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A NOVEL PLANAR ELECTROCHEMICAL CELL FOR VOLTAMMETRIC MEASUREMENTS IN THIN HYDROGEL FILMS

LÁSZLÓ KÉKEDY-NAGY[a*], FERNANDO GARAY[b] AND ERNŐ LINDNER[a]

ABSTRACT. The fabrication of a planar micro electrochemical cell is presented. The simplicity and the relative low cost of this kind of cells make them very interesting and promising in the development of chemical and biochemical sensors. The utilization of microelectrodes as working electrodes in planar electrochemical cells is preferred to the conventional macro electrodes because microelectrodes can be used in highly resistive media, have short response time, and excellent signal to noise ratio. In electrochemical sensor applications, the microelectrode surfaces are commonly modified with multiple layers to boost selectivity, control sensitivity, or to provide a biocompatible interface between the sensor and its environment. In this work, the fabricated set of bundled electrodes is covered with a hydrogel as an example of its potential use as electrochemical gas sensor. All micro electrochemical cells were characterized by cyclic voltammetry (CV) and the results were analyzed with different statistical methods.

Keywords: *Electrochemical gas sensor, microelectrode, planar micro electrochemical cell, cyclic voltammetry*

INTRODUCTION

Due to their unique advantages electrochemical (bio)sensors remained in the forefront of sensor research throughout the years [1,2].

Electrochemical gas sensors are widely used for the determination of different gases such as oxygen, carbon dioxide, or ammonia as well as for diagnostic purposes. In this regard, electrochemical sensors are considered to be selective tools for the determination of several analytes in a wide concentration

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[a] *University of Memphis, Department of Biomedical Engineering, Memphis, Tennessee 38152, USA*

[b] *INFIQC, CONICET, Dpto. de Físico Química, Fac. de Ciencias Químicas, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina*

* *Corresponding author: laszlo@inano.au.dk.*

range. Moreover, the robustness, low cost, and small size commonly associated to this kind of sensors make them suitable for the systematic analysis of small volumes of samples [3,4].

The most common gas sensor consist on a working electrode and a reference electrode, which are placed inside a cylinder filled with an electrolyte solution and separated from the sample by a thin gas permeable membrane. The working electrode is placed as close as possible to the membrane so that only a very thin film (~10 µm) of the electrolyte solution is sandwiched between the electrode surface and the gas permeable membrane. In this regard, the gas permeable membrane provides exceptional selectivity for this kind of sensors because only gas molecules can diffuse through the membrane and change the concentration in the thin layer of electrolyte immediately adjacent to the working electrode surface. Additionally, the system usually achieves steady-state conditions in a relatively short time (from few seconds to few minutes) depending on the thickness and resistance of the membrane [7,8]. In order to minimize this resistance, it is intended to add high concentration of the electrolyte into the film and it is also preferred the use of microelectrodes instead of conventional macro-electrodes. It is well-known that microelectrodes have smaller RC time constant and better signal-to-noise ratio than the larger electrodes. As a result, microelectrodes result quite suitable for the quantification of analytes in samples with relatively high resistive media.

Depending on the application, the fabrication strategy and the electrode material of a microelectrode can vary significantly [9]. Some few examples of microelectrode fabrication are the print and peel method [10], electrochemical deposition inside a microfluidic channel [11], electrochemical etching [12], inkjet printing with ultrashort pulsed laser ablation [13] and sonochemical patterning of microelectrode arrays [14].

In this work the development of a planar sensing platform that can be transformed into a variety of sensors by coating the surface with a task specific film is presented. This set of bundled electrodes is the scaffold for a micro-electrochemical cell that can be used for the determination of electroactive species in the gas phase. The bundled electrodes and the electrochemical cells are characterized by cyclic voltammetry and the results analyzed by different statistical methods.

