

Estimating Diffusion Coefficients of Probe Molecules into Polyelectrolyte Brushes by Electrochemical Impedance Spectroscopy

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Molecular transport through thin polymer films has become a subject with a variety of challenges and opportunities for chemists, physicists, and material scientists in recent years. The diffusion of probe molecules in and out of macromolecular environments plays a major role in the response of polymer-based sensor materials or the design of time-released drug delivery systems. Obtaining an improved understanding of the relevant dynamic phenomena, like transport of molecular probes, in boundary layers represents a crucial step to develop a clearer picture of the molecular transport processes taking place at interfaces modified with macromolecular assemblies. In this work, we present a new approach based on the derivation of the theoretical impedance transfer function to unambiguously describe the impedance response of gold electrodes modified with poly(methacryloyloxy)-ethyl-trimethyl-ammonium chloride (PMETAC) brushes. We demonstrate that this methodology not only enables the description of the experimental data but also provides insightful information about the dynamics of the diffusion of probe molecules inside the brush. More important, we show the capabilities of electrochemical impedance spectroscopy to gather information on a molecular transport process inside the brush under experimental conditions in which other electrochemical techniques are no longer applicable. As such, we consider that this experimental approach constitutes a new and powerful tool to estimate diffusion coefficients of probe molecules into interfacial macromolecular assemblies.

During the past decade, polymer brushes emerged as a new class of building blocks with outstanding characteristics to modify and control interfacial properties of materials.^{1,2} Polymer brushes refer to polymer chains tethered at one end to a solid substrate

forming a “brushlike” macromolecular film. The flexible nature of the polymer chains enables the reorganization of the macromolecular film upon environmental changes in order to minimize the system free energy.¹ This ability of the film to reorganize and adopt new conformational states depending on the surrounding determines its “responsive” behavior, which is widely exploited in the creation of “smart” interfaces.³ In particular, when dealing with polyelectrolyte brushes, their responsive behavior can be governed by a wide variety of environmental stimuli such as pH, salt concentration, solvent, or temperature. For example, weak polyelectrolyte brushes display significant reorganization processes at interfaces upon protonation/dissociation of their acidic/basic groups.^{4,5} As a consequence, the conformational state of the brush can change from the swollen to a totally collapsed state.

Within this framework, the development of switchable and tunable electrochemical interfaces turned into a research topic of increasing interest into the scientific community. Derivatizing or modifying electrode surfaces with responsive macromolecular architectures^{6,7} paves the way to the construction of novel electrochemical interfaces with tunable interfacial electron transfer properties that can be modulated or manipulated through environmental signals.

Triggering the collapse of a polyelectrolyte brush will lead to a more compact film and, consequently, from the electrochemical point of view, this conformational transition will affect the charge transfer process across the electrochemical interface. In other words, the brush interfacial reorganization can govern the access of diffusional redox species to the electrode surface, thus acting as a “molecular gate” of the electrochemical process. On the other hand, during the last years, electrochemical impedance spectroscopy (EIS) has grown in relevance and has been demonstrated to be a powerful tool to accurately monitor electron transfer processes at electrodes modified with self-assembled monolayers, polyelectrolyte multilayers, or biomolecular architectures.⁸

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More recently, EIS has been successfully extended to the study of electrodes modified with polymer brushes.⁹ Minko, Katz, and co-workers described a novel approach to create electrochemical gating systems using mixed polymer brushes grafted to an electrode surface.¹⁰ The morphological transitions in the mixed polymer brushes resulted in the precise tuning of their permeability for ion transport which was straightforwardly determined by EIS.¹⁰

On the other hand, Jennings and co-workers used EIS to evaluate the film performance and extract useful properties such as the film resistance and capacitance from ultrathin copolymer brushes acting as molecular barriers.¹¹ In addition, they also demonstrated the very interesting use of EIS to probe the rate of a pH-induced response of the copolymer brush by evaluating the impedance change at a fixed frequency.¹² In a similar fashion, Huck and co-workers recently described the application of EIS to probe the interfacial changes occurring at a polyelectrolyte brush bearing quaternary ammonium groups upon formation of strong ion pairs in different electrolytic environments.¹³ This increasing interest stems from the powerful capabilities of EIS to act as an electronic transducer of molecular level processes occurring into the brush environment. In most of the cases, the physicochemical information is obtained after fitting the complex impedance signal with a theoretical equivalent circuit which includes different elements representing physicochemical processes occurring at the interface.¹⁴ The choice of the suitable equivalent circuit must be done carefully in order to represent the actual physicochemical process taking place within the experimental system. The analysis could be even more complicated when different equivalent circuits, with reasonable physical meaning but different interpretation, can accurately describe the same set of experimental results.

