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Micro ring–disk electrode probes for scanning electrochemical microscopy

Peter Liljeroth, Christoffer Johans, Christopher J. Slevin, Bernadette M. Quinn *, Kyösti Kontturi

Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland

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Abstract

The construction and characterisation of ring–disk (RD) microelectrodes suitable for use in scanning electrochemical microscopy (SECM) is reported. Such RD electrodes are proposed as probes for novel generator–collector SECM experiments. In this case, the interaction of both the reactants and products with the substrate under investigation can be followed simultaneously from a single approach curve to the substrate. Examples of such approach curves to conducting and insulating substrates are given to demonstrate the potential of this new mode of SECM operation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ring–disk microelectrodes; Scanning electrochemical microscopy; Generator–collector approach curves

1. Introduction

The most common type of scanning electrochemical microscopy (SECM) tip used to date has been the planar disk-shaped microelectrode. This is due both to the relative ease of construction of robust tips and to the wealth of theoretical studies concerning their use in SECM. Other tip geometries (hemispherical, conical, spherical, ring) have been considered to a lesser extent, in particular for those in the nm range [1–7]. A recent report by Bard and co-workers [8] describes the construction and characterisation of ring microelectrodes for combined SECM and optical applications. The construction [9] and theoretical characterisation [10] of ring–disk (RD) microelectrodes has also been described, however, there are few reports concerning their use.

Here, we report the construction and use of a combined RD microelectrode suitable for SECM applications. Steady-state current vs. distance SECM approach curves recorded in the disk-generation/ring-collection (DG/RC) mode allow us to simultaneously follow the interaction of both the reactants and products with the substrate under study. With a conventional disk electrode, this can only be achieved using the method of double potential steps proposed by Unwin and co-workers [11]. The advantage of the steady-state response of the combined RD tip over transient based techniques is to simplify both the theoretical treatment and instrumentation requirements in terms of time resolution. This approach should prove useful for studies probing complex reaction mechanisms involving unstable intermediates, simultaneous topographical and reactivity imaging, and spontaneous reactions at interfaces. In this communication, we report a simple procedure for preparing RD microelectrodes for SECM. The measured response of these electrodes in DG/RC mode SECM is given for the limiting cases shown in Figs. 1(a) and (b). Preliminary theoretical results are presented while a detailed theoretical analysis will be published later [12].

2. Theory

The mass transport characteristics of SECM have been well studied theoretically for a number of different experimental conditions and geometries [13–16]. This section provides the theory for DG/RC experiments with RD SECM probes, in which a redox mediator, Red, initially present in solution at a concentration of c^b

* Corresponding author. Tel.: +358-9-4512579; fax: +358-9-4512580. *E-mail address:* bquinn@cc.hut.fi (B.M. Quinn).

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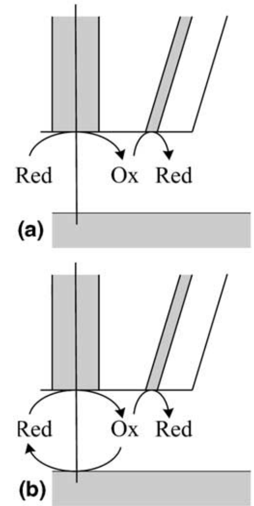

Fig. 1. Schematic of (a) the negative feedback and (b) positive feedback conditions.

reacts at the disk to form Ox initially at zero concentration. Ox further reacts at the ring to regenerate Red. Both electrodes operate under diffusion limited conditions. The geometry of the RD electrode with relevant symbols is shown in Fig. 2. The diffusion equation in dimensionless form in the cylindrical symmetry is

$$\frac{\partial^2 C(R,Z)}{\partial R^2} + \frac{1}{R}\frac{\partial C(R,Z)}{\partial R} + \frac{\partial^2 C(R,Z)}{\partial Z^2} = 0, \tag{1}$$

where $C = c/c^{\mathrm{b}}$, $R = r/r_{\mathrm{e}}$, $Z = z/r_{\mathrm{e}}$, and r_{e} is the radius of the microelectrode. The boundary condition at the disk electrode is $C(R,Z) = 0$ and at the ring electrode $C(R,Z) = 1$. The axis of symmetry $(R = 0)$ and the insulating glass sheath have the no flux boundary condition. The boundary conditions for the insulating (Eq. (2)) and conducting substrates (Eq. (3)) are

