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Influence of Finite Diffusion on Cation Insertion-Coupled Electron Transfer Kinetics in Thin Film Electrodes

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Materials that undergo ion-insertion coupled electron transfer are important for energy storage, energy conversion, and optoelectronics applications. Cyclic voltammetry is a powerful technique to understand electrochemical kinetics. However, the interpretation of the kinetic behavior of ion insertion electrodes with analytical solutions developed for ion blocking electrodes has led to confusion about their rate-limiting behavior. The purpose of this manuscript is to demonstrate that the cyclic voltammetry response of thin film electrode materials undergoing solid-solution ion insertion without significant Ohmic polarization can be explained by well-established models for finite diffusion. To do this, we utilize an experimental and simulation approach to understand the kinetics of Li⁺ insertion-coupled electron transfer into a thin film material (Nb₂O₅). We demonstrate general trends for the peak current vs scan rate behavior, with the latter parameter elevated to an exponent between limiting values of 1 and 0.5, depending on the solid-state diffusion characteristics of the film (diffusion coefficient, film thickness) and the experiment timescale (scan rate). We also show that values < 0.5 are possible depending on the cathodic potential limit. Our results will be useful to fundamentally understand and guide the selection and design of intercalation materials for multiple applications.

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Cyclic voltammetry is a powerful technique for characterizing the kinetic response of electrode materials for electrochemical devices such as batteries and electrochromic windows. As noted by Bard and Zoski,¹ voltammetry allows for mapping the three-dimensional space defined by potential, current, and time, the critical variables for electrochemistry. The rapid development of new materials for electrochemical devices relies heavily on easily-accessible electrochemical techniques to determine the rate-limiting step of the process (e.g. interface vs bulk) and kinetic parameters such as solid-state diffusion coefficients. This information is useful to identify the most promising materials for electrochemical applications. However, controversy and confusion have emerged in the analysis of cyclic voltammograms for electrochemical ion-insertion materials. Part of this stems from the application of analytical solutions originally developed for electrochemical processes occurring at ion blocking, electronically conductive electrodes in contact with a liquid electrolyte that provides a semi-infinite diffusion medium.

As illustrated in Fig. 1, the kinetic processes involved in ion-coupled electron transfer and non-Faradaic processes taking place at an ion blocking vs ion permeable electrode are related but different. At an ion-blocking electrode (Fig. 1a), there are two general electrochemical processes to consider: (1) mass transport of the ion in the liquid electrolyte towards the electrochemical interface and (2) specific or non-specific ion adsorption at the electrochemical interface. If process (1) is the rate limiting step, for instance via diffusion limitation in a quiescent solution, the voltammetric response will be characterized by the Randles-Ševcík equation:²

$$i_p = 0.4463 \left(\frac{F^3}{RT} \right)^{1/2} n^{3/2} A D^{1/2} C^* \nu^{1/2} \quad [1]$$

where i_p is the peak current, F is the Faraday constant, R is the ideal gas constant, T is the temperature, n is the stoichiometric number of

electrons in the electrochemical reaction, A is the geometric area of the electrode, D is the diffusion coefficient of the redox active species in the liquid electrolyte, C^* is bulk concentration of redox-active species, and ν is the linear scan rate. Importantly, this equation gives rise to a current proportional to $\nu^{1/2}$, an exponent that is characteristically found in diffusive systems with respect to the experimental time. If ion adsorption (process 2) is the rate limiting step, there are two possibilities. For non-specific or electrostatic ion adsorption, which involves no charge transfer between the electrode and the electrolyte ion, the relationship will be that of an ideal capacitor:²

$$i = AC_d \nu \quad [2]$$

where C_d is the double-layer capacitance. For specific ion adsorption, which involves charge transfer between the electrode and electrolyte ion (also termed pseudocapacitance), the current will be determined by:²

$$i = \frac{n^2 F^2 \nu A \Gamma^*}{4RT} \quad [3]$$

where Γ^* is the total surface concentration of adsorbed ions. Importantly, Eqs. 2 and 3 both give rise to a current directly proportional to ν which means that the scan rate dependence is the same whether the electrochemical process is due to non-specific or specific adsorption.

In the case of an insertion electrode (Fig. 1b) the same kinetic processes can be present as in Fig. 1a, with the addition of solid-state ion insertion. In the insertion electrode, ions adsorbed at the surface of the electrode diffuse further into the bulk because the structure has adequate insertion sites and transport pathways. In this situation, the solid-state insertion electrode provides another diffusion medium for ions. Unlike the electrolyte, this diffusion medium is not always semi-infinite for the diffusing ions. Due to the slower solid-state ion diffusion coefficients as compared to liquid electrolytes, thin films or small particle sizes (on the order of microns or smaller) are necessary. In electrochemical devices utilizing insertion electrodes,

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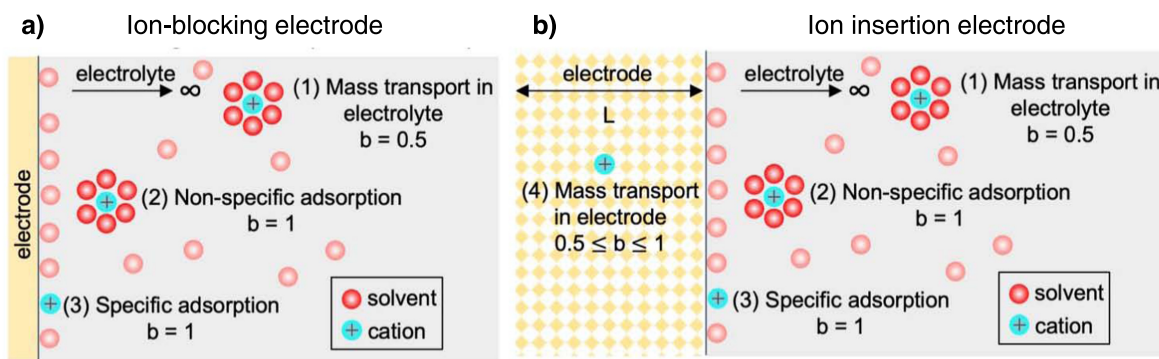


Figure 1. Comparison of ion-coupled electrochemical processes at (a) ion-blocking and (b) ion-insertion electrodes in contact with a liquid electrolyte in one dimension. Both cases feature a semi-infinite boundary for ion diffusion in the liquid electrolyte and allow for specific and non-specific ion adsorption at the interface. The ion-insertion electrode (b) further allows for solid-state diffusion of an inserting electrolyte ion, which leads to a finite diffusion boundary condition, here defined as the electrode length (L). For simplicity, we assume the presence of free ions or protons in the electrolyte and excess electrolyte, such that on the electrolyte side, the diffusing medium is semi-infinite with respect to the electrochemical interface.

the electrode can be either a thin film of the insertion material or a porous electrode composed of the active insertion material, conductive additive, and binder particles filled with a liquid electrolyte. There are many excellent reviews on the kinetics of such porous electrodes,³ which are not the focus here. Instead, we will consider the simpler case of thin film ion insertion electrodes which are frequently used in electroanalytical studies. Importantly, we will focus on insertion electrodes that do not undergo a solid-state phase transition during the ion insertion process, a situation that is often found in insertion materials and should also be considered in fully understanding the kinetic response.

