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The Electron as a Probe to Measure the Thickness Distributions of Electroactive Films

Darren Buesen, Huaiguang Li, Nicolas Plumeré*

Electron conducting films are ubiquitous in applications such as energy conversion, and their ability to fulfill their catalytic function can be greatly limited by inhomogeneities in their thickness or breaks within the film. Knowing the electroactive film thickness distribution would greatly facilitate optimization efforts, but techniques to measure this are lacking. Here, we present an electroanalytical method that provides the thickness distribution of the electrochemically accessible fraction of redox-active films in which the transfer of electrons is diffusional, i.e. by electron hopping. In this method, as the time scale of the experiment (the scan rate) is changed, the location of the diffusion layer boundary relative to the film roughness features is varied, allowing for the extraction of the film thickness distribution. In addition to being conveniently carried out in the solvated state, which is often the operational state of these conductive films, this approach is highly complementary to classical microscopy methods since it samples the entire modified electrode and is specific to the electroactive portions of the film. Therefore, this approach provides information on film morphology that is truly relevant for the catalytic processes being optimized, and thus can guide the optimization of catalyst integration in films towards macroscale cohesion and thickness homogeneity which are essential for optimal performances.

Introduction

Redox-active or conductive films assembled from synthetic or natural materials are ubiquitous as matrices for the immobilization and electrical wiring of catalysts or of light absorbing materials for technological applications. The most prominent of these are thin films based on perovskites and organic semiconductors for photovoltaics, as well as inorganic catalysts for reactions such as proton reduction and water oxidation. In addition, redox films containing biological or molecular catalysts immobilized on electrode surfaces have found numerous applications in sensing and recently, have also attracted interest in energy conversion as well as in the electrosynthesis of small molecules.  

While design and optimization is often focused on the active components embedded within the film, the geometry and dimensions of the redox-active matrix also play a central role in the resultant catalytic or photoactive properties. For example, film thickness can be modulated to maximize the overall performance with respect to electron transfer, mass transport and catalyst loading and thus exploit catalytic systems to their full potential. Recently, the properties and thickness of a redox-active film were engineered to provide protection to sensitive catalysts and may eventually serve to control reaction selectivity by regulating the local supply of electrons and reactants. Theoretical models describing reaction/diffusion processes in these systems as well as mechanisms for protection with film thickness as a major design parameter, are in place to enable the rational optimization of their catalytic properties. The central role of film thickness also means that the homogeneity of its distribution will likewise have a major impact on catalytic performance. For instance, a film with a highly heterogeneous thickness is detrimental because it may include areas where mass transport is limiting the catalytic performances due to excessive thickness, while on other areas of the same electrode, the catalyst loading may be limiting due to insufficient thickness. Therefore, for the optimization of such films, the homogeneity of the electroactive film thickness must be known.

A variety of confocal or atomic force microscopy (AFM) methods exists to characterize film morphology. However, these methods are often too complex for routine implementation or deliver only partial information. For instance, AFM is often applied, but only yields the top roughness of the sampled fraction of the film. Estimation of the thickness distribution is possible through profile measurements, but this requires partial film removal as an additional destructive step. Moreover, essential information, such as the thickness distribution of the electroactive fraction of the film, which is most relevant for electrocatalytic or light-induced charge transfer processes, remains inaccessible through AFM or confocal microscopy investigations.

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Here, we propose a straightforward and non-destructive electroanalytical method, based on linear sweep voltammetry, that delivers the electroactive film thickness distribution directly, and under the conditions relevant for the catalytic processes being optimized. Since the films under consideration for these applications are intrinsically electron conducting, we can use the electron as a probe for quantifying the locations of the film boundaries with respect to the electrode. Within redox-active films, electrons are transported by a hopping mechanism between the tethered redox moieties at a rate which is defined by the apparent diffusion coefficient of the electron $D$. For a given time scale ($\delta$) defined by the scan rate ($v$), the electron will travel a distance determined by the diffusion layer thickness ($\delta$) defined as $\delta = (D\cdot\delta)^{1/2} = (DRT/nFv)^{1/2}$. The key feature of our method is that the current response related to the electron transfer within the film depends on the relative dimension of $\delta$ with respect to the film thickness $d$ (Figure 1). In contrast to a smooth film (Figure 1A), the time scale window corresponding to $\delta$ values that reaches the outermost film boundaries is larger for rough films (Figure 1B). Accordingly, the current response for a rough film deviates from the one obtained for a smooth film (Figure 1C and 1D).

