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 cm² 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 $\text{Ru(bpy)}_3^{2+}$ (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]:

\[ i = (9.39 \times 10^5) v V C_0^* \]

where \( v \) is the scan rate (V s\(^{-1}\)), \( V \) is the volume of the film (cm\(^3\)) 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, \( \Phi \) (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]:

\[
D_{app} = \left(\frac{S \cdot \Phi}{(2.69 \times 10^3) \cdot m}\right)^2
\]
S5. Steady-state cyclic voltammogram measured at a 25 µm 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} cm^2 s^{-1}.