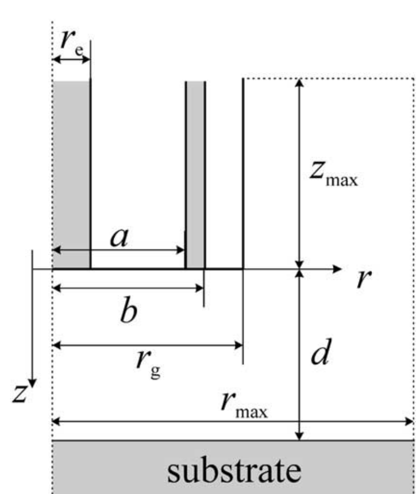

Fig. 2. Definition of the co-ordinate system and the symbols used in Section 2.

$$\left.\frac{\partial C(R,Z)}{\partial Z}\right|_{z=d/r_{\mathrm{e}}} = 0, \tag{2}$$

$$C(R, Z = d/r_{\mathrm{e}}) = 1. \tag{3}$$

The problem was solved numerically with Matlab® 5.3 equipped with the FEMLAB 1.0 toolbox for solving partial differential equations with the finite element method. The disk (I_{disk}) and ring (I_{ring}) currents were calculated from

$$I_{\mathrm{disk}} = 2\pi nFDc^{\mathrm{b}}r_{\mathrm{e}}\int_0^1 R'\left.\frac{\partial C(R',Z)}{\partial Z}\right|_{z=0}\mathrm{d}R', \tag{4}$$

$$I_{\mathrm{ring}} = -2\pi nFDc^{\mathrm{b}}r_{\mathrm{e}}\int_{a/r_{\mathrm{e}}}^{b/r_{\mathrm{e}}} R'\left.\frac{\partial C(R',Z)}{\partial Z}\right|_{z=0}\mathrm{d}R', \tag{5}$$

where n is the number of electrons transferred in the electrode reaction, F is the Faraday constant, and D is the diffusion coefficient of the species initially present. The tip and ring currents were normalised with respect to the diffusion limited current at the disk at distances far from the substrate under study.

3. Experimental

3.1. Preparation of electrodes

Disk-shaped Pt SECM probes were prepared as previously described [13]. Briefly, Pt wire (10 and 25 μm, Goodfellows, UK) was heat sealed in pulled borosilicate glass capillaries (Harvard GC200-10, UK) under vacuum followed by tip sharpening and polishing until the desired ratio of the overall tip diameter to that of the platinum disk was achieved. As the tip sharpening is done by hand, it is not possible to achieve absolutely uniform shape and perfect concentricity of the disk and ring. However, as will be shown in the results and discussion, the manufactured tips proved to be adequate for electrochemical studies. A thin gold film was subsequently sputtered (Balzers Union SCD 040, sputtering current 30 mA, sputtering distance 30 mm, and sputtering time 5 min) onto a continuously rotated tip, and electrical connections were made both to the disk and the gold film. With the sputtering parameters used, the thickness of the ring electrode was typically of the order of 500 nm. This can be altered by varying the sputtering time. The probe was then covered with insulating material, a commercial “nail-polish” (brand name SOHO New York, colour code 21, Interbeauty, Amsterdam, Holland), which was applied to the tip with a small brush by hand and allowed to dry in air at room temperature. The tip was then carefully polished with 0.3 μm aluminium oxide grinding paper (Buehler, US) until an RD electrode assembly was exposed. This grinding paper was found to be ideal in maintaining a good seal