This implies that gaining insight into the actual physicochemical processes governing the impedance response of polymer brushes can be significantly affected by the choice of the equivalent circuit. This will also affect the reliability of EIS to provide quantitative data about these processes. In this work, we put a particular emphasis on demonstrating the applicability of EIS to provide quantitative data about the relevant physical and chemical parameters of the system without requiring the use of an equivalent circuit as a first choice. In order to achieve an unambiguous description of the impedance response, we attempted the derivation of a theoretical impedance transfer function for the polyelectrolyte brush that describes the experimental data

and, more important, provides insightful information about the dynamics of the molecular transport inside the brush. The latter one represents a key aspect of this work considering that molecular transport of probe molecules through macromolecular assemblies plays a major role in the rational design of time-released drug delivery systems or the time-dependent response of polymer-based sensor materials, just to name a few examples. In this context, this work aims at providing new tools and methodologies to gain a better understanding of the diffusional phenomena taking place in boundary layers constituted of polymer brushes.

EXPERIMENTAL SECTION

Electrochemical measurements were carried out at room temperature in a conventional three-electrode cell. A large area platinum sheet was used as the counter electrode, and a saturated calomel electrode (SCE) was the reference electrode. All potentials are referred to the SCE. Working electrodes were obtained by modifying Au substrates after growing cationic brushes of poly-(methacryloyloxy)-ethyl-trimethyl-ammonium chloride (PMETAC) on the surface. The preparation method is described in detail elsewhere.^{14,15}

Solutions of KCl, KNO₃, and KClO₄ (or NaClO₄) were used as supporting electrolytes and prepared from analytical grade (Merck) reagents and Milli-Q water. Before performing each measurement, the working electrode was thoroughly rinsed with Milli-Q water and immersed in the supporting electrolyte solution for 10 min. Experiments were performed under purified N₂ gas saturation at 25 °C in the presence of a 1 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe in KCl and KNO₃ solutions at concentrations of 0.001, 0.1, and 1 M as well as in KClO₄ solutions (0.001 and 0.1 M) and a 1 M NaClO₄ solution.

Cyclic voltammetry measurements were obtained by scanning the potential between -0.5 and +0.9 V vs SCE, on modified gold electrodes.

Impedance spectra were obtained with a Zahner IM6d electrochemical workstation on modified gold electrodes with 0.56 cm² apparent area. The dc potential was held at the open circuit potential while a 10 mV amplitude ac potential was applied. The voltage signal frequencies used for EIS measurements ranged from 100 kHz to 1 mHz. Impedance data analysis was performed according to proper transfer function derivation and identification procedures with the use of complex nonlinear least-squares (CNLS) fitting based on the Marquardt–Levenberg algorithm.¹⁶ Nonlinear optimizations based on the Marquardt–Levenberg algorithm contained a weighting function that ensured a more uniform relative distribution of the differences over all frequencies.

RESULTS AND DISCUSSION

Using a PMETAC brush-modified gold electrode (Figure 1a), cyclic voltammograms were recorded at varying scan rates v (V s⁻¹) in a 0.001 M KClO₄ solution. The concentration of

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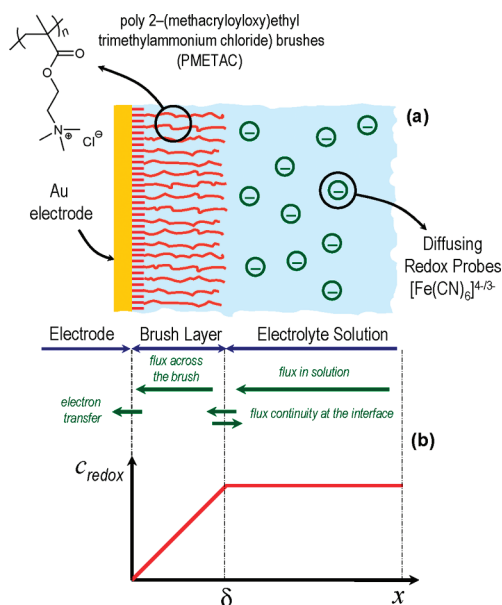


Figure 1. (a) Schematic illustration of a gold electrode modified with PMETAC brushes in the presence of redox probe molecules in solution (upper part). (b) Qualitative description of the steady-state concentration profile of redox species under finite-length diffusion conditions.