We exploit these deviations in peak currents obtained from linear sweep voltammograms to directly quantify the film thickness distribution. We demonstrate that the arrangement of the surface features does not significantly impact the accuracy of the thickness distribution determination when counter-ion transport is non-limiting. Major advantages of using this electrochemical method include i) its simplicity, since only voltammetric measurements are required, ii) its scope, since the thickness distribution is obtained for the entire film in contrast to a limited sampled area, and iii) its relevance to the intended electrocatalytic application, since it specifically probes the electroactive fraction of the film.

The Model

Linear sweep voltammetry with normalized parameters and a characteristic plot

For the case of planar diffusion in a perfectly smooth film, the theoretical position of the diffusion layer thickness ($\delta$) with respect to the film thickness ($d$) can be expressed in terms of a dimensionless parameter ($w^{1/2}$) according to equation (1). Since $w^{1/2}$ is proportional to $v^{1/2}$, $w^{1/2}$ can be regarded as a normalization of the square root of the scan rate.

$$ w^{1/2} = \frac{d}{\delta} = \frac{d}{\sqrt{DB}} = \frac{v}{(RT/nF) \cdot D}^{1/2} \quad (1) $$

$R$ is the gas constant, $T$ is the temperature, $F$ is the Faraday constant and $n$ is the number of electrons exchanged. The peak current ($i$) obtained at a given scan rate is normalized according to equation (2), and can be plotted against the dimensionless parameter ($w^{1/2}$), given by equation (1), to prepare the characteristic plot for this system.

$$ i_{p,n} = \frac{i_p}{nFAR(T/nF)^{-1/2}CD^{1/2}v^{1/2}} \quad (2) $$

$A$ is the surface area of the electrode and $C$ is the concentration of the redox-active species within the film. Although there are several variables in these expressions, a plot of $i_{p,n}$ vs $w^{1/2}$ can be regarded as essentially the normalization of an $i_p/v^{1/2}$ vs $v^{1/2}$ plot (Figure 1D).

Weibull distribution for the parameterization of film thickness variations

We use the Weibull distribution for the parameterization of film thickness distributions due to its ability to characterize films with extremely high inhomogeneity. The Weibull distribution is usually given as a shape factor (SF) which directly correlates with the relative standard deviation of the film thickness (see details in SI section S1). Low values of the shape factor correspond to high relative standard deviations. Therefore, low shape factors correspond to rough films, and high shape factors correspond to smooth films.

The deconstruction method for a planar electron diffusion reference
A straightforward approach for the prediction of the peak current for a rough film is to "deconstruct" it into a series of independent and perfectly smooth film sub-sections (Figure 2A).

The underlying assumption of planar (one-dimensional) electron transfer within each sub-section allows for the use of the algebraic equation for the peak current for a smooth film\(^2\) (Equation S2) for each of the sections, and then for the total current to be determined by taking the average. The theoretical electrochemical response of a perfectly smooth film in a LSV experiment was previously solved analytically using the Laplace Transform technique, resulting in integral equations for the theoretical LSV current-potential curves.\(^2\) This includes an algebraic expression for the peak current vs \(w^{1/2}\) for a series of shape factor values between 0.20 and 100, showing a systematic deviation from the results for a smooth film (uppermost curve) as the films become increasingly rough (decreasing shape factor values). (C) Normalized peak currents at \(w^{1/2} = 2\) (blue dashed line in panel B) plotted vs the Weibull distribution shape factor. This correlation enables for straightforward determination of the thickness distribution from the current response. (D) Predicted LSVs calculated from FEM for a series of shape factors (100, 2, 1, and 0.75) at \(w^{1/2} = 2\). The blue dots in figures (B) and (C) correspond to the normalized peak current from the LSVs shown in figure (D).

