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Capacitance Characterization of the Effect of pH Value on the Self-assembled Monolayers of Octadecanethiol

Ke Qiang DING[1], Qing Fei WANG[1], Ru Ting TONG[1], Hui Bo SHAO[2]*

[1]Chemistry College, Hebei Teachers' University, Shijiazhuang 050016
[2]Department of Chemistry, Capital Normal University, Beijing 100037

Abstract: In this paper, the membrane capacitance (C_m), which was obtained from the electrochemical impedance spectroscopy (EIS) method, was used to characterize the effect of pH value on the self-assembled monolayers (SAMs) of octadecanethiol(18SH) for the first time. The results not only strongly proved that inorganic ions could penetrate the SAMs of 18SH, but also ascertained that SAMs of 18SH were not an absolute of free of ion-penetration. Verifying the existence of pin-holes in the octadecanethiol SAMs was the main contribution of this paper, which coincided with the former conjecture very well.

Keywords: Octadecanethiol, SAMs, effect, pH value, capacitance characterization.

Octadecanethiol self-assembled monolayers (SAMs) are the most widely investigated SAMs. And most papers have pointed that 18SH SAMs are free of ion-penetration due to its well-ordered structure and density[1]. While, recently, the opinion that alkylthiol SAMs have pin-holes and defects has been proposed[2]. So far, the generally accepted view has not been presented yet.

The aim of this paper is to study the influence of pH value on 18SH SAMs, with an intention to confirm the existence of pin-holes. Here, the capacitance plot in the ac impedance measurement was used because membrane capacitance (C_m) is very sensitive to the conditions of interfaces.

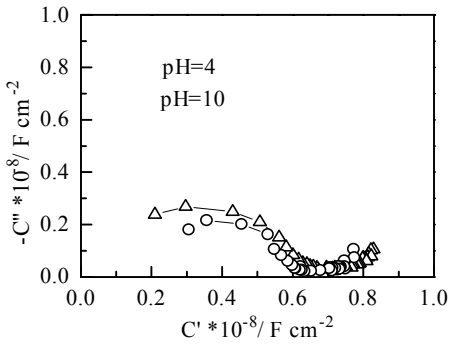
The measuring system is 0.1 mol/L KCl, where the value of pH was adjusted by adding HCl or NaOH. The preparation of 18SH SAMs on Au electrode and all other instruments are based on the previous report [3].

Results and Discussion

Figure 1 is the capacitance plots of 18SH modified Au electrode in 0.1 mol/L solution with various pH values. The membrane capacitance (C_m), presented by the semicircle diameter at the high frequency region, could be simulated conveniently[3]. At pH=4, C_m is about 6.2×10^{-9} F cm^{-2}, while when the pH was changed to 10, C_m was decreased to 4.6×10^{-9} F cm^{-2}, suggesting that the interfacial condition has been changed. The

*E-mail: Dkeqiang@263.net

Figure 1 The capacitance plots for 18SH SAMs modified on Au electrode recorded in 0.1 mol/L KCl solution with different pH values



formula, $C_m=\varepsilon_0\varepsilon_r/d$ [3], where ε_0 is the vacuum permittivity, ε_r the membrane permittivity and d is the thickness of the membrane, has illustrated the influencing factors to C_m. The thickness of studied 18SH SAMs, should remain unchanged due to strong S-Au chemical bonds, thus, the decrease of C_m in the case of pH=10 could only be attributed to the dropping of ε_r. Consequently, the expelling of inorganic ions was proved directly.

So it is reasonable believe that the change of C_m strongly confirms the existence of pin-holes in alkylthiol SAMs. Other detailed studies are being carried out in our laboratory.

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