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# Phase segregation on electroactive mixed SAMs: a numerical approach for describing interactions

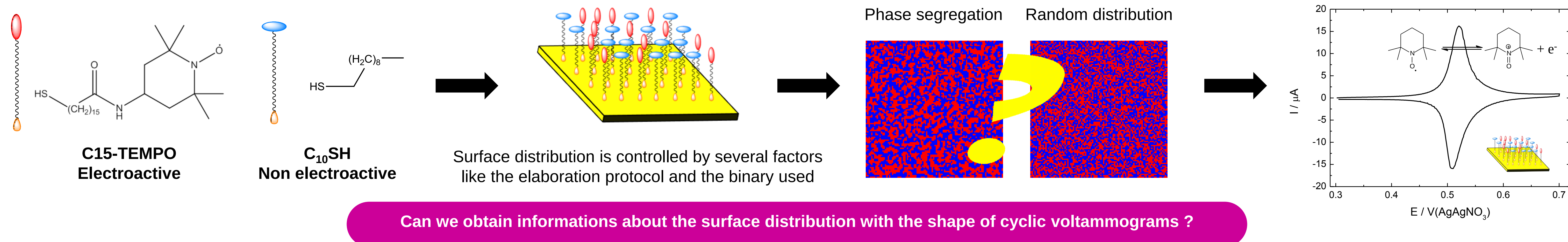
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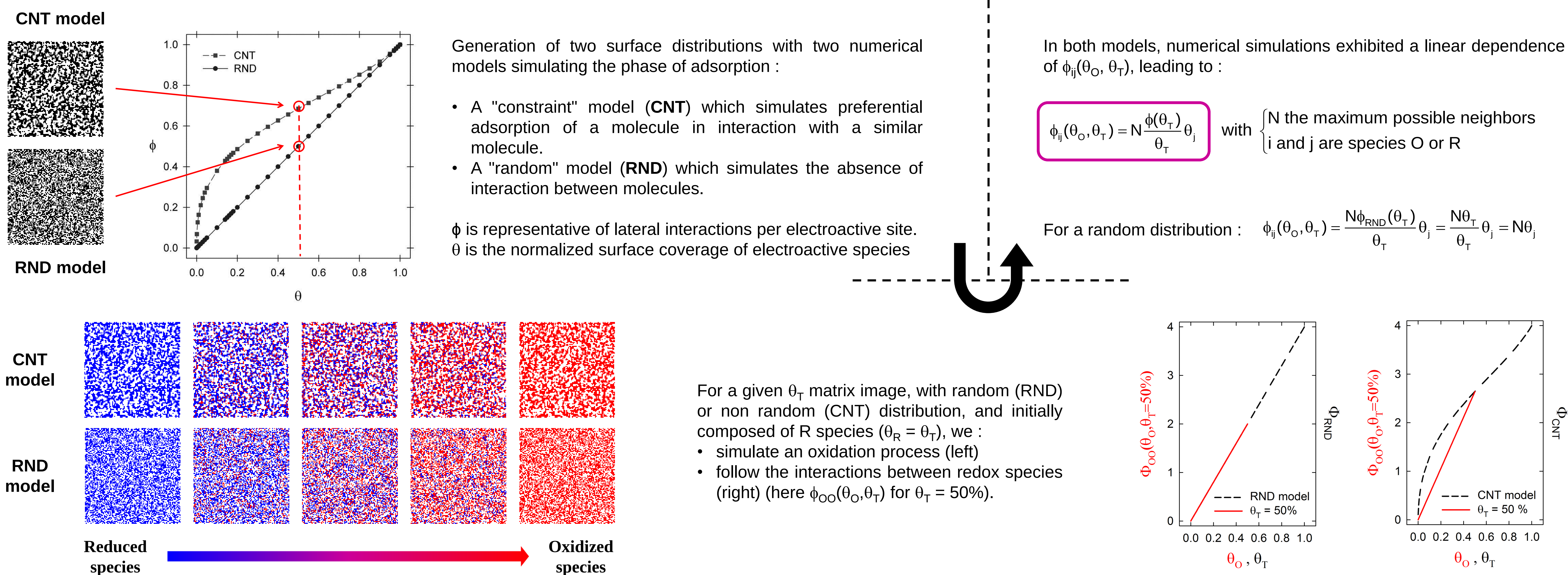
The Laviron's interaction model, dedicated to randomly distributed electroactive adsorbed species, was extended to a non-random distribution in order to extract the current-voltage characteristics from any surface distribution of electroactive centers on self-assembled monolayer (SAM). Confronted to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

