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Electrochemical Characteristics of Polyelectrolyte Brushes with Electroactive Counterions

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Cyclic voltammetry (CV) was employed to characterize the electrochemical behavior of polyelectrolyte brushes with immobilized electroactive counterions in response to external changes in concentration and composition of the supporting electrolyte and as a function of brush thickness. Poly(methacryloyloxy)ethyl-trimethyl-ammonium chloride (PMETAC) brushes were synthesized on Au substrates via atom transfer radical polymerization followed by ion-exchange with ferricyanide ions ($[\text{Fe}(\text{CN})_6]^{3-}$) as redox probes. CV measurements of the modified PMETAC brushes showed the typical electrochemical response corresponding to a surface-confined electroactive species and the redox counterions, as $[\text{Fe}(\text{CN})_6]^{3-}$ species form stable ion pairs with the quaternary ammonium groups of the brush. The electron-transfer features of PMETAC brushes with different thicknesses, as characterized by CV and UV-vis spectroscopy, revealed that the charge density probed by CV was lower than the charge density measured by UV-vis spectroscopy. The electrode current decreased significantly with increasing concentration of supporting electrolyte due to the effect of the Donnan potential. Hydrophobic counterions, ClO_4^- , which induced brush collapse, lead to significantly reduced electrode currents.

Introduction

Control over the electrochemical properties of polymer films is of importance in a wide range of technologies, including biosensors,¹ electrode materials for energy and data storage devices,^{2,3} electrochromic devices,⁴ and artificial muscles.⁵ Polyelectrolyte brushes, which consist of charged polymers densely end-grafted to surfaces of various geometries, are promising platforms for designing polymer films with tunable properties because environmental triggers, such as ionic strength, pH, and solvent properties, can promote changes in surface properties. Furthermore, the reversible swelling and collapse transitions of brushes can be exploited in the development of nanoscale actuators,⁶ especially if their response can be triggered upon an electrical stimulus. The responsive behavior of the polyelectrolyte brushes is governed by electrostatic interactions and osmotic pressure and depends strongly on polymer length and grafting density as well as density of charges along the polymer backbones.⁷ Despite extensive studies on a range of polyelectrolyte brushes, a detailed understanding of the kinetics of their swelling and collapse transitions is not known. The responsive properties of polyelectrolyte brushes have been studied using AFM,⁸ ellipsometry,⁹ quartz crystal microbalance with

dissipation,¹⁰ neutron reflectivity,¹¹ and the surface force apparatus.¹² We have previously used electrochemical analysis as a tool to study the internal structure of polymer brushes.¹³ The crucial development in the study reported here is the immobilization of the redox probes as counterions inside the brushes. As shown in Figure 1, cationic polyelectrolyte brushes were loaded with ferricyanide ions ($[\text{Fe}(\text{CN})_6]^{3-}$) via an ion-exchange reaction. This is in contrast to other studies, where the redox probes are free in solution and hence their diffusion through polyelectrolyte brushes is probed.^{13,14} In addition to obtaining information on the fundamental properties of polyelectrolyte brushes, we believe that the incorporation of electroactive species in the brushes provides a potential new route to fast switching and actuation of such brushes using electrochemistry.

Experimental Section

Preparation of Polyelectrolyte Brushes. Au was used as a substrate. The Au substrates were modified with thiol initiator ($\text{BrC}-(\text{CH}_3)_2\text{COO}(\text{CH}_2)_6\text{SH}$). Cationic brushes of poly(methacryloyloxy)-ethyl-trimethyl-ammonium chloride (PMETAC) bearing quaternary ammonium groups (QA^+) were grown from the Au surfaces using atom transfer radical polymerization (ATRP). The polymerization solution for METAC brush: METAC, 41.54 g; CuCl , 0.396 g; CuCl_2 , 0.268 g; BiPy (2,2'-bipyridyl), 1.562 g; MeOH , 32 g; H_2O , 8 g. The mixture was then stirred and de-oxygenated with a stream of dry N_2 (15 min). Initiator-coated Au substrates were sealed in Schlenk tubes, degassed, and left at 20 °C under N_2 . The polymerization solution

