Measurement of Apparent Diffusion Coefficients within Ultra-thin Nafion Langmuir-Schaefer Films: Comparison of a Novel Scanning Electrochemical Microscopy Approach with Cyclic Voltammetry

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Supporting Information



S1. Pressure-area isotherm of Nafion on a 0.1 M NaCl subphase; barrier speed: $100 \text{ cm}^2 \text{ min}^{-1}$.



S2. CVs of a 20-layer Nafion LS film during loading in 10^{-3} M FA⁺ (0.1 M NaCl supporting electrolyte). The scan rate was 0.05 V s⁻¹; 100 cycles.



S3. CVs of a 20-layer Nafion LS film during loading in 10^{-3} M Ru(bpy)₃²⁺ (0.1 M NaCl supporting electrolyte). The scan rate was 0.05 V s⁻¹; 100 cycles.

The concentrations of the electroactive species inside the Nafion films were calculated based on the relation [1]:

$$i = (9.39 \ 10^5) \ v \ V \ C_0 *$$

where *v* is the scan rate (V s⁻¹), *V* is the volume of the film (cm³) and C_0^* the concentration of FA⁺ within Nafion film. The number of the moles incorporated in the film, *m*, is given by the product of the volume of the film and the concentration of the electroactive species inside the film:

 $m = V C_0^*$

For reversible redox couples like FA⁺ incorporated inside Nafion LS films, the slope of the anodic current I_{pa} vs $v^{1/2}$ plot in the diffusion controlled region obeys the Randles-Sevcik equation [1]. When linear, the slope of these plots, *S*, combined with the films thickness, Φ (estimated by AFM), and amount of electroactive species (obtained by coulometric integration of the anodic peak current under thin-layer conditions) allows the evaluation of the apparent diffusion coefficient values within the coating based on the equation [2]:

$$D_{app} = \left[\frac{S \cdot \Phi}{(2.69 \cdot 10^5) \cdot m}\right]^2$$



S5. Steady-state cyclic voltammogram measured at a 25 μ m diameter UME in a solution containing 10⁻³ M FA⁺ and 0.1 M NaCl as supporting electrolyte; scan rate of 0.5 mV s⁻¹.

The diffusion coefficient was calculated from the limiting current of a steady-state voltammogram for FA⁺ oxidation (for example, see S5). Measurements were repeated with 5 freshly-prepared solutions of 10^{-3} M FA⁺, supporting electrolyte 0.1 M NaCl. The measured diffusion coefficient for FA⁺ was 6.1 (± 0.1) x 10^{-6} cm² s⁻¹.

Bard, A.J and Faulkner L.R. *Electrochemical Methods: Fundamentals and Applications*, Ch. 6, p.226, Wiley, New York, 2nd Edition, 2001.
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