The preceding review of fundamental electrochemical equations shows that in well-defined systems, the relationship between the electrochemical current and the cyclic voltammetry scan rate provides a diagnostic of the rate-limiting step (e.g. surface redox or capacitance vs semi-infinite diffusion in the electrolyte). These equations gave rise to a simple analysis, sometimes called “the b -value analysis,” to determine the power-law relationship between the current and scan rate of an electrochemical system:⁴

$$i = a\nu^b \quad [4]$$

The b -value can be obtained from the plot of $\log i$ vs $\log \nu$. The limiting values of $b = 0.5$ or 1 emerge from the Randles-Ševčík (Eq. 1) and surface adsorption (Eqs. 2 and 3) equations. However, intermediate values between 0.5 and 1 , or even below 0.5 , are often observed experimentally. Conway et al. proposed a related analysis by separating the cyclic voltammetry current at each potential into proportional amounts of ν and $\nu^{1/2}$:

$$i(V) = k_1\nu + k_2\nu^{1/2} \quad [5]$$

This model assumes that the overall electrochemical response of an electrode material is due to a linear combination of a surface process (e.g. non-specific or specific ion adsorption, surface redox) and a semi-infinite diffusion process from mass transport within the electrode. This has also been described as a “parallel” model⁶ because each process contributes separately to the total current. In this analysis, intermediate b -values between 0.5 and 1 arise from a linear combination of surface and semi-infinite diffusion limited currents, whose fractions can be obtained from solving for k_1 and k_2 . For example, this method was applied by Wang and Dunn⁷ to quantify the increase in surface storage in anatase TiO_2 due to a decrease in particle size. Since then, this analysis has been applied broadly to energy storage materials and electrodes, ranging from thin films⁸ to porous electrodes⁹ and from insertion to conversion mechanisms.^{10–16} The assumption that current can be separated in such a way and applied to battery and supercapacitor electrode materials has received criticism^{17,18} because it utilizes equations

derived for significantly simpler situations as described above. More recently, van den Bergh et al. proposed a mixed $\nu/\nu^{1/2}$ model of a different form, which approached the insertion electrode as having surface and diffusion processes occurring “in series” rather than “parallel,” as in the Conway model. The model assumes that a surface-limited insertion process is followed by semi-infinite diffusion into the bulk of the electrode material:

$$i = \left[\left(\frac{k_2}{\sqrt{\nu}} + R \right)^2 + \left(\frac{k_1}{\nu} + \frac{k_2}{\sqrt{\nu}} \right)^2 \right]^{-0.5} \quad [6]$$

This “series model” includes three fitting parameters: k_1 and k_2 , as well as a resistance term R . Combining $\nu/\nu^{1/2}$ in this manner leads to a sigmoidal $b(\nu)$ relationship whereby $b = 1$ at slow scan rates transitions to $b = 0.5$ at fast scan rates when $R = 0$. Non-zero resistance is shown to extend the b -value range in the model below $b = 0.1$. This is one of several recent works that examine the b -value response of $\text{T-Nb}_2\text{O}_5$ across varying length scales in different tunable morphologies.^{19–22}

The purpose of this manuscript is to demonstrate that the kinetic response of thin film electrode materials undergoing solid-solution ion insertion without significant Ohmic polarization can be explained by well-established models for finite diffusion. The model assumes a surface electrochemical reaction described by the Nernst equation, followed by mass transport into the electrode. Unlike the models proposed in Refs. 5 and 6 that assume the presence of semi-infinite diffusion (which gives rise to the analytical $\nu^{1/2}$ solution), finite diffusion models utilize numerical simulations to solve the mass transport problem in the thin film electrode. We performed a combined electrochemical and numerical simulation study utilizing Nb_2O_5 as the model insertion material and a numerical simulation model developed for ion insertion into Prussian blue thin films.²³ In addition to the Prussian blue study, we note the precedent of studies which have examined the interplay between a combination of diffusion, potential window, resistance, and interfacial kinetics (among other factors) in thin films using various diffusion-based CV simulation approaches.^{24–26} We chose Nb_2O_5 because it undergoes solid-solution Li^+ insertion over its entire composition range ($0 \leq x \leq 2$ for $\text{Li}_x\text{Nb}_2\text{O}_5$).²⁷ The fact that Nb_2O_5 does not undergo the nucleation and growth of a new lithiated phase decreases the complexity of the insertion kinetics. Our findings highlight the critical role of the dimensionless film thickness in determining the kinetic response of ion insertion thin film electrodes ($X = \frac{L}{\delta}$, where L is the film thickness and δ is the Nernst diffusion-layer thickness, vide infra). This parameter defines the kinetic response of an insertion electrode bound by semi-infinite diffusion and surface processes. Importantly, the agreement between the experimental and

simulation results shows that finite diffusion leads to intermediate behavior between surface adsorption and semi-infinite diffusion limitations. The simulated concentration profiles in the thin film electrode provide a physical basis for the intermediate behavior. We further show that the potential window of a cyclic voltammetry experiment can influence the kinetic response.

Methods

Thin film electrode deposition.—Thin films of orthorhombic $T\text{-Nb}_2\text{O}_5$ were prepared by electrophoretic deposition onto FTO-coated glass slides using a previously reported method.²² In summary, 33.75 mg of niobium (V) chloride (Fisher Scientific) was dissolved in 1 ml of methanol (Fisher Scientific) to form a 125 mM solution. The niobium chloride solution was rapidly injected into 24 ml of an aqueous 52 mM H_2O_2 (Sigma Aldrich) solution at 2 °C and aged for 3 h to form colloidal NbO_x . This solution was placed in a 50 ml glass three-neck flask (Kontes) for use in a two-electrode electrochemical cell with a FTO-coated glass (Sigma Aldrich, 7 Ω/sq) working electrode and a platinum wire counter electrode (Sigma Aldrich). A 17:3:1 “basic piranha” mixture of DI water, ammonium hydroxide (Fisher Scientific), and H_2O_2 was used to clean the 1 by 2 cm FTO-coated glass substrates while sonicating. Deposition was achieved by chronoamperometry at -2 V vs Pt for various times using a potentiostat (Bio-Logic MPG2). The deposition thickness was estimated by the amount of charge passed during chronoamperometry, from 0.15 to 9 C cm^{-2} . After deposition, the films were heat treated at 600 °C in air for 6 h to form $T\text{-Nb}_2\text{O}_5$.