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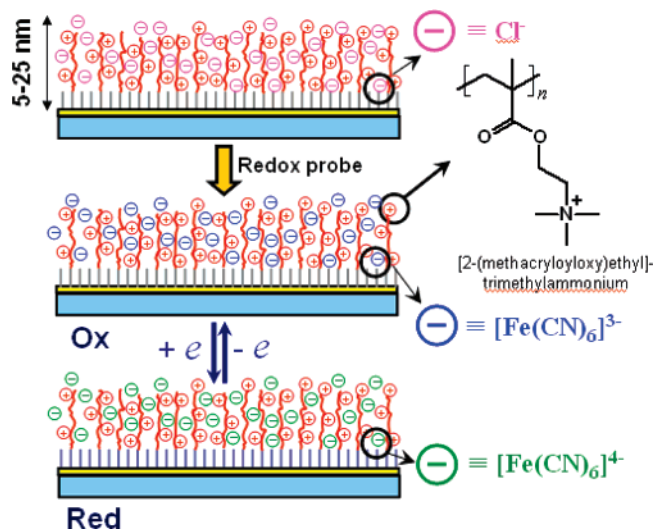


Figure 1. Schematic representation of brushes used in this study.

was then syringed into each Schlenk tube, adding enough solution to immerse each sample completely. After various polymerization times, the samples were removed, washed with water and then methanol, and dried under a stream of N_2 .

Characterization of a PMETAC Brush. The Au substrates used for CV measurements were prepared by evaporating 200 nm of Au on a silicon wafer with 2 nm of chromium as the adhesive layer. The pairing of the redox probe was obtained by immersing the as-synthesized Cl^- -coordinated PMETAC brush in 0.1 M $K_3Fe(CN)_6$ for 30 min. Figure 1 shows a schematic representation of the brushes under study. All CV measurements (measured on an Autolab PGSTAT 30 system) were carried out at room temperature in a three-electrode cell containing a PMETAC brush modified Au substrate as a working electrode, graphite as a counter electrode, and Ag/AgCl as a reference electrode. KCl, LiCl, and $LiClO_4$ solutions were used as supporting electrolytes. The electrochemical cell which was filled with supporting electrolyte and connected to the three electrodes was purged with nitrogen for 10 min before each measurement, and the cell was kept under flowing nitrogen for the duration of the experiment. The Au substrates for UV-vis spectroscopy were prepared by evaporating 20 nm of Au on a glass slide with 2 nm of chromium. Before scanning with UV-vis spectroscopy, in order to compare the charge density (Q) obtained from CV, the $[Fe(CN)_6]^{3-}$ -coordinated PMETAC brush (electroactive PMETAC brush) was immersed into the 5 mM KCl solution for 10 min. Great care was taken to measure an exact absorbance (420 nm) of $[Fe(CN)_6]^{3-}$ of the electroactive PMETAC brush. The samples of the brushes were rinsed abundantly with Milli-Q water and dried with a N_2 stream. Patterned substrates for AFM imaging were prepared. Bare Au substrates were washed with DI water and then with ethanol and dried in N_2 flow. Microcontact printing of patterned initiator SAMs was carried out using a PDMS stamp patterned with 10 μm lines with 10 μm spacing, which was inked with a 5 mM ethanolic solution of the thiol initiator (ω -mercaptoheptyl 2-bromo-2-methylpropanoate). The substrate was then washed again with ethanol and dried in N_2 flow. Polymer brushes were grown from the patterned substrates. AFM measurements were performed using an Agilent Series 4500 SPM (Agilent Technologies) in MAC mode with a scan rate of 0.8 Hz. The amplitude setpoint was adjusted to the minimum applied load required to acquire an image. The data was processed by baseline correction and fourth-order flattening using a homemade algorithm.

Results and Discussion

General Aspects. Figure 2a shows CV plots of electroactive PMETAC brushes (14 nm thick) using 5 mM KCl as the supporting electrolyte. The full width at half-height (fwhh), 136 mV, is larger than an ideal value for a Nernstian redox system,