RESULTS AND DISCUSSION

The obtained electrochemical cell consisted in a bundle of three electrodes and the details related to the electrode preparation are indicated in the experimental section. Figure 1 shows a scheme of the side view (A) and a picture of the surface of the bundled electrodes (B). It can be observed from Figure 1B that all three electrodes are relatively close to each other. The close proximity is beneficial, because it might minimize the ohmic potential drop of the solution. The integrity of the glass-platinum seal was investigated visually, using a digital microscope. There were no cracks or nicks observed around the working electrode, which might modify the surface and therefore the electrochemical characteristics of the working electrode. All indications showed a good seal between the glass and the metal, thus obtaining a microelectrode having disk geometry.

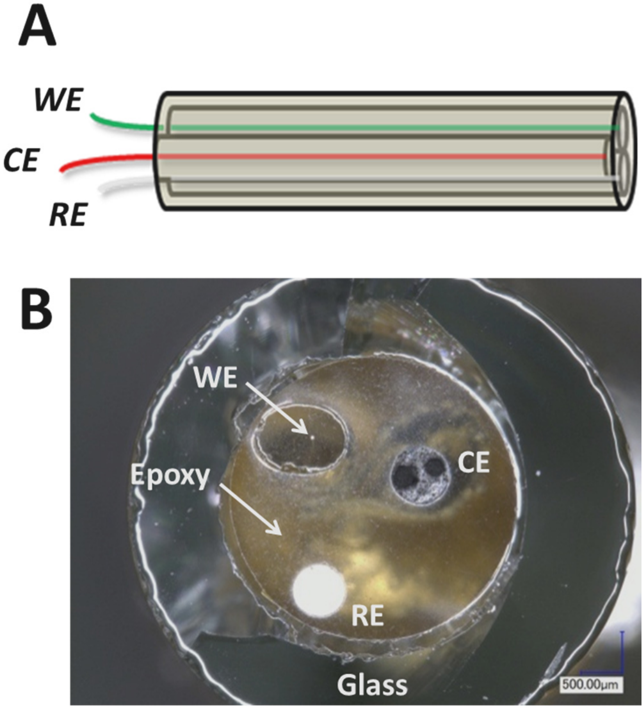

Figure 1. (A) Scheme of the planar micro electrochemical cell. (B) Photograph of a polished planar electrochemical cell surface, WE – working electrode (25 µm diameter Pt disc electrode); RE – reference electrode (0.5 mm diameter Ag disc electrode); CE – auxiliary electrode (0.6 mm diameter graphite disc electrode).

Every set of bundled electrode was tested/characterized by cyclic voltammetry (CV) [15, 16]. Figure 2 shows a cyclic voltammogram recorded in 1 mM FcMeOH in 0.1 M KCl, recorded from -0.1 V to +0.4 V (vs. Ag|AgCl|0.1M KCl) with a scan rate of 0.05 Vs^{-1}, while the solution was stirred vigorously for 10 seconds before each experiment. A very well developed sigmoidal voltammogram was observed, which is characteristic for microelectrodes having disk geometry.

The steady-state of limiting current for microelectrodes of disk geometry is expected to follow the equation [17-19]:

$$i_L = 4n\text{FDCr} \tag{1}$$

where, *I* is the steady state or limiting current (A), *n* is the number of electrons, *F* is the Faraday constant (96,485.3415 Asmol^{-1}), *D* is the diffusion coefficient of the FcMeOH in aqueous solution (7.6 ± 0.5×10^{-6} cm^{2}s^{-1}) [20], *C* is the concentration of the FcMeOH in the aqueous solution and *r* is the radius of the disk microelectrode. Using Equation 1, one can determine the actual radius of the working electrode.