The finite element method for the time and space dependent concentration profiles

The finite element method\(^2\) (FEM), was used by means of the Matlab\(^\circledR\) Differential Equations Toolbox to account for edge effects and non-planar diffusion. In contrast to the deconstruction method, in which the film is represented as a series of independent sections, the finite element method treats the entire film as one complete piece. In this approach, the time and space-dependent concentration profiles within the film are determined by solution of a partial differential equation (3), where the value for \(w^{1/2}\) from the problem for smooth films is replaced by \(w^{1/2}_{avg}\) according to equation (4), because the characteristic film thickness \(d\) is now the average film thickness \(d_{avg}\):

\[
\frac{\partial C_r}{\partial t} = \frac{\partial^2 C_r}{\partial x^2} + \frac{\partial^2 C_r}{\partial y^2} \tag{3}
\]

\[
w^{1/2}_{avg} = d_{avg}\left[\frac{v}{(RT/nF) \cdot D}\right]^{1/2} \tag{4}
\]

\[
i = \frac{1}{w^{1/2}_{avg} \cdot g_{th}} \int_0^{g_{th}} \frac{\partial C_r}{\partial y} \bigg|_{y=0}^{y=g_{th}} \ dx \tag{5}
\]

For each time point, the current was calculated by evaluating the concentration gradient at the electrode surface \((C_r\) is the concentration of the reduced form of the redox species within the film) and integrating the result according to equation (5), where \((g_{th})\) is the geometric length to height ratio of the film. The complete dimensionless formulation of the problem, as well as additional details regarding the finite element method implementation are included in the SI sections S3 and S4.

Results and discussion

Fig. 2: Film thickness distribution determination by the deconstruction method. A) Schematic illustration showing the “deconstruction” of a rough film (the shape factor is 2.5) into a series of individually independent smooth films. (B) Calculated normalized peak current vs \(w^{1/2}\) for a series of shape factor values between 0.20 and 100, showing a systematic deviation from the results for a smooth film (uppermost curve) as the films become increasingly rough (decreasing shape factor values). (C) Normalized peak currents at \(w^{1/2} = 2\) (blue dashed line in panel B) plotted vs the Weibull distribution shape factor. This correlation enables for straightforward determination of the thickness distribution from the current response. (D) Predicted LSVs calculated from FEM for a series of shape factors (100, 2, 1, and 0.75) at \(w^{1/2} = 2\). The blue dots in figures (B) and (C) correspond to the normalized peak current from the LSVs shown in figure (D).
The transition between the linear and plateau regime holds the factors from 100 to 3.5 in Figure 2B. The values also eventually reach the plateau for all other shape factors at high values. The electrons do not reach any of the boundaries of the film, whether the film thickness is 0.2–100. The resulting vs plot (Figure 2B) displays a similar trend for all shape factors. At low values, is proportional to within the linear region, the peak currents at a given high value at a reference line at (Figure 2C). In addition, FEM was used to calculate the entire LSVs for visualization of the effect of the shape factor (Figure 2D). Beside the peak current that decreases as the shape factor decreases, also the shape of the entire LSV changes when varying the shape factor while all other parameters are kept unchanged.

**Figure 1: Film thickness distribution determination by the Finite Element Method.** (A) Evidence for the presence of hemispherical diffusion from the curvature in the concentration profile and (B) from the concentration gradient flow for a film with sub-thicknesses arranged in an ascending order. (C) Concentration profile for the arrangements that minimize and (D) maximizes the contribution from hemispherical diffusion. (E) Normalized peak currents for various arrangements of 100 film sub-sections shuffled randomly, starting from either the most ordered arrangement (blue points), the most disordered arrangement (red points), or from the random arrangement (black points), in order to cover the entire range of possible degrees of disorder. The perimeter for each arrangement is normalized with respect to the minimum possible perimeter. The deconstruction result is shown as a dashed black line. (F) Correlation between the normalized peak currents and the Weibull distribution shape factor obtained from FEM in which deconstruction was used as an internal standard. Arrangements corresponding to the minimum and maximum of the plot in (E), shown in (C) and (D) respectively, and highlighted with green arrows in (E), were used for the construction of the upper and lower limits of the correlation shown in (F) as black dashed lines; the solid blue line is the average of these two results. An enlarged version of panel 3F is given in Figure S11. For panels (A)-(E), the shape factor was 1.5. Counter-ion transport is assumed to be non-limiting.