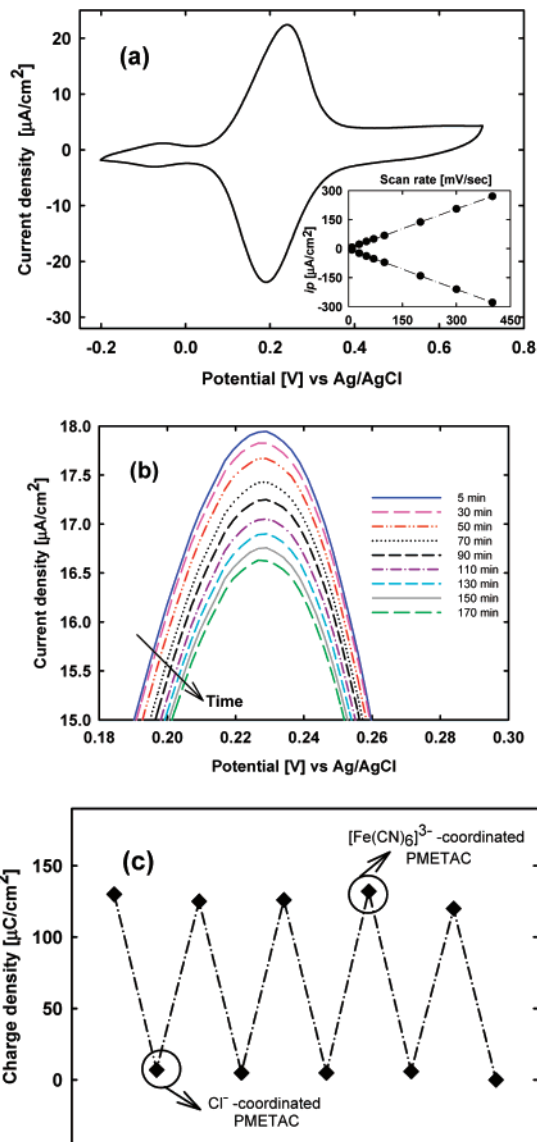


Figure 2. (a) Cyclic voltammogram corresponding to electroactive PMETAC brush (14 nm). v : 30 mVs^{-1} . Supporting electrolyte: 5 mM KCl. Inset: Plot of anodic and cathodic peak currents versus v . (b) Time-dependent anodic current peak of cyclic voltammogram corresponding to electroactive PMETAC brush (12 nm). v : 30 mVs^{-1} . Supporting electrolyte: 5 mM KCl. (c) Plot depicting the switching between the electroactive and nonelectroactive states of the PMETAC brush (15 nm) upon coordination with $[Fe(CN)_6]^{3-}$ (electroactive) and Cl^- (nonelectroactive). Supporting electrolyte: 0.1 M KCl. Immersion time: 5 min.

90 mV, indicating repulsive interactions between the redox sites.¹⁵ Highly reversible electron transfer between the ion paired redox centers and the electrode can be observed clearly. These voltammetric characteristics are typical electrochemical responses for surface-confined electroactive species, which has been described in detail in the literature.¹⁶ One distinctive feature of surface confined species is the linear response of the peak current density (i_p) with scan rate (v). In contrast, in the case of diffusing species, a $v^{1/2}$ dependence should be observed. Changes in the i_p with v were investigated and these results are shown in inset graph of Figure 2a. The linear response of the i_p with the v corresponding to the anodic and the cathodic process was observed

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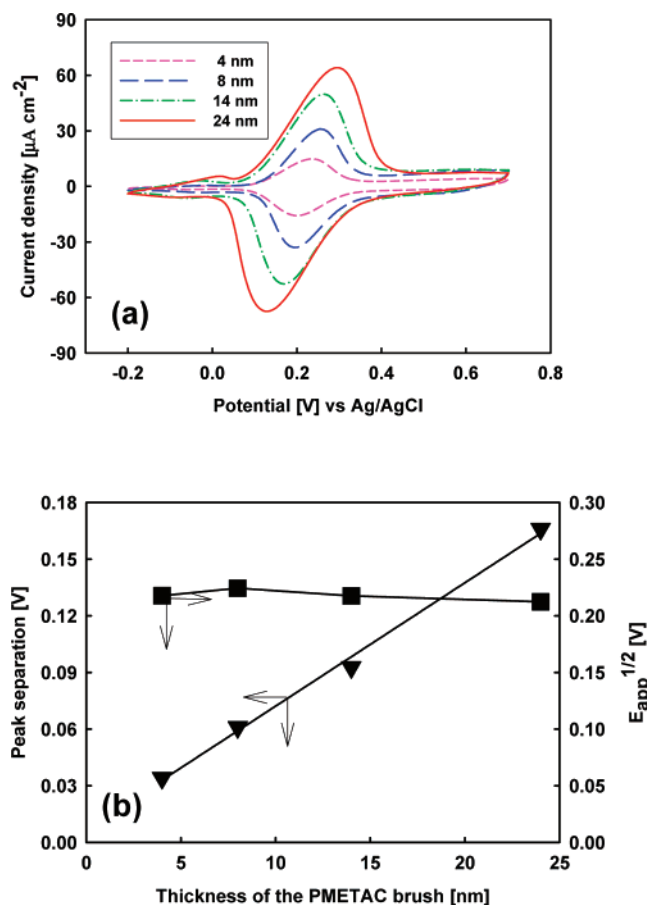


