

## Characterization of Formation Kinetics of Self-Assembled Thiol Monolayers on Gold by Electrochemical Impedance Spectroscopy

Peng DIAO<sup>1</sup>, Min GUO<sup>2</sup>, Ru Ting TONG<sup>1\*</sup>

<sup>1</sup> Department of Chemistry, Hebei Teacher's University, Shijiazhuang 050016

<sup>2</sup> Department of Traditional Chinese Pharmacy, Traditional Chinese Medicine College, Hebei Medical University, Shijiazhuang 050091

**Abstracts:** Self-assembled monolayers of octadecanethiol (ODT) on gold have been studied by electrochemical impedance spectroscopy (EIS). The fractional coverage has been examined as a function of immersion time of Au in ODT deposition solution. The fractional coverage exhibits two distinct adsorption steps: an initial rapid step followed by a slow one. The fractional coverage of ODT monolayer increases sharply from zero to more than 99% of its maximum within the first minute. However, it takes a day for the fractional coverage to approach its final value.

**Keywords:** Self-assembled thiol monolayer, electrochemical impedance spectroscopy, adsorption kinetics.

Interest in the properties of organized monolayers has grown enormously in recent years because these monolayers can provide a means to control the interface at a molecular level<sup>1</sup>. The self-assemblies of alkanethiols and their derivatives were probably the most intensively studied due to their stability, well-packed structure, ease in preparation, and flexibility in designing the tail group<sup>2</sup>. The adsorption kinetics of thiol monolayer has been studied by using several techniques, including constant angle and ellipsometry<sup>3</sup>, quartz crystal microbalance<sup>4</sup>, atomic force microscope<sup>5</sup> and second harmonic generation<sup>6</sup>. However, the adsorption rate is still in argument. In this paper, we present the results of adsorption kinetics of octadecanethiol (ODT) on gold by ac impedance.

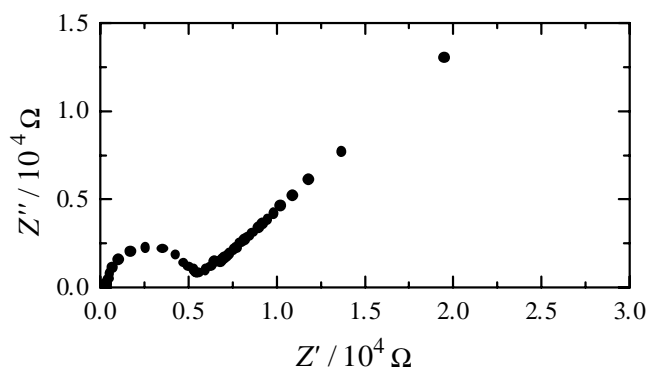
### Experimental

The octadecanethiol (ODT, Aldrich) was used as received. Other chemicals were of analytical grade. All aqueous solutions were prepared with redistilled water. The concentration of ODT in ethanol was 0.1 mmol/L. The formation process of ODT monolayer was described elsewhere<sup>7,8</sup>. Electrochemical impedance spectroscopy (EIS) was performed in 2 mmol/L Fe(CN)<sub>6</sub><sup>3-/4-</sup> in 0.1 mol/L KCl by using a PAR Model 388 electrochemical impedance system. The electrochemical cell used in EIS experiments was described in our previous works<sup>7,8</sup>.