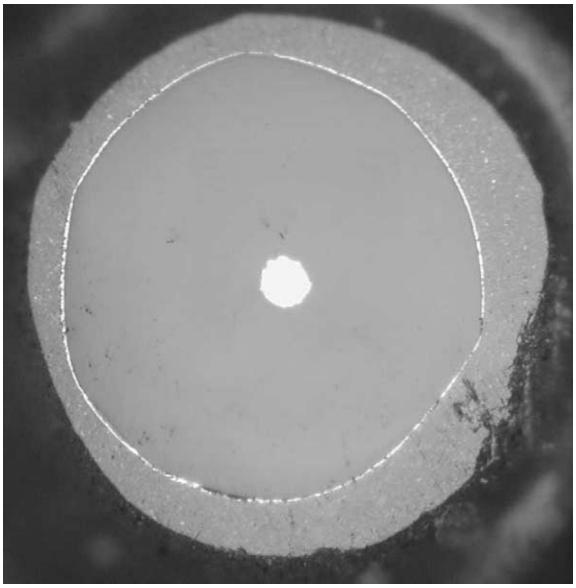

Fig. 3. A photograph of an RD electrode assembly. The diameter of the disk is 25 μm.

around the ring electrode. This resulted in a combined RD electrode suitable for use in SECM applications (Fig. 3).

3.2. Chemicals

Ferrocene methanol (FcMeOH) was purchased from Aldrich and used without further purification. All other chemicals were of the highest available commercial quality and were used as received. Solutions were prepared using MQ treated water (Milli-Q, Millipore).

3.3. Instrumentation

Cyclic voltammograms (CVs) and approach curves (tip (I_{disk}) and ring (I_{ring}) current vs. distance, d) were obtained using a CHI900 SECM instrument (CH-Instruments, Austin, TX). A bi-potentiostatic configuration was used where a Pt coil and Ag/AgCl wire served as counter and reference electrodes, respectively, while ring and disk electrodes were the working electrodes.

4. Results and discussion

In Fig. 4(a), typical CVs for FcMeOH oxidation at the ring (upper) and disk (lower) UMEs are given. The diffusion coefficient of ferrocene methanol can be calculated from the limiting current at the disk to be $D = 6.1 \times 10^{-6}$ cm^2/s. This compares favourably with the literature value of 6.7×10^{-6} cm^2/s [17]. The limiting current at the ring electrode can be predicted from the following equation [18]:

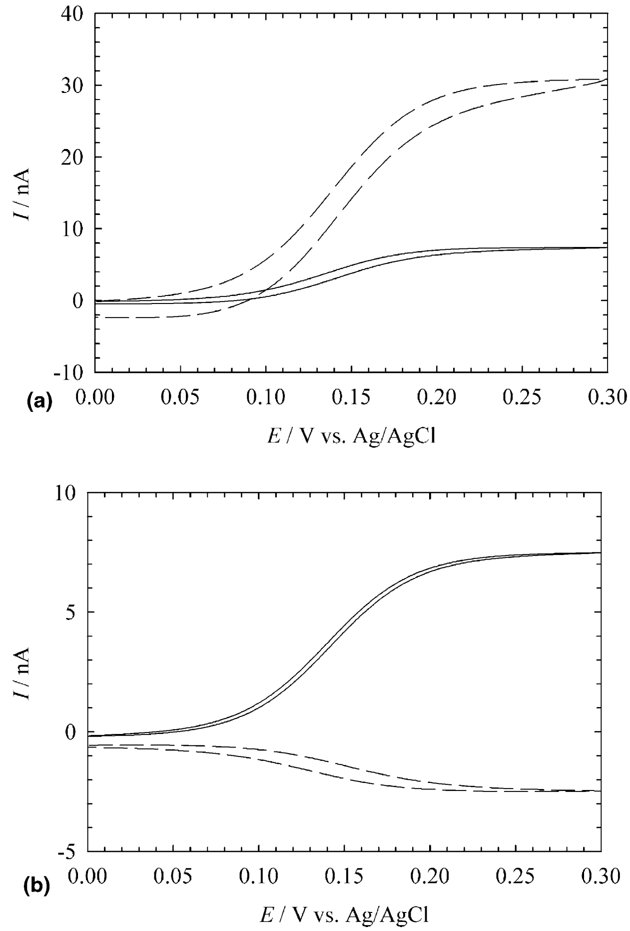

Fig. 4. (a) CVs of ferrocene methanol (2.5 mM) oxidation at the disk (———) and the ring (- - -). Sweep rate 25 mV/s. (b) CVs of a generation–collection experiment (disk (———), ring (- - -)): the potential of the disk is scanned while that of the ring is held at 0 V vs. Ag/AgCl. The disk diameter is 25 μm.

