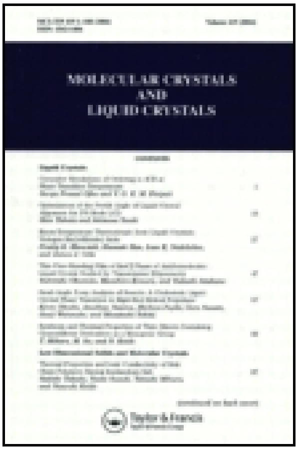

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Ferrocene Mediated Transmembrane Electron Transfer on Gold Electrode Modified by Hybrid Bilayer Membrane Consisting of Octadecanethiol and Phospholipid

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Supported hybrid bilayers consisting of octadecanethiol and phospholipid incorporated with ferrocene were fabricated through self-assembling methods. Its electrochemical behaviors in solutions containing different concentrations of $Fe(CN)_6^{3-/4-}$ were investigated by ac impedance and cyclic voltammetry. The transmembrane electron transfer across octadecanethiol self-assembled film and an adsorbed phospholipid layer mediated by ferrocene has been observed. It is determined that the apparent heterogeneous rate constant is 2.3×10^{-8} cm•s^{-1}.

Keywords: Hybrid bilayer membrane; Ferrocene; Cyclic voltammetry; Impedance spectroscopy; Transmembrane electron transfer

INTRODUCTION

Electron transfer and redox reactions play a central role in bioenergetics. Liposomes and BLMs were often used as models to study the process. Researches with vesicles do not allow a simple control of the applied potential and hence, limits the use of well-established electrochemical techniques. The fragility of conventional planar BLM also limits its applications[1]. Many attempts have been made to prepare synthetic bilayers using a solid electrode support. For instance, the group of Plant[2], using self-assembled layers of alkanethiol on gold as a phospholipid support to fabricate a hybrid bilayer membrane (HBM).

In our first report[3], we found that the formal potential of the redox couples in the solution has a great impact on the electron transfer rate. In this paper, the electron transfer resistance in different concentrations and the apparent heterogeneous rate constant of $Fe(CN)_6^{3-/4-}$ across the HBM mediated by ferrocene were obtained.

EXPERIMENTAL

Reagents and electrochemical methods were described previously[3]. Bilayer structure was prepared according to the literature [3]. The bilayer was assumed as satisfactory if its capacitance was close to 0.5 $\mu F \cdot cm^{-2}$, a series of electrochemical measurements were carried out.

RESULTS AND DISCUSSION

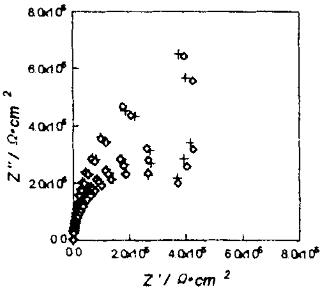
Figure 1 shows the complex-plane impedance plot for the ferrocene modified HBM electrode in the solution of different concentrations of $Fe(CN)_6^{3-/4-}$. Impedance data were analyzed by EQUIVCTR.PAS (EQU) which was programmed by Boukamp[4].The equivalent circuit that we used to model the HBM system is Rs(RrQ). Rs is the solution resistance, Rr is the apparent electron transfer resistance, The constant phase element (CPE) Q is corresponding to the membrane capacitance because the value of n is near to 1[4]. The CPE is independent of the concentrations of $Fe(CN)_6^{3-/4-}$ reflecting that the HBM are impermeable to the redox species in the solution. The whole electron transport basically consists of two processes. One is the electron-transfer reaction of redox couple at the HBM surface, and the other is the electron migration in the HBM interior[1]. The Rr value is a sum of the electron-transfer resistance (Rct) which decreases as the concentrations of the redox couple increase and the electron migration resistance (Rem) in the

HBM interior, which is independent of the concentration of redox couple. The relationship between Rct and concentration can be expressed as following.[1]

$$Rr = Rem + R\,T / (n^2\,F^2\,k_s\,c)$$

Where n is the number of electrons transferred, R, T and F have their usual electrochemical meanings, k_s is the heterogeneous electron-transfer rate constant, and c is the concentration of the redox couple in the solution. From the slope and intercept of the plot Rr vs $1/c$, the k_s and Rem value are found to be 2.3×10^{-8} cm·s^{-1} and 3.97×10^6 Ω·cm^2 respectively.

In order to expound the electron transfer mediation of ferrocene, a series of cyclic voltammetry were carried out in $Fe(CN)_6^{3-/4-}$ solution (Figure 2 a , b). With the addition of $Fe(CN)_6^{3-/4-}$ to the solution, an inverse sigmoidal cyclic voltammetric response is observed (Figure 2 b), which indicate that the electron transfer between electrode and redox couples in solutiuon is mediated by ferrocenes. In this case, the formal potential for $Fe(CN)_6^{3-/4-}$



FIGUER 1 The EIS of the ferrocene modified HBM derivatized gold electrode, the concentrations of $Fe(CN)_6^{3-/4-}$ from top to bottom are 0.99; 1.96; 3.84; 5.66; 7.41 mmol·L^{-1} respectively, (+) Experiment data, (◇) fit to equivalent circuit model from EQU

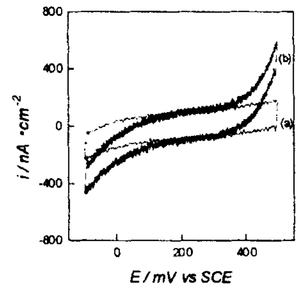


FIGURE 2 Cyclic voltammograms of the modified Au / octadecanethiol / lipid electrodes (no ferrocene) (a) and the ferrocene modified Au/octadecanethiol/ lipid electrode (b) in the solution of $Fe(CN)_6^{3-/4-}$ (7.41 mmol·L^{-1}), the scan rate is 0.1V / s.

(0.22V vs SCE)[1] is nearly coincident with that of ferrocene. The mediation of electron transfer is most effective because of the match in potential of the two redox couples. Both reductive and oxidative forms of the ferrocene in the bilayer may be present at equilibrium.

The mediated oxidation and reduction of $Fe(CN)_6^{3-/4-}$ by Fc / Fc^+ both can occur according to the following mechanism:

Anodic process

$Fc(o) = Fc^+(o) + e^-$

$Fc^+(o) + Fe(CN)_6^{4-}(w) = Fc(o) + Fe(CN)_6^{3-}(w)$

Cathodic process

$Fc^+(o) + e^- = Fc(o)$

$Fc(o) + Fe(CN)_6^{3-}(w) = Fc^+(o) + Fe(CN)_6^{4-}(w)$

The above experiments have shown that the transmembrane electron transfer across octadecanethiol self-assembled film and an adsorbed phospholipid layer mediated by ferrocene has been observed in the solution containing $Fe(CN)_6^{3-/4-}$. Further studies in other redox species solution and to clarify the detailed mechanism are under way in our laboratory.

Acknowledgements

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