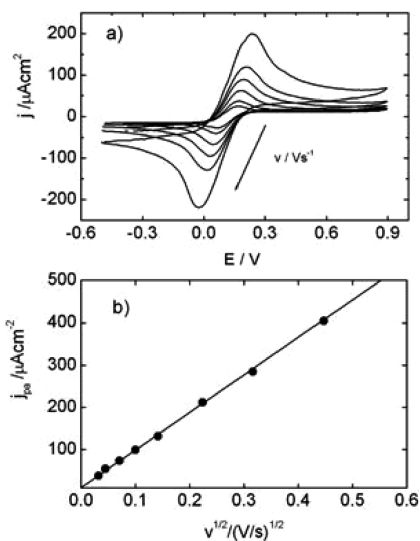


Figure 2. (a) Cyclic voltammograms of the PMETAC-modified electrode obtained upon application of different potential scan rates: 1, 2, 5, 10, 20, and 50 $\text{mV} \cdot \text{s}^{-1}$. The measurements were performed in 0.001 M KClO_4 + 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$. (b) Peak current density dependence on the square root of the potential scan rate.

$\text{K}_4\text{Fe}(\text{CN})_6$ (present in the solution as an electrochemically active molecular probe) was $C_0 = 1 \text{ mM}$. Typically, the voltammograms exhibit a conjugated pair of peaks corresponding to the reversible electron transfer of the redox couple on gold electrodes (Figure 2a). The recorded effect of the scan rate v on the baseline corrected oxidative peak current i_p can be accurately described by the Randles–Ševčík expression¹⁷ in eq 1 in the 1–50 $\text{mV} \cdot \text{s}^{-1}$ range, as shown in Figure 2b. According to eq 1, a diffusion coefficient $D = 1.08 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ was calculated.

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C_0 \quad (1)$$

Where n is the number of electrons involved in the electrode reaction, A is the electrode area, D is the diffusion coefficient of the electroactive species, v is the potential scan rate, and C_0 is the concentration of the electroactive species. In our experiments, $n = 1$ and $A = 0.56 \text{ cm}^2$.

The literature diffusion coefficient of $7.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for aqueous ferrocyanide is in good agreement with the value obtained from these experiments.^{18,19} Moreover, these voltammetric results indicate that, for 0.001 M NaClO_4 , a reasonably reversible electron transfer takes place subject to a semi-infinite planar diffusion regime.²⁰ Thus, diffusion of the redox probe does not slow down when it is surrounded by the swollen polymer brush, as compared to the aqueous solution.

On the other hand, increasing perchlorate concentrations in the electrolyte induce increasingly higher degrees of collapse of polymer brush structures and result in gradually more distorted voltammetric responses, characterized by noisy traces containing peaks that can no longer be clearly recorded and indicating a loss of signal transduction from the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe. These data indicate that both mass transport across the polymer film and electron reaction at the gold surface become gradually inhibited according to ClO_4^- concentration. This is owing to the formation of strong ion pairs between the PMETAC monomer units and the anions in the supporting electrolyte. In the case of ClO_4^- anions in the presence of the quaternary ammonium groups (QA^+), as those constituting the PMETAC chains, the ion-pairing interactions are strong enough to drastically change the properties of the polymer brush layer. In particular, the hydration of the polyelectrolyte brush is sharply changed upon coordination of ClO_4^- , giving the monomer units hydrophobic characteristics. This can be easily understood if we consider the fact that ClO_4^- salts of quaternary amines are water-insoluble compounds but highly soluble in chloroform or xylene. Within the traditional picture of polyelectrolyte brushes, the collapse is seen as a result of electrostatic screening of pendant charges by means of highly mobile counterions.^{21–24} However, in the case of the ion-paired ClO_4^- species, the brush experiences not only an electrostatic change but also a drastic (hydrophilic-to-hydrophobic) chemical change. As a consequence of this change, the brush suffers what has been called “hydrophobic collapse” instead of the traditional “electrostatic-driven collapse”.^{15,25,26} Brushes ion-paired with ClO_4^- anions behave like neutral brushes in a poor solvent, where the monomers try to exclude the solvent and effectively attract one

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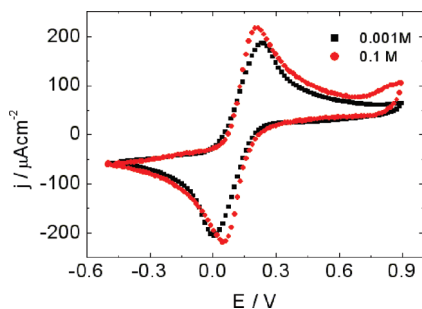


Figure 3. Cyclic voltammograms of the PMETAC-modified electrode obtained upon application of potential scans at $50 \text{ mV} \cdot \text{s}^{-1}$. The measurements were performed in (■) $0.001 \text{ M KCl} + 1 \text{ mM K}_4\text{Fe}(\text{CN})_6$ and (●) $0.1 \text{ M KCl} + 1 \text{ mM K}_4\text{Fe}(\text{CN})_6$.

