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Diffusional and migrational transport of ionic species affected by electrostatic interactions with an oppositely charged hydrogel layer attached to an electrode surface

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ABSTRACT

The effect of the presence of a charged thin gel layer on the electrode surface on mass transport of electroactive species of opposite charge was investigated. The layer was deposited using the electrochemically-induced free-radical polymerization method. The ferrocenyltrimethylammonium cation (FcN^+) served as the electroactive probe. Ionic accumulation of the anodic electrode product was observed in experiments with normal sized electrodes. Microelectrodes were used without supporting electrolyte to study the contribution of migration to the overall mass transport to the modified surface.

1. Introduction

Modification of an electrode surface usually results in the addition of new properties to the measuring system. Modification of the electrode surface with a material that is sensitive to changes in environmental conditions makes the electrode response sensitive to those changes as well [1–4]. The crosslinked sodium salt of poly(acrylic acid) (pAS) is a hydrogel sensitive to pH changes. Its pK_a value is ca. 4.7. At pH values higher than this, pAS is partially ionized and a negative, fixed charge appears in the polymer structure. Under such conditions the hydrogel is in a swollen state because the electrostatic repulsion of ionized carboxylic groups causes an increase in osmotic pressure. When the pH is lower than the pK_a, the carboxylic groups are protonated, the negative charges fixed on the polymer chains vanish, the osmotic pressure decreases, and, consequently, the swelling ratio (ratio of the volumes of the gels in their swollen and shrunken states) decreases.

Hydrogel-modified microelectrodes have been successfully applied in many research fields [5,6], including electrophysiology and neuroscience [7–9]. Due to their small size they have been used to increase spatial resolution and to minimize insertion trauma. An understanding of the mechanism of mass transport through the hydrogel layer in the presence of varying amounts of supporting electrolyte, including its absence, is crucial in all these applications.

The interactions between charged polymer layers/brushes and analytes and their practical applications in electroanalysis have already been reported in several papers [10–14]. The aim of this paper is to present the effect of the deposition of a charged microlayer not only on diffusional mass transport but also migration of electroactive species of opposite charge. The effect of a pAS layer on the diffusional and migrational transport of negatively charged electroactive species has been studied previously [15]. The degree of ionization of the carboxylic groups in the hydrogel layer can be controlled by selecting an appropriate solution pH. Here we demonstrate that ionization affects the transport of the positively charged probe due to the attraction between the negatively charged layer and the redox probe. In addition to the effects related to electrode modification, the micrometer scale of the electrodes allowed us to investigate the contribution of migration to the overall transport of charged species through the ionized hydrogel layer.

2. Materials and methods

The electrodes were modified with a cross-linked poly(acrylate sodium) layer. pAS layers were deposited on micro- and regular platinum electrode surfaces via an electrochemical free-radical polymerization process. Details of the deposition procedure and SEM characterization of the layers are described elsewhere [15,16]. The detached layers were quite uniform, with a thickness of ca. 40 nm. In the case of microelectrode the thickness of the dry polymer layer was ca. 30 nm [15].

The probe selected for the transport studies was the ferrocenyltrimethylammonium (FcN^+) cation, purchased as the iodide salt from Sigma. Iodide was replaced by hexafluorophosphate. In the three-electrode system either a Ag/AgCl electrode or a Pt wire was used as a reference or quasi-reference electrode, respectively.

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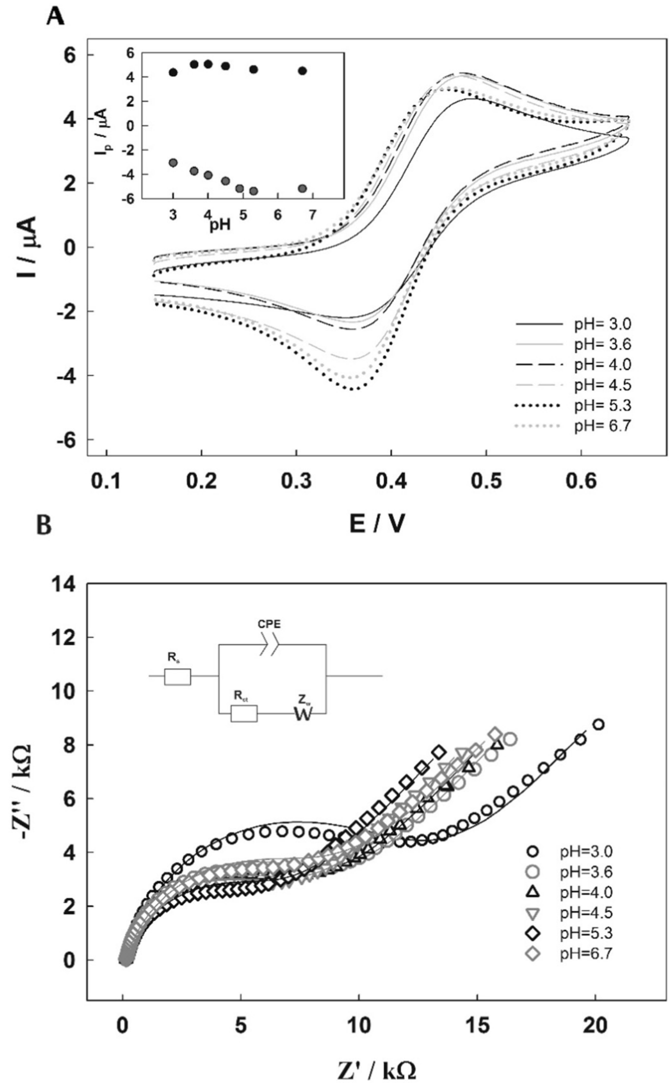

Fig. 1. (A) Cyclic voltammograms obtained with a pAS-modified Pt electrode at various pH values. Inset: oxidation and reduction peak currents plotted versus pH. (B) Nyquist plots for various pH values for the pAS-modified electrode, together with the equivalent circuit. Solution composition: 2 mM FcN^+ and 0.2 M $NaNO_3$ (ν = 50 mV·s^{-1}).

