAD^{1/2}C^*/\pi^{1/2}t^{1/2}$ , plots of  $i(t)$  versus  $t^{-1/2}$  for four different hydrogen peroxide concentrations showed good linearity at initial timings ( $t < 10 \text{ ms}$ ) and tended towards a plateau at higher values, as expected for a semi-infinite diffusion-controlled process. The diffusion coefficient from the linear portion of the plot is  $(2.48 \pm 0.64) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , which is very close to that on conventional electrodes,<sup>23</sup> and further indicates the suitability of the present system for analytical applications.

Before initiating analytical experiments, the influence of dissolved oxygen on the reduction of hydrogen peroxide was first investigated. Fig. 2 shows the typical responses of the CuSPE in pH 7.2 PBS with and without dissolved oxygen in the presence and absence of 1.62 mM hydrogen peroxide. It was expected that  $\text{Cu}_2\text{O}$  would assist in the oxygen reduction reaction with the formation of hydrogen peroxide.<sup>23</sup> A considerable increase in the hydrogen peroxide concentration near the electrode-electrolyte interface can lead to an increase in the current signal for bulk hydrogen peroxide reduction on the CuSPE. The sharp increase in the reduction current signals in the atmosphere and  $\text{O}_2$  purged solution, as shown in Fig. 2(A), confirms this expectation. Removal of oxygen from the cell can eliminate the underlying current from the  $\text{O}_2 + 2\text{Cu} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}_2$  reaction and leaves more Cu sites available for reaction with the externally added hydrogen peroxide. Hence the sensitivity is expected to increase with deoxygenation. Nevertheless, owing to the practical difficulty with the working solution in FIA, all the experiments were performed similarly with normal atmospheric conditions only.