Figure 3. (a) Cyclic voltammograms of the electroactive PMETAC brushes with different thicknesses. v : 70 mV s⁻¹. Supporting electrolyte: 5 mM KCl. (b) Effect of the thickness of the electroactive PMETAC brushes on the peak separation and $E_{app}^{1/2}$ of cyclic voltammogram.

and it verifies that the redox centers are confined in the polymer film and do not significantly diffuse into solution at the timescales of these experiments (several of minutes). The linear response of i_p with v is given by

$$i_p = \frac{n^2 F^2}{4RT} v \Gamma_0 \quad (1)$$

where F is the Faraday constant, T , the temperature, and Γ_0 , the density of surface-confined electroactive species. The Q of the PMETAC brush can be calculated from the cyclic voltammograms. For both the positive and negative scans, a linear background is first subtracted to remove the charging current. The area under the peaks is then integrated and divided by v to obtain the amount of charges. From the data shown in Figure 2a, we estimate Q to be 93 μC cm⁻² that, in our case, is equivalent to having 5.8×10^{14} redox centers per cm² confined in a 14 nm-thick PMETAC brush. This population of redox centers is comparable to other covalently modified electroactive organic films (compare for example ferrocene-terminated thiol monolayers¹⁷ or electroactive organometallic dendrimer films,¹⁸ with 2.8×10^{14} and 1.6×10^{14} redox centers per cm², respectively).

PMETAC brushes collapse either in high ionic strength solutions due to charge screening or via specific interactions in the presence of certain ions like ClO₄⁻, SCN⁻, and I⁻.¹⁹ Scarcely

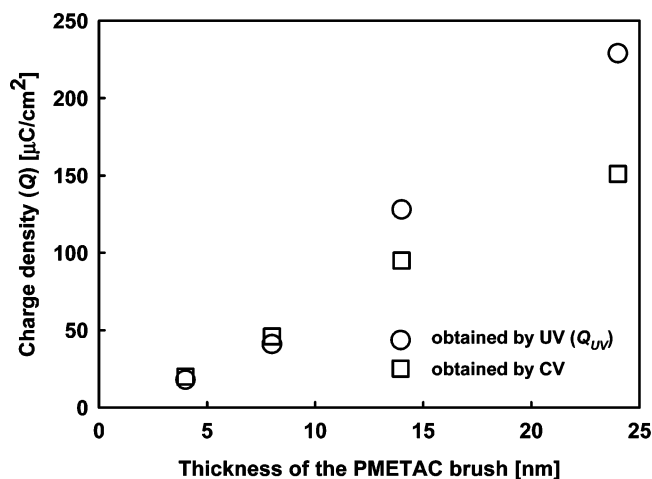


Figure 4. (a) UV-vis spectrum of a 24 nm electroactive PMETAC brush. (b) The comparison of the Q of the PMETAC brushes probed by CV with that Q_{UV} (measured by UV-vis).

hydrated, large, and highly polarizable species interact very strongly with the QA⁺ groups leading to the formation of stable ion pairs. The voltammetric characteristic shown in Figure 2a imply that the redox counterions, [Fe(CN)₆]³⁻ species, form moderately stable ion pairs with the QA⁺ moieties of the brush.²⁰ In other words, the QA⁺-bearing monomers turned into new electroactive monomer units upon ion pairing. In spite of the stable ion pairs of QA⁺ moieties of the brush with [Fe(CN)₆]³⁻ species, time-dependent CV peaks show that electroactive counterions slightly decreased with time. As shown in Figure 2b, the i_p decreased over time (6.6% after 170 min) due to the displacement of the counterion from electroactive species ([Fe(CN)₆]³⁻) to nonelectroactive species (Cl⁻) of supporting electrolyte. The displacement was also observed by immersing the electroactive PMETAC brush in KCl solution. Figure 2c depicts the switching in film electroactivity after repeated changes in brush counterions. Immersing the [Fe(CN)₆]³⁻-coordinated PMETAC brush in a 0.1 M KCl solution for 5 min leads to the complete removal of the electroactive species. The electroactivity can be easily restored by exchanging the nonelectroactive Cl⁻ with [Fe(CN)₆]³⁻ counterions. In other words, the electroactivity of the brush layer can be easily tuned by choosing the respective counterions. It can be observed that repeated switching of the counterion does not affect the charge-transfer characteristics of the brush layer upon coordination with the redox probe.