## Nitroxyl radical self-assembled monolayers on gold



## Generalization of Lateral Interaction Model for any surface distribution

### FIRST STEP : NUMERICAL MODEL



### SECOND STEP : GENERALIZATION OF THE MODEL

$$\begin{cases}
 i(t) = nFAk_s \Gamma_{\max} \left[ \theta_O(t) \eta^{-\alpha} \exp \left[ -2a_{OO} \frac{\phi(\theta_T)}{\theta_T} \theta_O(t) - 2a_{OR} \frac{\phi(\theta_T)}{\theta_T} \theta_R(t) \right] - \theta_R(t) \eta^{1-\alpha} \exp \left[ -2a_{RR} \frac{\phi(\theta_T)}{\theta_T} \theta_R(t) - 2a_{RO} \frac{\phi(\theta_T)}{\theta_T} \theta_O(t) \right] \right] \\
 i(t) = nFA \frac{d\Gamma_O}{dt} = nFA \Gamma_{\max} \frac{d\theta_O}{dt}
 \end{cases}$$

where  $\eta = \exp \left( nF \frac{(E - E^0)}{RT} \right)$  and  $E^0 = E_0 - \frac{RT}{nF} \ln \left( \frac{b_O}{b_R} \right)$

and  $n, F, A, R, k_s, T, E^0$  have their usual meanings.

We generalized the LAVIRON's interaction model by introducing the  $\phi$  parameter calculated in the first step.

$\theta_O$  and  $\theta_R$ , normalized surface coverage of oxidized and reduced species  
 $\theta_T = \theta_O + \theta_R$ , normalized surface coverage

$a_{OO}, a_{RR}, a_{OR}$  and  $a_{RO}$  are the interaction constants between molecules of O, molecules of R and molecules of O and R respectively.

$a_i$  is positive for an attraction and negative for a repulsion. The  $a$  values are assumed to be independent of the potential.

$\phi(\theta_T)$ , "segregation factor", is representative of the average number of lateral interactions per electroactive site

For a fast reversible system ( $k_s = \infty$ ), the  $i$ - $E$  characteristics can be expressed as :

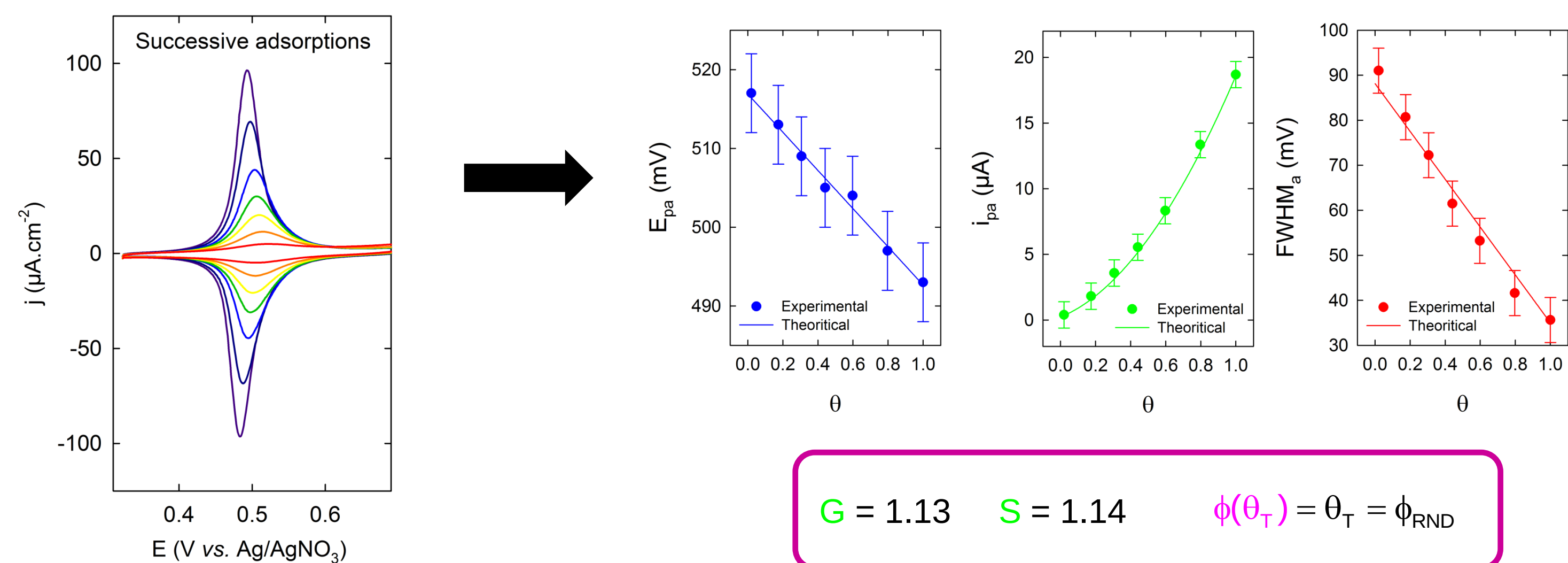
$$\begin{aligned}
 E_p(\theta_T) &= E^0 - \frac{RT}{nF} S \phi(\theta_T) \\
 i_p(\theta_T) &= \frac{n^2 F^2 v A \Gamma_{\max}}{RT} \frac{\theta_T}{2(2 - G \phi(\theta_T))} \\
 FWHM(\theta_T) &\approx \frac{RT}{nF} \left[ 2 \ln(2\sqrt{2} + 3) - \frac{3\sqrt{2}}{2} G \phi(\theta_T) \right]
 \end{aligned}$$