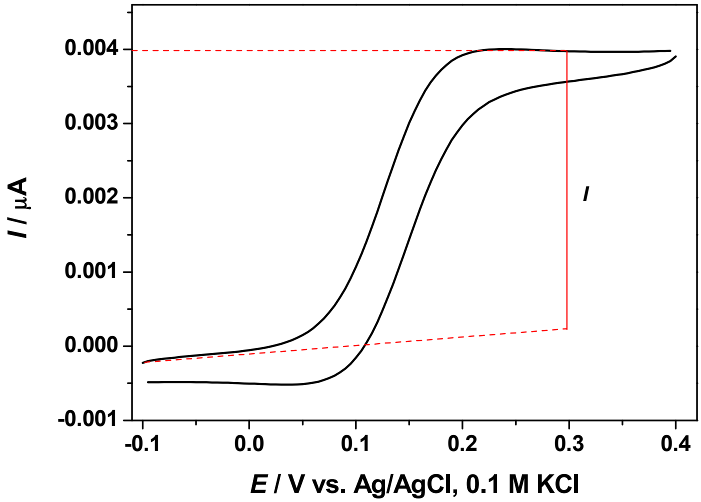

Figure 2. Representative CV recorded with a fabricated micro-electrochemical cell in 1 mM FcMeOH and 0.1 M KCl background electrolyte. Scan rate 0.05 Vs^{-1}.

The steady state current obtained with the Pt disk microelectrode was compared to the expected (theoretical) current obtained from Equation 1. The results are shown in Figure 3. The current expected from the equation was 0.00367 µA.

The average diameter of the fabricated Pt disk microelectrodes was (23.9 ± 0.5) µm after they were bundled to the reference and counter electrodes. Although the obtained average diameter was 4.4% smaller than the 25.0 µm informed by the manufacturer of the Pt wire, a one way analysis of variance (ANOVA) points out no significant difference between the steady state currents of the different microelectrodes and the theoretical steady state current. The statistical study was performed for $\alpha = 0.05$. Tukey and Levene's tests were also in agreement with ANOVA analyses indicating that the newly fabricated set of bundled electrodes were performing as expected for microelectrodes having disk geometry and also, statistically they were no different from the theoretically calculated values (steady state current or radius).

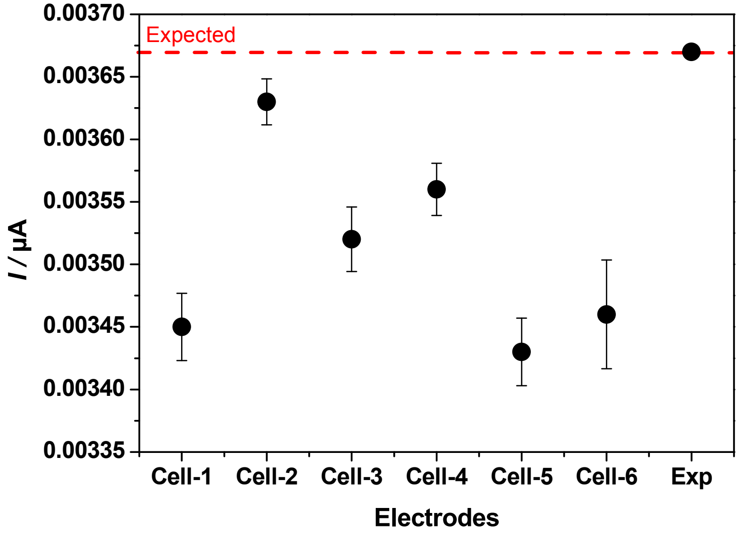

Figure 3. Steady state current values obtained for independently fabricated bundled electrodes. All measurements were in 1.0 mM FcMeOH and 0.1 M KCl as background electrolyte. Experimental results are compared to the expected value of a 25 µm diameter Pt disk.

Once this platform was ready, the electrodes were covered with a hydrogel. In this case, the hydrogel was composed by 0.045 g/mL (3x) gelatin. The hydrogel was placed by drop casting on the surface of the bundled electrodes. Thus, the volume of hydrogel defined the size of planar electrochemical cell.