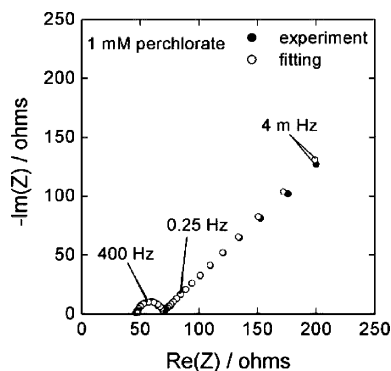


Figure 4. Nyquist plots of impedance data for PMETAC-modified electrodes in 0.001 M KClO_4 containing a $1 \text{ mM K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture. Experimental data (●) and fit results (○) according to eq 21.

another. Interestingly, this phenomenon is observed even under low concentration conditions.^{15,26a} As a result, the flexible chains form compact architectures in such a way that minimizes the interaction between the ion-paired monomers and the solvent. From an electrochemical point of view, this new conformational state represents a compact layer in which the diffusion and the electron transfer of the redox probe are strongly hindered, as evidenced by the absence of an appreciable voltammetric signal. The distortion of the voltammetric peaks should be ascribed to the fact that, within the time window of the experiment, only negligible amounts of redox probes reached the gold surface. This indicates that, in spite of its ease and versatility, cyclic voltammetry is not always the best choice to explore in detail the molecular transport of the redox probes in highly collapsed brushes.

When chloride or nitrate replaced perchlorate as the species interacting with the brush in the supporting electrolyte, the voltammetric response, although qualitatively similar, was barely affected by the anion concentration, in the 1 mM to 1 M concentration range, as opposed to ClO_4^- . (Figure 3). This can be explained considering that, in contrast to ClO_4^- , these counterions do not form ion pairs with QA^+ groups. Voltammetric data for equivalent systems can be found elsewhere.^{13,14,27}

To further explore and gain insight on the physicochemical characteristics of the brush-coated electrodes, we proceeded to use electrochemical impedance spectroscopy. Figures 4, 5, and 6 display experimental and fitted impedance spectra for gold electrodes modified with a surface-tethered PMETAC brush in

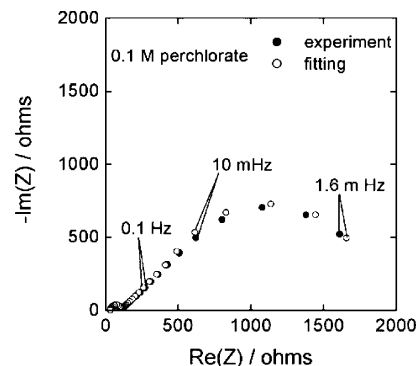


Figure 5. Nyquist plots of impedance data for PMETAC-modified electrodes in 0.1 M KClO_4 containing a $1 \text{ mM K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture. Experimental data (●) and fit results (○) according to eq 21.

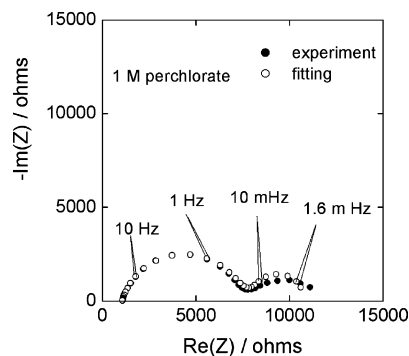


Figure 6. Nyquist plots of impedance data for PMETAC-modified electrodes in 1 M NaClO_4 containing a $1 \text{ mM K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture. Experimental data (●) and fit results (○) according to eq 21.

ClO_4^- -containing solutions with concentrations of 1 mM KClO_4 , 0.1 M KClO_4 , and 1 M NaClO_4 , respectively. All spectra exhibit a high-frequency capacitive contribution and a distinctive contribution at low frequencies that suggests Warburg-type behavior in the electrolyte with lower concentration (Figure 4), while this contribution becomes related to finite-length diffusion with an increase in the anion concentration (Figures 5 and 6). Thus, the high-frequency contribution can be associated with the relaxation of the charge transfer process at the surface and the charging of the interfacial capacitor, while the second contribution at low frequencies can be related to ionic transport of the electroactive probe through the polyelectrolyte brush. These results fully agree with cyclic voltammetric responses presented above, although the observed finite-length diffusion is at variance with that predicted by some existing theories.^{10,11,13,28} At this point, it is probably worth introducing a brief qualitative analysis of data presented in Figures 4–6, before attempting to derive the impedance transfer function and to apply identification procedures.