**Normalized peak current plots for films of increasing inhomogeneity in their thickness**

Prediction of the peak current for a given experimental time scale was carried out with the deconstruction method (Figure 2A), using 50000 film subsections, for a series of shape factors in the range of 0.2–100. The resulting vs plot (Figure 2B) displays a similar trend for all shape factors. At low values, is proportional to within the linear region, the peak currents at a given high value at a reference line at (Figure 2C). In addition, FEM was used to calculate the entire LSVs for visualization of the effect of the shape factor (Figure 2D). Beside the peak current that decreases as the shape factor decreases, also the shape of the entire LSV changes when varying the shape factor while all other parameters are kept unchanged.

**Quantitative evaluation of hemispherical diffusion contributions**

Although the calculation procedure afforded by the deconstruction method is especially fast and convenient to obtain the normalized peak current variation as a function of normalized scan-rate (vs plot), the accuracy of the resulting film thickness distribution is bound to the assumption of planar electron diffusion through the film. In order to quantitatively account for the contribution of hemispherical electron diffusion, the finite element method (FEM) was used for generating the concentration profiles and gradients at...
the time of peak current for a film thickness distribution with a shape factor of 1.5 (Figure 3). This shape factor was selected because the effects of hemispherical diffusion were greatest at this value, according to the comparison of deconstruction and FEM results for the entire range of Weibull distribution shape factors (see details in SI section S5.2).

The film sub-sections were first ordered in an ascending order to reveal insights into the contour line curvature. For the case of planar electron transfer, the contour lines of the concentration profile would be entirely flat throughout the film. Instead, the concentration profile for the ordered arrangement (Figure 3A) revealed curvature, which can be attributed to contributions from hemispherical diffusion. This was confirmed by the non-planar direction of the electron flow depicted in the flow profile (Figure 3B). Moreover, comparison of the concentration profile from an arrangement having a strong planar diffusion character (Figure 3C) with the one from a highly disordered arrangement having strong hemispherical character (Figure 3D) showed substantial differences in their curvatures. This qualitatively demonstrates that film sub-section arrangements have an impact on the resulting electron-transfer within the film. This implies that the various possible arrangements of the film sub-sections for a single thickness distribution affect the resulting normalized peak currents from which the shape factor is extracted.

For a quantitative evaluation of the effect of film sub-section arrangement on the resulting hemispherical diffusion, a set of 100 sub-sections for a film with a shape factor of 1.5 was generated and shuffled randomly between two extreme configurations containing minimum and maximum disorder (Figure 3E). The objective was to identify the minimum and maximum \( i_{p,n} \) values obtained for a given shape factor as a function of the arrangement and, by extension, the minimum and maximum thickness distribution values related to these \( i_{p,n} \) values. The normalized peak currents were calculated and plotted versus the normalized total perimeter, which was used as a general measure of film sub-section disorder. The minimum \( i_{p,n} \) value (0.320) was obtained from a cluster of values with a perimeter ratio of 2.6, while the maximum \( i_{p,n} \) (0.334) was derived from a cluster of values with a perimeter ratio of 8.7. The minimum value, being closest to the deconstruction result (black dashed line in Figure 3E), represents the film configuration that corresponds to a condition of mostly planar diffusion, and the maximum value represents the film configuration that corresponds to a maximum contribution from hemispherical diffusion.

Through these calculations, the impact of hemispherical diffusion on \( i_{p,n} \) was quantified, allowing for the calculation of a correlation between \( i_{p,n} \) and shape factor based on FEM results that includes lower and upper confidence limits. For the calculation of these limits, one representative configuration from the minimum and maximum value clusters was identified (Figure 3C and 3D). Then, for each shape...
factor, the sampled sub-sections were rearranged according to these limiting configurations before calculation of the \( i_{p,n} \) values by FEM, and the difference between this result and the deconstruction result (which was used as an internal standard that depends on planar diffusion only), was used to add lower and upper limits to the correlation (Figure 3F). The average of the two results is reported as the center line. Probability distribution functions (PDFs) at the lower and upper limits at three points in the correlation (nominal shape factor = 0.5, 1.5, and 7.0) were compared to the PDFs corresponding to the mean values and did not look substantially different (See SI section S5.3). This means that although the film sub-section arrangement impacts the peak current and thus the resulting film thickness distribution value, it remains relatively minor.

