Probing the distribution of redox in the diffusion layer of the substrate electrode by the scanning electrochemical microscopy

Haixia Guo, Huibo Shao*

Key Laboratory of Cluster Science (Ministry of Education), Beijing Key Laboratory of Photoelectronic and Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 102488, P.R. China

* Corresponding author: hbs@bit.edu.cn

Abstract. Taking advantage of the dual working electrodes and the precise positioning of the tip electrode of the scanning electrochemical microscopy, the distribution of ferrocenemethanol in the diffusion layer of the substrate electrode is studied when the substrate potential is applied. When the co-directional potential is applied to the substrate, the closer to the surface of the substrate electrode, the less the amount of ferrocenemethanol. Because the reaction of the substrate electrode and the tip electrode is the same, they compete with each other. When the reverse potential is applied to the substrate electrode, the closer to the surface of the substrate electrode, the more the amount of ferrocenemethanol. Because the reaction of the substrate electrode can regenerate ferrocenemethanol.

1. Introduction

Scanning electrochemical microscopy (SECM) is an electrochemical in-situ detection method based on ultramicro tip electrodes and scanning tunneling microscopy[1,2]. Compared with traditional electrochemical workstations, SECM contains two working electrodes. Normally, the tip electrode is the first working electrode and the substrate electrode is the second working electrode. SECM has an obvious advantage because of the dual working electrodes. Electrochemical reactions can occur simultaneously on the tip electrode and the substrate electrode, so in-situ detection can be realized. In SECM, the tip electrode obtain the limit steady-state diffusion current at a position far away from the substrate electrode (to avoid the influence of the substrate electrode feedback), and the substrate electrode is at open circuit potential[3]. Or the tip electrode is placed near the substrate electrode for generation/collection mode[4] and competition mode[5]. It is worth noting that these two modes require the distance between the two electrodes to be less than 30 μm. Bard group studied the tip voltammograms when the distance between the tip and the substrate is smaller than the radius of the tip electrode. Studies have shown that the tip voltammograms will be completely shielded by the substrate electrode, partial feedback/partial shielding or complete feedback, which is determined by the potential applied to the substrate electrode[6]. However, when a potential is applied to the substrate, the tip voltammograms at a position far away from the substrate electrode (greater than 30 μm) is unknown, which needs to be explored and discussed.

In this paper, ferrocenemethanol is used as the redox molecule. A constant potential is applied to the substrate electrode, and the tip electrode is linearly scanned at different positions away from the substrate.
electrode (greater than 30 μm). By analyzing the tip voltammograms, the distribution of ferrocenemethanol in the diffusion layer of the substrate electrode surface is explored when a constant potential is applied to the substrate electrode.

2. Materials and Methods

2.1 Reagents and electrodes
Ferrocenemethanol (FcCH₂OH, 98%) and potassium chloride (KCl, 99.8%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. The reagents were used directly without further purification. Water was purified by a Milli-Q filter (18.2 MΩ·cm, Shanghai Hetai Instrument Co., Ltd.). A polycrystalline gold disk substrate electrode with a radius of 1 mm was used as substrate working electrode. A platinum disk electrode with a radius of 5 μm was used as tip working electrode. A Ag/AgCl electrode (3 M KCl) was used as the reference electrode, and a platinum wire was used as the counter electrode. All of the electrodes were purchased from Shanghai Chenhua Instrument Co., Ltd.

2.2 Experiments procedures and setup
Electrochemical experiments were conducted by a CHI920C SECM at room temperature. The gold disk electrode was first polished with 1.0, 0.3 and 0.05 μm alumina for 30 min, respectively, and then treated with ultrasound. After rinsed with ultrapure water, the gold electrode was cleaned by an electrochemical method: cyclic voltammetry at the potential from 0 V to 1.6 V (vs. Ag/AgCl) at a scan rate of 0.05 V/s in a solution of in 0.5 M H₂SO₄.

The distance between the tip and substrate electrode was obtained from comparing experiment approaching curve to theoretical ones. Then, the tip was moved to the gold part and drawn back using stepper motor for the subsequent experiments[^7]. A constant potential was applied to the substrate electrode, and a linear sweep potential was applied to the tip electrode in a solution of 0.5 mM FcCH₂OH in 0.2 M KCl electrolyte. The potential window was from 0 V to 0.5 V, and the scan rate was 0.01 V/s.

