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Study of the ion-channel behavior on glassy carbon electrode supported bilayer lipid membranes stimulated by perchlorate anion

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ABSTRACT

In this paper, a kind of didodecyldimethylammonium bromide (DDAB) layer membranes was supported on a glassy carbon electrode (GCE). We studied the ion channel behavior of the supported bilayer lipid membrane by scanning electrochemical microscopy (SCEM) in tris(2,2′-bipyridine) ruthenium(II) solution. Perchlorate anion was used as a presence of stimulus and ruthenium(II) complex cations as the probing ions for the measurement of SECM, the lipid membrane channel was opened and exhibited the behavior of distinct SECM positive feedback curve. The channel was in a closed state in the absence of perchlorate anions while reflected the behavior of SECM negative feedback curve. The rates of electron transfer reaction in the lipid membranes surface were detected and it was dependant on the potential of SECM.

1. Introduction

Since the reconstituted bilayer lipid membrane (BLM) that separates two solutions was first reported in 1962 [1], BLM system has been employed extensively as an experiment model of biomembranes [2–5]. The membrane allows selective transport of ions and molecules; property of ion channel can be utilized as a philosophy for the construction of devices useful for monitoring a large number of biochemical of clinical, environmental and agricultural interest or for being used in food and pharmaceutical analysis [6–8].

Supported on some ideal solid substrates, such as metal [9,10], hydrogel [11], Si [12,13], GC [14] and polymer [15], the ion channel behavior of the mechanically stable BLMs have aroused the research interest of more scientists at present. Many measurement methods were used to study the interaction and the reaction kinetics between the surface of s-BLM and the probe species in solution. In those methods, electrochemical methods, e.g., cyclic voltammetry (CV) [16] and electrochemical impedence spectroscopy (EIS) [14,17], were widely used to research the performance of s-BLM. For the study of ion-channel behavior, CV can only estimate the k_{app}, while the EIS can only suppose the kinetic trends. The key of the study deficiency of the conventional electrochemical measurements is that the k_{app} is the average kinetics of the total interface without considering the surface reaction intensity at the inhomogeneous morphology. As is known to all, the rate of electron transfer of the conventional probe molecular, such as $K_3[Fe(CN)_6]$ and $Ru(bpy)^{3+}$, can be calculated by CV technique or simulated by CV_{sim} software for an ideal electrochemical system. In this system, a precise initial concentration and diffusion coefficient of the probe molecular and a precise electrochemical active area and so on must be needed. However, it is very difficult in confirming the electrochemical area of the s-BLMs in this system [16]. Accordingly, it is the inaccurate electrochemical area of the s-BLMs to lead to an incorrect kinetics value by the CV technique. Combining the conventional electrochemical techniques, Atomic Force Microscopy (AFM) [17] was usually used to character the morphology of the s-BLM, thus it does work only to assist other measurement techniques. An accurate kinetic value for the probe molecular can perform the ion-channel behavior of s-BLM in details, so seeking a novel technique which can measure not only an accurate kinetic value but also the morphology is a problem to be solved.

Scanning electrochemical microscopy (SECM) provides a novel way for electrochemical research with high spatial resolution. It combines the advantages of ultramicroelectrodes (UMEs) and scanning probe microscopes (SPMs), which has been demonstrated to be a powerful tool to confirm the accurate heterogeneous kinetic parameters from the I_T–L curves without accurate electrochemical active area [18–29].

In this work, perchlorate anion was used as presence of stimulus and ruthenium (II) complex cation was selected as the probe species in the solution. An Au microelectrode and SECM were employed to study the reaction kinetics of ruthenium (II) complex cation reduction on the surface of lipid coated GCE. The rate constant k_f can be evaluated by fitting

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the experimental I_T–L curves with theoretical values under different concentration of perchloride anion and externally controlled substrate potentials (Es). The standard rate constant k^0 can be calculated by the use of the Butler–Volmer equation, and we also evaluated the relation of k^0 depending on the concentration of perchloride anion in the solution.

2. Experimental

2.1. Chemicals

Didodecyldimethylammonium bromide and tris(2,2′-bipyridine) ruthenium(II) were supplied by ACROS (Belgium). Sodium perchlorate of analytical grade was supplied by Beijing Chemicals Co., China. Chloroform was analytical grade. All aqueous solutions were prepared from deionized water (Milli-Q, Millipore Corp.).

2.2. Electrodes and electrochemical Cell

A 15 μm-diameter Au microelectrode ($RG < 3$, $RG = b/a$, a is the radius of the electrode and b is the radius of the electrode + the thickness of the insulating layer), was used as the working electrode (SECM tip), and it was made using the procedure described in the reference [30]. A diameter of 0.2 mm Ag wire coated with AgCl was used as a reference electrode, and a 0.12 cm-diameter Pt wire served as the counter electrode.

All electrochemical and SECM measurements were performed using a CHI 900 system (CHI Instrument, USA). All of the experiments were carried out at the room temperature (20 ± 2 °C).