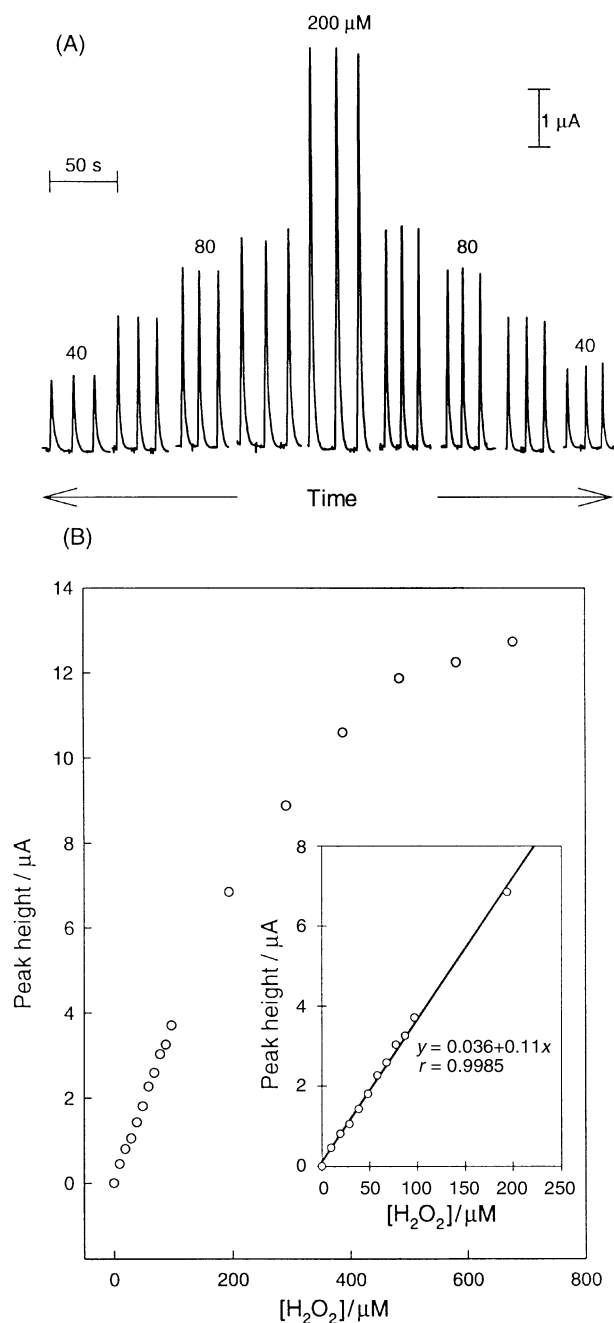
### Flow injection analysis

Hydrodynamic voltammograms for  $0.32 \mu\text{M}$  hydrogen peroxide under various poised potentials (0 to  $-1.3 \text{ V}$ ) and flow rates ( $0\text{--}4 \text{ ml min}^{-1}$ ) are shown in Fig. 3. The optimized values were chosen based on the peak resolution ( $R_p$ ,  $\mu\text{A s}^{-1}$ ), calculated by dividing the peak current by the peak width. A poised potential of  $-0.3 \text{ V}$  and a flow rate of  $2 \text{ ml min}^{-1}$  gave the best  $R_p$  and these conditions were therefore used to construct the calibration graph. It is important that the optimized poised potential of  $-0.3 \text{ V}$  matches exactly the redox potential of the  $\text{Cu}_2\text{O}/\text{Cu}$  transition and thus indicates that the surface poisoning due to CuO is negligible in the present method. Fig. 4 shows typical FIA responses and a calibration plot for hydrogen peroxide under the optimized conditions. The linear range is up to  $200 \mu\text{M}$  and the sensitivity is  $0.0345 \mu\text{A } \mu\text{M}^{-1}$  ( $r = 0.9985$ ) with a detection limit of  $0.97 \mu\text{M}$  ( $S/N = 3$ ). The RSD obtained for continuous injection ( $n = 10$ ) of  $10 \mu\text{M}$  hydrogen peroxide was 1.10%, demonstrating the high precision of the present method.

The hydrodynamic voltammograms in FIA are similar to those for the operation of a rotating disc electrode.<sup>32,33</sup> Thus,

under steady hydrodynamic conditions, the peak current ( $i_{pa}$ ) obtained was taken as the limiting kinetic current to arrive at some further important mechanistic information. A double logarithmic plot of  $i_{pa}$  versus  $[\text{H}_2\text{O}_2]$  yielded a slope very close to 1 for  $[\text{H}_2\text{O}_2]$  up to  $300 \mu\text{M}$ , and subsequently the slope decreased to zero. This result indicates a first order reaction mechanism for  $[\text{H}_2\text{O}_2]$  up to  $300 \mu\text{M}$  and a surface saturation effect at high  $[\text{H}_2\text{O}_2]$  for the CuSPE. The surface concentration ( $\Gamma$ ) of  $\text{Cu}_2\text{O}$  at the CuSPE can be calculated according to  $Q = nF\Gamma$ ,<sup>32,41</sup> where  $Q$  is the anodic charge at  $v = 10 \text{ mV s}^{-1}$ . The  $\Gamma$  value obtained is  $5.08 \times 10^{-9} \text{ mol cm}^{-2}$ , which is about three orders of magnitude lower than the hydrogen peroxide working concentrations. It is therefore concluded that the overall rate of the reduction depends directly on  $[\text{Cu}_2\text{O}]$  and is a typical example of a pseudo-first order mechanism.

Finally, the influence of interfering compounds was studied and the results are summarized in Table 1. Compounds such as



**Fig. 4** (A) FIA response of the CuSPE with various  $[\text{H}_2\text{O}_2]$ . (B) Plot of  $i_{pa}$  versus  $[\text{H}_2\text{O}_2]$  on the CuSPE by FIA. The inset shows the calibration plot for hydrogen peroxide in the concentration range  $10\text{--}200 \mu\text{M}$ . Other experimental conditions as in Fig. 3 Applied potential =  $-0.3 \text{ V}$ ; flow rate =  $2 \text{ ml min}^{-1}$ .