For a typical electrochemical gas sensor, the electrodes are placed in a cylinder which contains the electrolyte. In our case this electrolyte solution was replaced by the hydrogel which was spin coated on the surface of this electrochemical cell. In this setup, the reproducibility of the sensor it doesn't only depend on the radius of the working micro electrode, but the thickness of the hydrogel as well. The changes within the humidity of the room might drastically influence the thickness of the hydrogel, hence the electrochemical response of the sensor as well. Thus the feasibility of using the planar electrochemical cell as a sensor in the gas phase was evaluated by studying the effect of humidity in the environment. To do this, 1 mM FcMeOH and 0.1 M KCl were added to the composition of the hydrogel. Then the hydrogel film coated electrochemical cell was placed in a sealed 20 mL vial over 5 mL of 0.1 M KCl. Under this condition, the hydrogel of the sensor slowly incorporates water from the environment. As a result, gradual swelling of the hydrogel occurs until its saturation with water and the current response of the sensor decreases due to the dilution of the electroactive species into the film. Figure 4 shows CVs performed with the planar electrochemical cell every 30 minute. During the first 3 hours, the volume of the hydrogel changes linearly with time. Then, the swelling effect slows down and after 6 hours the humidity of the hydrogel is close to its equilibrium value.

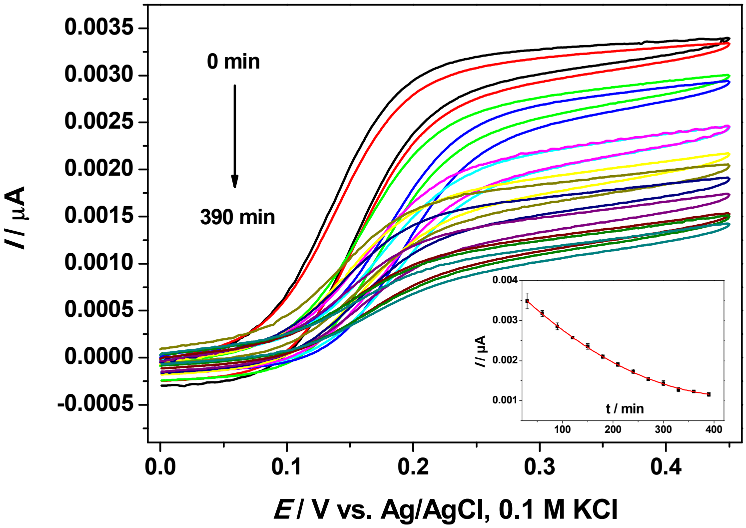

Figure 4. Representative CVs recorded with a gelatin film coated planar electrochemical cell exposed to a humid environment. The gelatin film contained 1 mM FcMeOH as analyte and 0.1 M KCl as background electrolyte. The inset shows the decrease of the steady state current with time. Scan rate 0.05 Vs^{-1}.

Since the decrease of the signal in the first 30 minutes was not significant it projects promising feasibility for the utilization of the homemade planar micro electrochemical cell as a platform for the development of membrane coated gas sensors. The optimization of the experimental protocol and hydrogel film coating was out of scope for this work.

CONCLUSIONS

A novel planar electrochemical cell has been presented. In this work it is shown its preparation and characterization by cyclic voltammetry. In order to minimize IR drop and to maximize the signal to noise ratio a 25 µm Pt microdisk electrode is used as working electrode. No statistical difference was found between the theoretically expected and experimentally determined steady state currents. The set of bundled electrodes is robust and the surface can be renewed any time simply by polishing with alumina.

The electrochemical measurements showed clearly that the newly prepared electrochemical cells could be a viable option in the development of electrochemical (bio)sensors of species dissolved in the gas phase.