While it is possible to determine the shape factor (and therefore the distribution) using only the value of \( i_{p,n} \) at \( w_{avg}^{1/2} = 2 \) (Figure 3F), a peak current overlay plot similar to that of Figure 2B, but which uses FEM and deconstruction was calculated (Figure S9) to enable extraction of the shape factor using \( i_{p,n} \) values at any \( w_{avg}^{1/2} \) values in the transition region. This is useful when the exact value of \( i_{p,n} \) at \( w_{avg}^{1/2} = 2 \) is not available experimentally (the exact value of the scan rate corresponding to \( w_{avg}^{1/2} = 2 \) cannot be predicted beforehand since the values of \( d_{avg} \) is typically unknown, see equation 4). In Figure S11, deconstruction was used for shape factors below 0.75 and FEM was used for shape factors 0.75 and greater. This was possible because the average FEM values (when using deconstruction as an internal standard) were the same as the deconstruction values for shape factors below 0.75 (see SI figure S8 and SI section S5.4). Physically, this means that the effects of hemispherical diffusion are negligible for shape factors below 0.75.

**Experimental example and comparison with AFM**

As an experimental example showing the usefulness of the electroanalytical approach, as well as its complementarity with AFM, both methods were applied for the characterization of redox-active films assembled from viologen modified macromolecules. We compare previously reported data\(^{20}\) for smooth films (Figure 4) assembled from the drop-casting of viologen-modified dendrimers (Figure 4A) as well as for rough films (Figure 5) made from the drop-casting of viologen-modified polymers (Figure 5A).

Optical microscopy of the smooth film revealed surface homogeneity over a large area (Figure 4B), which was confirmed by AFM on a smaller sampled area (Figure 4C). The probability distribution function of the surface height (Figure 4D) and roughness parameters were calculated using Gwyddion software.\(^{25}\) The average value of the surface height is 0.75 µm and the root mean square roughness is 0.20 µm. For electrochemical determination of the thickness distribution, the peak currents were extracted from both the anodic and cathodic scans of the cyclic voltammograms obtained for the same redox film at various scan rates (Figure 4E). The normalized dimensionless peak values obtained according to equation (2), are

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**Figure 5: Comparison of electrochemistry and AFM results for a rough polymer film.**

(A) Structure of the viologen modified polymer used for film assembly by means of drop-casting. (B) Optical microscope image with the approximate area imaged by AFM framed in orange, (C) AFM image (bottom panel) with line scan (upper panel), and (D) resulting surface height distribution based on AFM (See SI Section S1.1 for definition of the probability variable), (E) Linear sweep voltammograms at increasing scan rates (from 2 to 700 mV s\(^{-1}\)). (F) The corresponding normalized peak current plot generated using the peak currents from the LSVs in (D) (open dots) and theoretical \( i_{p,n} \) vs \( w_{avg}^{1/2} \) curve for a perfectly smooth film (solid line). The plot is depicted with both dimensionless (bottom x axis and left y axis, black) and dimensional (top x axis and right y axis, blue) axes. (G) Normalized film thickness distribution resulting from the LSV measurements (bottom x axis and left y axis, black) and the corresponding absolute film thickness distribution obtained by multiplying with the film thickness (top x axis and right y axis, blue). The experimental data are from reference (20).
plotted against the normalized scan-rates obtained according to equation (4) (Figure 4F). The experimental data are in close agreement with the theoretical ip,n vs W1/2 avg plot (blue trace) expected for a perfectly homogenous film. Using the ip,n value at W1/2 avg = 2, a Weibull distribution shape factor value of 14 was directly determined based on the correlation given in Figure 3F and was used to generate the probability distribution function (See Section SI 1.1) shown in Figure 4G (black trace). The relative standard deviation for the thickness distribution of the electroactive fraction of the film obtained directly from the shape factor (Figure S11) was 9 %.