**Table 1** Interference study in FIA on the CuSPE in pH 7.4 PBS

Compound	Peak current ratio (%)		
	$\times 10^a$	$\times 100^a$	$\times 1000^a$
NaHCO <sub>3</sub>	0	0	0
NaClO <sub>4</sub>	0	0	0
Methylviologen	0	0	0
Na <sub>2</sub> SO <sub>4</sub>	0	0	0.8
KNO <sub>3</sub>	0	15.0	31.7
Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0	21.1	499.7
KCl	-2.2	-9.8	-9.7
NaOH	-25.9	-33.4	238.2

<sup>a</sup> In excess with respect to 100  $\mu$ M H<sub>2</sub>O<sub>2</sub>.

NaHCO<sub>3</sub>, NaClO<sub>4</sub> and methylviologen did not interfere, and SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> had little influence when in 100-fold excess. On the other hand, Cl<sup>-</sup> and OH<sup>-</sup> had a considerable effect in altering the detection signals, which can be explained as follows. If Cu<sub>2</sub>O reacts with anions at the electrode-solution interface to form a more soluble complex, then the Cu<sup>I</sup> may dissolve from the electrode before it is reduced. This is the source of interference for Cl<sup>-</sup> and OH<sup>-</sup> since the copper salts of these anions are highly soluble.<sup>42</sup>

Considering that the CuSPE offers an effective route for the sensitive determination of H<sub>2</sub>O<sub>2</sub>, this same system can be further developed to obtain biosensors for glucose and alcohol by coupling with glucose oxidase and alcohol oxidase on its interface. Fortunately, the CuSPE is a metal-based sensor, so that enzymes can easily be coated on the surface. The construction of biosensors based on the CuSPE is in progress.

## Conclusion

The disposable CuSPE combined with FIA was successfully demonstrated to be suitable for hydrogen peroxide detection by effective catalytic reduction through Cu<sub>2</sub>O mediation. The kinetic parameters obtained such as the transfer coefficient ( $\alpha_c$ ) and electrochemical rate constant ( $k_c$ ) indicate the suitability of the CuSPE in FIA applications. The reduction mechanism was pseudo-first order with respect to the Cu<sub>2</sub>O concentration. Since the reduction process on the CuSPE is diffusion-controlled, the electrode renewal is very fast (<20 s) with good repeatability (<1.5%) and low signal-to-noise ratio. The detection limit is 0.92  $\mu$ M (S/N = 3) and is comparable to that in previous work using HRP. It is worth noting that most applications in clinical and pharmacological practice require hydrogen peroxide determination at neutral pH, and this FIA method can obviously fit this requirement well. Furthermore, the CuSPE can be constructed simply and inexpensively, and thus offers an easy route to extension to real applications.

## Acknowledgement

The authors gratefully acknowledge financial support from the National Science Council of the Republic of China.

