STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLIV, 1-2, 1999

ELECROSYNTHESIS OF HYDROGEN PEROXIDE BY PARTIAL REDUCTION OF OXYGEN IN ALKALINE MEDIA. PART III. WALL-JET RING ELECTRODE FOR HYDROGEN PEROXIDE AMPEROMETRIC DETECTION

VICTOR ROSCA, PETRU ILEA and IONEL CATALIN POPESCU

Department of Physical Chemistry, University "Babeş–Bolyai", 3400 Cluj-Napoca, Romania

ABSTRACT. A wall-jet ring electrode system was selected as a convenient electrochemical device for amperometric detection of hydrogen peroxide, particularly when it was "in situ" generated by partial electro-reduction of dissolved oxygen in a flow-injection set-up. Steady-state amperometric measurements were performed at an applied potential corresponding to the diffusion-controlled plateau, previously reported for hydrogen peroxide oxidation on stainless steel ring electrode. The experimental parameters, electrolyte flow rate and inlet capillary nozzle to ring electrode distance, were established to ensure a wall-jet hydrodynamic regime. In these experimental conditions, a good linear dependence between the ring limiting current *vs.* hydrogen peroxide concentration was observed. Thus, it was proved that the hydrogen peroxide obtained during electro-reduction of dissolved oxygen at wall-jet disc electrode could be successfully monitored at a ring electrode, part of a wall-jet ring disc electrode.

INTRODUCTION

Because of environmental pressure on the use of chlorine chemistry, hydrogen peroxide has been displacing some uses of chloride based chemicals in the paper and pulp industry (bleaching of mechanical pulp, brightening of chemical pulp etc.) [1-4], as well as in wastewater treatment as an oxidizing agent for electrochemical and chemical incineration of various pollutants [5-9]. These and many other reasons motivate continuous interest in electrosynthesis and detection of H_2O_2, particularly in alkaline media. Electrosynthesis of H_2O_2 by partial electro-reduction of oxygen (PERO) and the subsequent use of H_2O_2 solutions in industrial processes require a rigorous control of its concentration [10].

Several techniques, as for example thermometric, potentiometric, optical, conductivity measurements etc. were adapted to measure H_2O_2 concentration. However, until now, none of them gave satisfactory results in terms of continuous and/or in-line monitoring, reliability, stability, and low cost. An important advance along this line was achieved by elaboration of new modified electrodes for H_2O_2 selective detection. For example, should be mentioned amperometric sensors based on glassy carbon electrodes modified with nickel tetra-aza-macrocyclic complexes [12], polyaniline films and platinum particles co-modified carbon fiber microelectrodes [13], peroxidase based biosensors [14,15] etc. This approach permits to improve especially the selectivity of the H_2O_2 detection.

On the other hand, electrochemical sensors are easily adapted to measurements in flow-injection systems. Thus, they can satisfy most of requirements for an ideal flow-through cell as, for example, good washing characteristics, low dead volume, fast response, and simple maintenance [16, 17]. Among the different used hydrodynamic configurations, the wall-jet one was recognized as one of the most convenient for a flow-injection detector [18]. That is why, a wall-jet electrochemical system was selected in our investigation of PERO on carbonaceous materials [18,10].

In this context, the present work was done in order to prove that the hydrogen peroxide obtained during electro-reduction of dissolved oxygen at wall-jet disc electrode could be successfully monitored by measuring the limiting current developed at ring electrode during its oxidation on a wall-jet ring disc electrode (WJRE). For this purpose, the influence of the main experimental parameters, electrolyte flow rate, inlet capillary nozzle to ring electrode distance, and hydrogen peroxide concentration, on the sensor out-put was investigated.

EXPERIMENTAL

Reagents and materials

All reagents were of analytical grade and used without any further purification. 1M NaOH aqueous solution was used as supporting electrolyte for all electrochemical measurements. All solutions were prepared with doubly distilled water.

The working ring electrode was made of stainless steel (AISI 304).

Electrochemical measurements

The wall-jet ring disc electrode was a part of a wall-jet electrochemical cell [19] (Figure 1) equipped with a homemade ring disc electrode [18]. Accordingly to the purpose of this study the disc electrode was deactivated, and hence the WJRE resulted. A Pt wire was used as counter electrode and an Ag/AgCl, KCl 1M served as reference electrode.

In order to construct the ring working electrode (r_{out} = 3 mm, r_{inn} = 2 mm) a stainless steel ring was mounted in a Perspex body, and was sealed with epoxy resin. Before use, the ring electrode was carefully wet polished with emery paper (grit 400 and 600, Carbochim, Romania) and Al_2O_3 (1 μm).