In the case of this smooth film, both of the limiting regions (the linear dependence at low scan-rate and the plateau at high scan rate) are experimentally accessible (Figure 4F). Information from the two limiting regions (the slope at low scan-rates and the plateau value at high scan-rates) were used for the determination of two combinations of variables (davg/D1/2 and CD1/2) which can be used to convert the ip/nb1/2 vs V1/2 plot to the normalized plot of ip,n vs W1/2 avg (see SI section S6.1). This means that the peak currents from the voltammetric measurements alone directly enable the determination of the film thickness distribution without the need to determine any of the individual parameter used for normalization of the peak current and of the scan rate. An additional benefit from the determination of the film thickness distribution being independent of film parameters such as D, davg, and C is that the method is independent of the electrolyte composition which may impact the latter film parameters.

Knowledge of D is however useful for extracting the absolute film thickness davg from the electrochemical data according to a previously reported method24 or more conveniently from the intersection of the extrapolated plateau and linear region in Figure 5F (See SI section S6.2). In the case of this particular film based on redox-active dendrimers, the value of D was determined previously.25 The resulting davg value extracted from the electrochemical data is 1.2 µm and was used to dimensionalize the probability distribution function of the film thickness (Figure 4G). To allow for a direct comparison with AFM surface measurements, the film thickness distribution can be further converted to a dimensional surface distribution (see SI Section S1.1). The resulting average surface height value (0.88 µm) and the root mean square roughness (0.10 µm) are in good agreement with the corresponding values obtained from AFM considering the different characterization conditions (dry vs solvated state).

One additional parameter of interest is the resolution of the electrochemical method. This was determined by analyzing the variations of the electrochemistry derived film thickness distributions (relative standard deviation of the film thickness). After preparation of a single smooth film, a series of nine successive CVs (Figure S10) were taken at a scan rate corresponding to W1/2 avg = 2 for this film preparation (V = 10 mV s−1). Data treatment for each CV was then performed separately, resulting in a series of nine individual shape factor determinations with their corresponding normalized RSD values. The standard deviation of these nine RSD values was found to be 1% (Table S1).

In the case of rough films (Figure 5) with very low shape factors, the two limiting regimes for the experimental ip,n vs W1/2 avg plot may not be accessible. This is illustrated with the example based on the film fabricated through drop-casting of a viologen modified polymer. Both the optical images (Figure 5B) and the AFM images (Figure 5C) revealed the presence of large aggregates of polymer. The probability distribution function of the height features on the surface was subsequently extracted using Gwydion software26 (Figure 5D). The average value of the surface height is 0.31 µm and the root mean square roughness is 0.17 µm. The cyclic voltammetry measurements of this same film (Figure 5E) were used for extraction of the peak currents and for construction of the experimental ip,n vs W1/2 avg plot (Figure 5F). Both the linear region and the plateau were not accessible experimentally via the scan rate. Nevertheless, the transition region was sufficient for the determination of the film thickness distribution because the normalization of ip,n and W1/2 avg can be performed independently. To this end, the values of D, davg, and C which are needed for normalization must be determined individually from separate experiments. The value for D for films made of the same redox polymer was determined previously24 and was used to determine C. The value of davg (7.32 µm) was obtained from C and the surface concentration in viologen according to a previously reported procedure.14,20

The dimensionless normalized ip,n vs W1/2 avg plots (Figure 5F) constructed based on D, davg, and C values were used for extraction of the value of ip,n at W1/2 avg = 2 from which a Weibull distribution shape factor of 60.60 was directly determined from the correlation given in Figure 3F. The probability distribution function corresponding to the determined shape factor was then generated (Figure 5G) as described in SI section S1.1. The relative standard deviation for the film thickness distribution obtained from the shape factor using the correlation in Figure S1 was 176 %. To allow for a direct comparison with AFM results, as in the case of the dendrimer, the dimensional film thickness distribution was generated (Figure 5G) and then converted to a surface distribution (see SI Section S1.3). The average surface height value (7.32 µm) and the root mean square roughness (12.87 µm) are substantially different from the corresponding values obtained from AFM. This discrepancy is attributed to the selection of a relatively smooth region for AFM imaging (orange frame in Figure 5B) in comparison to the large aggregates in other regions of the same sample as observed in the optical image (Figure 5B).