Thin film electrode characterization.—The Nb_2O_5 film thickness was determined via confocal laser scanning microscope (CLSM) profilometry (Keyence VKx1100). 10 μm by 10 μm regions were analyzed from larger 95 μm by 75 μm scans at 150 $\times$ magnification. Average height was gauged by comparing “crack height” to “island height” across 5 different regions in 3 different scan locations per film. Characterization of the thin film morphology was performed with scanning electron microscopy (FEI Verios 460 I). The $T\text{-Nb}_2\text{O}_5$ structure was confirmed using confocal Raman spectroscopy (Witec Alpha300 M) using a 532 nm laser, 100 $\times$ magnification, and an 1800 g cm^{-1} grating.

Electrochemical characterization.—Cyclic voltammetry was performed in a three-electrode configuration in 1 M LiClO_4 in propylene carbonate (PC) (Sigma Aldrich, anhydrous, 99.7%) electrolyte between 1.2 and 3 V vs Li/Li^+ using a potentiostat (Bio-Logic VMP3). A Nb_2O_5 thin film deposited on FTO-coated glass served as the working electrode, and lithium metal (Sigma Aldrich, 99.9%) was used for the counter and reference electrodes. The electrochemical cell was assembled in a 50 ml glass three-neck flask (Kontes). Each electrode was subject to conditioning at 10 mV s^{-1} for 5 cycles before further analysis. Apparent diffusivity values for Li^+ (D_{Li}) in the Nb_2O_5 films were calculated using a modified Cottrell analysis;^{28,29} further details are provided in the Supplementary Information. All electrochemical characterization was performed in an argon-filled glovebox (MBraun Labstar Pro) with O_2 and H_2O levels of <1 ppm.

Numerical Simulation

Numerical simulation of cyclic voltammograms was carried out using the method proposed by Garcia-Jareño et al.²³ A thin-film electrode of finite thickness L was defined with a fixed concentration of electroactive species C^* , equal to the sum total of oxidized and reduced redox centers, C_{O} and C_{R} respectively. In the context of the Nb_2O_5 insertion electrode, C_{O} would correspond to the concentration of Nb^{5+} and C_{R} to that of Nb^{4+} . Boundary conditions were set for the thin film such that ion diffusion was blocked at one end ($x = L$), representative of the electrode/current collector interface,

$\left(\frac{\partial C_{\text{O}}}{\partial x}\right)_{x=L} = 0$. C_{O} and C_{R} were defined at the other boundary ($x = 0$) as a function of the electrode overpotential ($E^{\text{eff}} - E^{\circ}$) assuming Nernstian behavior at the electrode/electrolyte interface:

$$\frac{C'_{\text{O}}}{C'_{\text{R}}} = \exp\left(\frac{nF}{RT}(E^{\text{eff}} - E^{\circ})\right) \quad [7]$$

Ions were allowed to diffuse into or out of the film at this interface, modeled by solving Fick's equations in one-dimension using the Crank-Nicolson numerical method. This method approximates the thin film as a series of finite elements spaced Δx in one-dimension, and reports the local value of C_{O} for each finite element, yielding a time-dependent concentration profile of the film's local oxidation/reduction due to ion (de)insertion. For each time-step, the derivative of the profile at the electrode/electrolyte interface ($x = 0$) was used to calculate the amount of current passed:

$$i = -nFAD_{\text{O}}\left(\frac{\partial C_{\text{O}}}{\partial x}\right)_{x=0} \quad [8]$$

Mechanistically, this model is representative of a system which consists of a surface insertion process coupled with a bulk diffusion process. This contrasts with the previously mentioned models of Conway and van den Bergh, respectively, which consider a thin “near-surface” charge-storage region for surface-limited current. Comparatively, this model simplifies the surface and near-surface insertion processes, exploring the effects of bulk diffusion at confined length scales.

We also utilized a set of dimensionless parameters to contextualize the simulated cyclic voltammogram results in relation to the Nb_2O_5 thin films used in the experiment. Multiple examples of dimensionless cyclic voltammogram models exist,^{30,31} and here we follow the recommendations of D. Britz.³³ Dimensionless potential p is the result of normalizing the overpotential by the factor nF/RT . The potential scan rate is also normalized by the factor nF/RT to yield a scan rate a with units of s^{-1} . Taking the reciprocal of a yields a time constant τ , in seconds. Taken together with the diffusivity D , we define a Nernst diffusion-layer thickness δ of the form $\delta = \sqrt{D\tau}$. This may also be written as:

$$\delta = \sqrt{\frac{DRT}{nF\nu}} \quad [9]$$

The ratio between the film thickness L and this diffusion-layer thickness is the dimensionless film thickness X , given by

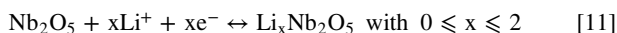
$$X = \frac{L}{\delta} \quad [10]$$

It is important to note that a single thin film will take on different values of X based on the scan rate used due to the changing diffusion-layer thickness. Further details including a schematic of the diffusion geometry are in the SI section S1. The full simulation code used here is freely available on GitHub.³²

Results and Discussion

We performed SEM, Raman spectroscopy, and optical profilometry to characterize the Nb_2O_5 before and after thermal treatment (Figs. S4–S7). As-deposited thin films were hydrous and amorphous with a granular microstructure. Thermal treatment led to the formation of $T\text{-Nb}_2\text{O}_5$ with a “cracked mud” microstructure because of the volume change upon crystallization and dehydration. SEM and profilometry show that the average island size and film thickness increased as a function of total electrodeposition charge. Using profilometry, we establish a general trend of film thickness as a function of deposition charge. The film thickness is used to vary the solid-state Li^+ diffusion distance and to determine D_{Li} using the modified Cottrell analysis.

We used cyclic voltammetry to quantify the electrochemical kinetics of the Nb₂O₅ thin film electrodes (see SI section S2 for further details). The typical CV response of the Nb₂O₅ thin film is shown in Fig. S2. The reversible current response between $\sim 1.2 - 2$ V occurs from ion insertion-coupled electron transfer via a solid-solution mechanism into the oxide host over the entire composition range. The Li⁺-coupled electron transfer reaction for Nb₂O₅ can be written as:



We determined the effective diffusion coefficient for Li⁺ in Nb₂O₅ between 10^{-10} and 10^{-11} cm² s⁻¹ using a modified Cottrell analysis, described in further detail in section S3. The magnitude of this value agrees with the reported diffusion coefficients for Li⁺ in niobium oxides in the literature (Table S1). The structure of *T*-Nb₂O₅ consists of corner and edge-sharing NbO₆ octahedra with interstitial sites that allow for Li⁺ insertion. The structure can intercalate up to 2 Li⁺ per Nb₂O₅ without undergoing a structural transition, a broad solid-solution regime that occurs from the unique “pillared layer” arrangement of the crystal structure.^{27,34} This leads to fast ion insertion into the structure which is desirable for high power energy storage devices.^{35,36}

Next we consider the effect of two experimental variables on the electrochemical response: the Nb₂O₅ film thickness, which determines the diffusion length (*L*) and the scan rate ν , which determines the diffusion-layer thickness (δ). As film thickness increases (Fig. 2a), the amount of electroactive Nb₂O₅ increases which leads to an increase in current density. The increased film thickness also leads to increased resistance, as shown by the decrease in the potential of the cathodic peak. This is expected because Nb₂O₅ is a semiconductor with a band gap of ~ 3.2 eV.³⁷ On the other hand, Li_{*x*}Nb₂O₅ is a metallic conductor and there is a decrease in resistivity of up to two orders of magnitude from Nb₂O₅.³⁸ This could explain why the anodic peak does not exhibit a major shift in potential as a function of film thickness. As ν increases at a constant film thickness of 250 nm (Fig. 2b), the current increases and the cathodic and anodic peaks shift to lower and higher potentials, respectively. For most films (those with thickness > 100 nm), the cathodic peak is not fully resolved within the potential window as scan rate increases. The cathodic potential limit is limited to 1.2 V by experimental constraints from the electrochemical activity of the FTO, irreversible phase transitions of Nb₂O₅ when *x* of Li⁺/e⁻ is > 2 , and contribution from electrolyte reduction. We explore the

implication of the incomplete cathodic peak on its scan rate behavior using numerical simulations (vide infra).

