Effective diffusion of electroactive species on hydrogel modified ultramicroelectrodes

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Abstract

Potential step experiments on microelectrodes permit determination of both the effective diffusion coefficient (D) and the concentration of redox sites in gel matrix (C^{gel}). This benefit arises because the potential step experiment can be performed in two time regimes by applying short and long potential pulses. The effective diffusion of ferrocyanide and ferrocene carboxylic acid was investigated by the reliable potential step measurements for the determination of D and C^{gel}. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

There has been dramatic developments in recent years in the use of polymer gels [1–3]. However, from an electrochemical view point, the limited diffusion within the gel phase causes a reduced mass transfer rate for low molecular-weight compounds. This in turn diminishes the chances of interaction between the molecules within the gel and those in the bulk solution [4]. This situation can be improved significantly by incorporation of appropriate electron transfer mediator into gel matrix.

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Such gel–mediator system will possess a polymer composite structure and a unique dynamic electrical properties. These properties are of considerable importance particularly when linked with an ultramicroelectrode, where the diameter of the electrode is much smaller than the diffusion distance within the time scale of typical electrochemical experiment [5, 6]. Owing to the size of this electrode, its electrochemical response is considerably different from conventional voltammetric electrodes, and its prediction are based on new electrochemical theory.

When incorporated into a gel matrix potential step measurements on microelectrodes permit estimation of both the effective diffusion coefficient and the concentration of redox sites in the gel. The two time regimes usually employed in potential step experiments by applying short and long potential pulses are particularly beneficial in accomplishing this goal [7]. Since two distinct mass-transfer patterns (linear and spherical) apply in the different regimes, there are two different equations that can be solved simultaneously for the two unknown parameters: the concentration and the effective diffusion coefficient [7–10].

In this paper, the reliability of potential step measurements for the determination of these two parameters and their physicochemical significance will be investigated on microelectrodes incorporated into a gel matrix in the presence and absence of mediator. In particular, the influence of two kinds of mediators on the effective diffusion coefficient within the gel matrix will be considered.

2. Experimental

2.1. Reagents

Acrylamide (AA) (FW 71.08), N,N′-methylene-bis-acrylamide (MBA) (FW 154.2) and N,N,N′,N′-tetramethyl ethylenediamine(TEMED) (FW 116.2) were purchased from SIGMA Chemical Company and were used for the preparation of gels without further purification on treatment. Ammonium persulfate (AR, Ajax) and potassium ferricyanide (Sigma) were used as received.

2.2. Preparation of modified electrodes

The platinum ultramicroelectrodes (50 μm diameter) were polished on 0.3 and 0.05 μm alumina-water slurry oxide powder, successively. The electrodes were then ultrasonicated in Milli-Q water, and then dried at room temperature.

Polyacrylamide gel was synthesised using 0.5 g AA, 6.5 mg MBA (as the crosslinker) and 2.5 mg ammonium persulfate (as the initiator). TEMED (5 μL) was added to 5mL aqueous solution to initiate the gelation at room temperature. Gelation was completed in 30 min. The electrodes were then cast with approximately 1.5 mm thick hydrogel. The modified hydrogel electrodes were immersed either in 0.1 M KCl or in 1 mM $K_3Fe(CN)_6$/0.1 M KCl for 24 h while stirring with a magnetic stirrer. The two resulting types of gel were used for background and redox sites measurement,

respectively. The same fabrication procedures were applied to ferrocene caboxylic acid modified electrodes.

2.3. Electrochemical measurement

A conventional three-electrode system was used with the BAS C2 Cell Stand. The counter and reference electrodes were a platinum wire and Ag/AgCl/3M NaCl, respectively. Cyclic voltammetric and amperometric experiments were performed on BAS CV-27 with PA-1 PreAmplifer coupled with a MacLab/8e system (AD Instruments Pty Ltd, NSW, Australia).

