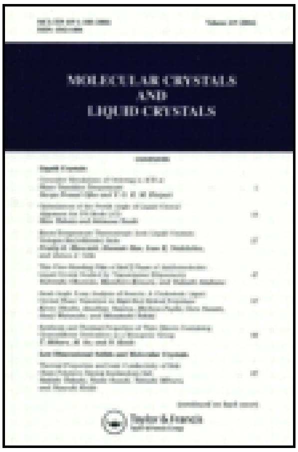

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Ionomer Film-Coated Electrodes as Electrochemical Sensors

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Recent studies have shown that perfluorosulfonate ionomer film-coated electrodes have potential applications as electrochemical sensors. This paper reports on fundamental investigations of the response characteristics of electrochemical sensors prepared by coating glassy carbon electrode surfaces with films of the perfluorosulfonate ionomer Nafion. The effects of various experimental parameters on sensitivity, detection limit and linear response range of the Nafion-coated electrodes were studied. The experimental parameters investigated included film thickness, duration of exposure of the film to the analyte solution, and electrochemical detection method. These studies have shown that Nafion-modified electrodes can be extremely sensitive electrochemical sensors. Differential pulse detection at the Nafion-film coated electrode provided the lowest detection limit (10^{-9} M). Methods of purging the analyte cation from the Nafion film were also studied.

BRIEF

Effects of various experimental parameters on sensitivity, detection limit and linear response range of Nafion film-coated electrodes were investigated. Parameters studied included film thickness, duration of exposure to the analyte solution and electrochemical detection method.

INTRODUCTION

Substantial research effort is currently being devoted to the development of chemically modified electrode sensors.[1-17] A number of recent investigations have suggested that ion exchange polymer-modified electrodes might be useful as sensors for electroactive ions.[2,3,6-9,15-17] We, for example, are investigating the possibility of using perfluorosulfonate ionomer (PFSI)[18] film-coated electrodes as sensors for organic cations.[6–8] PFSI's, such as Nafion (Nafion is a trademark of E.I. du Pont de Nemours and Co., Inc.), are strong acid cation exchange polymers. We have shown that PFSI's are unusual ion exchange materials in that they prefer to incorporate large, hydrophobic cations rather than small, hydrophillic cations.[6,19] For example, the ion exchange selectivity coefficient for the replacement of Na^+ with $Ru(bpy)_3^{2+}$ (byp = 2,2'-bipyridine) in a Nafion membrane is 6×10^6.[6] Furthermore, we have shown that ion exchange selectivity coefficients increase as the hydrophobicity of the exchanging counterion increases.[19]

Because ion exchange selectivity coefficients for hydrophobic cations are large, PFSI films will *preconcentrate* such ions, even in the presence of huge excesses of inorganic cations. This preconcentration effect will cause the electrochemical detection limit (DL) for a hydrophobic cation at a PFSI film-coated electrode to be orders of magnitude lower than the DL at an analogous uncoated electrode.[6–8] For example, the DL for the protonated form of dopamine at a Nafion-coated electrode is over two orders of magnitude lower than the DL at the uncoated electrode.[7]

In addition to showing lower DL's, PFSI film-coated electrodes provide greater selectivity than uncoated electrodes.[5] Enhanced selectivity is obtained because the polycationic film rejects anions and, as noted above, because PFSI's show tremendous preference for hydrophobic cations over inorganic cations. While these are rudimentary forms of selectivity, for many applications this level of discrimination is sufficient. For example, ascorbate is a strong interferant in the in vivo electrochemical determination of dopamine at an uncoated ultramicroelectrode.[5,7,20] In contrast, because Nafion rejects anions, dopamine is easily detected, in vivo, at a Nafion film-coated ultramicroelectrode.[5] Furthermore, the PFSI film can protect the substrate electrode from foulants present in the contacting solution phase. For example, Wightman has recently demonstrated that Nafion-coated ultramicroelectrodes show longer lifetimes in in vivo applications than corresponding naked electrodes.[21]

We have suggested that ionomer film-coated electrodes could be used as sensors in a new, extremely sensitive, electroanalytical technique called ion exchange voltammetry.[8] Because ion exchange voltammetry entails an equilibration step, during which the analyte cation is preconcentrated into the film, followed by an electrochemical step, during which the analyte in the film is assayed, ion exchange voltammetry is similar to anodic stripping voltammetry.[8] The two techniques are, however, complementary in that anodic stripping voltammetry is used for analyses of inorganic ions (usually metal cations); whereas, ion exchange voltammetry is best suited for analyses of organic ions.