EXPERIMENTAL SECTION

Micro Electrochemical Cell Fabrication

The planar micro electrochemical cell consists of three electrodes, each of them were prepared individually. The working microelectrode (WE) consists of a 25 μm Ø Pt wire, which was inserted in a borosilicate glass tubing (OD = 1.0 mm and ID = 0.5 mm). Before the electrode preparation the glass tubing was cleaned with 1:10 dilute nitric acid solution, and de-ionized water. After several rinses the glass capillaries were dried for 1 hour in an oven at 100° C. The cleaned capillaries were pulled with a Sutter Instruments pipette puller (Model P-30) using the following settings: $HEAT_1$ = 825; $HEAT_2$ = 100; PULL = 800. The pulling provided a pair of capillaries of approximately the same length (5 cm) with a short tapered end. The tapered end of the pulled capillaries was sealed with an open flame produced by a Bunsen burner.

The Pt wire was cut into sections of ~2 cm, straightened, cleaned in methanol, dried and inserted into the pulled glass capillary tubes. For visual confirmation a microscope was used to check if the Pt wire had fully descended to the tip of the closed glass capillary tubing. The open ends of the glass tubing were attached then to a vacuum pump for 30 minutes. Heat was carefully applied to the tips of the closed end of the glass tubing, using the same Bunsen burner. The glass tubing was heated slowly, first at the top of the flame, and was pulled in and out of the flame. It was also rotated during the process so that the tubing would not bend. This process was continued until approximately one centimeter of the glass tubing had collapsed around the platinum wire. Finally, each microelectrode was checked with a microscope to ensure that no air bubbles were formed between the glass and the Pt wire. The working electrode was connected to a thin cable by injecting silver epoxy (EPO-TEK H2OE) into the open end of the glass capillary.

The reference electrode was a 0.5 mm Ø Ag wire while the counter electrode was a 0.6 Ø mm spectral purity graphite rod. The connections were prepared by careful alignment of the electrode piece with the copper connecting wire, followed by the sealing with the silver epoxy. The silver epoxy was cured overnight at 100° C.

The set of three electrodes were bounded together as tight as possible with parafilm, in order to fit in an external glass tubing (OD = 5.1 mm, ID = 3.0 mm), which was pre-cleaned in a 1:10 dilute HNO_3 solution. The side of this external glass tube that contains the three electrodes was temporarily sealed with scotch tape. Then epoxy resin Epon 828 was prepared according to a protocol by Wightman et al [21]. It consisted of a preheated (~70°C) mixture of m-phenylenediamine and in a weight ratio of 0.16/1.0. Once the resin was prepared, it was injected into the glass tubing containing the electrodes and the epoxy was cured over a period of two days, first overnight at room temperature, and then at 150° C.

After complete curing the scotch tape was removed from the end of the glass tube and the planar electrochemical cell was polished manually using sandpaper of decreasing coarseness in order to obtain a flat smooth surface for each of the three electrodes. Then, the set of bundled electrodes was polished with alumina slurry of 1.0 µm and 0.3 µm. This polishing was performed on a machine-rotating polisher. Prior to each electrochemical experiment, the planar electrochemical cell surface was polished with 0.05 µm grade alumina slurry. This last step was done by hand, and the electrodes were rinsed and sonicated in de-ionized water to ensure that no alumina particles remained on the surface.

Materials

The following chemicals were used: potassium chloride-extra pure (KCl) from Acros Organics (New Jersey, US); ferrocenemethanol (FcMeOH) 97% from Aldrich (St. Louis, MO). For the preparation of the hydrogel film commercially available gelatin was used from a local store. The electrodes of the planar micro cell were fixed together with an epoxy resin constituting of m-phenylenediamine 99+%, from Acros Organics (Belgium); Epon resin 828 from Miller-Stephenson chemical company (Danbury, CT). The tight electric contact of the cell electrodes with the Cu connecting wires was realized via silver epoxy H20E, from Epoxy Technology (Conroe, TX). All solutions were prepared by using de-ionized water (18 MΩ cm) from a Millipore Milli-Q system.

The electrodes prior measurements were polished on the polishing cloth by using wet Alpha micropolish II deagglomerated alumina (1 µm, 0.3 µm, 0.05 µm) powder (Buehler, Lake Bluff, IL).