3. Results and discussion

3.1. Characterization of hydrogel modified microelectrodes by cyclic voltammetry

Hydrogel membranes have been proven to be good carriers for mediators, such as ferricyanide and ferrocene carboxylic acid. Their high water-containing structure provides a favorable hydrophilic environment for electron shuttle. Fig. 1 shows that the electroactivity of ferrocyanide and ferricyanide is evident on the hydrogel-ferricyanide modified electrode (Fig. 1e), but not as pronounced as the one obtained in absence of gel (Fig. 1f). This may be due to the presence of less effective concentration of ferricyanide at the hydrogel modified electrode surface. The presence of KCl as supporting electrolyte improved electroactivity on bare electrode (Fig. 1f vs. d) and hydrogel modified electrode (Fig. 1e vs. c). Ferrocene carboxylic acid redox behaviors in the presence of gel and on the bare platinum electrodes are illustrated in Fig. 2.

3.2. Determination of the effective diffusion coefficient and concentration of ferricyanide and ferrocene caboxylic acid in the redox sites

An important feature of the potential step chronoamperometry experiment on an ultramicroelectrode is that the nature of mass transport depends on the time t domain (Figs. 3 and 6 in the absence of gel, Figs. 4 and 7 in the presence of gel).

To simplify calculations and interpretations, chronoamperometric mode was employed. The potential was stepped to 0.00 V, i.e. to a potential that is slightly more negative than the reduction process in Fig. 1. Fig. 4B gives the cumulative $i(t)$ passed in reducing ferricyanide that are effectively transported to the ultramicroelectrode by linear diffusion along the concentration gradient within the gel. The observed $i(t)$ can be described by Cottrell equation [6]