With reference to the increase in impedance values observed for increasing perchlorate concentration in solution, the following discussion provides a plausible explanation. The ClO_4^- -driven collapse of the PMETAC leads to a scenario in which the partial blockage/coverage (θ) of electroactive area is sensitively increased and, as such, the passage of Faradaic current is

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strongly blocked. It is worth mentioning that the increased blockage is not due to an increase in surface coverage of grafted polyelectrolyte chains at the metal/film interface. The density of anchoring/grafting points of the polymer chains does not change when the brush collapses. The increased blockage results from an increase in film rigidity/density owing to the strong conformational changes of the polymer chains in the presence of strong ion pairing interactions.

The “blocked” surface here is independent of the potential.²⁹ Assuming, as a first approximation, that partial coverage does not affect significantly linear conditions for the mass-transport step at a planar electrode, the effect of the partial coverage is simply to reduce the active area. All impedances are inversely proportional to the active area; thus, if the capacity of the covered surface can be neglected with respect to the double layer capacity of the active surface, all impedance values are inversely proportional to the fractional area of active surface ($1 - \theta$). In particular, these circumstances enable one to explain the observed larger charge transfer resistances R_{ct} (Ω) and smaller double layer capacitances C_{dl} (F) for increasing θ , i.e., for an increasing degree of collapse of the polyelectrolyte brush.

Regarding the second time constant at low frequencies, it corresponds to a uniformly accessible electrode to mass transfer through a polyelectrolyte brush of finite thickness. The diffusion impedance response of the brush-containing electrode, when the resistance of the brush to diffusion is much larger than that of the bulk electrolyte, can be approximated by the diffusion impedance of the brush. Moreover, the thickness of the diffusion layer depends significantly on the time scale of a transient experiment or equivalently on the frequency scale of impedance experiments. If there is a finite length associated with the diffusion layer beyond which the electrode process can have no effect on concentrations, then there is a frequency range for sufficiently low frequencies where impedance response departs from a pure Warburg behavior. Noteworthy, for our experiments, we set the lowest measurement frequency at a lower value than that used in comparable experiments from the literature.¹³ Thus, it can be anticipated that the brush layer represents a diffusion-limiting barrier of finite thickness for electroactive molecular probes (Figure 1b). Also, when additional negative charges are present in the form supporting electrolyte anions, the diffusion constant of the probe anion is expected to further decrease.³⁰ In fact, several arguments were advanced in the literature indicating that ion diffusion rather than electron hopping is the charge transport mechanism in $[\text{Fe}(\text{CN})_6]^{3-}$ -coordinated PMETAC brushes.²⁷

Figures 7 and 8 display experimental and fitted impedance spectra for gold electrodes modified with surface-tethered PMETAC brush in Cl^- - and NO_3^- -containing solutions with concentrations of 1 M, respectively. Again, when chloride or nitrate replace perchlorate, the impedance response, although exhibiting qualitatively similar dynamics, is quantitatively less affected by the anion concentration, in the 1 mM to 1 M concentration range, as compared to ClO_4^- and in agreement with voltammetric data.

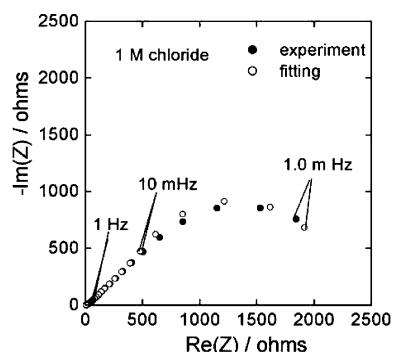


Figure 7. Nyquist plots of impedance data for PMETAC-modified electrodes in 1 M KCl containing a 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture. Experimental data (●) and fit results (○) according to eq 21.

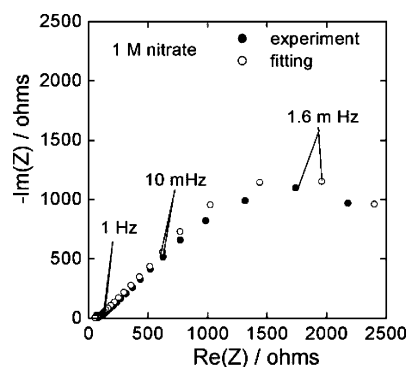


Figure 8. Nyquist plots of impedance data for PMETAC-modified electrodes in 1 M KNO_3 containing a 1 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ (1:1) mixture. Experimental data (●) and fit results (○) according to eq 21.