3. Results and discussion

3.1. Diffusion of charged redox probe to modified regular electrodes

Dissociation of carboxylic groups in the hydrogel network should affect the electrochemical signals of positively (and negatively) charged redox probes. The effect of ionization of a pAS layer on the transport of a positively charged redox probe, FcN^+, is illustrated in Fig. 1. At pH values higher than the pK_a most of the pAS carboxylic groups are ionized, and therefore the hydrogel layer possesses the opposite charge to the redox probe, FcN^+.

At pH equal to 3.0 (carboxylic groups are protonated), the cyclic voltammograms were quasi-reversible; the anodic to cathodic peak separation was 114 mV (compared to 59 mV expected for a reversible process) and the ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}) of FcN^+ was equal to 1.44 (compared to a value of 1 for an ideally reversible process and equal electroactive species diffusion coefficients). The corresponding ratio of peak currents for the unmodified electrode, under the same conditions, was 1.17. This change may be related to possible differences in the mobilities of the monovalent cationic substrate and the divalent product. At pH 3.0 the hydrogel layer had shrunk due to a decrease in osmotic pressure, so the diffusion of the redox probe to and from the electrode surface was somewhat sterically impeded. The results presented in Fig. 1 reveal that the cathodic peak current increased with an increase in pH due to ionization of the hydrogel network and the appearance of attractive interactions. The observation of larger cathodic currents at increased pH values was probably related to slightly stronger interactions between the negatively charged polymer chains and the product of the electrode process. In particular, the oxidized form of the positively charged probe was more strongly attracted by the negatively charged polymer network on the electrode surface. This resulted in a decrease in the I_{pa}/I_{pc} ratio. The corresponding data are listed in Table 1. In fact, the ratio of peak currents is a function of several variables, including diffusivity (which reflects changes in molecular structure and charge), sterical limitations in the matrix due to swelling/shrinking effects, the nonuniform concentration/distribution of the species, and permanent immobilization of a fraction of the molecules. Therefore, the direct interpretation of the obtained data is not straightforward.

Table 1
Ratio of anodic and cathodic peak currents and peak-potential separation for FcN^+. Voltammograms were obtained with a pAS-modified electrode in 0.2 M $NaNO_3$ at various pH values. Data in parentheses, marked with an asterisk, refer to an unmodified Pt electrode.

pH	3.0	3.6	4.0	4.5	5.3	6.7
I_{pa}/I_{pc}	1.44 (1.17*)	1.34	1.23	1.07	0.86 (1.18*)	0.86
ΔE_p/mV	114 (59*)	105	104	101	88 (59*)	94

Electrochemical impedance spectroscopy was then used to examine the electrode modified with a pAS layer. Nyquist diagrams were obtained for solutions with various pH values and are presented in Fig. 1B. The EIS measurements were performed at the FcN^+/Fc^+N^+ formal potential, in a frequency range from 1 MHz to 0.1 Hz, using an alternating voltage of 10 mV. The electron-transfer resistance was the highest (R_{ct} = 12 kΩ) for the most acidic solution (pH = 3.0) due to the shrunken structure of the layer. R_{ct} decreased to 6.5 kΩ when the pH was increased to 5.3 (compared to the unmodified electrode value of 0.1 kΩ). It seems that the appearance of negative charge on the polymer network favoured the electron transfer of oppositely charged species at the electrode surface. The double layer capacitance, C_{dl}, increased its value circa 2 times. This change was caused by ionization of the carboxylic groups in the layer at pH 5.3. For the unmodified electrode, the capacitance was two orders of magnitude smaller (9.45·nF). The values of the Warburg coefficient, A_w, and solution resistance, R_s, remained almost unchanged after the increase/decrease in pH. These two parameters did not differ substantially from the results obtained for the unmodified electrode. The impedance parameters for both pH values are given in Table 2. The analysis of the impedance data was carried out using methods described elsewhere [17,18].

3.2. Transport of positively charged redox probe to the microelectrode surface in the presence and absence of supporting electrolyte

The use of microelectrodes allowed us to perform measurements without deliberately adding supporting electrolyte and hence to

Table 2
Impedance parameters obtained by fitting the Randles equivalent circuit to experimental data. pAS-modified electrode in 0.2 M $NaNO_3$ solution containing FcN^+ at pH 3.0 and 5.3.

	pH = 5.3	pH = 3.0
R_s/Ω	149	134
R_{ct}/Ω	6556	12,141
A_w/Ω·s$^{-1/2}$	5775	6445
C_{dl}/F	8.67·10^{-7}	5.54·10^{-7}