$$i(t) = n\pi^{1/2} F D^{1/2} C^{gel} r^2 t^{-1/2},\tag{1}$$

where n is the number of electrons per mole, F is Faraday's constant, D is the diffusion coefficient of the reactant, C^{gel} is the reactant concentration in gel, and r is the electrode radius. As the experimental time scale increases, spherical diffusion
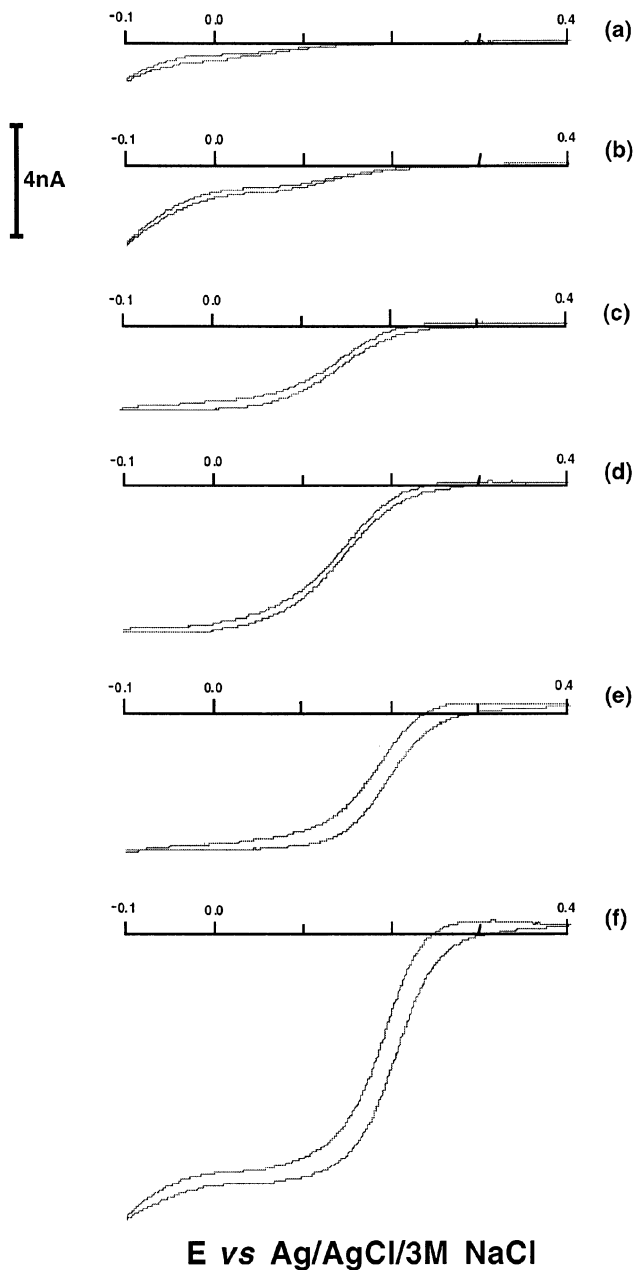
Fig. 1. Cyclic voltammetry of hydrogel modified platinum microelectrode and bare platinum microelectrode: (a) hydrogel-KCl electrode in 0.1 M KCl; (b) bare electrode in 0.1 M KCl; (c) hydrogel-ferricyanide electrode in 1 mM $K_3Fe(CN)_6$; (d) bare electrode in 1 mM $K_3Fe(CN)_6$; (e) hydrogel-KCl-ferricyanide electrode in 1 mM $K_3Fe(CN)_6$/0.1 M KCl and (f) bare electrode in 1mM $K_3Fe(CN)_6$/0.1 M KCl. Scan rate: 10 mV/s.
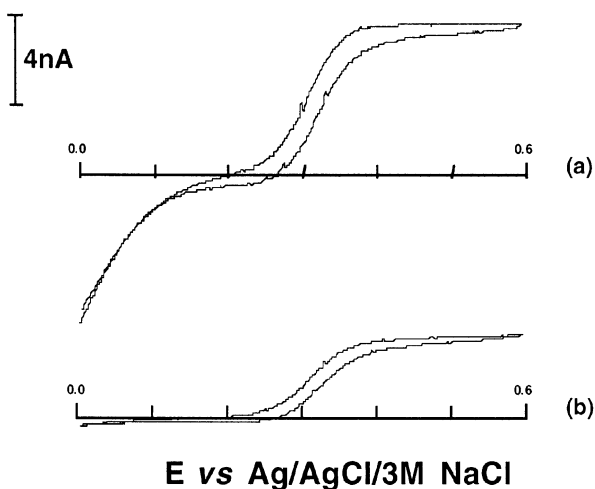
Fig. 2. Cyclic voltammetry of hydrogel modified platinum microelectrode and bare platinum microelectrode: (a) bare electrode in 1 mM ferrocene carboxylic acid/0.1 M phosphate buffer (pH 8.0) and (b) hydrogel-phosphate-ferrocene electrode in 1 mM ferrocene carboxylic acid/0.1 M phosphate buffer (pH 8.0). Scan rate: 10mV/s.
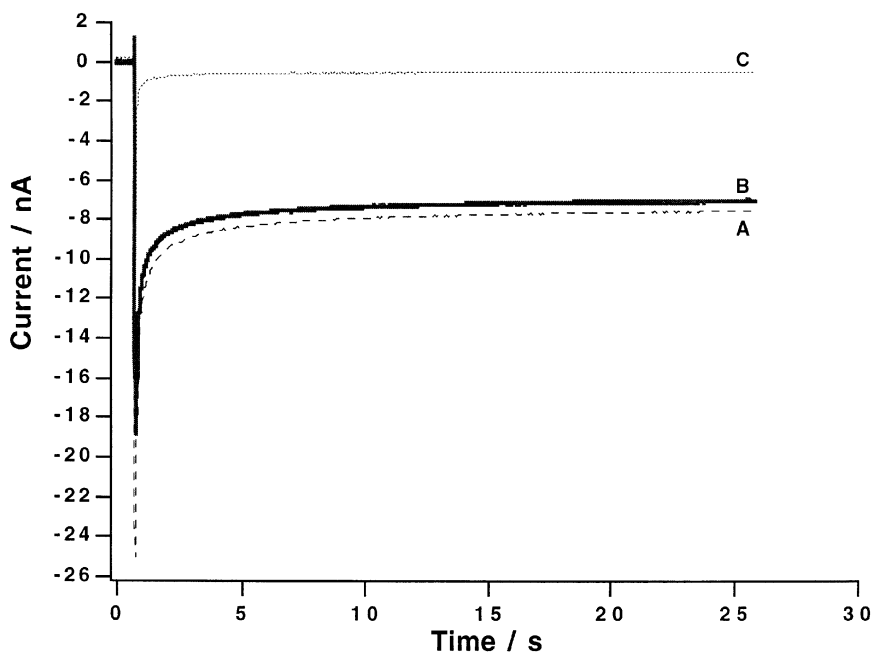