## Results and discussion

**Figure 1** shows the complex impedance plots of Au|ODT monolayer in  $\text{Fe}(\text{CN})_6^{3-/4-}$  solution when assembling time of ODT monolayer is 5 s. A rational parameter that can be used to characterize adsorption kinetics is the fractional coverage of the monolayer,  $\theta$ <sup>6</sup>. However, for film coated electrode, Amatore and co-workers<sup>9</sup> pointed out that  $\theta$  can not be simply obtained from the equation  $1 - \theta = R_{\text{app}}^0 / R_{\text{app}}$  (where  $R_{\text{app}}^0$  and  $R_{\text{app}}$  are the apparent charge transfer resistances at bare and film covered electrode) when  $\theta$  is close to unit ( $\theta > 0.9$ ). If we use the above-mentioned equation to calculate  $\theta$ , we find  $\theta > 0.98$  for the case shown in **Figure 1**. This means we have to use another method, which is appropriate for the case that  $\theta$  is close to unit, to determine the value of  $\theta$ . The Warburg lines in **Figure 1** indicates thiol monolayer contains pinholes. Finklea *et al.*<sup>10</sup> demonstrate that the pinholes in thiol monolayers can be regarded as microarray electrodes. The equivalent circuit, which contains a solution resistance  $R_s$  in series with a parallel Faradaic impedance  $Z_f$  and an interfacial capacitance  $C$ , can be used to model these microarray electrodes. The Faradaic impedance  $Z_f$  is actually composed of a charge transfer resistance  $R_{\text{ct}}$  in series with a mass-transfer impedance containing linear and nonlinear diffusion terms.

**Figure 1** Complex plan plots of total impedance of ODT coated gold electrodes in 0.2 mmol/L each  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 0.1 mol/L KCl. The frequency range is 0.05 Hz – 100 kHz. The adsorption time is 5 s. Electrode area 0.02 cm<sup>2</sup>.



Finklea *et al.*<sup>10</sup> have studied the Faradaic impedance  $Z_f$  and obtained that the real part of  $Z_f$  can be expressed as the following at high frequencies:

$$Z'_f = R_{\text{ct}} / (1 - \theta) + \sigma \omega^{-1/2} + \sigma (1 - \theta)^{-1} \omega^{-1/2} \quad (1)$$

$$\sigma = 1.414 RT / (n^2 F^2 A c D^{1/2}) \quad (2)$$

$$R_{\text{ct}} = RT / (n^2 F^2 A k^0 c) \quad (3)$$

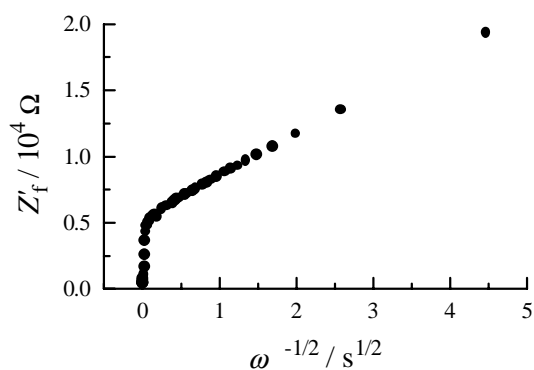
where  $\omega$  is the radial frequency,  $\sigma$  is the Warburg impedance slope,  $A$  is the geometric area of electrode,  $c$  is the concentration of the redox couple,  $D$  is the diffusion coefficient of redox couple (assuming  $D_{\text{O}}$  equals  $D_{\text{R}}$ ), and  $R$ ,  $T$ ,  $n$ ,  $F$  and  $k^0$  have their usual significance.  $\sigma \omega^{-1/2}$  represents the linear diffusion and the last term in the eqns.(1) corresponds to the effect of non-linear diffusion. While at low frequencies  $Z'_f$  is

expressed as:

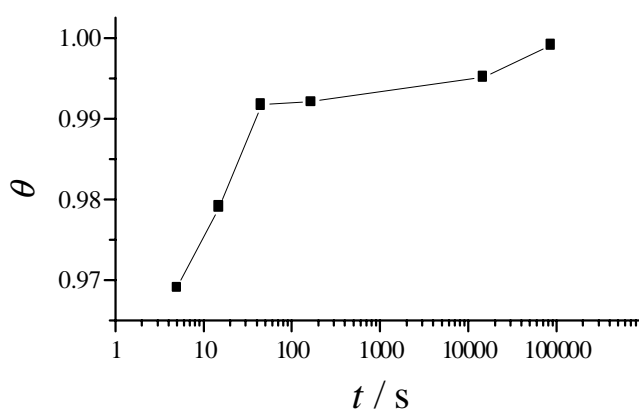
$$Z'_f = R_{ct}/(1-\theta) + r_a(0.72/D)^{1/2} \sigma(1-\theta)^{-1} + \sigma\omega^{-1/2} \quad (4)$$

