



# An electrochemical approach tunes the electric property of benzoylferrocene-modified supported lipid membrane

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## ARTICLE INFO

### Article history:

Received 28 June 2008

Received in revised form 23 July 2008

Accepted 25 July 2008

Available online 3 August 2008

### Keywords:

Benzoylferrocene

Bilayer lipid membrane

Membrane conductance

## ABSTRACT

A benzoylferrocene (BFC) supported 3-sn-phosphatidylcholine (PC) film electrode was prepared by casting the solution of BFC and PC in chloroform onto the surface of platinum (Pt). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results showed that BFC, retained in the biological membrane, acted as a shuttle for electron transfer across the supported bilayer lipid membranes (s-BLMs). Doping of BFC increased membrane conductivity, while electrochemical oxidation of BFC greatly changed the membrane conductivity, the membrane impedance characterized by charge transfer resistance ( $R_{ct}$ ) dramatically increased about 400 times (from 10.32 to 3919.67 k $\Omega$ ). Interestingly, the electrochemical oxidized BFC buried in the membranes could be reduced by applying a low potential, and this led to recurrent of a conductive membrane. The conductivity of the s-BLMs could be controlled by the redox status of embedded BFC molecules. The approach provided a facile and novel way to electrochemically control the membrane conductance of s-BLMs by embedding BFC as a switchable redox mediator.

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## 1. Introduction

The cell surrounded by a limiting plasma membrane is an essential element of all living organisms. The membrane is an array of lipids, proteins, and carbohydrates that carries out functions including molecularly specific transport, receptor binding, enzymatic activity, and control of cell–cell interactions. Formation of a bilayer lipid membrane (BLM or planar lipid bilayer) *in vitro* as a model of biomembrane has made it possible to extend the experimental methods used in the studies of membrane phenomena [1–3].

BLMs modified with some functional materials are very useful in numerous research areas. This is owing to the fact that specific modifiers mediate the functions of biomembranes. Modifiers, such as electron mediators or carriers (e.g. tetracyanoquinone and fullerene), can facilitate electrons transfer and oxidation–reduction (redox) reaction process [4]. One of the mediators extensively used is ferrocene [5]. Ferrocene is a hydrophobic molecule, which can be retained in lipid bilayer, and this molecule gives a couple of irreversible peaks and electrocatalyses the oxidation of ascorbic acid [6]. Substituted ferrocenes are interesting molecules which can be incorporated as electron mediators inside s-BLMs. Vinylferro-

cene embedded s-BLMs showed that (i) ferrocene can be very easily embedded in the lipid bilayer and (ii) ferrocene in the lipid bilayer membrane increases about two orders of magnitude of the potassium ferri/ferrocyanide ion sensitivity more than that of the Pt electrode [3]. It seems evident that ferrocene and the substituted ferrocenes are compounds suitable for embedding in s-BLMs for basic studies as well as for practical exploitation.

In this paper, we describe the incorporation of BFC into lipid to control the electric properties of s-BLMs. Furthermore, the electric properties of s-BLMs can be altered by electrochemical redox reaction of BFC inside the BLMs. Scheme 1 illustrates a schematic representation of the electrochemical tuning on the electric properties of s-BLMs. The phase separations of s-BLMs were formed by the self-assembly of lipid after the modified electrode was immersed into PBS.

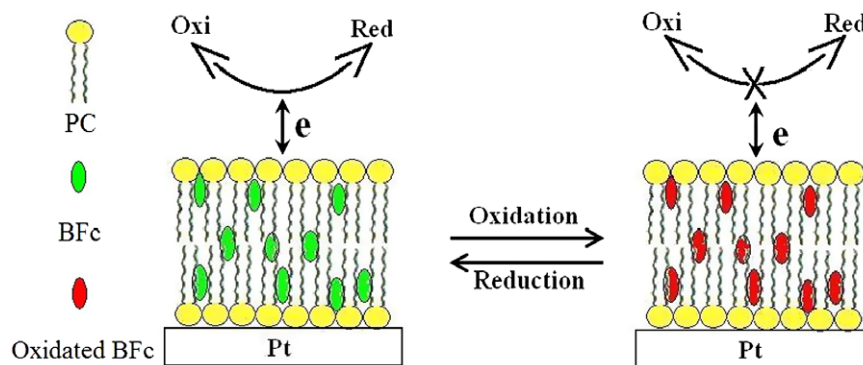
## 2. Experimental

PC ( $\geq 99\%$ , TLC) and BFC were purchased from Sigma. Phosphate buffer solution (PBS) contains: 8 g/L NaCl, 0.2 g/L KCl, 1.44 g/L  $\text{Na}_2\text{HPO}_4$ , 0.24 g/L  $\text{KH}_2\text{PO}_4$  with pH 7.2. All other chemicals were analytical grade. Super purified water was used throughout.

The three-electrode system consisted of the lipid-modified electrode as the working electrode, an Ag/AgCl reference electrode and a Pt auxiliary electrode. CV measurements were performed on an e-corder (ED401) electrochemistry equipment (eDAQ Pty Ltd., Australia). Impedance measurements were performed on Auto

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**Scheme 1.** Schematic representation of an electrochemical tuning on the electric property of s-BLMs.

LAB PGSTATA30 (Metrohm Ltd., The Netherlands) with the frequency range of 0.01 Hz–100 KHz. A 5 mV amplitude sine with the open circuit potential wave was applied between the working and reference electrode.