Effect of Thickness of the Polyelectrolyte Brush. Figure 3a presents the cyclic voltammograms of the electroactive PMETAC brushes with different thicknesses. The current increases with an increase in the thicknesses of the PMETAC brush because there are more redox centers in thicker brushes. The peak separations between the cathodic peaks and the anodic peaks of cyclic voltammograms shown in Figure 3a are depicted in Figure 3b. The peak separation increases with an increase in the thickness of the brush. The peak separation of CV reflects the rate of electron transfer. No peak separation between the oxidation and reduction peaks is expected for noninteracting electroactive groups attached to the surface and in rapid equilibrium with the electrode.^{21,16} Figure 3b shows the effect of the thickness of the

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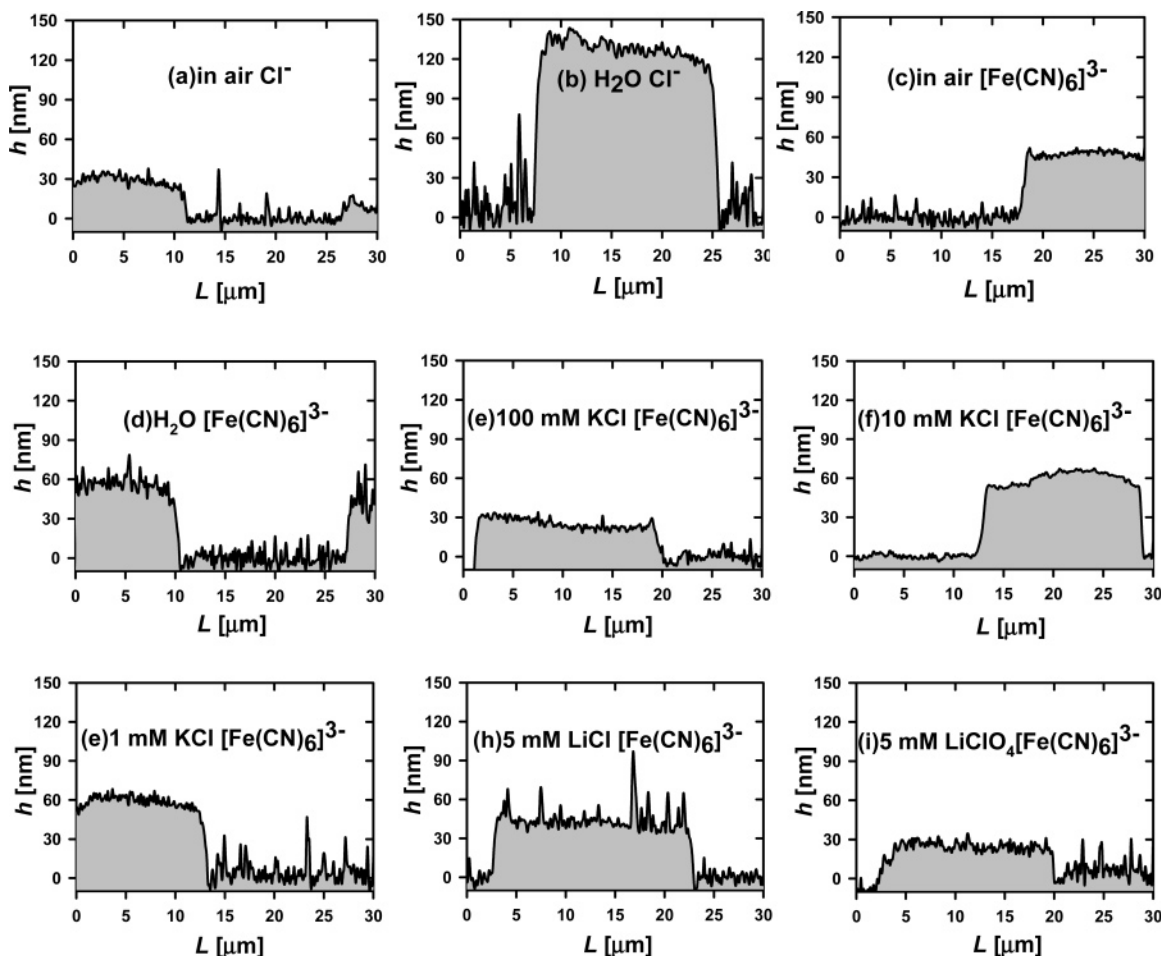


Figure 5. AFM cross-sections of patterned PMETAC on Au substrate: as synthesized (a) in air and (b) in DI water; after immersion for 30 min in 0.1 M $K_3[Fe(CN)_6]$ solution: (c) in air, (d) in DI water, (e) in 100 mM KCl, (f) in 10 mM KCl, (g) in 1 mM KCl, (h) in 5 mM LiCl, and (i) in 5 mM $LiClO_4$. h , vertical displacement [nm]; L , horizontal displacement [μm].

