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Studies of Structural Disorder of Gold Supported Thiol-Lipid Bilayers

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Electrochemical impedance spectroscopy was used to investigate the structural disorder of Au supported octadecanethiol-phosphatidylcholine (Au/ODT-PC) bilayers. Results of experiments indicate that collapsed-sites and pinholes exist in octadecanethiol monolayer (ODTM) and phosphatidylcholine monolayer (PCM), respectively.

Keywords: supported bilayer membrane; thiol; lipid

INTRODUCTION

Supported bilayer membranes, which were developed in order to overcome the extreme fragility of the classical bilayer lipid membranes, are now becoming particularly attractive as model systems that can be used to mimic many roles of biological membranes. In this paper, a.c. impedance was used to investigate the structural disorder of Au/ODT-PC bilayer.

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EXPERIMENTAL

The octadecanethiol (ODT) and L-α phosphatidylcholine (PC) (99% TLC) were purchased from Aldrich and Sigma, respectively. Other chemicals were of analytical grade. The Au supported ODTMs were prepared as described elsewhere[1]. The Au/ODT-PC bilayers were formed by depositing PCM on ODTM[2]. Electrochemical impedance spectroscopy (EIS) were performed with an a.c. impedance system (EG&G, Model 388).

RESULTS AND DISCUSSION

It has been demonstrated in our previous studies that pinhole defects do not exist in ODTM but collapsed-sites do[3]. The main way for charge transfer across ODTM is electron tunneling at collapsed-sites.

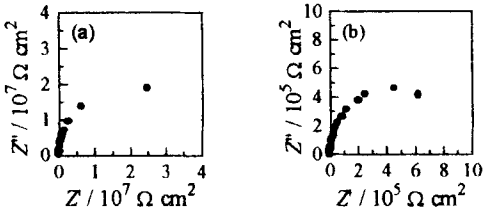

FIGURE 1 Nyquist plots of (a) Au/ODT-PC and (b) Au/ODTM in 1 mM $Fe(CN)_6^{3-/4-}$ + 0.1 M KCl. Frequency range: (a) 65 kHz — 0.005 Hz, (b) 65 kHz — 0.01 Hz.

Fig.1 shows the Nyquist plots of Au/ODT-PC and Au/ODTM in 1 mM $Fe(CN)_6^{3-/4-}$ solution. The Faraday resistance of Au/ODT-PC obtained from Fig.1a is $3.9\times10^7\Omega cm^2$, which is much greater than that of Au/ODTM ($9.0\times10^5\ \Omega\ cm^2$ obtained from Fig.1b).

Since the theoretical Faraday resistance of structural-disorder-free Au/ODT-PC bilayer, $R_f^{ODT\text{-}PC}$, which is calculated from electron tunneling

model, is greater by a factor of > 10^9 than the apparent one R_{app}^{ODT-PC} obtained from experiments, it is rational to conclude that electron tunneling across bilayer contributes little to the redox current (see Fig.2 b).

If the redox couple in solution could permeate through PCM, the equivalent circuit should contain Warburg impedance, Z_w^{PC}, (see Fig.2c). Under the conditions of $R_{app}^{ODT} >> Z_w^{PC}$, $R_{app}^{ODT} << Z_w^{PC}$, and $R_{app}^{ODT} \approx Z_w^{PC}$, the Nyquist plot of Au/ODT-PC will be a semicircle with about the same diameter as that of Au/ODTM, a unit-sloped line, and a semicircle in the high frequency range and a unit-sloped line in the low frequency range, respectively (see Fig.2 c and a). However, none of the above three cases is observed in Fig.1a, so we believe $Fe(CN)_6^{3-/4-}$ cannot permeate through PCM.

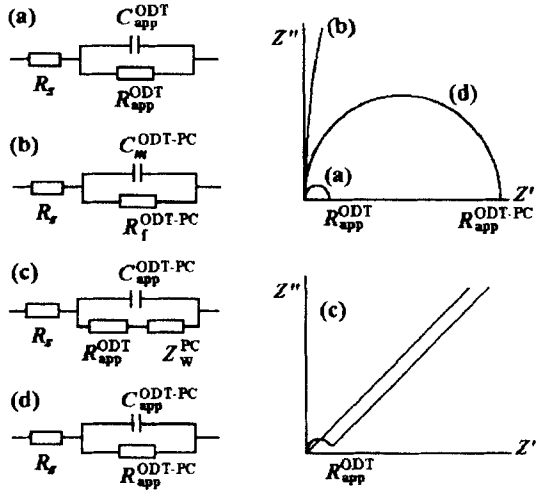

FIGURE 2 Equivalent circuit and impedance plots for (a) Au/ODTM with collapsed-sites, (b) Au/ODT-PC without structural disorder, (c) Au/ODT-PC when redox couples being able to permeate through PCM, and (d) Au/ODT-PC with collapsed-sites in ODTM and pinholes in PCM, respectively

Then, the only way left for charge transfer reaction to occur at Au/ODT-PC is that electroactive species could diffuse through pinholes in PCM and reach collapsed-sites where electrons tunnel across a relatively thin ODTM. In this mechanism, the electron tunneling process is the rate-limiting step, otherwise the mass transfer effects would be observed in EIS experiments. This means that only a semicircle should be obtained in Nyquist plot, which is just the case of our experimental results (Fig. 1a). The fact that R_{app}^{ODT-PC} is much greater than R_{app}^{ODT} can be attributed to the great decrease of the area of collapsed-sites exposed to the solution after the deposition of PCM on ODTM. To summarize briefly, EIS experimental data provide definite evidence that pinholes exist in PCM.

We attribute the existence of pinhole defects in PCM to the following reason: on the collapsed-site-free domains of Au/ODTM, PC and ODT molecules may form well-assembled bilayer. While, at collapsed sites, it is difficult for PC molecules to form a compact and orderly monolayer because of the structure disorder of ODTM. We believe that the main course of redox current at Au/ODT-PC is that electroactive species diffuse through pinholes in PCM and reach collapsed-sites in ODTM where electron transfer occurs via a tunneling process.

Acknowledgments

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