To understand the physical origin of this behavior, we simulated the cyclic voltammetry response of a thin electroactive film using the method of García-Jareño et al.²³ The details of the numerical simulation are described in the Methods and SI section S1. Using the simulated CVs, we can obtain the concentration profiles in the film as a function of applied potential. We can also determine the sweep-rate dependence of the current (*b*-value), peak potential, and capacity, and compare these to our experimental results. First, we check that the simulated CVs show the expected behavior in the kinetic extremes of either surface reaction or semi-infinite diffusion limitation. Figure 3 shows the simulated CVs at 1 and 100 mV s⁻¹ for a 300 nm thin film, with a diffusivity that is within the experimental range for solid-state diffusion of Li⁺ in Nb₂O₅ ($D_{\text{Li}} = 5 \times 10^{-11}$ cm² s⁻¹). Varying the scan rate leads to two extremes at a constant thickness (*L* = 300 nm): when the diffusion-layer thickness ($\delta = 358$ nm) is greater than the film thickness (1 mV s⁻¹; Fig. 3a) and when the diffusion-layer thickness ($\delta = 35.8$ nm) is much smaller than the film thickness (100 mV s⁻¹; Fig. 3c). At 1 mV s⁻¹, the simulated CV shows almost no peak separation and a near-uniform distribution of oxidized/reduced species (C_0/C^* ; Fig. 3b) at each applied potential. This means that when $\delta > L$, the surface concentration is close to the bulk concentration at each applied potential. Under these conditions, the surface reaction is the rate limiting step. At 100 mV s⁻¹, the simulated CV shows a peak separation of 59 mV and concentration gradients in the film become more pronounced near the redox peaks (Fig. 3d). Proportionally less of the film is accessible on the shorter timescales imposed by the faster scan rates. Under these conditions, mass transport in the film is the rate limiting step. The simulated CVs lack the characteristic peak width and extended peak separation of the experimental, and these simulations do not capture all the complexities of ion insertion materials. However, they provide quantitative information on the predicted trends in peak current magnitude and potential as a function of scan rate depending on the diffusion parameters of the thin film.

Using the above method for simulating CVs, we probe the effects of three parameters: film thickness *L*, scan rate ν , and ion diffusivity D_{Li} . The effects of these parameters are gauged in the voltammetry response via the *b*-value, peak separation ΔE_p , and normalized capacity Q/Q_{max} . Our findings are summarized in Fig. 4, with generalized trends shown as a function of each parameter changing the overall dimensionless film thickness *X*. Each of these outcomes are discussed in more detail in later sections.

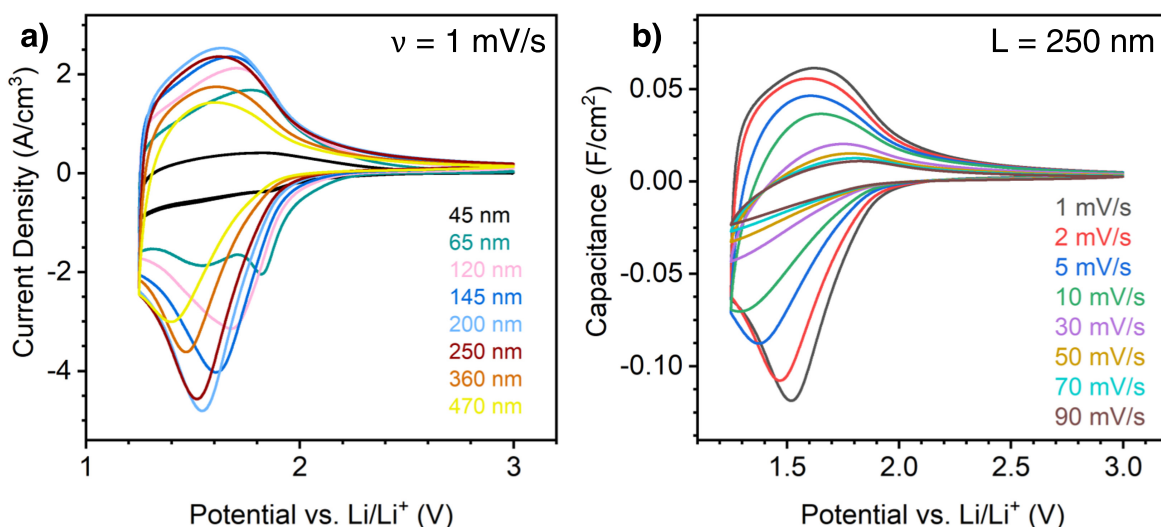


Figure 2. (a) Experimental CVs at 1 mV s⁻¹ for different Nb₂O₅ film thicknesses. Current per unit area is normalized by the approximate film thickness to yield current per unit volume. (b) Experimental CVs for a Nb₂O₅ film thickness of 250 nm at different scan rates; current was normalized by scan rate to yield the units of capacitance.