PMETAC brushes on the peak separation and $E_{app}^{1/2}$. The peak separation of 4 nm-thick brushes shows only 0.034 V but the peak separation increases proportionally to the thickness of the brush, whereas $E_{app}^{1/2}$ shows similar values for all thicknesses of the PMETAC brushes. It implies that all of the PMETAC brushes with different thicknesses require the same electronic energy for the electron transfer between the PMETAC brushes and the electrode but the electron transfer was more significantly hindered with thicker brush. Hindrance of electron transfer with thick PMETAC brushes was confirmed by measuring their charge densities Q by UV-vis absorption (Q_{UV}) and comparing it with Q obtained from CV. The Q_{UV} of the PMETAC brush was estimated using eqs 2 (Beer-Lambert law) and 3²²

$$\bar{c}_x = \frac{A}{\epsilon L} \quad (2)$$

$$Q_{UV} = \bar{c}_x LF \quad (3)$$

where A is the absorbance of the $[Fe(CN)_6]^{3-}$ at 420 nm, ϵ , the a molar extinction coefficient of $1000 M^{-1}cm^{-1}$, L , the thickness of the polyelectrolyte brush (cm), and F , the Faraday constant. The UV-vis absorption of each brush was measured three times, and the average value was used to calculate the Q_{UV} . In Figure 4, the Q_{UV} of the PMETAC brushes obtained by UV-vis spectra

was compared with the Q probed by the CV. Clearly, Q_{UV} 's for the thick PMETAC brushes (14 and 24 nm) were higher than Q 's. This difference indicates increasing difficulty for the electron-transfer reaction between the redox centers of the PMETAC brush and the electrode with increasing the thickness. In the case of thin brushes, the agreement between Q_{UV} and Q indicates that all of the electroactive species are participating in the electron-transfer process. When the brush thickness is increased, the discrepancy between Q_{UV} and Q indicates that a fraction of the electroactive species is no longer participating in the electron-transfer process or they lost the connectivity with the other redox centers or the electrode. This result was consistent with the result of the peak separation shown in Figure 3b. The difficulty of electron transfer might be ascribed to the distance of the redox centers from the electrode. Since the maximum distance an electron can tunnel is a few angstroms in bulk films of redox polymers,²³ the electron transfer to distant redox centers in thick brushes is limited. Another contributing factor might be related to the hydrophobic characteristics of the PMETAC brush bearing the $[Fe(CN)_6]^{3-}$. The $[Fe(CN)_6]^{3-}$ is scarcely hydrated, large, and highly polarizable, forming stable ion pairs with QA^+ groups of the PMETAC brush. The stable ion pairs with scarcely solvated counterions can enhance the hydrophobic characteristics of the

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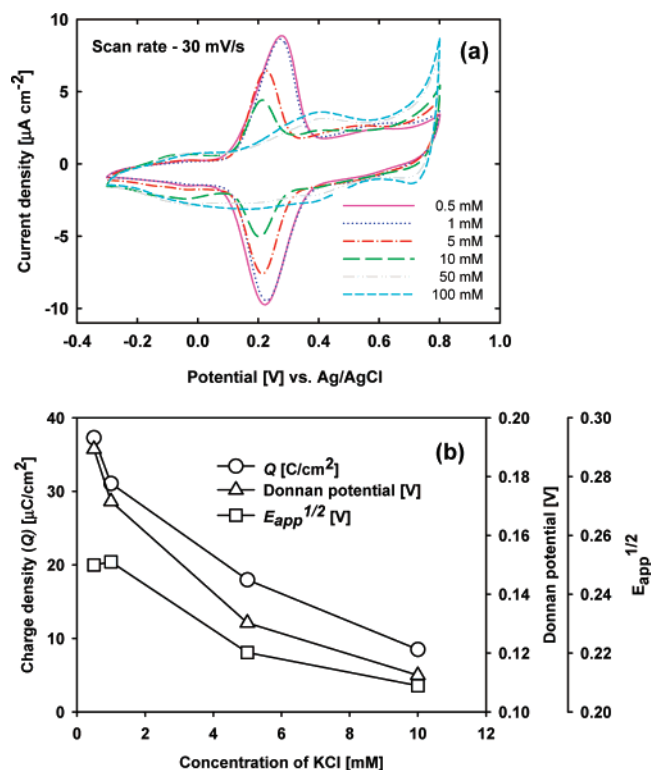