A number of important questions regarding analyses at ionomer film-coated electrodes remain to be answered. These questions include—what electrochemical technique (e.g., linear sweep voltammetry,[6-8] differential pulse voltammetry[3,9,12] etc.) is best for assaying the quantity of analyte partitioned into the polymer film? What film thickness is best? What is the effect of analyte/film exposure time on sensitivity and DL at the polymer film-coated electrode? How can the analyte be expelled from the polymer film after analysis? Note that these questions are not unique to the ionomer-coated electrode but apply to nearly any type of polymer-modified electrode sensor.

We have begun a series of investigations aimed at providing answers to these questions. In the first phase of this research effort, we chose two common voltammetric wave forms (linear sweep and differential pulse) and assessed the effects of film thickness, exposure time, and scan parameters on sensitivity, DL and linear response range (LRR) observed for a test analyte cation at the Nafion film-coated electrode. We have also compared sensitivities and DL's obtained from the linear sweep and differential pulse methods at the film-coated electrode. We report the results of these investigations in this paper.

EXPERIMENTAL SECTION

Materials and equipment

$Ru(NH_3)_6Cl_3$ (Strem Chemicals), $Ru(bpy)_3Cl_2$ (G. Frederick Smith Chemical) and $NaClO_4$ (Aldrich) were used as received. High purity water was obtained by circulating house distilled water through a Milli-Q (Millipore) water purification system. Glassware used for preparation and storage of highly dilute solutions was cleaned and preconditioned as described previously.[6] Nafion (1100 equivalent weight) was obtained from du Pont. A 0.6 wt./vol. % Nafion solution was prepared using the standard procedure (22). Glassy carbon rods were obtained from Tokai.

A Bioanalytical Systems CV-27 Voltammograph was used to conduct the linear sweep experiments. Differentials pulse experiments utilized an EG&G PAR 174A Polarographic Analyzer. Data were recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder or a Nicolet Explorer oscilloscope. A conventional 3 electrode electrochemical cell was used; a Nafion film-coated glassy carbon rod,[23] a Pt flag and a SCE served as the working, counter and reference electrodes, respectively.

Procedures

Glassy carbon rods were polished, coated and preconditioned as described previously.[23] Electrodes were coated with films of 0.2, 0.4, 0.8 and 1.6 μm. Film thicknesses were calculated assuming a density of 1.58 g/cm^3.[23] $Ru(NH_3)_6^{3+}$ was chosen as the test analyte cation because it undergoes a simple, chemically and electrochemically reversible, one electron reduction. Furthermore, $Ru(NH_3)_6^{3+}$ has a relatively large aqueous/Nafion partition coefficient.[6] $Ru(NH_3)_6^{3+}$ solutions were prepared by serial dilution from a 1 mM stock; all solutions were 0.1 M in $NaClO_4$, which served as the supporting electrolyte. Solutions were degassed with prepurified N_2 prior to electrochemical analysis.

A voltammetric experiment yields a faradaic current, associated with the oxidation or reduction of the analyte, which is linearly related to the analyte concentration. This faradaic signal is superimposed on a background current and must be extracted from this background. The conventional background subtraction procedure which was used here involves extrapolation of the background current envelope and subtraction of this envelope from the total current at the voltammetric peak.[24]

The general strategy in this work was to use calibration-type experiments to demonstrate the effects of the various experimental variables on the sensitivity, DL and LRR of the Nafion-coated electrode. Two types of calibration experiments were employed. The first type (Figures 1, 2, and 4) focused on a specific variable and illustrated the effect of that variable on sensitivity. A limited and relatively high concentration range was employed in these studies. The intent of the second type of calibration experiment (Figures 5, 6, and 8) was to evaluate the DL and LRR[25,26] of the Nafion-coated electrode. These experiments utilized the information obtained from the type-one experiments and involved much larger analyte concentration ranges.

RESULTS AND DISCUSSION

Linear sweep voltammetry at the Nafion film-coated electrode

While linear sweep voltammetry (LSV) is not the most sensitive electroanalytical technique, it is rapid and convenient, requires inexpensive and readily available equipment, and yields qualitative information about the nature of the electrochemical process. For these reasons, LSV was used to evaluate the effects of exposure time and film thickness on sensitivity, DL and LRR at the Nafion film-coated electrode. Since LSV is used only to assay the quantity of analyte in the film, the conclusions reached are valid when other electroanalytical methods (e.g., differential pulse voltammetry) are used at the film-coated electrode.