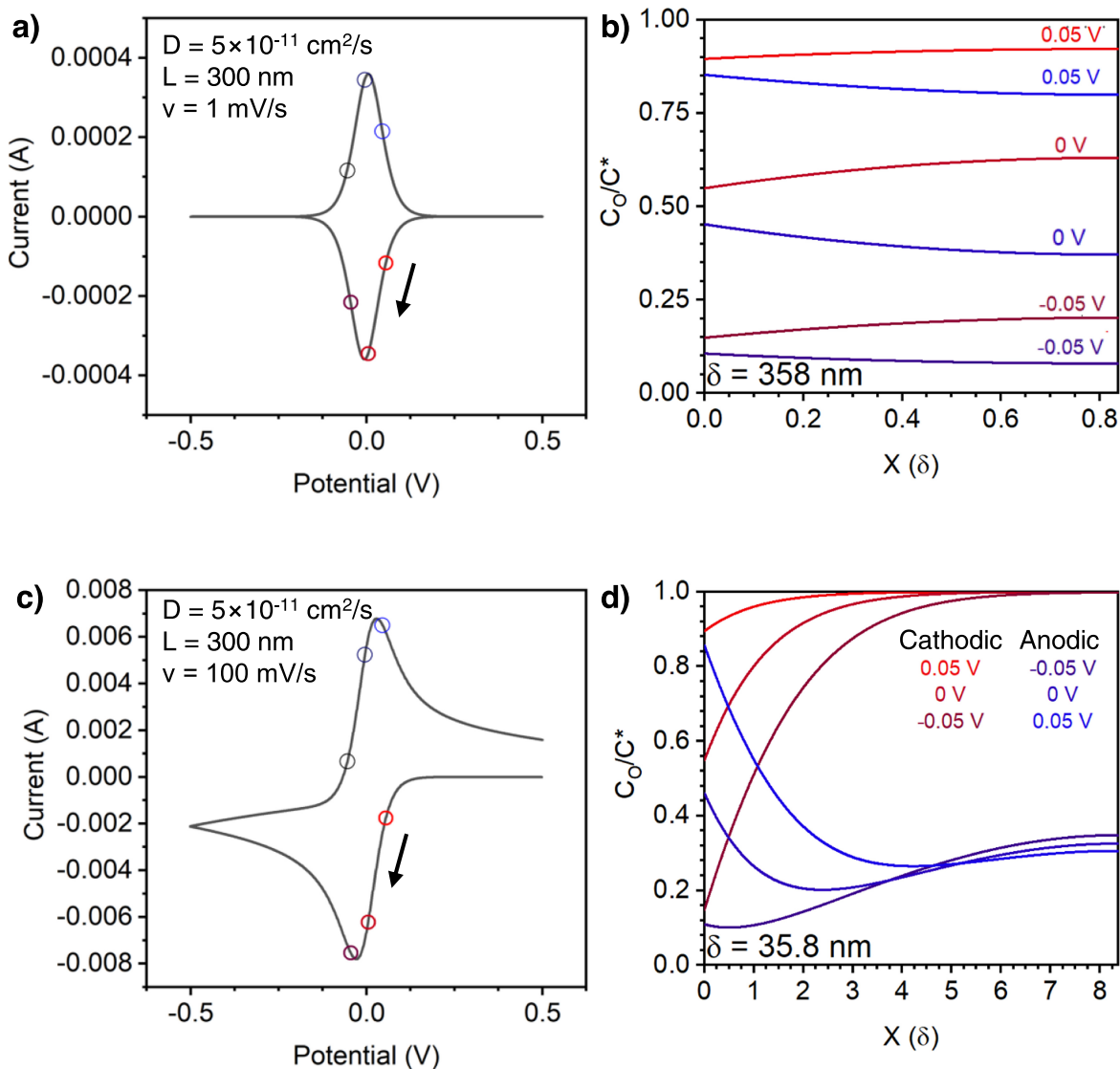


Figure 3. CVs for a simulated 300 nm film with kinetics controlled by (a) the surface reaction (1 mV s^{-1}) and (c) semi-infinite diffusion (100 mV s^{-1}). Concentration profiles for circled voltammogram points on (a) and (c) are shown in (b) and (d) respectively, in units of diffusion layer length. The profiles in (c) are more uniform than (d), due to the longer timescale allowed for diffusion into the electrode at the slower scan rate.

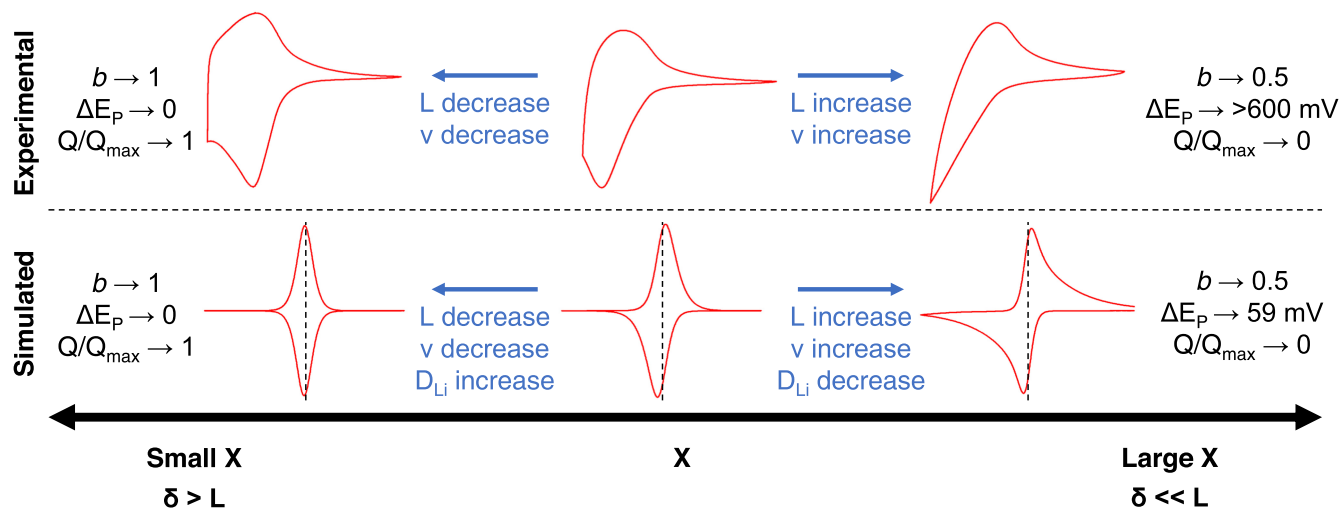


Figure 4. Overview of the parameters that determine the kinetic response of the thin film insertion electrode (L , v , & D), and their overall effects on the cyclic voltammetry response in both experimental and simulated voltammetry. At a fixed value of D , the limiting behavior is dictated by the relative magnitude of the film thickness L and δ , the diffusion-layer length, whose ratio gives the dimensionless film thickness, X .

Scan rate dependence of the peak current.—We first determine and compare the behavior of the peak current with the scan rate between experiment and numerical simulation, since this has given rise to the popular b -value and k_1/k_2 methods. Commonly, a single b -value will be assigned to a sample as a function of its performance over a range of scan rates. However, we find that this relationship between peak current and scan rate is not necessarily linear for all systems at all scan rates. Thus, assigning a single b -value to a sample may over-simplify the kinetic response, undermining the utility of b -values as kinetic descriptors.

Stefik et al. reported a method for assigning b -values to specific scan rates rather than an entire range.⁶ The approach requires taking the derivative of experimental log-peak-current data with respect to log-sweep-rate over a range of scan rates which have even logarithmic spacing. We follow this procedure with three Nb₂O₅ films of different thicknesses to explore the variable b -value response between $b = 0.5$ and $b = 1$ (Fig. 5a). The derivative was taken using the “differentiate” function in the OriginLab software, which averages the slope between a point and its two neighbors. An apparent diffusivity of $6 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is within the range of diffusivities we determined experimentally (section S3), was used to convert film thickness into the dimensionless X .