Figure 6. (a) Effect of the concentration of KCl on the cyclic voltammogram of electroactive PMETAC brush. Thickness of the brush: 9 nm. v : 30 mV s⁻¹. (b) Q , $E_{app}^{1/2}$, and Donnan potential ($\Delta\phi_D$) as function of concentration of KCl.

brush, which leads to collapse. The electron transfer between the electrode and the polyelectrolyte is hindered in its collapsed state compared to the stretched state.¹³ AFM experiments were performed to study the responsive nature of electroactive brushes in some more detail. As can be seen in Figure 5, panels a and b, PMETAC brushes with Cl⁻ counterions swell up to five times their dry thickness when placed in water. However, after exchange with [Fe(CN)₆]³⁻ ions, the brushes swell only slightly (from ~50 to 60 nm, Figure 5, panels c and d). This indicated tight ion-pairing in the brush, leading to a hydrophobically collapsed state. The AFM images reveal very clearly though that these brushes still contain a significant amount of water, since imaging the same brushes under varying concentrations of KCl shows significant changes in thickness. In 100 mM KCl, the brushes collapse further (down to ~30 nm), but in 1 mM and 10 mM, the brushes swell to around 60–65 nm (Figure 5, panels e–g). On the other hand, low concentrations (5 mM) of LiCl show brushes collapsing to around 40 nm, and when LiClO₄ is used as the electrolyte, the brushes do collapse again to ~30 nm, even at 5 mM concentration (Figure 5, panels h and i). These results on the effect of different electrolytes will be explored electrochemically in more detail below.

Effect of Concentration of the Supporting Electrolyte.

Figure 6a shows the CV data of the electroactive PMETAC brushes measured at various concentrations of KCl (0.5, 1, 5, 10, 50, and 100 mM). The current decreases with increasing concentrations of KCl, and breakdown as well as irreversibility of the CV peak were observed at high concentrations (50 and 100 mM). The increasing concentration of supporting electrolyte leads to the depletion/exchange of the ion-paired redox centers by no electroactive species, i.e., replacement of [Fe(CN)₆]^{3-/4-} by Cl⁻ ions. As shown in Figure 6b, this is reflected in a marked decrease on Q upon increasing changes in KCl concentration. In addition, changes in electrolyte concentration evidenced a

decrease in formal potential ($E_{app}^{1/2}$) which was taken as the average of the reduction and oxidation potentials. These changes can be interpreted in terms of the Donnan potential. Polyelectrolyte brushes can be considered as a membrane exhibiting permselectivity properties. In the case of PMETAC brushes, they act as an anion-exchange membrane permitting the transport of Cl⁻ ions into the highly positively charged brush environment and hindering the transport of K⁺ species (Donnan exclusion). This exclusion process due to the permselectivity properties introduces the presence of a Donnan potential which affects the formal potential of the redox centers. A similar effect has been reported for the case of electroactive self-assembled polyelectrolyte multilayers.²⁴ Assuming that the change in the resolution energy of ions in the solution and polyelectrolyte brush and the difference in the activity coefficient in the two phases can be disregarded, the Donnan potential, $\Delta\phi_D$, can be described as²⁵

$$\Delta\phi_D = \frac{\omega RT}{F} \ln \left\{ \frac{\bar{c}_x}{2c^s} + \left[1 + \left(\frac{\bar{c}_x}{2c^s} \right)^2 \right]^{1/2} \right\} \quad (4)$$

where \bar{c}_x is the concentration of the ionic sites in the ionic polymer, c^s , the concentration of the 1:1 electrolyte, and ω , the ionic charge of the fixed ionic charges in the ionic polymer. In our case, the decrease in the $E_{app}^{1/2}$ with electrolyte concentration is in complete agreement with a scenario where the film is bearing fixed positive charges and exchanging Cl⁻ upon oxidation–reduction cycles.²⁴ The effect of the electrolyte concentration on the Donnan potential was further corroborated using eq 4 with $\bar{c}_x = 0.8$ M and $\omega = 1$. \bar{c}_x was obtained from the UV–vis absorption (data not shown). As expected, Figure 6b shows a decreasing trend in $\Delta\phi_D$ with increasing concentration of supporting electrolyte. It can be seen that the magnitude of the estimated $\Delta\phi_D$ is in good agreement with the experimentally observed $E_{app}^{1/2}$ shifts.