Fig. 3. Chronoamperometry of a bare ultramicroelectrode: forward potential step from +0.4 to 0.0 V. (A) in 1 mM $K_3Fe(CN)_6$/0.1 M KCl; (C) in 0.1 M KCl; and (B) = (A)–(C), background corrected chronoamperommogram.
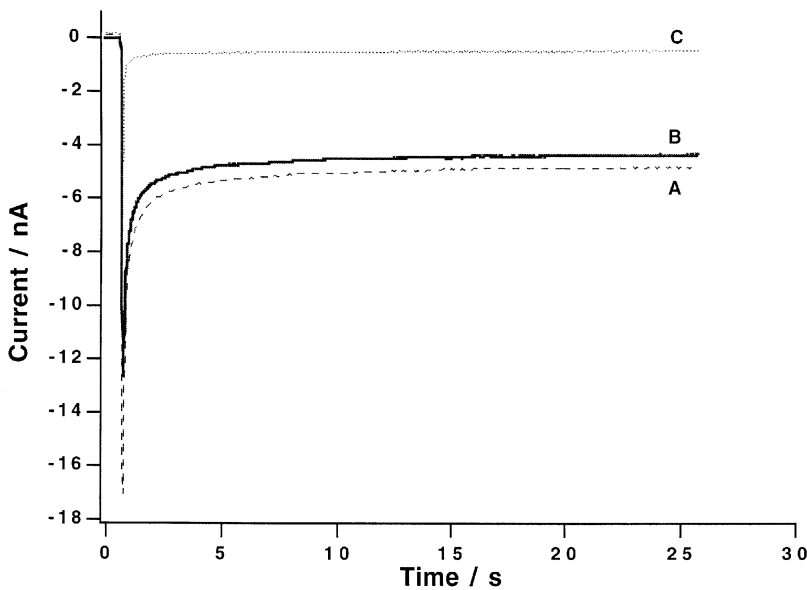
Fig. 4. Chronoamperometry of the gel matrix using an ultramicroelectrode: forward potential step from +0.4 to 0.0 V. (A) in 1 mM $K_3Fe(CN)_6$/0.1 M KCl gel matrix; (C) in 0.1 M KCl gel matrix; and (B) = (A)–(C), background corrected chronoamperommogram.
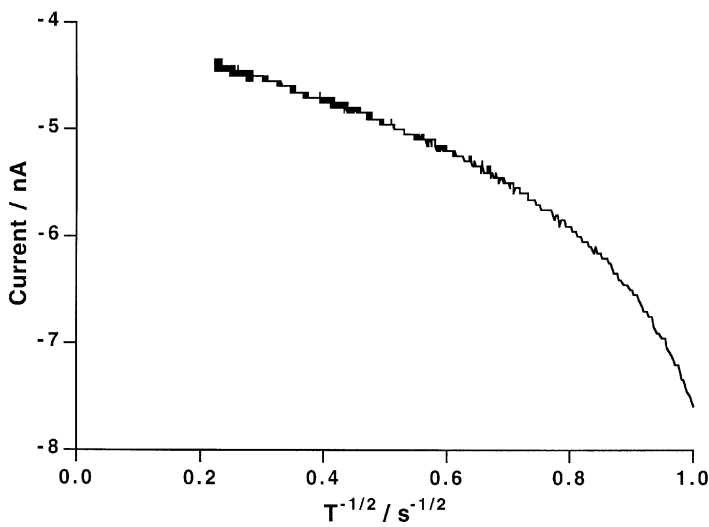

Fig. 5. Background corrected chronoamperometric current for the reduction of $K_3Fe(CN)_6$ in KCl with a platinum gel ultramicroelectrode. $E_{step} = -0.4$ V.