3. Results and Discussion

3.1 Electrochemical characterization of the tip electrode
The tip electrode needs to be characterized before use to determine whether it meets the experimental requirements. Fig. 1 is the steady-state cyclic voltammogram of the tip electrode in 0.5 mM FcCH₂OH solution, showing the S-shaped characteristic curve of a typical ultramicro disk electrode. And the limit steady-state diffusion current value also conforms to the equation \( i = 4nFcDa \), where \( i \) is the current of the tip electrode, \( n \) is the number of electron transfer, \( F \) is the Faraday constant, \( c \) is the concentration of the redox, \( D \) is the diffusion coefficient of the redox, \( a \) is the radius of the tip electrode[^3]. It shows that the tip electrode has good sealing performance and meets the experimental requirements.

![Fig. 1 Steady state voltammogram of the tip electrode in a solution of 0.5 mM FcCH2OH in 0.2 M KCl electrolyte. Scan rate: 0.01 V/s. (ET: the potential of the tip electrode, iT: the current of the tip electrode)](image)

[^7]: The reference to the paper number is not provided in the text.
[^3]: The reference to the paper number is not provided in the text.
3.2 Electrochemical characterization of the tip electrode at different positions when a potential applied to the substrate electrode

3.2.1 The substrate electrode is at open circuit potential

Fig. 2 is the linear sweep voltammogram of the tip electrode in 0.5 mM FcCH₂OH at different positions when the substrate electrode is at an open circuit potential (0.152V). The distance between the tip and the substrate is 50, 100, 200 and 500 μm, respectively. Although the distance between the tip and the substrate is different, it can be seen that the limit steady-state diffusion current on the tip electrode almost coincides when the substrate electrode is at open circuit potential. This is because the maximum feedback distance is 40 μm when the substrate is at open circuit potential. So the substrate electrode can’t give feedback to the tip electrode when the distance is 500 μm. Then the diffusion flow of FcCH₂OH to the surface of the tip electrode is the same.

Fig. 2. The linear sweep voltammogram of the tip electrode in 0.5 mM FcCH₂OH solution. The substrate electrode is at open circuit potential and the distance between the tip and the substrate is 50, 100, 200, and 500 μm, respectively.

3.2.2 The co-directional potential is applied to the substrate electrode

Fig. 3 is the linear sweep voltammogram of the tip electrode. The distance between the tip and the substrate is 500 μm and different constant potentials are applied to the substrate electrode. Although different constant potentials are applied to the substrate electrode, it can be seen that all of the limit steady-state diffusion current value is the same. That is to say, when the distance between the tip and the substrate is 500 μm, the potential applied to the substrate electrode has no effect on the electrochemical behavior of FcCH₂OH near the tip electrode. Because the diffusion layer of the substrate electrode is less than 500 μm.

Fig. 3. The linear sweep voltammogram of the tip electrode in 0.5 mM FcCH₂OH solution. The distance between the tip and the substrate is 500 μm, and different constant potentials are applied to the substrate electrode. (ES: the potential of the substrate electrode)
Fig. 4 is the linear sweep voltammogram of the tip electrode at different positions when the same constant potential is applied to the substrate electrode. The substrate potential is set so that the reaction at the substrate is the same as that occurring on the tip electrode (named co-directional potential). The red line is 0 nA, which is the baseline here. Fig. 4a is the linear sweep voltammogram of the tip electrode, and the distance between the tip and the substrate is 500, 200, 100 and 50 μm, respectively, when 0.2 V co-directional potential is applied to the substrate electrode. When the distance is 200, 100, or 50 μm, it can be observed that the initial current and the limit steady-state diffusion current of the tip electrode are less than that when the substrate electrode is at the open circuit potential (which is equal to the value when the distance between the tip and the substrate is 500 μm). This is because the FeCH$_2$OH near the substrate electrode is oxidized to Fe$^+$CH$_2$OH when the co-directional potential is applied to the substrate electrode. When the tip electrode potential scans from 0 V to 0.5 V, the first reaction on the tip electrode is to reduce the Fe$^+$CH$_2$OH generated by the substrate electrode to FeCH$_2$OH. So the initial current is below 0 nA and it is the reduction current of Fe$^+$CH$_2$OH. When the sweep potential gradually increases, the reaction on the tip is to oxidize the FeCH$_2$OH in the solution to Fe$^+$CH$_2$OH. As the distance between the tip and the substrate decreases, the initial current and the limit steady-state diffusion current of the tip electrode also decrease. Because the distribution of Fe$^+$CH$_2$OH generated by the substrate electrode conforms to Fick’s law. That is, the concentration of Fe$^+$CH$_2$OH decreases from the surface of the substrate electrode to the bulk solution. Therefore, the closer the tip electrode is to the substrate electrode, the more Fe$^+$CH$_2$OH is in the gap between the tip and the substrate. So the more Fe$^+$CH$_2$OH is reduced when the tip electrode starts electrochemical sweep, and the lower the initial current on the tip electrode.

