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Short communication

Electroactive self-assembled monolayers: A versatile function to fit symmetric voltammetric peak

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ABSTRACT

We propose a versatile function to fit adsorption voltammetric peak in order to extract the characteristic parameters such as the full width at half maximum, the peak potential, the peak current and the surface coverage. Based on the generalized Gaussian function and supported by generalized lateral interaction model, this method has been tested on different electroactive self-assembled monolayers (i.e. ferrocene, bithiophene, tetrathiafulvalene and radical aminoxyl units).

1. Introduction

Current–voltage behaviors of electroactive self-assembled monolayers (SAMs) can be simple or complex with sharp, normal or broad shapes [1,2] and one of the major obstacles facing those who wish to analyze raw data is how to extract characteristic parameters (E_p, i_p, and FWHM) from experimental cyclic voltammograms (CVs). The only alternative to CV peak analysis is often to use the graphical powerful analysis tools of the Turnkey instrument control software (i.e. EC-Lab from Biologic, VersaStudio Software from Princeton Applied Research).

Previous works [3–7] have proposed to fit unusual CV peaks via usual or unusual functions such as Gaussian, Lorentzian, or Extreme function but these calculations were either very intricate or not based on a theoretical support.

Herein, we propose a versatile method to fit experimental peak in order to extract characteristic parameters (E_p, i_p, FWHM and Γ) of cyclic voltammograms (CVs), especially for non-ideal voltammograms where no algebraic equation exists. This approach is compared to the extended Laviron's interaction model [8,9] and then to electrochemical data obtained from several electroactive SAMs.

2. Generalized lateral interaction model

In a previous work [8,9], we have presented a theoretical study to complete the lateral interaction model proposed by E. Laviron [10], by extending this initial model to non-random distributions of electroactive sites adsorbed on surface. This model enables current–voltage behaviors to be simulated and allows extracting characteristic parameters of cyclic voltammograms (CVs) obtained from any surface distribution of electroactive SAM.

To summarize, the generalized lateral interaction model can be defined according to the main following hypotheses [9–12]:

- The electroactive centers are distributed on substrate with a unimodal statistical distribution of electroactive neighbors. A parameter $\phi(\theta)$, between 0 and 1, defined for a normalized surface coverage θ, quantifies the segregation level of the electroactive centers. 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 ($k_s \rightarrow \infty$), CVs are reversible, and the characteristic parameters such as full width at half maximum (FWHM), peak potential E_p and peak current i_p are defined as:

$$E_p(\phi(\theta)) = E'_0 + \frac{RT}{nF} S\phi(\theta) \quad (1)$$

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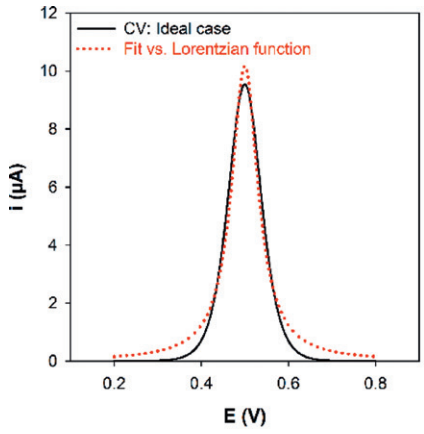
$$\mathrm{FWHM}(\phi(\theta)) = \frac{2\ RT}{nF}\left[\ln\left(\frac{1+\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}}{1-\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}}\right) - G\sqrt{\frac{2-G\phi(\theta)}{4-G\phi(\theta)}}\phi(\theta)\right] \overset{|G\phi(\theta)<1|}{\approx} \frac{RT}{nF}\left(2\ln\left(2\sqrt{2}+3\right)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

$$i_p(\phi(\theta)) = \frac{n^2 F^2 v A \Gamma_{max}}{RT}\frac{\theta}{2(2-G\phi(\theta))} \quad (3)$$

