Electrochemistry Communications 12 (2010) 1462–1466

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electroactive self-assembled monolayers: Laviron's interaction model extended to non-random distribution of redox centers

Olivier Alévêque, Pierre-Yves Blanchard, Christelle Gautier, Marylène Dias, Tony Breton *, Eric Levillain *

Laboratoire CIMA, Université d'Angers-CNRS, 2 boulevard Lavoisier 49045, Angers cedex, France

ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form 13 July 2010
Accepted 22 July 2010
Available online 12 August 2010

Keywords:
Tempo
Self-assembled monolayers
Cyclic voltammetry
Interaction model

ABSTRACT

The Laviron's interaction model, dedicated to randomly distributed electroactive adsorbed species, was extended to a non-random distribution in order to extract the current–voltage characteristics from any surface distribution of electroactive centers on self-assembled monolayer (SAM). Confronted to electrochemical behaviour of nitroxyl radical SAMs, the *agreement* observed between *theory* and experiments provides evidence of a distribution independence of the interaction parameters.

1. Introduction

Since the pioneering work by Nuzzo and Allara in 1983 [1], self-assembled monolayers (SAMs) of alkanethiols have gained much attention in the interfacial electrochemistry and other research fields [2]. Previous works [3] were dedicated to confront Laviron's interaction model and electrochemical data from nitroxyl radical SAMs on gold in order to provide evidence of a random distribution of electroactive centers on surface. To extend this approach to non-random distribution of electroactive sites on SAMs, we developed an empirical numerical model combined with electrochemical data from nitroxyl radical SAMs. This work allowed to differentiate a random distribution from a non-random distribution [4].

Here, we propose to develop an extension of the Laviron's model to a non-random distribution in order to extract the current–voltage characteristic (*i*–*E*) from any surface distribution of electroactive centers.

2. Experimental procedures

2.1. Compounds

The synthesis and electrochemical characterizations of nitroxyl radical (TEMPO) derivative 1 (*N*-(TEMPO)16-mercaptohexadecanamide) were described in reference [5].

Elaboration and electrochemical characterizations of SAMs prepared from Route 1 and from Route 2 were described in references [3,4].

Route 1: Successive adsorptions of 1 and dodecanethiol (C12) for the formation of binary SAMs were performed by immersing the Au/glass substrate for 15 min in a millimolar solution of 1 in dichloromethane and then in a millimolar solution of C12 in dichloromethane. The time in the C12 solution varied from 1 min to 48 h in order to obtain the expected **1** surface coverage.

Route 2: Partial desorption of a densely packed SAM of 1 was performed by immersing the Au substrate for 15 min in a millimolar solution of 1 in dichloromethane and then in pure dichloromethane under ultrasonication (40 kHz) for a time varying from 5 to 120 min to obtain the desired 1 surface coverage.

2.2. Numerical models

The SAMs were modeled by a square matrix $M(X,Y)$ composed of "1" (site occupied by an electroactive species) and of "0" (site not occupied or site occupied by a non-electroactive species). The relation between the number of "1" and the "total number of sites" experimentally corresponds to the normalized surface coverage θ_T [0,1]. A matrix exclusively composed of "1" corresponds to a SAM whose number of electroactive sites is maximum with $\theta_T = \theta_{max} = 1$. A mixed SAM is represented by a matrix whose θ_T is included in the interval [0,1[. To generate a non-unitary matrix with a fixed θ_T value from a unitary matrix, we used a pseudorandom number generator (PRNG).

---

* Corresponding authors. Tel.: +33 241735095; fax: +33 241735405.
E-mail addresses: tony.breton@univ-angers.fr (T. Breton), eric.levillain@univ-angers.fr (E. Levillain).

1388-2481/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2010.07.039

2.3. Surface distribution

Two numerical models were developed [4] in order to generate two different molecular surface distributions. The RND model was dedicated to random distribution and the CNT model to phase segregation. The two models were used to generate matrices $M(X,Y)$ with a normalized surface coverage θ_T between 0 and 1. The binary images from calculated matrices are represented in Fig. 1 for a 0.5 normalized surface coverage.

A dimensionless quantity ϕ, "segregation factor", representative of the average number of lateral interactions per electroactive site, allowed quantifying distributions from RND and CNT models.

$$\text{For the RND model, } \phi_{RND}(\theta_T) = N\ \theta_T$$

$$\text{For the CNT model, } \phi_{CNT}(\theta_T) = N\left(\frac{\theta_T}{1+\theta_T}\right)^{0.4} exp\left[\left(1.44\frac{\theta_T}{1+\theta_T}\right)^{4}\right] \qquad (1)$$

with N = the maximum number of nearest neighbours on a full-covered surface ($\theta_T = \theta_{max} = 1$).

3. Results and discussion

3.1. Interactions calculation

The influence of the initial molecular distribution on the molecular distribution of reduced and oxidized species during the oxidation (or reduction) step was studied *via* a reversible *n*-electron redox reaction of adsorbed electroactive species:

$$R_{ads} \rightleftharpoons O_{ads} + ne^{-} \qquad (2)$$

Hypotheses [6,7] were the following:

- The sum of surface concentrations Γ_O and Γ_R of O and R respectively, is constant and equal to Γ_T. Γ_{max} designates the maximal steady state surface coverage of O and R. The coverage θ_O and θ_R being defined by: $\theta_O = \Gamma_O/\Gamma_{max}$, $\theta_R = \Gamma_R/\Gamma_{max}$ and $\theta_T = \Gamma_T/\Gamma_{max}$,
- The surface occupied by one molecule of O is equal to the surface occupied by one molecule of R.