Table 1 lists the limit steady-state diffusion current values corresponding to different distances between the tip and the substrate when the co-directional potential is applied to the substrate electrode. It is clear that when the co-directional potential is applied to the substrate, the smaller the distance between the tip and the substrate is, the smaller the limit steady-state diffusion current value on the tip electrode is.

From Fig. 4a to 4f, the co-directional potential applied to the substrate electrode increases sequentially. When the distance between the tip and the substrate is 50 μm (green line), it can be clearly observed that as the co-directional potential increases with the substrate, the limit steady-state diffusion current on the tip electrode decreases. Combined with the data in Table 1, this rule is also reflected when the distance between the tip and the substrate is 100 or 200 μm. This is because as the co-directional potential applied to the substrate electrode increases, the energy barrier for the oxidation reaction of FeCH$_2$OH gradually decreases. That is, the higher the co-directional potential applied to the substrate electrode, the more easily FeCH$_2$OH is oxidized on the surface of the substrate electrode. Therefore, in the same time, the higher the co-directional potential is applied to the substrate electrode, the more Fe$^+$CH$_2$OH is generated on the substrate electrode. When the tip electrode scans from 0 V, the amount of Fe$^+$CH$_2$OH undergo reduction reaction is large. Therefore, the smaller the initial value of the current on the tip electrode is, the smaller the corresponding limit steady-state diffusion current value is.
Fig. 4. The linear sweep voltammogram of the tip electrode at different positions in 0.5 mM FcCH2OH when the co-direction potential is applied to the substrate electrode. The substrate potential is (a) 0.2 V, (b) 0.23 V, (c) 0.24 V, (d) 0.25 V, (e) 0.3 V, and (f) 0.4 V. The distance between the tip and the substrate: green line, 50 μm; blue line, 100 μm; pink line, 200 μm; black line, 500 μm.

3.2.3 The reverse potential is applied to the substrate electrode

When the potential of the substrate is set so that the reaction at the substrate is opposite to that on the tip electrode (named reverse potential), the linear sweep voltammogram of the tip electrode at different positions is shown in Fig. 5. Fig. 5a is the linear sweep voltammogram when -0.1 V reverse potential is applied to the substrate electrode. The inset is an enlarged view of the limit steady-state diffusion current of the tip electrode at different distances. It can be seen that the limit steady-state diffusion current value on the tip electrode is related to the distance between the tip and the substrate when -0.1 V reverse potential is applied to the substrate electrode. The smaller the distance is, the greater the steady-state diffusion current on the tip.

Table 1 The limit steady-state diffusion current value when the co-direction potential is applied to the substrate electrode and the tip electrode is at different positions