predominates and a steady-state plateau current is produced, as expected for chronoamperometry at an ultramicroelectrode [7]. It is known [11] that steady-state current of an inlaid disk microelectrode is proportional to the radius of the disk and is governed by the expression:

$$I_{ss} = 4nFDC^{gel}r. \tag{2}$$

As a result, the two equations can be solved for the variables, C^{gel} and D, as all other parameters are known (n, π, F, and r) or can be measured. This approach permits the absolute determination of the concentration of the redox sites (C^{gel}) as well as the effective diffusion coefficient (D) in the gel. As shown in Fig. 5, a linear regression of the current vs. $t^{-1/2}$ should give a straight line with a slope which can be used to determine the D and C^{gel}, associated with I_{ss} in Fig. 4. Based on this approach the estimated values for the two parameters were: $D = 6.8 \times 10^{-6}$ cm^2/s, $C^{gel} = 0.66$ mM. The concentration of ferricyanide in redox sites (C^{gel}) is 66% of the bulk concentration (1 mM) of $K_3Fe(CN)_6$. This may account for the differences in the magnitude of current observed on the cyclic voltammograms (Fig. 1b and d) obtained in the absence and presence of the gel. The steady-state current ratio in the presence:absence of gel is $4.35/7.05 = 0.62$. The diffusion coefficient (D) in the absence of gel can be calculated from the background corrected steady-state current in Fig. 3B and Eq. (2).

The same method is applied to determine the effective diffusion coefficient and concentration of ferrocene carboxylic acid in the redox sites, according to I_{ss} in the absence of gel, I_{ss} in the presence of gel and a slope as illustrated in Figs. 6, 7 and 8,
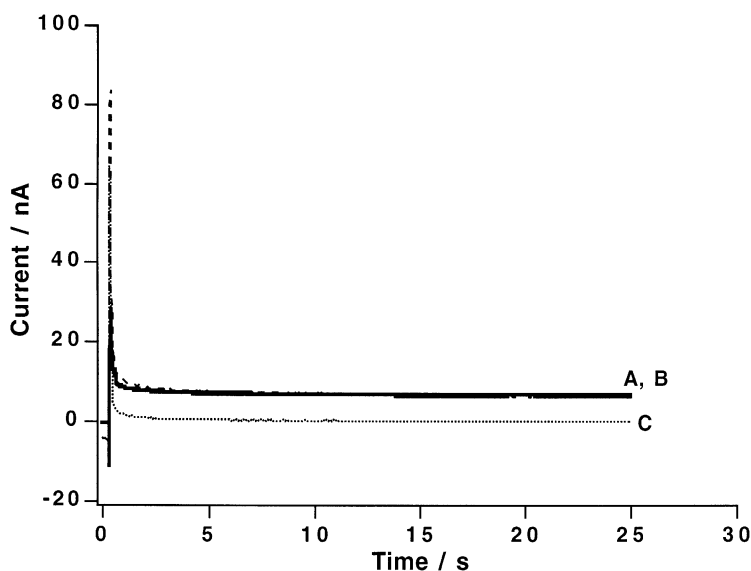

