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A generalized lateral interactions function to fit voltammetric peaks of self-assembled monolayers

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ABSTRACT

From the generalized lateral interactions model and via a few mathematical approximations, a suitable regression function has been developed in order to fit voltammetric peak of redox responsive SAM for extracting the characteristic parameters. The efficiency of the generalized lateral interactions function was tested on simulated and raw data.

1. Introduction

Since their initial discovery in 1946 [1], self-assembled monolayers (SAMs) have become an ideal system for the theoretical study of interfacial phenomena, especially in the field of electrochemistry when they are immobilized on conductive substrates like gold [2,3]. A major constraint to obtain a fine characterisation of electroactive SAMs is the dispersion of the current–voltage characteristics around the fully solved theoretical one [4]. Indeed, cyclic voltammograms (CVs) of SAMs are most often complex with sharper or broader voltammetric peaks than in the ideal case [5–8].

Some of these electrochemical behaviours can be explained by several theories/models, like the generalized lateral interactions model (GLI model) [7]. They allow to clarify deviations from ideality and define characteristic parameters of theoretical voltammograms like peak potential (E_p), peak intensity (i_p) and full width at half maximum (FWHM) in the case of infinite electron transfer.

However, using the GLI model to perform a global fit of experimental CVs is impossible, because the expression of I-V curves leads to a recursive function, excluding a curve fitting analysis.

A first alternative to analyse CV peaks consists in using the graphical analysis tools of the commercial instrument control software. This method allows determining characteristic parameters (E_p, i_p and FWHM) of the CVs but do not allow determining if a particular experimental profile follows a theoretical curve.

A second alternative, detailed in previous work, proposed to fit CV peaks via usual or unusual functions [9,10] such as Gaussian [11–13], Lorentzian [11–13], or Generalized Gaussian Function [14] but these calculations were either very complex or not based on a theoretical support.

Herein, we propose a regression function, derived from the GLI model [6], which allows extracting characteristic parameters of a voltammetric peak and interaction constants of an electroactive system by curve fitting.

2. The GLI model

In previous works, we presented theoretical studies to complete the lateral interaction model proposed by E. Laviron [5], by extending this initial model to non-random distributions of electroactive species and by taking into account the interactions between redox and non-redox species [7].

In the case of interactions between redox species only, this model enables current–voltage behaviours to be simulated and allows extracting characteristics parameters of CVs obtained from any surface distribution of electroactive SAM.

For a better reading of the article, we must summarize previous works.

The generalized lateral interactions model can be defined according to the main following hypotheses:

- The electroactive species are distributed on substrate with a unimodal statistical distribution of electroactive neighbours. A parameter $\phi(\theta)$, between 0 and 1, defined for a normalized surface coverage $\theta = \frac{\Gamma}{\Gamma_{max}}$,

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quantifies the segregation level of the electroactive species. For a randomly distributed SAM, $\phi(\theta)=\theta$, and when a segregation exists on the surface, $\phi(\theta)>\theta$,

- The sum of normalized surface coverage θ_O and θ_R of oxidized (O) and reduced (R) species is constant and equal to θ,
- The surface occupied by one molecule of O is equal to the surface occupied by one molecule of R,
- The electrochemical rate constant k_s is independent of the coverage,
- a_{OO},a_{RR} and a_{OR} are the interaction constants between molecules of O, molecules of R and molecules of O and R, respectively. a_{ij} is positive for an attraction and negative for a repulsion.

For a full reversible reaction ($\frac{k_s}{v}\to\infty$), CVs are perfectly reversible and the current can be expressed as a function of θ_O:

$$i(\theta_O)=\frac{n^2F^2Av\Gamma_{\max}}{RT}\frac{\theta_O(\theta-\theta_O)\theta}{\theta^2-2G\theta_O\phi(\theta)(\theta-\theta_O)} \tag{1}$$

The characteristic parameters of CVs as full width at half maximum (FWHM), peak potential (E_p) and peak current (i_p) can be extracted and defined as:

$$E_p(\phi(\theta))=E_0^{'}+\frac{RT}{nF}S\phi(\theta) \tag{2}$$

$$FWHM(\phi(\theta))=\frac{2RT}{nF}\left[\ln\left(\frac{1+\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}}{1-\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}}\right)-G\phi(\theta)\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}\right]\underset{|G\phi(\theta)<1|}{\approx}\frac{RT}{nF}\times\left(2\ln\left(2\sqrt{2}+3\right)-\frac{3\sqrt{2}}{2}G\phi(\theta)\right) \tag{3}$$

$$i_p(\theta,\ \phi(\theta))=\frac{n^2F^2vA\ \Gamma_{\max}}{RT}\frac{\theta}{2(2-G\phi(\theta))} \tag{4}$$