| The distance between the tip and the substrate / μm | Limit steady-state diffusion current on the tip electrode / nA |
|-----------------------------------------------|-----------------------------------------------|
|                                              | 0.20 V | 0.23 V | 0.24 V | 0.25 V | 0.30 V | 0.40 V |
| 500                                          | 0.8984 | 0.8993 | 0.8891 | 0.8993 | 0.8958 | 0.8936 |
| 200                                          | 0.8508 | 0.8296 | 0.8104 | 0.8042 | 0.7899 | 0.7906 |
| 100                                          | 0.7208 | 0.5899 | 0.5511 | 0.4856 | 0.3919 | 0.3483 |
| 50                                           | 0.7026 | 0.4867 | 0.4168 | 0.3581 | 0.1912 | 0.1303 |
electrode is. Fig. 5b is the linear sweep voltammogram of the tip electrode when -0.2 V reverse potential is applied to the substrate electrode. It can be observed that the limit steady-state diffusion current on the tip electrode when the distance is 200, 100, or 50 μm is greater than when the substrate electrode is at the open circuit potential. This is because the reverse potential applied to the substrate electrode is beneficial to the reduction of Fe'CH₂OH generated on the tip electrode and to regeneration FcCH₂OH. Therefore, the diffusion flow of FeCH₂OH to the surface of the tip electrode increases, and the limit steady-state diffusion current value increases. And the smaller the distance between the tip and the substrate is, the greater the limit steady-state diffusion current shows. This is because the closer to the surface of the substrate electrode, the more the amount of regenerated FeCH₂OH. The amount of FeCH₂OH decreases from the surface of the substrate electrode to the solution. The phenomenon is obviously different from that when the co-directional potential applied to the substrate electrode. When the reverse potential is applied to the substrate electrode, the initial current on the tip electrode is almost the same, all starting from 0 nA. This is because the regeneration reaction of FeCH₂OH occurs on the substrate electrode. FeCH₂OH is distributed in the solution between the tip and the substrate, and there is no Fe'CH₂OH. So when the potential on the tip electrode starts from 0 V, no reduction reaction occurred. Therefore, the currents all started from 0 nA.

Fig. 5. The linear sweep voltammogram of the tip electrode in 0.5 mM FeCH₂OH at different positions when the reverse potential is applied to the substrate electrode. The substrate potential is (a) -0.1 V, (b) -0.2 V. The distance between the probe and the substrate: green line, 50 μm; blue line, 100 μm; pink line, 200 μm; black line, 500 μm.

4. Conclusions
The SECM is used to study the distribution of redox molecule in the diffusion layer of the substrate electrode when a potential is applied to the substrate electrode. In this work, a constant potential is applied to the substrate electrode. The experimental results show that the closer to the surface of the substrate electrode, the less the amount of ferrocenemethanol when the co-directional potential is applied to the substrate electrode. The closer to the surface of the substrate electrode, the more the amount of ferrocenemethanol when the reverse potential is applied to the substrate electrode. Knowing the concentration distribution of redox molecule when the potential is applied to the substrate electrode is helpful for us to better develop new models and place the tip electrode in suitable position.

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References
[1] Bard A J, Fan F, Kwak J, et al. (1989) Scanning electrochemical microscopy. Introduction and principles [J]. Analytical Chemistry, 61(2): 132-138.
[2] Izquierdo J, Knittel P, Kranz C. (2018) Scanning electrochemical microscopy: an analytical perspective [J]. Analytical and Bioanalytical Chemistry, 410(2): 307-324.
[3] Bard A J , Cliffel D E , Demaille C , et al. (1994) Advances in scanning electrochemical microscopy. Plenary lecture[J]. Analyst, 119(1):15-31.
[4] Fernández J L, Bard A J. (2003) Scanning electrochemical microscopy. 47. Imaging electrocatalytic activity for oxygen reduction in an acidic medium by the tip generation-substrate collection mode. [J]. Analytical Chemistry, 75(13):2967-2974.

[5] Eckhard K, Chen X X, Turcu F, et al. (2006) Redox competition mode of scanning electrochemical microscopy (RC-SECM) for visualisation of local catalytic activity [J]. Physical Chemistry Chemical Physics, 8(45): 5359-5365.

[6] Zoski C G, Luman C R, Fernández J L, et al. (2007) Scanning electrochemical microscopy. 57. SECM tip voltammetry at different substrate potentials under quasi-steady-state and steady-state conditions. [J]. Analytical Chemistry, 79(13): 4957-4966.

[7] Shao Y, Mirkin M V. (2014) Probing ion transfer at the liquid/liquid interface by scanning electrochemical microscopy (SECM) [J]. Journal of Physical Chemistry B, 102(49):9915-9921.