Cyclic Voltammetric Model and Simulation of Inert, Graded Density Films on Electrodes

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A computer simulation and diagnostics for cyclic voltammetric responses of redox probes that permeate inert, thin films of graded density are provided. Applications for film characterization include electroactive films analyzed in a nonelectroactive potential window. Control of the diffusion profile by a density gradient could provide a new approach for research in pharmaceutical drug delivery matrices and fuel cell mass transport.

The density profile of a film can affect the kinetics, equilibria, and mass transport of an electrochemical reaction by changing how the electroactive species approaches the electrode surface. The diffusion of molecules through a variety of polymer films with uniform density has been studied extensively, and cyclic voltammetric diagnostics for inert, uniform density films on electrodes have been established.[1] However, diffusion through films with a graded density remains uncharacterized. A density graded film on an electrode in which the highest density is at the electrode film interface and the lowest density is at the film solution interface induces passive, near steady state transport of the electroactive species through the film to the electrode.
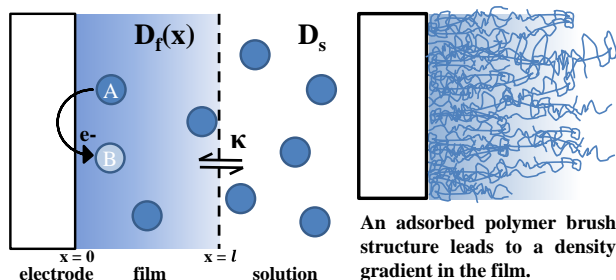

Figure 1. Redox probe A with diffusion coefficient D_S in solution extracts across a density graded film. Extraction is characterized by the extraction parameter κ. A diffuses in the film with diffusion coefficient $D_f(x)$ and undergoes a reversible heterogeneous electron transfer reaction at the electrode to become B. $D_f(x)$ is defined in Equation 4. B has the same κ, D_S, and $D_f(x)$ as A.

The diffusion coefficient D of a probe through a particular density of polymer can be related to the viscosity η of the polymer by the Einstein Smoluchowski relation for ion mobility and Stoke's Law for the drag coefficient through a low Reynolds number medium; k_B is Boltzmann's constant, T is absolute temperature, and r is the radius of the probe.[2]

$$D = \frac{k_B T}{6\pi\eta r} \tag{1}$$

In the case of the proposed density graded film, as the scan rate slows, flux approximates a steady state and the cyclic voltammogram approaches a sigmoidal shape. For a density gradient in which the highest density is at the film solution interface, the cyclic voltammogram approaches a Gaussian shape and flux approximates a thin layer case with slower scan rate. Simulated examples are provided in Figure 2.
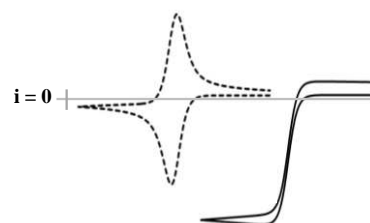

Figure 2. Simulated cyclic voltammograms of reversible redox probe at graded density film modified electrodes. For highest density at film solution interface, shape approaches Gaussian (dashed line). For highest density at electrode film interface, shape approaches sigmoidal (solid line). Current is dimensionless.

A computer simulation was developed using well-established finite difference methods.[3] The system is specified by partial differential equations, explicitly expressed by finite difference. In the simulation, redox probes pre-equilibrate in the film, extract at the film solution interface, and diffuse to the electrode to undergo heterogeneous electron transfer. Inert films are not electroactive in the probe electrolysis window.

An expanded version of Fick's second law, which takes into account spatial variation, elucidates the changes in current as related to the diffusion coefficient gradient.

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(x)\frac{\partial(x,t)}{\partial x}\right] \tag{2}$$

$$\frac{\partial c(x,t)}{\partial t} = D(x)\frac{\partial^2 c(x,t)}{\partial x^2} + \frac{\partial D(x)}{\partial x}\frac{\partial c(x,t)}{\partial x} \tag{3}$$

$D(x)$ can be described by any equation, dependent on the characteristics of the film. Here, the density of the film is assumed to vary linearly for the purpose of simplicity. D_0 is the diffusion coefficient in the film at the electrode surface, D_s is the diffusion coefficient in solution, and ℓ is the film thickness.

$$D(x) = D_s \pm ax\frac{D_0 - D_s}{\ell} \tag{4}$$

The simulation and diagnostics are vetted with experimental data[4] for tetramethyl phenylenediamine (TMPD) in Ficoll®. Ficoll is a synthetic copolymer of epichlorohydrin and sucrose that forms a graded density film. As shown in Figure 3, cyclic voltammogram morphologies approach sigmoidal as scan rate slows.
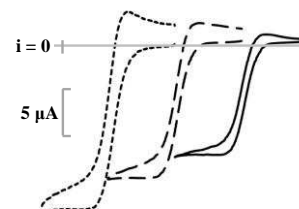

Figure 3. Cyclic voltammograms of 0.1 mM TMPD (in acetonitrile, 0.1 M TBABF₄ electrolyte) at a Ficoll film modified electrode for scan rates 200, 20, and 2 mV/s, from left to right. Potential scanned from -0.1 to 0.5 V vs Ag/AgO QRE.

1. Knoche, K. L.; Hettige, C.; Moberg, P. D.; Amarasinghe, S.; Leddy, J., Cyclic Voltammetric Diagnostics for Inert, Uniform Density Films. Submitted to Anal Chem **2012**.
2. Israelachvili, J., Intermolecular and Surface Forces. 2nd ed.; Academic Press: London, 1992.
3. Bard, A. J.; Faulkner, L. R., Electrochemical Methods, Fundamentals, and Applications. 2 ed.; John Wiley & Sons, Inc: New York, 2001.
4. Knoche, K. L.; Moberg, P. D.; Leddy, J., Graded Density Films: Cyclic Voltammetry of Ficoll Modified Electrodes. In preparation **2012**.