With n, F, v, A, R, T, E, $E_0^{'}$ have their usual meanings

And $G=a_{OO}+a_{RR}-2a_{OR}$ *and* $S=a_{RR}-a_{OO}$ *with* |G| and |S| ≤ 2

G and S are defined as "global interaction" parameters and play an important role when associated with $\phi(\theta)$. Indeed, $G\cdot\phi(\theta)$ defines the shape of the peak and modulates the FWHM and the peak intensity (i_p), whereas $S\cdot\phi(\theta)$ only defines the position of the peak potential (E_p).

3. The generalized lateral interactions function (GLI function)

3.1. Introduction to the GLI function

The GLI model is very useful to predict characteristic parameters of CVs but, in order to fit CVs, and contrary to the expression 1, the current needs to be expressed as a function of the applied potential (E).

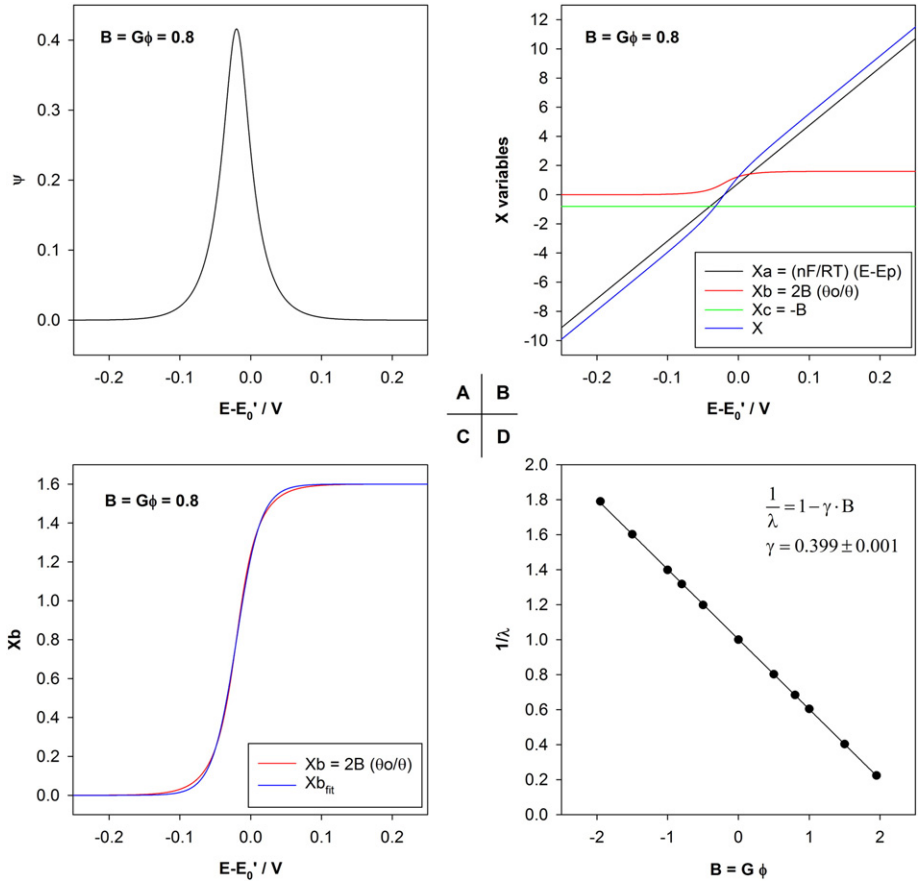

Fig. 1. (A) Dimensionless simulated current of a SAM vs. ($E-E_0'$) using B = Gϕ = 0.8 (and Sϕ = −0.8). (B) Decomposition of the different components of the variable X (X = Xa + Xb + Xc) vs. ($E-E_0'$) in the case of the simulation performed in A). **(C)** Xb component (red) and fitted curve of Xb component (blue) using a generalized sigmoid vs. ($E-E_0'$) in the case of the simulation performed in A). **(D)** λ parameter of generalized sigmoids extracted from a set of simulations vs. B parameter.