Permeability of Alkanethiols Self-Assembled Monolayers on Gold Prepared by Neat Thiols and Ethanolic Thiols

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In this article we investigated the permeability of alkanethiols (C_nSH , $n = 6, 10, 12, 16$) self-assembled monolayers (SAMs) on gold prepared by neat thiols and ehanolic thiols. The electrochemical parameters (interfacial capacitance C_d , phase angle $\Phi_{1\text{ Hz}}$ and ions transfer resistance R_{it}^* at 1 Hz, current density difference Δj and charge transfer resistance R_{ct}) from cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to explore the permeability of SAMs. Results indicated that alkanethiols SAMs prepared by neat thiols had smaller C_d than by ehanolic thiols. Thus, the neat thiols SAMs were more compacted than ehanolic thiols SAMs. The dielectric constant ϵ of alkane chain in SAMs were calculated to be 1.2 (neat thiols) and 3.0 (ehanolic thiols) respectively based on the linear slopes of $C_d^{-1} \sim n$ plots. A hydrophobic gap possibly existed on neat thiols SAMs-water interface, which might lead to smaller ϵ (1.2) than the reported value (2.3) by literatures. The $\Phi_{1\text{ Hz}}$ of neat thiols SAMs were bigger and close to 88° as an ions insulator and the ehanolic thiols SAMs were ions permeable SAMs. The permeable constants (p) of neat thiols SAMs and ehanolic thiols SAMs on gold were 0.097/ CH_2 and 0.111/ CH_2 respectively based on the linear slopes of $\ln R_{it}^* \sim n$ plots. However, to our surprise, the tunneling constant β of neat thiols SAMs was calculated to be 0.238/ CH_2 based on the linear slopes of $\ln R_{ct} \sim n$ plots (R_{ct} was the charge transfer resistance of $Fe(CN)_6^{3-/4-}$), which was much smaller than 1.0/ CH_2 from literatures. We considered that there might be two main reasons: 1) The hydrophobic layer existed on the neat thiols SAMs possibly influenced the R_{ct} of $Fe(CN)_6^{3-/4-}$; 2) The neat thiols SAMs was not an ideal tunneling system with the collapsed sites possibly existed in SAMs, which might influence the R_{ct} of $Fe(CN)_6^{3-/4-}$. These conclusions provided the important reference for understanding the interfacial characteristics of alkanethiols SAMs on gold in depth.

Keywords: self-assembled monolayers, permeability, neat thiols, ehanolic thiols, gold electrode

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