For a given θ_T matrix image, with random (RND) or non-random (CNT) distribution, and initially composed of R species ($\theta_R = \theta_T$), the oxidation process is simulated by the random replacing of R species by O species (Fig. 1). At each step of the replacement (*i.e.* for various θ_O), we calculated interactions between redox species by means of four dimensionless quantities $\phi_{OO}(\theta_O,\theta_T)$, $\phi_{OR}(\theta_O,\theta_T)$, $\phi_{RR}(\theta_O,\theta_T)$, and $\phi_{RO}(\theta_O,\theta_T)$. $\phi_{ij}(\theta_O,\theta_T)$, representative of the average number of interactions between a species i (O or R) and a species j (O or R). Taking into account only the nearest neighbours interactions, $\phi_{ij}(\theta_O,\theta_T)$ can be expressed by:

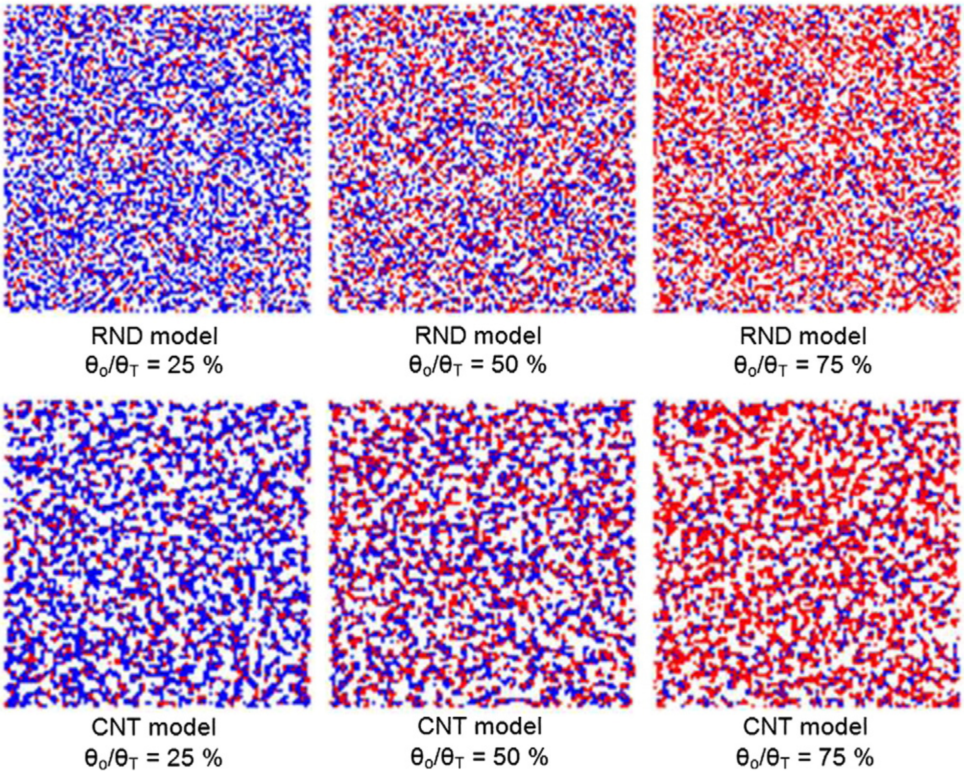
$$\phi_{ij}(\theta_O,\theta_T) = \frac{\sum_{x}^{X}\sum_{y}^{Y}\sum_{M_{\theta_O,\theta_T}(X,Y)=i} M_{\theta_O,\theta_T}(X,Y)N_j(X,Y)}{\sum_{x}^{X}\sum_{y}^{Y}\sum_{M_{\theta_O,\theta_T}(X,Y)=i} M_{\theta_O,\theta_T}(X,Y)} \qquad (3)$$

with

$M_{\theta_O,\theta_T}(X,Y)$ Matrix generated for given surface coverages θ_O and θ_T.
$N_j(X,Y)$ Number of direct neighbours j close to $M(X,Y)$
$\Phi_{ij}(\theta_O,\theta_T)$ varies between 0 and N. In our case, with a square matrix, $N=4$.

$\phi_{ij}(\theta_O,\theta_T)$ values *vs.* θ_T were calculated from RND and CNT models. In both models, numerical simulations exhibited a linear dependence of $\phi_{ij}(\theta_O,\theta_T)$ *vs.* θ_T (Fig. 2), leading to:

$$\phi_{ij}(\theta_O,\theta_T) = \frac{\phi(\theta_T)}{\theta_T}\theta_j \qquad (4)$$



RND model θ_o/θ_T = 25 %
RND model θ_o/θ_T = 50 %
RND model θ_o/θ_T = 75 %
CNT model θ_o/θ_T = 25 %
CNT model θ_o/θ_T = 50 %
CNT model θ_o/θ_T = 75 %

Fig. 1. Binary images obtained from calculated matrix during an oxidation step for θ_T = 50%. (Up) random and (Down) segregated distribution of electroactive centers for different values of θ_O. For each matrix, R species are represented in blue, O species are represented in red and free sites are represented in white. he size of the matrix is (100 × 100).