These experimental facts suggest that increasing Cl^- and NO_3^- concentrations determines a less efficient collapse of the brush structure, and in turn, the electrode active area becomes less blocked, as compared to perchlorate ion. As previously discussed, the distinctive action of different anionic species in solution is originating from ion-pairing interactions between the QA^+ monomer units and the different K counterions.¹⁵

The electrochemical reaction can formally be written as



where O is the $[\text{Fe}(\text{CN})_6]^{3-}$ species and R represents the $[\text{Fe}(\text{CN})_6]^{4-}$ species.

The potential (V) dependence of the rate constants can be expressed by an exponential law:

$$k_a = k_a^0 \exp[b_a(V - V_r)] \quad (3)$$

$$k_c = k_c^0 \exp[b_c(V - V_r)] \quad (4)$$

where $b_c = -\alpha_c F/RT$ and $b_a = \alpha_a F/RT$, k^0 is a constant independent of V , α is the transfer coefficient, and V_r is the Nernst equilibrium potential.

Charge balance is given by:

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(30) Reznik, C.; Darugar, Q.; Wheat, A.; Fulghum, T.; Advincula, R. C.; Landes, C. F. *J. Phys. Chem. B* **2008**, *112*, 10890–10897.

$$I_f = -A_e F [k_c C_O(0) - k_a C_R(0)] \quad (5)$$

where $C_O(0)$ and $C_R(0)$ represent concentrations of the oxidized and reduced species at the surface and A_e is the apparent electrode area. The negative sign arises from the assumed convention in which the cathodic current is negative.

When a small ac perturbation signal $\Delta V = \tilde{V} \exp(j\omega t)$ is applied, the current and concentrations oscillate around steady-state values: $I_f = I^{dc} + \Delta I$, $C = C^{dc} + \Delta C$ (for both O and R), where the superscript dc indicates a parameter that changes only slowly with time (i.e., either a steady-state term or one that does not change with the frequency of the perturbation ω), and the symbol Δ indicates a parameter oscillating periodically with time t . The resulting oscillations with time may be written as $\Delta I = \tilde{I} \exp(j\omega t)$ and $\Delta C = \tilde{C} \exp(j\omega t)$. \tilde{V} and \tilde{I} represent the phasors of potential and current. Taking \tilde{V} as the reference signal and considering the phase shift ϕ between them results in $\tilde{E} = E_o$ and $\tilde{I} = I_o \exp(j\phi)$, where E_o and I_o are the amplitudes of the applied potential and the resulting current waves, respectively.

For simplicity, we write a single generic expression for O and R mass balances according the second Fick's law, as

$$\frac{dC}{dt} = -\nabla J = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

for the flux J along the x coordinate perpendicular to the electrode surface or, equivalently,

$$\frac{d\Delta C}{dt} = D \frac{\partial^2 \Delta C}{\partial x^2} \quad (7)$$

which in the Fourier domain can be expressed as

$$j\omega \Delta C(x, \omega) = D \frac{d^2 \Delta C(x, \omega)}{dx^2} \quad (8)$$

with $j = (-1)^{1/2}$.

The general solution of the second-order differential eq 8 is

$$\Delta C(x, \omega) = P \exp\left(x \sqrt{\frac{j\omega}{D}}\right) + Q \exp\left(-x \sqrt{\frac{j\omega}{D}}\right) \quad (9)$$

subject, in this case, to the following boundary conditions (eqs 10 and 11) corresponding to a finite-length diffusion in a system having a transmissive boundary,

$$x = 0 \quad F\Delta J = \Delta I_f \quad (10)$$

which expresses the flux continuity condition at the interface, and

$$x = \delta \quad \Delta C = 0 \quad (11)$$

which indicates that transfer of electroactive species O and R is possible at $x = \delta$ (thickness of the diffusion layer), while for $x \geq \delta$, C remains unaltered and equal to C^{dc} .

Interestingly, deviations from the straight line in a Cottrell representation at long times in $[\text{Fe}(\text{CN})_6]^{3-}$ -coordinated PMETAC brushes were interpreted by Spruijt et al.²⁷ as due to the confinement of the electroactive species in a finite layer. In

contrast with the impedance response derived in this work, the limit of the diffusion zone is considered impermeable to the diffusing species.³¹ Thus, these authors describe the system with a zero-flux boundary condition for $x = \delta$, claimed to be valid at least on the time scale of the chronoamperometric experiments. However, the experimental conditions used in this work represent a different scenario in which the flux continuity at the interface provides a more realistic framework.