## References

- 1 F. A. Armstrong and A. M. Lannon, *J. Am. Chem. Soc.*, 1987, **109**, 7211.
- 2 D. Belenger, J. Nadreau and G. Fortier, *J. Electroanal. Chem.*, 1989, **274**, 143.
- 3 T. Tatsuma, Y. Okawa and T. Watanabe, *Anal. Chem.*, 1989, **61**, 2352.
- 4 U. Wollenberg, V. Bogdonovskaya, S. Bobrin, F. Scheller and M. Tarasevich, *Anal. Lett.*, 1990, **23**, 1795.
- 5 B. A. Gregg and A. Heller, *J. Phys. Chem.*, 1991, **95**, 5970.
- 6 M. Vreeke, R. Maidan and A. Heller, *Anal. Chem.*, 1992, **64**, 3084.
- 7 S. Pan and M. A. Arnold, *Anal. Chim. Acta*, 1993, **283**, 663.
- 8 E. Csoregi, L. Gorton, G. Marko-Varga, A. J. Tudos and W. T. Kok, *Anal. Chem.*, 1994, **66**, 3604.
- 9 J. Razumas, R. Kazlauskaitė and R. Vidziunaite, *Bioelectrochem. Bioeng.*, 1996, **39**, 139.
- 10 V. Luovich and A. Scheeline, *Anal. Chem.*, 1997, **69**, 454.
- 11 A. Navas Diaz, M. C. Ramos Peinado and M. C. Torrijas Minguez, *Anal. Chim. Acta*, 1998, **363**, 221.
- 12 S. Yabuki, F. Mizutani and Y. Hirata, *J. Electroanal. Chem.*, 1999, **468**, 117.
- 13 N. Oyama and F. C. Anson, *J. Electroanal. Chem.*, 1984, **169**, 315.
- 14 J.-M. Zen, S.-H. Jeng and H.-J. Chen, *J. Electroanal. Chem.*, 1996, **408**, 157.
- 15 Q. Chi and S. Dong, *Anal. Chim. Acta*, 1995, **310**, 429.
- 16 A. A. Karyakin, O. V. Gitlemacher and E. E. Karyakina, *Anal. Chem.*, 1995, **67**, 2419.
- 17 C. Sun, J. Zhao, H. Xu, Y. Sun, X. Zhang and J. Shen, *J. Electroanal. Chem.*, 1997, **435**, 63.
- 18 S. Lj. Gojkovic, S. Gupta and R. F. Savinell, *Electrochim. Acta*, 1999, **45**, 889.
- 19 F. Mizutani, S. Yabuki and S. Iijima, *Electroanalysis*, 1995, **7**, 706.
- 20 L.-T. Cai and H.-Y. Chen, *Sens. Actuators B*, 1999, **55**, 14.
- 21 U. Scharf and E. W. Grabner, *Electrochim. Acta*, 1996, **41**, 233.
- 22 E. R. Savinova, S. Wasle and K. Doblhofer, *Electrochim. Acta*, 1998, **44**, 1341.
- 23 M. Somasundrum, K. Kirtikara and M. Tanticharoen, *Anal. Chim. Acta*, 1996, **319**, 59.
- 24 F. A. Cotton and G. Wilkinson, *Basic Inorganic Chemistry*, Wiley, New York, 1976, p. 303.
- 25 S. M. Abdel Haleem and B. G. Ateya, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **117**, 309.
- 26 L. D. Burke, G. M. Bruton and J. A. Collins, *Electrochim. Acta*, 1998, **44**, 1467.
- 27 Y. Zhou and J. A. Switzer, *Scr. Mater.*, 1998, **38**, 1731.
- 28 B. Millet, C. Fiaud, C. Hinnen and E. M. M. Sutter, *Corros. Sci.*, 1995, **37**, 1903.
- 29 M. V. Vazquez, S. R. de Sanchez, E. J. Calvo and D. J. Schiffrin, *J. Electroanal. Chem.*, 1994, **374**, 179.
- 30 O. Bagel, B. Limoges, B. Schollhorn and C. Degrand, *Anal. Chem.*, 1997, **69**, 4688.
- 31 Z. T. Liu, D. Lai and J. D. Osterloh, *Anal. Chem.*, 1997, **69**, 3569.
- 32 J. Wang, *Analytical Electrochemistry*, VCH, New York, 1994, p. 57.
- 33 A. A. Karyakin, E. E. Karyakina and L. Gorton, *J. Electroanal. Chem.*, 1998, **456**, 97.
- 34 O. Bagel, B. Limoges, B. Schollhorn and C. Degrand, *Anal. Chem.*, 1997, **69**, 4688.
- 35 S. Hartinger and K. Doblhofer, *J. Electroanal. Chem.*, 1995, **380**, 281.
- 36 R. A. Van Leeuwen, C. J. Hung, D. R. Kammiller and J. Switzer, *J. Phys. Chem.*, 1995, **99**, 15247.
- 37 B. E. Breyfogle, C. J. Hung and M. G. Switzer, *J. Electrochem. Soc.*, 1996, **143**, 2741.
- 38 U. Stimming, *Langmuir*, 1987, **3**, 423.
- 39 S. R. de Sanchez and D. J. Schiffrin, *Corros. Sci.*, 1988, **28**, 141.
- 40 E. Laviron, *J. Electroanal. Chem.*, 1979, **101**, 19.
- 41 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- 42 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 80th edn., 1999–2000, 4-54–4-56.