Fig. 6. Chronoamperometry of a bare ultramicroelectrode: forward potential step from 0.0 to +0.6 V. (A) in 1 mM FCA/0.1M phosphate buffer (pH 8.0); (C) in 0.1 M phosphate buffer (pH 8.0); and (B) = (A)–(C), background corrected chronoamperommogram.
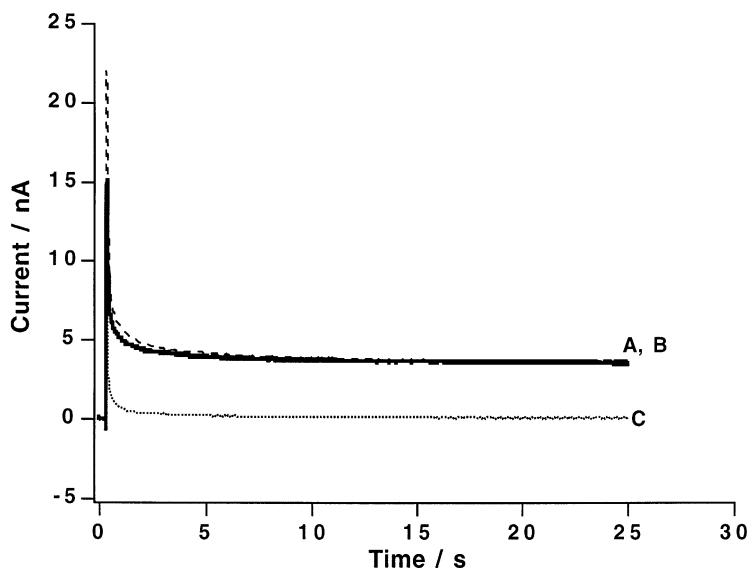
Fig. 7. Chronoamperometry of the gel matrix using an ultramicroelectrode: forward potential step from 0.0 to +0.6 V. (A) in 1mM FCA/0.1 M phosphate buffer (pH 8.0) gel matrix; (C) in 0.1 M phosphate buffer (pH 8.0) gel matrix; and (B) = (A)–(C), background corrected chronoamperommogram.
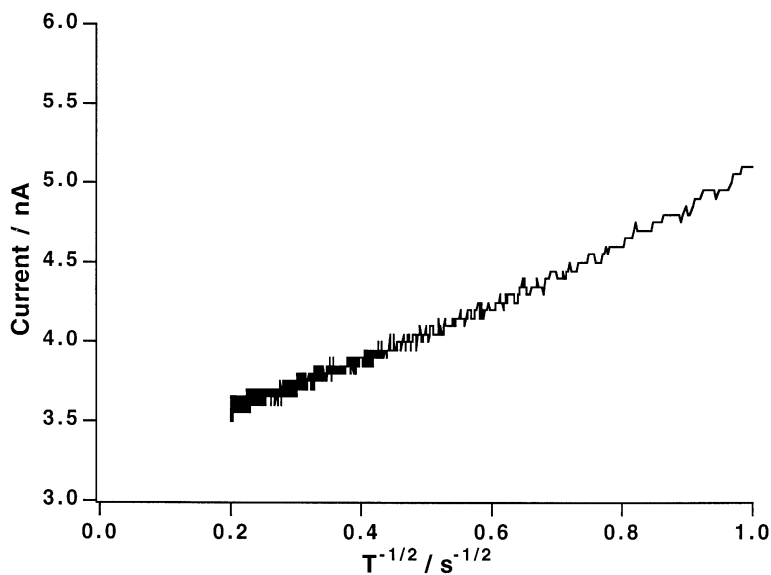

Fig. 8. Background corrected chronoamperometric current for the oxidation of FCA in phosphate buffer (pH 8.0) with a platinum gel ultramicroelectrode. $E_{step} = +0.6$ V.

Table 1
Diffusion coefficient of ferricyanide and ferrocene (cm^2/s)

Mediator	Presence of Gel	RSD[a] ($n = 3$)	Absence of Gel	RSD[a] ($n = 3$)
Ferricyanide	6.8×10^{-6} (0.66 mM)	1.7%	7.3×10^{-6} (1.0 mM)	0.5%
Ferrocene	6.3×10^{-6} (0.59 mM)	2.0%	6.8×10^{-6} (1.0 mM)	0.4%

[a] Relative standard deviation.

respectively. The calculated values of the effective diffusion coefficient are summarized in Table 1. The high value of the effective diffusion coefficient indicates that the hydrogel composite structures have very good electronic conductivity.

4. Conclusions

The surprising result is that the hydrogel has little effect on the diffusion coefficent of species investigated, such as ferricyanide and ferrocene. This may be one of the most interesting and important subjects in the development of functional immobilized biocatalysts. When immobilizing biocatalysts within polymer gels using physical entrapment methods, we may take advantage of the great resistance to the diffusion of macromolecular substances due to the gel porosity.

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