$$I_{ring} = nFDc^{b} \frac{\pi^2(a+b)}{\ln(16(a+b)/(b-a))}. \quad (6)$$

The result with the measured diffusion coefficient, $b/r_e = 9$ and $a/b = 0.995$ (vide infra) is 37.2 nA with a difference of 16% as compared to the result from the CV, 31.3 nA. This difference is probably due to the non-ideality of the ring electrode surface and the non-uniformity of the thickness of the ring electrode, see Fig. 3. In Fig. 4(b), the results of a generation–collection voltammogram are shown; the potential of the disk is scanned to a potential region where FcMeOH is oxidised while that of the ring is held at a potential where $FcMeOH^+$ is reduced at a diffusion controlled rate (0 V vs. Ag/AgCl). The collection efficiencies, defined as $\eta = |I_{ring}/I_{disk}|$, are lower than predicted by the model in [10], but in line with the numerical solution to the diffusion problem with the chosen tip geometry. This difference is in part due to the finite r_g in the present case, which was not considered in [10]. It should be noted that any imperfection in the shape of the RD assembly will affect the absolute value of the collection efficiency. Our main goal, however, is to study processes occurring at the substrate. Thus, the changes due to the presence of a surface with respect to the bulk solution are of greatest interest and the geometrical complications can be accommodated as average values of the parameters (ring radius and thickness and r_g) characterising the RD electrode assembly.

Experimental generator–collector approach curves (disk (○) and ring (□)) are given in Fig. 5 for tip approach to an insulating (a) and conducting (b) substrate. In this case, $FcMeOH^+$ is generated at a diffusion limited rate at the disk and collected at the ring. The experimental curves are compared to theory (solid lines) as outlined in Section 3 for $a/b = 0.995$, $b/r_e = 9$, and $r_g/r_e = 15$.

The current response at the disk is as expected for a conventional disk SECM tip: negative feedback for an approach to an insulator due to hindered reactant diffusion at the tip and positive feedback for an approach to a conductor due to reactant regeneration [14]. For the collector ring electrode, as the tip approaches an insulator, diffusion of $FcMeOH^+$ away from the disk is also blocked by the substrate and initially, the ring current increases. At closer distances, however, the ring current decreases as the amount of disk-generated $FcMeOH^+$ is reduced. In contrast to an approach to a conducting substrate, the concentration changes due to the reaction at the disk are localised in the disk-substrate gap and, thus the collection current at the ring decreases to zero as positive feedback at the disk increases. Corresponding collection efficiencies for insulating (a) and conducting substrates (b) are shown in Fig. 6. At the insulator, when the tip is located close enough to the substrate, all the mediator species converted at the disk will be regenerated at the ring, and the collection efficiency approaches unity. On the other hand, with a conducting substrate, the ring current decays to zero and so does the collection efficiency. The slight deviation between theoretical and experimental responses can be explained by the presence of trace amounts of $FcMeOH^+$ in bulk solution. This affects the ring current, especially at close distances to an insulating sub-