where  $r_a$  is the radius of pinhole. Based on eqns.(1)  $\theta$  can be obtained from the plot of  $Z'_f$  vs  $\omega^{-1/2}$ . **Figure 2** shows the  $Z'_f$  vs  $\omega^{-1/2}$  plot of Au|ODT monolayer whose assembling time is 5 s. The Faradaic impedance is obtained from the corresponding impedance data shown in **Figure 1**. The removal of solution resistance  $R_s$  and interfacial capacitance  $C$  from the total impedance is done by Equivcrt.pas software<sup>11</sup>. The values of  $R_s$  and  $C$  needed for the correction are obtained at the highest frequencies, where it is accurate enough to simplify the equivalent circuit to  $R_s$  and  $C$  in series.

**Figure 2** Real part of Faradaic impedance ( $Z'_f$ ) vs  $\omega^{-1/2}$  for ODT coated gold electrodes in 2 mmol/L each  $\text{Fe}(\text{CN})_6^{3-/4-}$  in 0.1 mol/L KCl. The values of  $Z'_f$  are obtained from the corresponding impedance data in **Figure 1** after correcting for  $R_s = 370 \Omega$  and  $C = 1.7 \times 10^{-8}$  F.



**Figure 3** The fractional coverage of ODT monolayer as a function of adsorption time.



From **Figure 2**, we note that there are two linear domains at high and low frequencies, which is in good agreement with the theoretical prediction of eqns. (1) and (4). The slope of high-frequency line whose correlation factor is greater than 0.98 is used to calculate  $\theta$ . We can also obtain the  $Z'_f$  vs  $\omega^{-1/2}$  plots with different adsorption time and get the corresponding values of  $\theta$  by using the similar method mentioned above.

Then, we can examine  $\theta$  as a function of assembling time. The plot of  $\theta$  vs the logarithm of assembling time is shown in **Figure 3**. **Figure 3** exhibits distinct two adsorption steps: an initial rapid step that lasts less than a minute and a slow one that takes hours. During the initial rapid step,  $\theta$  reaches ca. 99% of its limiting value, which is in agreement with the adsorption kinetics studied by using contact angle and ellipsometry measurement<sup>3</sup>. The determination of adsorption rate constant from  $\theta$  is in progress.

### Acknowledgments

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### References

1. A. Ulman, *Chem. Rev.*, **1996**, *96*, 1533.
2. H. O. Finklea, in: A. J. Bard (Ed.), *Electroanalytical Chemistry, Vol. 19*, Marcel Dekker, New York, **1996**, pp 109.
3. C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.*, **1989**, *111*, 321.
4. D. S. Karpovich, G. J. Blanchard, *Langmuir*, **1994**, *10*, 3315.
5. K. Hu, A. J. Bard, *Langmuir*, **1998**, *14*, 4790.
6. O. Dannenberger, M. Buck, M. Grunze, *J. Phys. Chem.*, **1999**, *B103*, 2202.
7. P. Diao, D. Jiang, X. Cui, D. Gu, R. Tong, B. Zhong, *J. Electroanal. Chem.*, **1999**, *464*, 61.
8. P. Diao, M. Guo, D. Jiang, Z. Jia, X. Cui, D. Gu, R. Tong, B. Zhong, *J. Electroanal. Chem.*, **2000**, *480*, 59.
9. C. Amatore, J. M. Saveant, D. Tessier, *J. Electroanal. Chem.*, **1983**, *147*, 39.
10. H. O. Finklea, D. A. Snider, J. Fedyk, E. Sabatani, Y. Gafni, I. Rubinstein, *Langmuir*, **1993**, *9*, 3660.
11. B. A. Boukamp, Equivalent Circuit (Distributed by EG&G-PARC, Version 4.51), Users Manual, University of Twente, The Netherlands, 2nd. edn. **1993**.

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