The planar electrochemical cell was constructed by using a Pt wire of 25 µm Ø and 99.95% purity from Alfa Aesar (Ward Hill, MA), a silver wire of 0.5 mm Ø and 99.99% purity manufactured by Aldrich, and a graphite bar of 0.6 mm Ø, spectral purity by Aldrich, as auxiliary electrode.

Apparatus and Methods

The electrochemical measurements were performed using a potentiostat Model 760C (CH Instruments, Austin TX).

For the electrochemical cell preparation the following instruments were used: P-30 pipette puller; Pittsburgh Universal Bunsen burner; Cooltech (Ashford, Middlesex, UK) high performance vacuum pump Model No. 15600; rotating polisher ST-707B from Sharpner (Saddle Brook, NJ). The electrodes surfaces were observed with the digital microscope VHX-1000 Keyence (Itasca, IL).

REFERENCES

[1]. A. Turner, *Trends in Biotechnology*, **2013**, *31*, 119.

[2]. A.J. Bandodkar, J. Wang, *Trends in Biotechnology*, **2014**, *32*, 363.

[3]. J.R. Stetter, W.R. Penrose, S. Yao, *Journal of The Electrochemical Society*, **2003**, *150*, S11.

[4]. C.M.A. Brett, *Pure Appl. Chem.*, **2001**, *73*, 1969.

[5]. D. Grieshaber, R. MacKenzie, J. Voros, E. Reimhult, *Sensors*, **2008**, *8*, 1400.

[6]. S.D. Collyer, F. Davis, S.P.J. Highson, *Sensors*, **2010**, *10*, 5090.

[7]. B.D. Pendley, H.D. Abruna, *Anal. Chem.*, **1990**, *62*, 782.

[8]. J.R. Stetter, J. Li, *Chem. Rev.*, **2008**, *108*, 352.

[9]. R.D. O'Neill, S.C. Chang, J.P. Lowry, C.J. McNeil, *Biosensors and Bioelectronics*, **2004**, *19*, 1521.

[10]. C. Hong, D. Bao, M. S. Thomas, J.M. Clift, V.I. Vullev, *Langmuir*, **2008**, *24*, 8439.

[11]. A.D. Bani-Yaseen, *Int. J. Electrochem. Sci.*, **2010**, *5*, 1837.

[12]. H.J. Lim, Y.M. Lim, S.H. Kim, *Jpn. J. Appl. Phys.*, **2003**, *42*, 1479.

[13]. S.H. Lee, D.J. Lee, Y.H. Lee, S.T. Wereley, J.H. Oh, *Phys. Status Solidi A 209*, **2012**, *11*, 2142.

[14]. S.D. Collyer, F. Davis, S.P.J. Higson, *Sensors*, **2010**, *10*, 5090.

[15]. C.M.A. Brett, A.M. O. Brett, "Electrochemistry - Principles, Methods and Applications", Oxford University Press, New York, **1993**, chapter 13.

[16]. P.T. Kissinger, W. R. Heinman, "Laboratory techniques in electroanalytical chemistry", Marcel Dekker, Inc., New York, **1996**, chapter 12.

[17]. J. Wang, "Analytical Electrochemistry", A John Wiley & Sons, Inc., New York, **2000**, chapter 6.

[18]. A.J. Bard, L.R. Faulkner, "Electrochemical Methods Fundamentals and Applications", John Wiley & Sons, Inc., New York, **2001**, chapters 1 and 14.

[19]. C.G. Zoski, “Handbook of Electrochemistry”, Elsevier B. V., Amsterdam, **2007**, chapter 2.
[20]. C. Amatore, C. Pebay, L. Thouin, A. Wnag, J.S. Warkocz, *Anal. Chem.*, **2010**, *82*, 6933.
[21]. R.M. Wightman, A. Hermans, A.T. Seipel, C.E. Miller, *Langmuir*, **2006**, *22*, 1964.