Using eqs 9 and 11, we can write,

$$\Delta C(0, \omega) = -2Q \exp\left(-\delta \sqrt{\frac{j\omega}{D}}\right) \sinh\left(-\delta \sqrt{\frac{j\omega}{D}}\right) \quad (12)$$

and calculate ΔJ at the surface in the Fourier domain

$$\begin{aligned} \Delta J(0, \omega) &= -D \frac{d\Delta C(x, \omega)}{dx} \Big|_{x=0} \\ &= 2QD \sqrt{\frac{j\omega}{D}} \exp\left(-\delta \sqrt{\frac{j\omega}{D}}\right) \cosh\left(-\delta \sqrt{\frac{j\omega}{D}}\right) \end{aligned} \quad (13)$$

Let us call $M(0, \omega)$ the mass transfer function, defined as in refs 32 and 33

$$M(0, \omega) = \frac{\Delta C(0, \omega)}{\Delta J(0, \omega)}$$

Considering the boundary condition at the surface (eq 10), results in

$$M(0, \omega) = \frac{\Delta C(0, \omega)}{\Delta J(0, \omega)} = \frac{F\Delta C(0, \omega)}{\Delta I_f} = \frac{1}{D \sqrt{\frac{j\omega}{D}}} \tanh\left(\delta \sqrt{\frac{j\omega}{D}}\right) \quad (14)$$

In order to calculate the reaction impedance Z_r , eq 5 describing the rate of charge transfer should be linearized, according to the Taylor series expansion, retaining only terms with first-order derivatives, giving

$$\begin{aligned} \frac{1}{Z_f} = \frac{\Delta I_f}{\Delta V} &= \left(\frac{\partial I_f}{\partial V}\right)_{dc} + \left(\frac{\partial I_f}{\partial C_O(0)}\right)_{dc} \frac{\Delta C_O(0)}{\Delta I_f} \frac{\Delta I_f}{\Delta V} + \\ &\quad \left(\frac{\partial I_f}{\partial C_R(0)}\right)_{dc} \frac{\Delta C_R(0)}{\Delta I_f} \frac{\Delta I_f}{\Delta V} \end{aligned} \quad (15)$$

Derivatives in eq 15 correspond to stationary conditions and may be obtained from eq 5.

$$\left(\frac{\partial I_f}{\partial V}\right)_{dc} = \frac{1}{R_{ct}} = A_e F \left[C_O(0) \left(\frac{k_c \alpha_c F}{RT}\right) + C_R(0) \left(\frac{k_a \alpha_a F}{RT}\right) \right] \quad (16)$$

$$\left(\frac{\partial I_f}{\partial C_O(0)}\right)_{dc} = -A_e F k_c \quad (17)$$

$$\left(\frac{\partial I_f}{\partial C_R(0)}\right)_{dc} = A_e F k_a \quad (18)$$

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Table 1. Fitting Parameters R_{Ω} , C_{dl} , and Those from the Reaction Impedance Z_f According to Eq 21 for the Experimental Spectra Shown in Figures 4–8

	R_{Ω} (Ω)	C_{dl} (μF)	R_{ct} (Ω)	B ($\text{s}^{1/2}$)	δ (cm)	D ($\text{cm}^2 \text{s}^{-1}$)
KClO ₄ (1 mM)	48	21.5	20		27×10^{-7}	7.6×10^{-6a}
KClO ₄ (0.1 M)	32.5	13.4	72	9.96	24×10^{-7}	5.8×10^{-14}
KClO ₄ (1 M)	1070	8.7	6440	10.47	23×10^{-7}	4.8×10^{-14}
KCl (1 M)	8.4	23.6	15.4	13.34	32×10^{-7}	5.75×10^{-14}
KNO ₃ (1 M)	53.8	18.0	24	14.4	30×10^{-7}	4.3×10^{-14}

^a This value was obtained from data in Figure 2b.

and eq 15 becomes

$$\frac{1}{Z_f} = \frac{1}{R_{ct}} + \left(\frac{\partial I_f}{\partial C_O(0)} \right)_{dc} \frac{M_O(0)}{F} \frac{1}{Z_f} + \left(\frac{\partial I_f}{\partial C_R(0)} \right)_{dc} \frac{M_R(0)}{F} \frac{1}{Z_f} \quad (19)$$

For simplicity, we assume $D_O = D_R = D$, and so $M_O(0) = M_R(0) = M(0)$ that can be calculated according to eq 14.