The upper part of the electrochemical cell, where the WJRE was inserted, has a thread with 1 mm step, allowing a fine-tuning of distance (d) between the inlet capillary nozzle (ϕ = 0.5 mm) and the WJRE surface. The electrochemical cell was inserted into a single line flow system, consisting of a peristaltic pump (Alitea-XV, Sweden), equipped with a silicone tubing (0.16 $cm^3\ m^{-1}$).

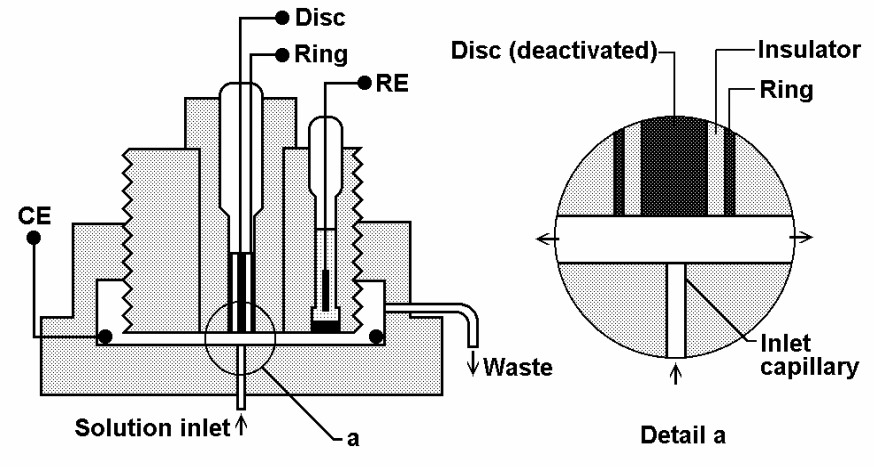

Figure 1. Scheme of the wall-jet electrochemical cell equipped with a ring disc electrode.

The three electrodes of the electrochemical cell were connected to a low current custom-made potentiostat, controlled by an IBM-PC (Olivetti 486/33) through a data acquisition card (AT-MIO-16F-5, National Instruments, USA). The software for monitoring the set-up and to perform data acquisition was based on LabVIEW 3.1 software [20].

Steady-state amperometric measurements were performed at an applied potential selected in the diffusion-controlled plateau, previously observed for hydrogen peroxide oxidation on stainless steel electrode [18].

RESULTS AND DISCUSSIONS

The limiting current, observed in a WJRE system is strongly influenced by the hydrodynamic conditions under which the system is operated [21]. In addition, the potential of the ring electrode has to be established in the domain controlled by mass transfer.

In this context, for this work an alternative procedure to that described previously [18] was followed. Thus, basically hydrogen peroxide was oxidized at WJRE when its potential was linearly swept with a slow rate, between + 0.1 and + 0.48 V *vs.* Ag/AgCl, KCl 1M. Modifying the hydrogen peroxide concentration, the distance between the inlet capillary nozzle and the ring plane for different electrolyte flow rate it was tried to establish simultaneously two goals: (i) the optimum hydrodynamic regime; (ii) the linear range of the dependence between the limiting current and the hydrogen peroxide concentration.

In order to check the assumption that, for the selected experimental conditions, the WJRE is working under wall-jet hydrodynamic regime the following equation was used [22]:

$$i_L = 1.59knFCD^{2/3}\upsilon^{-5/12}a^{-1/2}A^{3/8}V_f{}^{3/4}r_{in}{}^{3/4}\beta^{2/3}$$

where, $\beta = (r_{out}^q - r_{in}^q)/r_{in}^q$ and for a wall-jet system q = 9/8 [22]

k is a constant determined by experimental way to be 0.86 [23];
a – inlet capillary nozzle diameter, cm;
A – electrode aria, cm^2;
C – concentration, mol cm^{-3};
F – Faraday constant; C eq^{-1}
D – diffusion coefficient; cm^2 s^{-1};
ν – cinematic viscosity; cm^2 s^{-1};
V_f – volume flow rate; cm^3 s^{-1}
n – number of exchanged electrons.

In Table 1 are presented the slopes and the correlation coefficients of the regression lines obtained for linear fitting of log i_L *vs.* log V_f, at two values of the distance between the inlet capillary nozzle and the ring electrode. It can be seen that for the distance of 2 mm, the hydrodynamic regime is well a wall-jet one: the slope of the log i_L *vs.* log V_f dependence is closed to the theoretical value (0.75). For a smaller value of the distance, 1 mm, the hydrodynamic regime was not well defined (experimental data are not shown). For a higher value, 3 mm, the hydrodynamic regime starts to deviate significantly from a wall-jet one (the slopes differ significantly from 0.75).