Our approach to this problem is to leverage the CV simulation to approximate $\frac{\partial \log i_p}{\partial \log \nu}$, the derivative of the peak current-scan rate relationship. The theoretical approach is akin to the limit definition of a derivative. We simulate multiple CVs within a narrow range of scan rates $\nu_1 \dots \nu_n$ and apply a linear fit to determine the b -value $\frac{\Delta \log i_p}{\Delta \log \nu}$ for the range of scan rates. By incrementally narrowing the range of scan rates $\Delta \nu = \nu_n - \nu_1$, we observe convergence to a uniform b -value. The $\Delta \nu$ threshold for convergence is roughly 1 mV s^{-1} (Fig. S8). One can utilize this approach to plot b -values as a function of scan rate when film thickness and diffusivity are known. This trend is made more general by plotting the instantaneous b -values as a function of the dimensionless thickness ratio X , as shown in Fig. 5b. Once this curve is established, it is evident that the curve is constant for any film thicknesses, scan rates, and diffusivities. Moreover, this curve is bound by the limiting conditions discussed earlier that result in $b = 1$ and $b = 0.5$. Varying any or multiple of these parameters moves data points along the curve, but the shape of the curve itself is conserved.

The simulation-derived b - X relationship in Fig. 5b affords a good fit for the transformed 125 nm film data shown in Fig. 5a. In both cases, the b -values traverse between 0.5 and 1, though the same dimensionless transformation yields a curve for the 250 nm film which is shifted towards the right. Additionally, the experimental curve also exhibits the characteristics of a cyclic voltammogram which reached its turnover potential before fully reducing the film, in that the higher- X values exhibit $b < 0.5$. We can mimic this

experimental behavior in our simulations by imposing a turnover potential which is close to E^0 . We observe in Fig. 5c when the turnover potential is limited to $-0.25 \text{ V vs } E^0$ and further limited to $-0.1 \text{ V vs } E^0$ that the b -value becomes depressed further below 0.5 as the cathodic sweep is increasingly restricted. We discuss this situation in more detail below.

Influence of the potential limit on the peak current.—Figures 5a and S2b show that experimentally obtained b -values can be < 0.5 . This is surprising at first since a b -value of 0.5 corresponds to semi-infinite diffusion, meaning that the bulk concentration does not change as a function of time or potential far from the interface. Experimental b values of < 0.5 have been reported for other systems,³⁹ often attributed to ohmic losses or charge transfer limitations.³⁸ Utilizing the 1-D film model, we show that $b < 0.5$ may arise in a system with no ohmic drop and no charge transfer limitations, solely due to the influence of the turnover potential on the concentration profile developed in the film electrode.

When the potential window is large enough that the film is completely oxidized or completely reduced at the beginning of a potential sweep, the simulated concentration profile evolves in a simple manner. If diffusion occurs rapidly, or the film is particularly thin, the concentration profile will be nearly uniform throughout the film, roughly equivalent to the concentration at the interface. If diffusion is sluggish, or the film is very thick, the concentration near the interface will change much more rapidly than the concentration further into the film, and a large gradient will develop, slowly extending further into the film. Given enough time, the concentration would be expected to equalize. If the potential sweep is reversed before the film is fully oxidized or reduced, which is achieved in the simulation by imposing turnover potential near E^0 , then a unique concentration profile may form (Fig. 6c). The near-surface concentration will respond rapidly to the reversal of the potential sweep, but the bulk concentration far from the interface will take much longer to equilibrate with the surface concentration. In some intermediate distance, a pocket of especially high (or especially low) concentration relative to its surroundings will develop, which had not equalized with the bulk concentration on the previous sweep and is now not yet in equilibrium with the near-surface concentration, as pictured in Fig. 6d. At this point, in a 1-D context, the modeled film will experience bi-directional diffusion from this high concentration region, as species diffuse both towards the interface and into the bulk film. It is this bi-directional diffusion which depresses the b -values below 0.5. A minimum b -value = 0.5 occurs when mass transport is in only one direction (interface to film bulk or vice versa). b -values < 0.5 may be attained in the CV simulation by imposing a sufficiently high cathodic turnover potential. This corresponds well with our experimental cyclic voltammetry where the cathodic potential limit is restricted by irreversible electrochemical reactions of the FTO glass substrate at low potentials.

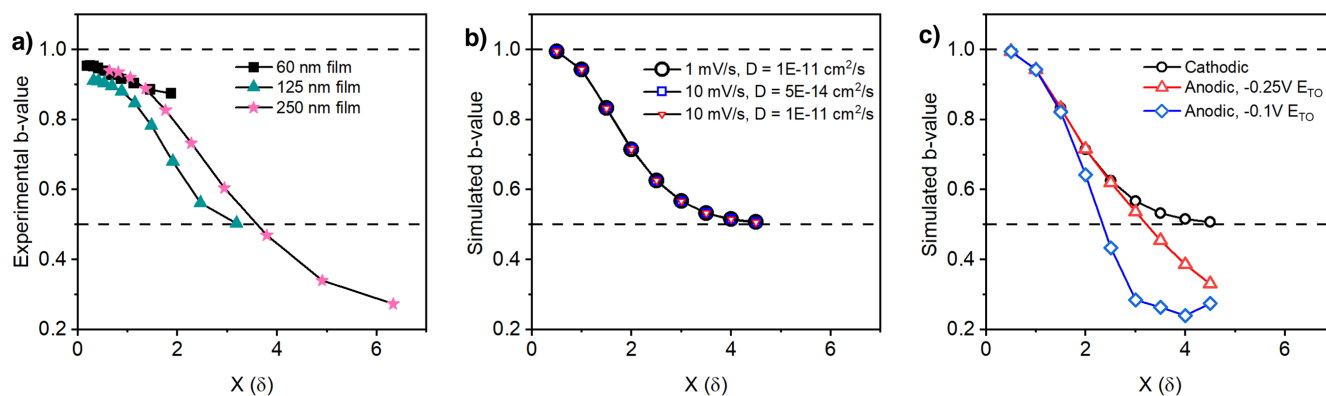


Figure 5. (a) Experimental instantaneous anodic b -values as a function of X for three different film thicknesses. (b) Simulated instantaneous cathodic b -values as a function of X demonstrate the relationship is conserved across varied scan rates and diffusivities. (c) Simulated anodic b -values demonstrating the effect of narrower potential windows using turnover potentials (E_{TO}) of -250 and -100 mV . The narrower potential windows depress the reported b -values below 0.5.