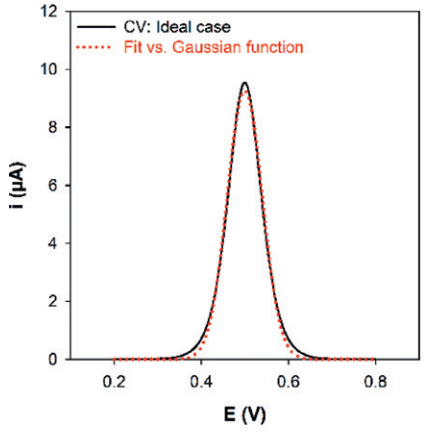
with, $G = a_{OO} + a_{RR} - 2a_{OR}$ et $S = a_{RR} - a_{OO}$ ($|G|$ and $|S| \leq 2$) G and S play a primordial role and can be defined as "interaction" parameters of O and R, respectively.

The parameter G defines the shape of the peak (FWHM) and the peak intensity (i_p) and the parameter S, the peak potential (E_p) as a function of θ.



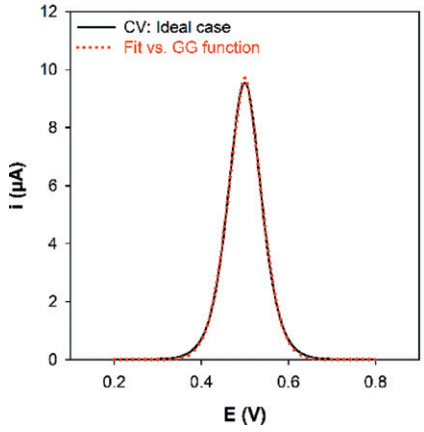
(A)

$$f\ E = \frac{a}{\pi b.\left[1+\left(\frac{E-E_0}{b}\right)^2\right]} \quad with \begin{cases} E_0 \\ FWHM = 2.b \\ i = \frac{a}{\pi b} \\ \Gamma_{SG} = \frac{a}{n\ F\ S\ v} \end{cases}$$



(B)

$$f\ E = \frac{a}{b.\sqrt{\pi}}e^{-\left(\frac{|E-E_0|}{b}\right)^2} \quad with \begin{cases} E_0 \\ FWHM = 2.b.\sqrt{\ln\ 2} \\ i = \frac{a}{b.\sqrt{2\pi}} \\ \Gamma_{SG} = \frac{a}{n\ F\ S\ v} \end{cases}$$



(C)

$$f\ E = \frac{a.c}{2.b.\Gamma\ 1/c}e^{-\left(\frac{|E-E_0|}{b}\right)^c} \quad with \begin{cases} E_0 \\ FWHM = 2.b.\left[\ln\ 2\right]^{\frac{1}{c}} \\ i = \frac{a.c}{2.b.\Gamma\ 1/c} \\ \Gamma_{SG} = \frac{a}{n\ F\ S\ v} \end{cases}$$

Fig. 1. A comparison of peak fitting from an ideal CV (n = 1, k = 1000 s^{-1}, E_0 = 0.500 V, T = 293 K, v = 0.1 V·s^{-1}, A = 0.2 cm^2, FWHM = 0.089 V and $\Gamma_{SG} = 5.00 \cdot 10^{-10}$ mol·cm^{-2}). (A) Fit vs. Lorentzian function (3 unknown parameters): E_0 = 0.500 V, FWHM = 0.074 V and $\Gamma_{SG} = 6.15\ 10^{-10}$ mol.cm^{-2}. (B) Fit vs. a Gaussian function (3 unknown parameters): E_0 = 0.500 V, FWHM = 0.095 V and $\Gamma_{SG} = 4.85 \cdot 10^{-10}$ mol·cm^{-2}. (C) Fit vs. a GG function (4 unknown parameters): E_0 = 0.500 V, FWHM = 0.088 V and $\Gamma_{SG} = 4.95 \cdot 10^{-10}$ mol·cm^{-2}. Note that E_0 = 0.500 V, FWHM = 0.086 V and $\Gamma_{SG} = 5.02 \cdot 10^{-10}$ mol·cm^{-2} for a GG function at 3 unknown parameters.