The second step consisted of the analysis of i_L *vs.* hydrogen peroxide concentration dependence in the domain of wall-jet hydrodynamic regime predomination. In figure 2 are represented i_L *vs.* C_m (H_2O_2) plots for 6 volume flow rates and two different distances.

First of all, we can notice a good linearity between the limiting current and H_2O_2 concentration, for all flow rates when the distance was 2 mm (see also Table 2). This fact can be attributed to the stability of the wall-jet regime in the selected working conditions.

Table 1.

Linear fitting parameters of log i_L *vs.* log V_f dependencies.

d = 2 mm		d = 3 mm	
$[H_2O_2]$ mM	**Slope / R / N**	**$[H_2O_2]$ mM**	**slope / R / N**
1.5	0.7845 / 0.97824 / 5	1.5	0.7826 / 0.9484 / 5
2.3	0.7536 / 0.9859 / 5	2.3	0.6821 / 0.9716 / 5
3.1	0.7832 / 0.9969 / 5	3.1	0.8164 / 0.9819 / 5
3.8	0.7445 / 0.9982 / 5	3.8	0.5894 / 0.9713 / 5
4.6	0.7817 / 0.9817 / 5	4.6	0.70655 / 0.9678 / 5
R – the correlation coefficient N – the number of experimental points			

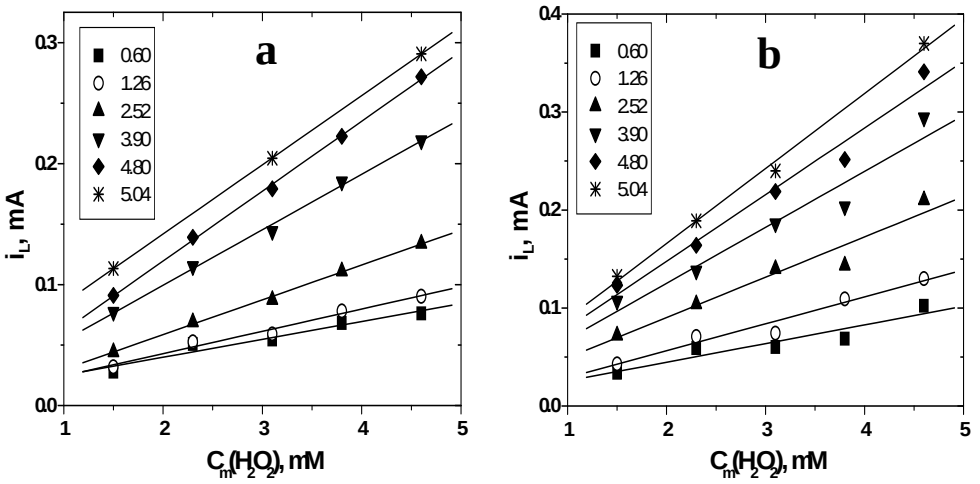

Figure 2. Dependence of the WJRE limiting current *vs.* hydrogen peroxide concentration: (*a*) d = 2 mm; (***b***), d = 3 mm. Numbers in the legend are the values of volume electrolyte flow rate (cm^3 min^{-1}). Experimental conditions: applied potential, + 400 mV *vs.* Ag/AgCl, KCl 1M; flow carrier, 1M NaOH solution.

The best linear fittings are observed for intermediate flow rates. This can be explained by the instability of the hydrodynamic regime at low flow rates, and by the decrease of the limiting current plateau at high flow rates, both involving an increasing error in the evaluation of the limiting current value. Analyzing the similar data for the distance of 3 mm it can be noticed that for a mixed hydrodynamic regime a worse linearity was observed.

In order to demonstrate the performances of the investigated system, the values of main analytical parameters are given below. Thus, for an electrolyte flow rate of 4.80 cm^3 min^{-1}) we found: the minimum sample volume, 500 μL; number of samples per hour, 30 s/h; sensitivity, 15.5 mA/mM;

detection limit, 0.71 mM (for S/N = 3). It should be added the an important advantage of the proposed detection technique is the possibility to slightly increase the system sensitivity by increasing the electrolyte flow rate.

Table 2.

Parameters of linear regression lines for i_L *vs.* C_m (H_2O_2) dependencies.