PC and BFc were dissolved in chloroform to give a final concentration of (a) 2 mg/mL PC and (b) 1 mg/mL BFc with 2 mg/mL PC. Prior to s-BLMs formation, the solid substrate electrodes (Pt electrode, 2.0 mm diameter from CH instruments, USA) were polished with 0.3 and 0.05  $\mu\text{m}$  alumina slurry repeatedly, then sonicated for 5 min in super purified water and acetone successively. The electrodes were dry in air. The 10  $\mu\text{L}$  aliquot of the lipid solution was dropped onto the surface of the electrode by a microsyringe. After the chloroform was evaporated gradually in air, the lipid-coated electrode was immersed into PBS for 10 min, in which s-BLMs was formed spontaneously. All the measurements and experiments were performed at room temperature.

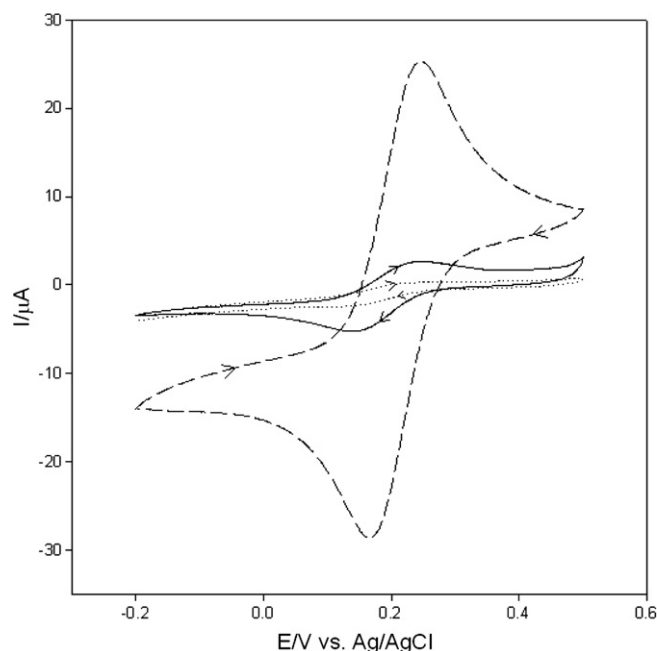
### 3. Results and discussion

For investigation of the properties of BLMs, electrochemical techniques such as CV techniques [5,7] and impedance techniques [8], have been applied at the very beginning. For instance, EIS was used to investigate the influence of  $\text{Ca}^{2+}$  ions on the electron transfer of  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple on Pt supported BLMs [9]. More recently, impedance technique was used to demonstrate that layers of dimyristoylphosphatidylcholine (DMPC) at the surface of GC electrode were bilayer lipid membranes with 5 nm thickness for DMPC membrane [10].

In this study, we selected Pt electrode as a substrate and employed CV and EIS ( $\text{Fe}(\text{CN})_6^{3-/4-}$  as a marker molecule) to characterize the electric properties of s-BLMs with and without doping of BFc. (PC modified Pt electrode was described as PC/Pt; while PC with BFc modified Pt electrode was described as BFc@PC/Pt.)

#### 3.1. Formation and characterization of s-BLMs

Fig. 1 shows the CV of bare Pt electrode (dash line), PC/Pt electrode (dotted line) and BFc@PC/Pt electrode (solid line) in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution with PBS as supporting electrolyte. Comparing the CV of bare Pt and PC/Pt electrode, the PC/Pt electrode shows a sharp decrease (from 28.6 to 0.2  $\mu\text{A}$  for cathodic current) in the current response. This is caused by the formation of BLMs and the BLMs insulated the electrode and precluded redox reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  occurring on the electrode surface [8,10]. Besides, the low current response of PC/Pt is owing to the pinholes formed during the immersion process. While in the case of BFc@PC/Pt electrode, redox current response increased (5.2  $\mu\text{A}$  for cathodic current, compared to 0.2  $\mu\text{A}$  for cathodic current at PC/Pt electrode), indicating that electrons appeared to be transferred between the redox couples and the Pt substrate via BFc embedded in



**Fig. 1.** CV of (a) bare Pt electrode (dashed line), (b) BFc@PC/Pt electrode (solid line), or (c) PC/Pt electrode (dotted line) in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution containing PBS as supporting electrolyte. Scan rate: 100 mV/s. Arrows indicate the direction of the initial scan.

the lipid bilayer [5]. Besides, the peak-to-peak separation of Pt, PC/Pt or BFc@PC/Pt electrode is 77, 117, or 96 mV, respectively. The heterogeneous electron transfer rate of PC/Pt or BFc@PC/Pt is estimated to be 0.17 or 0.08  $\text{s}^{-1}$ . This result indicates that BFc inside s-BLM increases the electron transfer rate.

#### 3.2. Electrochemical tuning on the conductivity of BFc supported BLMs

Fig. 2 is the CVs of BFc@PC/Pt electrode in 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with PBS as supporting solution. We observed that current response for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was controlled by the potential range. When potential scanning between  $-0.20$  and  $+0.50$  V, the symmetric redox peaks at  $+0.14$  and  $+0.24$  V was recorded (inserted dotted line). However, when potential scanning between  $-0.20$  and  $+1.20$  V, BFc@PC/Pt electrode showed current response for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (peak I) only at the first scan (red line). The current response for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  disappeared when potential scan was from  $+1.20$  back to  $-0.20$  V even in the first potential scan and in the following scans (black line). The current response could not be recovered during the potential scans, indicating that the change of the structure or/and the composition inside the lipid bilayer. The observed irreversible peaks (at  $+0.68$  V peak II and  $+0.50$  V peak III for anodic and cathodic

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