2.3. Formation of supported bilayer lipid membranes on GCE

Before the formation of lipid bilayer, a glassy carbon electrode was prepared as literature [14]. A 3-μL lipid solution (5 mg mL^{-1} didodecyldimethylammonium bromide chloroform solution) was dropped onto the surface of the GC electrode by a microsyringe and the electrode was immediately immersed into 0.1 mol L^{-1} KCl solution, in which the supported lipid layer was formed spontaneously. Then keep it in a cleaning beaker and used as the SECM substrate.

3. Results and discussion

3.1. Formation of supported bilayer lipid membranes on GCE and its characterization by SECM and cyclic voltammetry

Fig. 1 shows the schematics diagram of the electrochemical cell and the setup used to investigate the ion-channel behaviors of supported bilayer lipid membranes on glassy carbon electrode. The feedback curve of SECM and cyclic voltammetry curve were employed to characterize the electrochemical performances of the lipid coated GC electrode. The feedback mode is a quantitative operation mode of SECM. The positive feedback curve indicates that the substrate is conductive, whereas the negative feedback one is observed when the substrate is insulating.

Fig. 2 shows the approach curves and cyclic voltammograms (inset) of bare and lipid coated GC electrode in a ferricyanide aqueous solution. Both results indicate that the electron transfer (ET) of ferricyanide anions on the lipid coated GC electrode could be blocked, and also that there was no block effect on bare GC electrode at the same conditions. When ruthenium(II) complex cation was used as marker ion in the solution for SECM and CV detection, positive feedback curve of SECM can be obtained when perchloride anion was used as supporting electrolyte in the solution (Fig. 3), while the CV curve that gave the same result indicates that perchloride anions play an important role to open the ion channel of bilayer lipid membrane supported on the GC electrode.

3.2. Measurements of the kinetic parameters of the oxidation of ruthenium(II) complex cation on the lipid coated GC electrode by SECM

For a redox couple in this paper, k^0 is the standard kinetics constant, while k_f is the kinetics constant when the interface is blocked [16,30]. From this we can know that the k_f would equal to k^0 when there is no blocks on the electrode surface.

Without electrochemical active area, the k_f can be calculated from the equation I_T–L in the approach experiment.

$$I_T(E,\mathrm{L}) = \frac{0.68 + 0.78377/\mathrm{L} + 0.3315\ \exp(-1.0672/\mathrm{L})}{\theta + 1/k}$$

where $\theta = 1 + \exp\left[nf\left(E - E^{0'}\right)\right]D_O/D_R$, and $\mathrm{L} = d/a$; a is the radius of the tip.

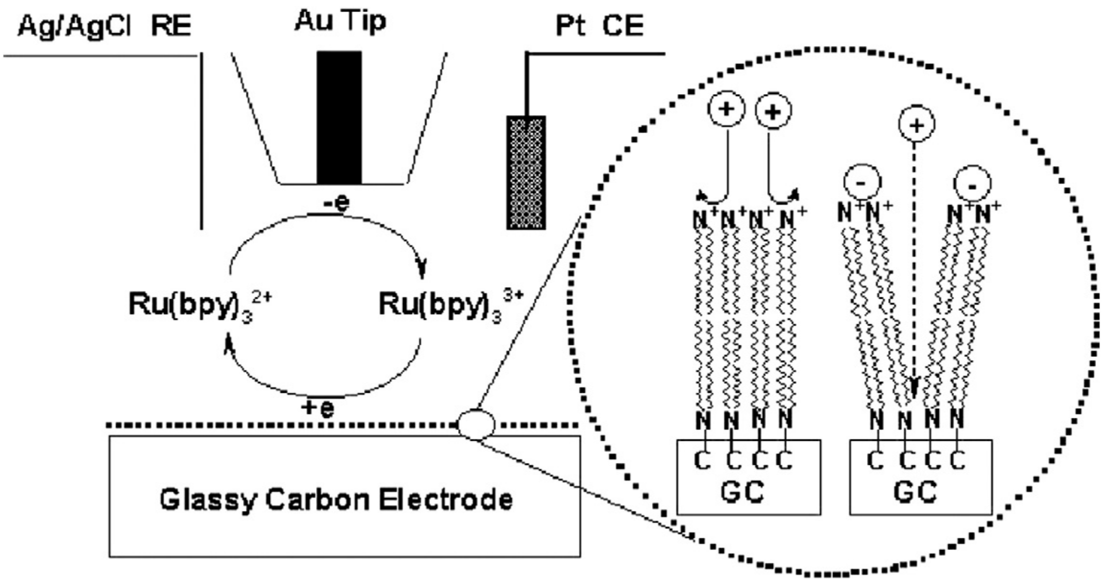

Fig. 1. Schematic diagram for the study of ion investigations of the ion-channel behavior of s-BLM on glassy carbon electrode by SECM.