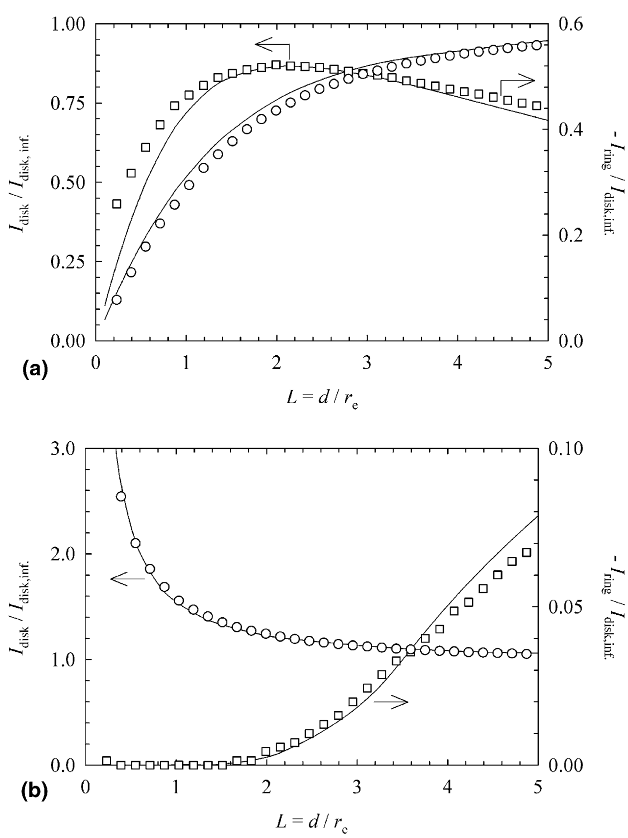

Fig. 5. Experimental approach curves (disk (○) and ring (□)) to (a) an insulating and (b) a conducting substrate. $E_{disk} = 0.3$ V vs. Ag/AgCl, $E_{ring} = 0$ V vs. Ag/AgCl. The disk diameter is 25 μm. The solid lines are from numerical simulations with $a/b = 0.995$, $b/r_e = 9$, and $r_g/r_e = 15$. All the curves are normalised with the limiting current at the disk far from the substrate, $I_{disk,inf.}$.

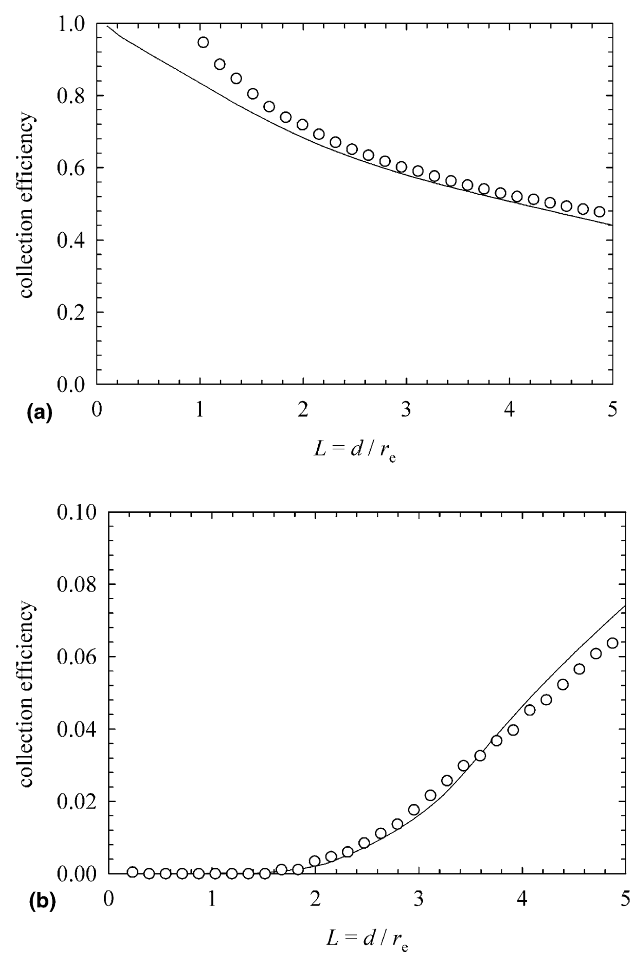

Fig. 6. The collection efficiencies ($\eta = |I_{ring}/I_{disk}|$) calculated from the approach curves to an insulating (a) and conducting (b) substrate. Experimental data are represented by circles while the solid lines are from the numerical simulation.

strate when the amount of disk-generated $FcMeOH^{+}$ is decreased.

5. Conclusions

This report illustrates the potential of generator–collector RD UMEs for SECM applications. Theoretical approach curves can be calculated enabling full characterisation of the RD response. In comparison to conventional disk UME tips, additional information on product interaction with the substrate under study can be obtained from a single approach curve. RD SECM tips should be useful for following spontaneous reactions, partitioning across interfaces and detection of reaction intermediates.

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