Inlet capillary nozzle to ring electrode distance			
2 mm		**3 mm**	
V_f (cm^3 min^{-1})	**Cor. coeff. / No. of points**	**V_f (cm^3 min^{-1})**	**Cor. coeff. / No. of points**
0.60	0.9822 / 5	0.60	0.9411 / 5
1.26	0.9940 / 5	1.26	0.9778 / 5
2.52	0.9988 / 5	2.52	0.9802 / 5
3.90	0.9981 / 5	3.90	0.9813 / 5
4.80	0.9994 / 5	4.80	0.9868 / 5
5.04	0.9999 / 3	5.04	0.9976 / 4

CONCLUSIONS

Experimental data demonstrate two important points:

(i) The wall-jet hydrodynamic regime is remarkably stable at small variations of the electrolyte flow rate and the distance between the inlet capillary nozzle and the electrode.

(ii) For the wall-jet hydrodynamic regime (d = 2 - 3 mm and V_f = 2.5 - 5.0 cm^3 min^{-1}) a strong linear regression between the ring limiting current (i_L) and the H_2O_2 concentration (up to 5 mM) was observed.

Taking into consideration these electroanalytical characteristics we can conclude that the wall-jet configuration render to the electrochemical response of the WJRE a high stability and a good sensitivity, qualities that often are decisive to establish the level of performance for a flow-injection method of analysis. Concluding, the WJRE system can by recommended as an alternative method for "in-line" amperometric detection of H_2O_2.

ACKNOWLEDGEMENT

Financial support from CNCSIS (Grant 53/109-1999) is gratefully acknowledged. The single line flow system is a kindly gift from Dr. Lo Gorton, Lund University, Sweden. The authors thank Adrian Nicoara for the data acquisition software. We also thank Sorin Dorneanu for his technical assistance.

REFERENCES

1. E.E. Kalu and C. Oloman, J. Appl. Electrochem., 1990. **20.** 932.
2. B.V. Tilak, in "Electrochemistry for a Cleaner Environment", J.D. Genders and N.L. Weinberg (eds.), p. 387, The Electrosynthesis Company Inc, New York, 1992.
3. J.A. McIntyre, The Electrochemical Society Interface, 1995, **4**(2), 29.
4. O. Savadogo and S. Leclerc, Résumés des Comunications, Journées d`Electrochimie, Montréal, 1997.
5. P. Westbroec, E. Temmerman and P. Kiekens, Anal. Commun., 1998, **35**, 21.
6. J.-S. Do and C.-P. Chen, J. Appl. Electrochem., 1994, **24**, 936.
7. C. Ponce de Leon and D. Pletcher, J. Appl. Electrochem., 1995, **25**, 307.
8. Y.-L. Hsiao and K. Nobe, J. Appl. Electrochem., 1993, **23**, 943.
9. J.-S. Do and W.-C. Yeh, J. Appl. Electrochem., 1996, **26**, 673.
10. O. Serdan, C. Ghiurutan, P. Ilea and I.C. Popescu, unpublished results.
11. R. Toniolo, N. Comisso, G. Bontempelli, G. Schiavon, Electroanalysis, 1996, **8**,151.
12. J. Taraszewska and G. Roslonek, J. Electroanal. Chem., 1994, **371**, 223.
13. Yu. Wang, J. Huang, J. Wei and X. Zhou, Electroanalysis, 1998, **10**, 776.
14. D. Wilke, H. Muller and N. Kolytsheva, Fresenius J. Anal. Chem., 1997, **357**, 534.
15. Z. Zhang, C. Lei, W. Sun, H. Liu and J. Deng, J. Electroanal. Chem., 1996, **419**, 85.
16. W. Frenzel, Analyst, 1988, **113**, 1039.
17. J.G. Douglas, Anal. Chem., 1989, **61**, 922.
18. P. Ilea, S. Dorneanu and I.C. Popescu, J. Appl. Electrochem., 2000, **30**, .
19. R. Appelqvist, G. Marko-Varga, L. Gorton, A. Torstensson and G. Johansson, Anal. Chim. Acta, 1985, **169**, 237.
20. A. Nicoara, L. Oniciu and S. Dorneanu, Rev. Roumaine Chim., 1998, **43**, 823.
21. H. Gunasingham and B. Fleet, in A.J. Bard (Ed.) "Electroanalytical Chemistry", vol. 16, Marcel Dekker, New York. 1989, 96.
22. W.J. Albery and C.M.A. Brett. J. Electroanal. Chem., 1983, **148**, 201.
23. D.C. Johnson and R.E. Allen, Talanta, 1973, **20**, 305.