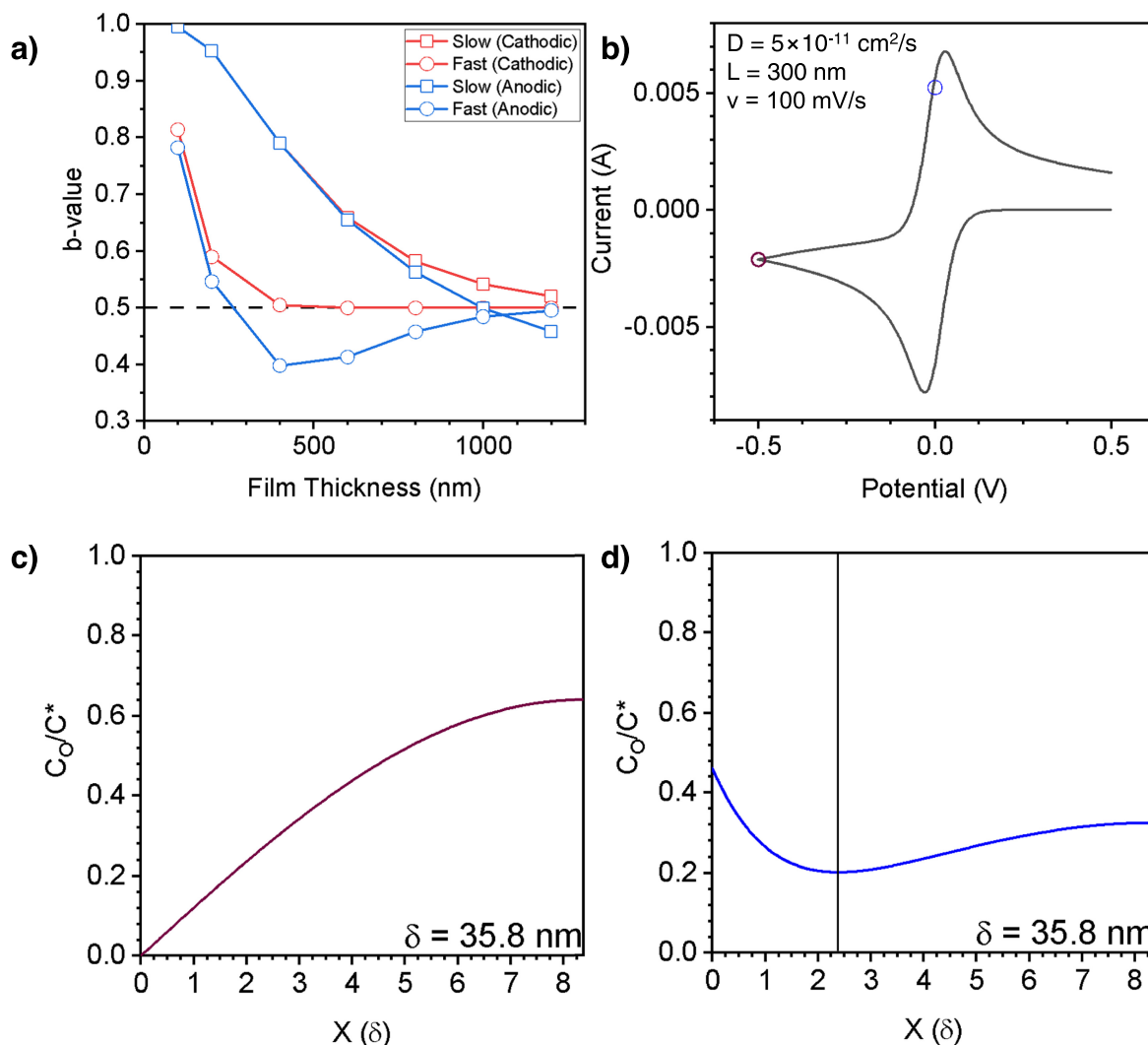


Figure 6. (a) Simulated cathodic and anodic b -values for a given system at slow ($\leq 10 \text{ mV s}^{-1}$) and fast ($\geq 30 \text{ mV s}^{-1}$) scan rates. Anodic b -values may exist below $b < 0.5$ but converge at $b = 0.5$ for the thicker films. (b) Sample cyclic voltammogram for a modeled 300 nm film; circled points indicate potential for the concentration profiles. (c) Simulated concentration profile at the turnover potential of -0.5 V , showing the film fully reduced at the interface $X = 0$, with partial reduction deeper into the film. (d) Modeled concentration profile at 0 V during the anodic sweep. The local concentration minimum at $X \sim 2.3$ is highlighted, showing the change in the direction of concentration gradient which yields bi-directional diffusion based on Fick's laws.

Bi-directional diffusion alone is not responsible for $b < 0.5$ behavior. We know this from the observation that a standard, purely diffusive Nernstian CV at an ion-blocking electrode will experience bi-directional diffusion in the solution phase upon the reverse sweep, but does not show $b < 0.5$. We conclude then that bi-directional diffusion in the finite geometry is the key factor in our modeled system. In a modeled classical Nernstian diffusional CV, the diffusion medium (e.g. electrolyte) is assumed to be semi-infinite. In both our experimental and modeled systems, we observe that the b -value decreases as a function of the dimensionless length ratio. However, in cases where the b -value decreases below 0.5, we observe a convergence back towards 0.5 when X is sufficiently large (fast sweep rate, fast diffusion, or large film thickness). This trend is represented in Figs. 6a and S2b for the simulated and experimental cases, respectively. For the b -value to converge back towards 0.5, there must be little-to-no change in concentration at the maximum distance from the electrochemical interface ($x = L$) during the voltammetry experiment (Fig. S9). In other words, to replicate the convergence to $b = 0.5$, the modeled films must become sufficiently thick that the system operates under the semi-infinite diffusion condition. Until such a condition is reached, the existence of bi-

directional diffusion under finite diffusion yields a region where b can be < 0.5 .

Scan rate dependence of the peak potential.—Next, we determine the peak separation behavior as a function of film thickness and scan rate from both experiment and simulation. Experimentally, we see an increase of peak separation which follows a sigmoid curve from slow to fast scan rates. At a fixed scan rate, thicker films also have larger peak separations. The deviation between thick and thin films appears largest at intermediate scan rates where $0.5 \leq \log(\nu) < 1.5$ and convergence is observed when peak separation approaches 600 mV (Fig. 7b). It is salient to note here that the peak separation values converge in the same range as the cathodic peak cut off by the limited turnover potential. As such, the turnover potential is artificially limiting and possibly obscuring any underlying trend in the peak separation. We explore this further by comparing the simulated peak separation values for 3 films with varying X ratios (Fig. 7a). All three films exhibit a similar sigmoid curvature, but the magnitude is much smaller: no simulation ever exceeds a 58 mV peak separation. This limitation can be tied to the two assumptions of (1) Nernstian kinetics at the film/electrolyte interface and (2) no