Effect of the Type of Supporting Electrolyte. The nature of the counterion significantly affects the characteristics of the collapsed state of polyelectrolyte brushes. The interaction between QA⁺ groups in the PMETAC brushes and the surrounding counterions plays a main role in determining the change in the collapsed state. The electrochemical behavior of electroactive PMETAC is sensitively affected by the nature of the counterions. Figure 7 shows voltammograms of electroactive PMETAC in the presence of 5 mM LiCl and LiClO₄ as supporting electrolytes. It can be observed that, in comparison to LiCl, the LiClO₄ electrolyte leads to a marked decrease in Q from 76.3 to 37.1 μC cm⁻². In addition, there is a sensitive shift in $E_{app}^{1/2}$ from 0.21 to 0.15 V. This fact can be explained in terms of the strong interaction between the ClO₄⁻ anions and QA⁺ moieties in the polymer layer leading to the formation of ion pairs. This strong interaction is the driving force for the significant replacement of [Fe(CN)₆]^{3-/4-} by ClO₄⁻, which is evidenced as a marked decrease of electroactive species into the brush. The strong ClO₄⁻–QA⁺ interaction is also responsible for the sensitive shift in $E_{app}^{1/2}$. ClO₄⁻ ions are more tightly bound to the brush in comparison to Cl⁻, thus promoting a more efficient screening of strong positive charges in the brush. This leads to a scenario similar to that of NaCl but resembling a higher ionic strength environment. In a recent publication, we reported on the critical role of the specific ionic interactions on determining the effective electrostatic environment of polyelectrolyte brushes.^{19a} For

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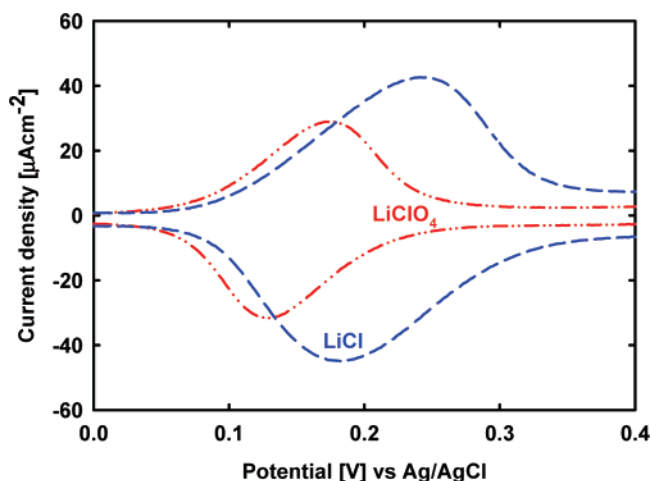


Figure 7. CVs using LiCl or LiClO₄ as the supporting electrolyte. Concentration of electrolyte: 5 mM. Thickness of the brush: 14 nm.

example, the ζ -potential of PMETAC brushes in 0.1 M NaCl was +26.7 mV in contrast to the +7.9 mV measured on similar brushes in 0.1 M LiClO₄. When working at ionic strengths as low as 10^{-4} M, the ζ -potential changed from +44 to +22 mV when changing from NaCl to LiClO₄. These results strongly support the idea that the $E_{app}^{1/2}$ shift due to the Donnan potential is sensitively affected by the nature of counterions and especially by the specific interactions between the fixed charges and the ionic surrounding. That is, the Donnan potential is correlated to the electrostatic characteristics of the brush environment and especially the outer layer.^{26,27} Under same ionic strength conditions, ionic species leading to stronger ion pairs (better

screening) would lead to a different electrostatic environment, which is reflected in a different Donnan potential.

Conclusions

In this study, the electrochemical properties of electroactive PMETAC brushes as a function of a range of parameters were investigated. Cyclic voltammetry revealed that the electroactive PMETAC brushes are very stable and have excellent electron-transfer characteristics. The repeated switching of the counterion did not affect the charge-transfer characteristics of the brush layer upon coordination with the redox probe. We found that the electroactivity of the brushes is strongly dependent on the thickness of the layers, which indicates that the “direct communication” between electrochemical species and electrode is lost toward the surface of thicker brushes, or that ions are free to move into solution. Experiments probing the role of the supporting electrolyte clearly revealed marked changes in electrochemical properties when ClO₄[−] was used as a strongly coordinating anion. These results show that CV provides a route for switching the electroactivity of the polymer film without using covalent interactions and a tool to study the internal structure of polyelectrolyte brushes. We also believe that these experiments provide a framework for electrochemical actuation of polyelectrolyte brushes via the rapid cycling of electroactive counterions between different redox states.

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