with  $G = a_{OO} + a_{RR} - a_{OR} - a_{RO}$  and  $S = a_{OO} - a_{RR} + a_{OR} - a_{RO}$

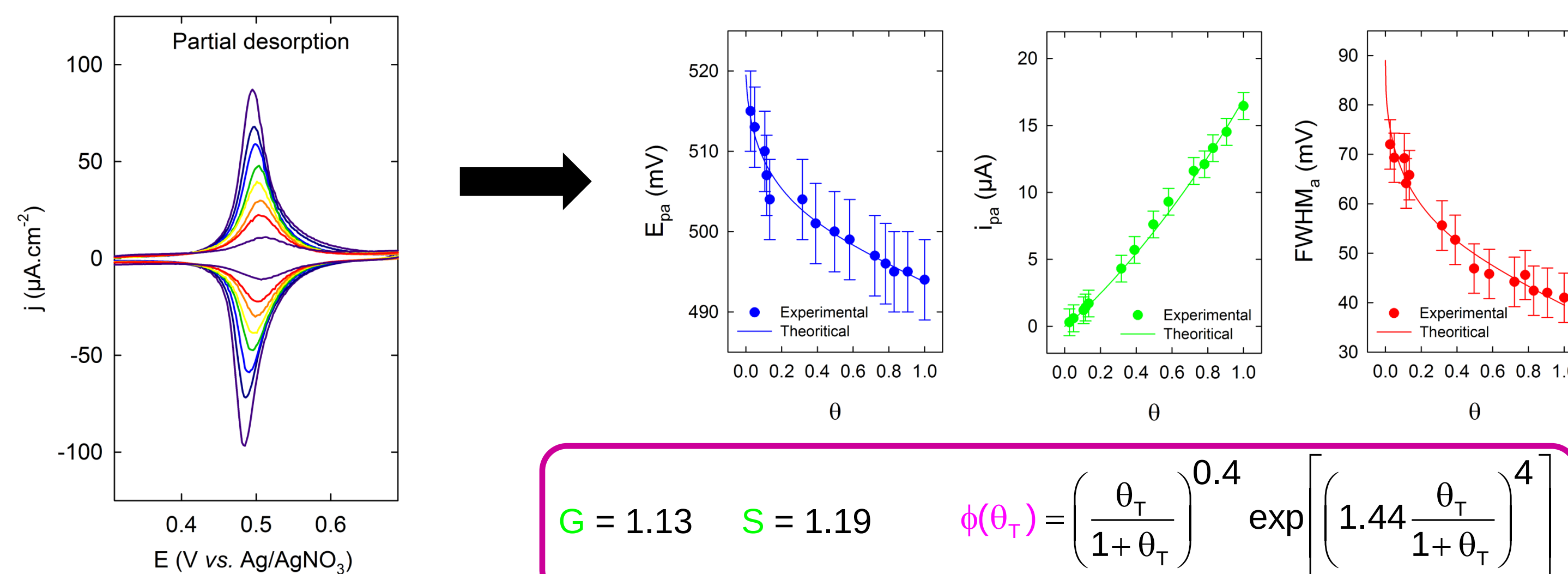
## Application

In order to test this new model, we elaborate C15-TEMPO mixed SAMs using two protocols leading to two surface distributions.

Successive adsorptions of C15-TEMPO and C<sub>10</sub>SH  
 Favors random distribution



Partial desorption of a densely packed SAM of C15-TEMPO under ultrasonication  
 Favors surface segregation



Distribution independence of G and S parameters. The surface distribution  $\phi$  can be deduced with the shape of cyclic voltammograms.