Consequently, the reaction impedance can be identified as

$$Z_f = R_{ct} + R_{ct} \frac{A_e(k_c - k_a)}{D\sqrt{j\omega}} \tanh\left(\delta\sqrt{\frac{j\omega}{D}}\right) \quad (20)$$

which, after rearranging reduces to

$$Z_f = R_{ct} + \frac{\sigma}{\sqrt{\omega}} \tanh(B\sqrt{j\omega})(1 - j) \quad (21)$$

where the so-called mass transfer coefficient σ contains the contributions of the forms O and R and $B = \delta/(D)^{1/2}$.

Finally, the electrode impedance consists of the electrolyte resistance R_{Ω} connected in series with a parallel connection of the double layer capacitance C_{dl} and the reaction impedance Z_f .

Fitting experimental impedance spectra in Figures 4–6 to the theoretical model allows one to estimate the parameters assembled in Table 1. Included in this table are the brush thickness values δ that were measured using protocols described in the literature.¹⁴

Double layer capacitance values derived from the fit in a 0.001 M KClO₄ solution are in good agreement with the 25–40 $\mu\text{F cm}^{-2}$ capacitance value range measured on gold single crystals in perchloric acid solutions.³⁴ Thus, this value confirms that diluted KClO₄ solutions correspond to near nonblocked electrode surfaces or, equivalently, to a swollen brush in which mass transport and electron transfer of electroactive probes are not hindered. Decreasing C_{dl} values (expressed in Farads) were observed for increasing blocking of the active surface area as explained above. A noteworthy fact is that this decrease was also informed in the literature, although it was interpreted in terms of partial exclusion of water from the brush and a decrease in charge density.¹³

A most relevant parameter obtained from the fitting procedure was the diffusion coefficient D , derived at a different anion type concentration and, thus, reflecting various states of the polymer brush swelling. In principle, D values are markedly smaller than those expected for diffusion in aqueous solutions and only negligible variations were measured according to the anion present in the supporting electrolyte. All calculated D values for the different anions in the supporting electrolyte and varying degrees of swelling are within the $4\text{--}8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ range. Interestingly, we reproducibly observed a sharp difference between coefficient diffusion values of the redox probes obtained in 1 mM ClO₄[−] and the rest of the supporting electrolytes, including 1 mM Cl[−] and NO₃[−], i.e., the same ionic strength but different ions. This particular diffusional behavior observed in 1 mM ClO₄[−] is supported separately by CV and EIS in which the former describes a well-defined diffusional voltammogram of the redox probes and the latter displays the typical impedance response of a semi-infinite diffusional process. Even though the origin of these particular transport properties of PMETAC brushes in the presence of 1 mM ClO₄[−] is beyond the scope of this work, we should refer to the seminal work of Anson and co-workers³⁵ on copolymer film-modified electrodes. These authors encountered that, by randomly incorporating small amounts of hydrophobic comonomers into hydrophilic polymer films, the diffusion of the redox probes was sharply enhanced, even surpassing the transport properties of fully hydrophilic films. They attributed this observation to the creation of phase-segregated interconnected hydrophilic domains that facilitated the motion of the redox ions through the film. In close resemblance to the observations reported by Anson et al., the presence of small amounts of ClO₄[−] would probably generate ion-paired hydrophobic domains delimiting interconnected hydrophilic domains which could facilitate the transport of the electroactive species. However, since D decreases only slightly with the anion concentration, it is clear that, under our working conditions, the brush structure readily becomes compact enough to inhibit at a similar extent the mass transport of redox species through the polymer brush. Conversely, regardless of the ionic strength, the diffusion coefficient values of the redox probes in supporting electrolytes containing Cl[−] and NO₃[−] anions are $\sim 5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$.³⁶

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CONCLUSIONS

The simplified theoretical description presented in this work is adequate to clearly show the simultaneous effect of the collapse of a polyelectrolyte brush on decreasing the active surface and on inhibiting diffusive transport within the brush matrix. Swelling–collapse transitions seem to be more efficient at blocking the electrode surface area when they result from the presence of perchlorate ions in the electrolyte, as compared to chloride or nitrate ions. The degree of diffusive transport inhibition is comparable for all three anions in the supporting electrolytes considered in this work. One valuable feature of the impedance technique relies on its ability to separate both effects.

Data analysis was performed according to proper transfer function derivation and identification procedures, while avoiding the use of ambiguous equivalent circuit models. Moreover, this analysis provides a plausible explanation for the distinct features of the experimental impedance data recorded under different working conditions, something that was lacking in the literature. However, full capabilities of the electrochemical approach were obtained, as usual, with complementary results from other measuring techniques. Within this framework, we have shown that EIS provides a powerful alternative tool for exploring

dynamical aspects and elucidating the magnitude of the molecular transport process occurring at macromolecular interfaces and polymer thin films.^{37,38}

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