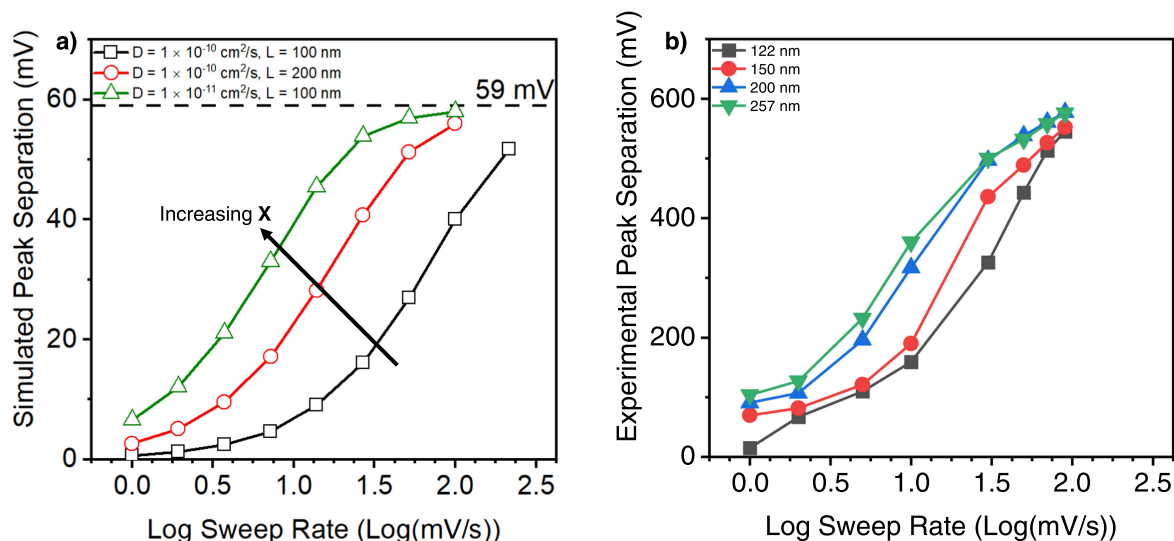


Figure 7. (a) Simulated and (b) experimental peak separation as a function of scan rate for different thicknesses.

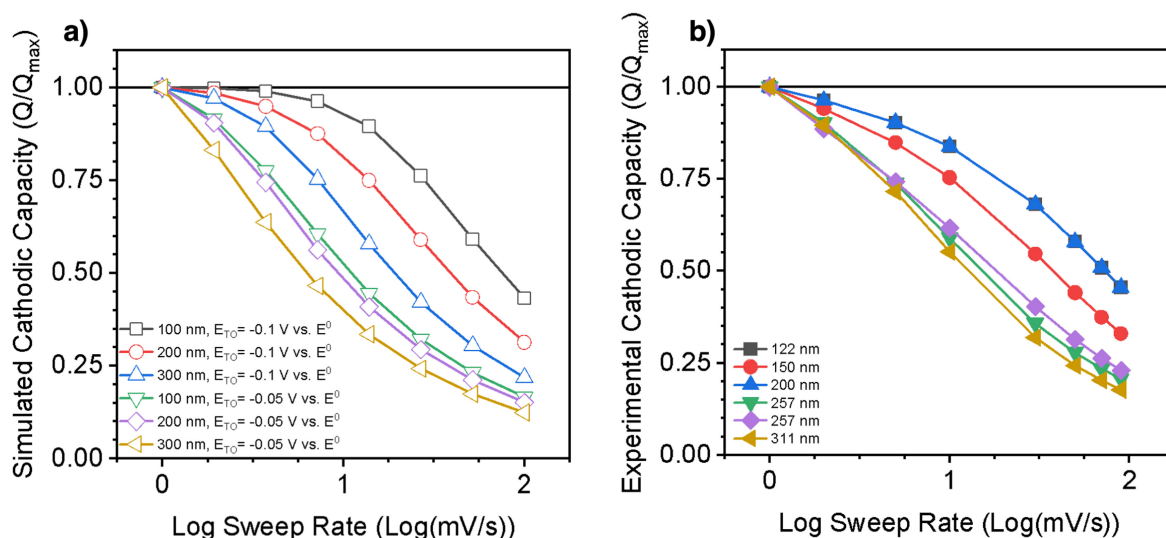


Figure 8. (a) Simulated and (b) experimental cathodic capacity vs scan rate for different thicknesses. Here Q_{max} represents the maximum capacity achieved for a particular sample, rather than the maximum theoretical capacity.

ohmic drop for the simulated cyclic voltammograms. Peak separation of larger than 58 mV has been shown for similar modeling studies which incorporated either more sluggish kinetics at the interface or ohmic drop within the system.^{40,41} An important trend noted for both the experimental and simulated results is that the curve shifts upwards for higher values of X . This is demonstrated by varying film thickness and assuming constant values of D_{Li} for the experimental films, and varying both the thickness and diffusivity parameters in the simulation. For a fixed scan rate, an increase in either thickness or diffusivity will increase X , which in turn is shown here to be coupled with an increased peak separation. Further insight into the peak separation behavior beyond this general trend would likely require a different representation of the interfacial kinetics (for example, Butler-Volmer kinetics), or an ohmic drop implementation within the model.

Scan rate dependence of the capacity.—Cathodic capacities were calculated for both experimental and simulated CVs by taking the integral of current passed with respect to time during the cathodic sweep. Here, the capacities are compared for simulated voltammograms of three different film thicknesses and two different turnover potentials (Fig. 8a). All CVs shown exhibit some capacity

loss at faster scan rates, with increased capacity loss as a function of both increasing film thickness and narrowing the potential window by moving the turnover potential from $-100 \text{ mV vs } E^0$ to $50 \text{ mV vs } E^0$. When similar analysis is performed on the experimental cathodic capacities, the same correlation between increased film thickness and decreased capacity is observed (Fig. 8b). Given the previous section's results which show increased peak separation as a function of film thickness, we also infer that there are potential window effects at play due to the cathodic peak migrating towards the turnover potential. While the simulation is shown here to be capable of capturing capacity loss as a function of potential window and timescale limitations, it does not model capacity loss which arises from other processes, such as electrode degradation or ion trapping.

Conclusions

In conclusion, we demonstrate a framework for understanding the ion-insertion kinetic behavior of thin-film electrodes by combining experimental Nb_2O_5 voltammetry data with a voltammetry model built on diffusion in one dimension. Herein, we highlight the commonly used method of “ b -value analysis,” and show that the

b -value response may be modulated both experimentally and in silico by altering the diffusion length scale, as characterized by the dimensionless film thickness X , the ratio between the film thickness and the diffusion-layer length. The entire range between the theoretical extrema of $b = 0.5$ and 1 is shown to be accessible as a function of X . We elucidate that in an ion-insertion electrode, intermediate b -values between 0.5 and 1 arise due to finite diffusion and that the buildup of a non-monotonic concentration profile in the electrode can lead to b -values < 0.5 . The finite diffusion model serves as a useful first step in predicting the kinetic response of an electrode undergoing ion-coupled electron transfer. The electrode experimental variables, film thickness and diffusivity, can be readily obtained from physical or electrochemical methods. The results inform the selection of scan rates to observe, for example, surface-limited kinetics. The employed voltammetry model is powerful in its simplicity, but is limited by the assumptions of Nernstian behavior at the surface, a constant diffusion coefficient throughout cycling, zero ohmic drop, and single-crystal 1-D geometry. We regard these as opportunities for further improvement.

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