This result highlights an important advantage of the electrochemical method, which is that it is naturally an ensemble method, i.e. it samples the entire surface, rather than a subsection. Although direct observation of the surface by AFM or optical methods is highly desirable, in particular, for its ability to show the sizes and spatial locations of aggregates, the results are highly dependent on the selection of the sampling area (typically only up to 100 µm × 100 µm). Conversely, although the electrochemistry measurements are representative of the entire surface, the exact locations and geometries of the aggregates are not available. This emphasizes the complementary nature of the two methods and highlights the unique information derived from electrochemistry. Moreover, the electrochemical method measures from the bottom of the film at the electrode surface upwards through the film. Therefore, it naturally probes the film thickness distribution, in contrast to AFM which directly gives surface roughness information but requires scratching of the sample to access thickness information. Furthermore, while AFM can be performed on solvated samples or
in presence of electrolytes, soft samples such as the hydrogel films used in the present study can be particularly challenging to image.\textsuperscript{26} The electrochemical method, in contrast, is intrinsically performed in presence of the electrolyte, which correspond to the operational conditions for the applications of the film. Therefore, optimization of the solvent composition and evaluation of solvent effects is convenient when using the electrochemical method.

Although the method presented in this work is broadly applicable to redox-active films, the limitations of the scope of this model should be noted. Firstly, the time-scale of the electron transfer within the film needs to be sufficiently slow so that the diffusional regime is accessible within the time scale of the linear sweep voltammetry experiment. In other words, diffusion layer thicknesses with dimensions in the range of the thicknesses of all film sub-sections must be accessible via the scan rate (see Equation 1). Generally, films in which electrons are transported by diffusional, or “electron-hopping” types of mechanisms are covered by this model. Second, the accuracy of the peak current analysis depends on the ease of subtraction of the baseline related to the capacitive current. In particular, possible interferences may arise from non-uniform capacitance (i.e. potential dependent capacitance at the underlying electrode) that would distort the cyclic voltamograms and therefore adversely affect the peak current analysis. Additionally, since the model assumes electrochemical reversibility for the electron transfer at the electrode/film interface, peak currents from films that have slow heterogeneous electron transfer rates cannot be analyzed with the current version of the model.

In general, the design requirements of redox active films for electrocatalytic applications include high loading of the redox moiety (catalyst and/or electron relays) and fast charge transfer at the electrode interface, implying that the peak to baseline ratio is therefore adversely affect the peak current analysis. Additionally, from a plot of the normalized peak current versus the experimental working conditions of the modified electrode. This is ultimately useful for the optimization of the performance of these films, in which the film thickness is a critical parameter defining the catalytic or light-induced current output and the fraction of catalyst effectively contributing to the reaction.

Experimental Section
Materials and methods Unless stated otherwise, all reagents used in experiment were purchased from Sigma-Aldrich. All the materials were directly used as received without further purification.

Film preparation The preparation and characterization procedure for the redox-active films used to illustrate the application of the present method for determination of the thickness distribution was previously reported in detail\textsuperscript{20}. We recall here the film preparation corresponding to the specific data used in the present study: viologen modified dendrimer\textsuperscript{22} (200 µg cm\textsuperscript{-2}) was cast from a 2 µL droplet onto a gold electrode (2 mm diameter) with 0.5 µL Tris-buffer (0.1 M, pH 9.0), and allowed to dry in a closed container at room temperature under a water saturated atmosphere for 24 h. The electrode was then dried in the air for another hour. Viologen modified polymer\textsuperscript{19} (200 µg cm\textsuperscript{-2}) was cast from a 2.5 µL droplet onto a glassy carbon electrode (3 mm diameter), and dried using the same conditions as that of the dendrimer.

Electrochemical Characterization Cyclic voltamograms were performed in phosphate buffer (0.1 M, pH 7.2) under anaerobic conditions at room temperature using Gamry Potentiostats and an Autolab PGSTAT12 Biptotentistat. A platinum wire and Ag/AgCl/3 M KCl were used as the counter and reference electrodes, respectively. Before preparation of the characteristic normalized peak current plot, interactions were accounted for using slow scan-rate LSVs, in which the experimentally determined peak currents were converted to their Langmuir equivalents (see details in SI section S7).

AFM Characterization. The AFM measurements were conducted in the AC mode by NanoWizard 3 (JPK) with cantilever of the type NSC15 (MikroMarsch).

Conflicts of interest
There are no conflicts to declare.

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