Effect of duration of exposure of the film to the analyte solution

When Na^+-form Nafion is exposed to an aqueous solution containing $Ru(NH_3)_6^{3+}$, the need to establish ion exchange equilibrium will cause $Ru(NH_3)_6^{3+}$ to be partitioned into the film. The time required to achieve equilibrium depends on the film thickness and on the concentrations of Na^+ and $Ru(NH_3)_6^{3+}$ in the solution phase.[6] The effect of duration of exposure on LSV peak current (for a given film thickness) is shown in Figure 1. Each data point represents an average of peak currents obtained at three identical electrodes. Furthermore, a fresh set of three electrodes was used to obtain each point. Thus, Figure 1 represents data from 36 different electrodes.

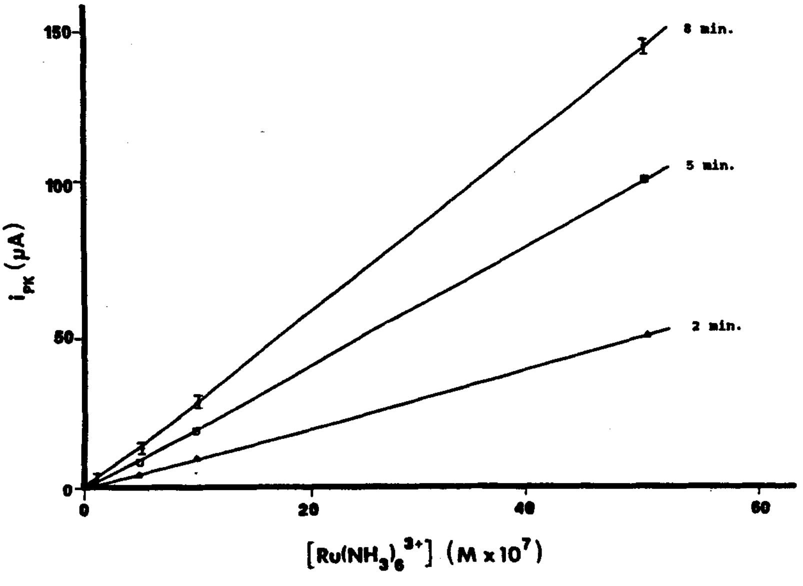

FIGURE 1 Effect of exposure time on sensitivity at the Nafion film-coated electrode. Analyte = $Ru(NH_3)_6^{3+}$; film thickness = 0.4 μm; scan rate = 500 mV s^{-1}. Data obtained as described in the text. Typical error bars (equivalent to 2 times the standard deviation for currents at three electrodes) are shown for the 8 min experiment.

Figure 1 shows that sensitivity increases with exposure time. This is not surprising since prolonged exposure allows a larger quantity of analyte to partition into the film. While these data suggest that long exposure times are preferable, there are two caveats. First, if the concentration of analyte in the solution phase is high, or if the Nafion film is very thin, prolonged exposure will result in saturation of the film (i.e., all of the $-SO_3^-$ sites will become occupied by the analyte cation). If this happens, the concentration of analyte in the film will become fixed and independent of the solution concentration (vide infra). Second, prolonged exposure increases analysis time and thus decreases sample throughput.

The above discussion illustrates an important point. The variables—solution concentration, film thickness and equilibration time—are all interrelated. For example, in the context of optimization of exposure time, thick films can tolerate longer exposure times than thin films, and longer exposure times can be used at lower concentrations than at higher concentrations. This makes delineation of optimal analytical conditions difficult, since optimization would require a priori knowledge of the analyte concentration. This, this paper will point out general trends in the experimental data and will then discuss caveats associated with these trends.

Effect of film thickness

The effect of film thickness on sensitivity, at constant (2 min) exposure time, is illustrated in Figure 2. Again, each data point represents an average of peak currents obtained at three identical electrodes and a fresh set of electrodes was used to obtain each point. Thus, Figure 2 represents data from 24 electrodes.

Figure 2 shows that sensitivity increases as film thickness decreases. There are two reasons for the enhanced sensitivity of the thin film-coated electrode; the first involves the film volume. Assume, for the moment, that there is a steady-state flux of analyte cation into the film (regardless of thickness), throughout the duration of exposure of the film to the analyte solution. If this is the case, the fluxes of analyte cation into the 1.6 and 0.2 μm films (Figure 2) are the same. Furthermore, since both films are exposed to the solution for the same amount of time (2 min) and both films have the same surface area, the thick and thin films imbibe the same number of moles of analyte cation. However, because the volume is smaller, the concentration of analyte in the thin film is higher. Thus, the thin film-coated electrode would be expected to show greater sensitivity.

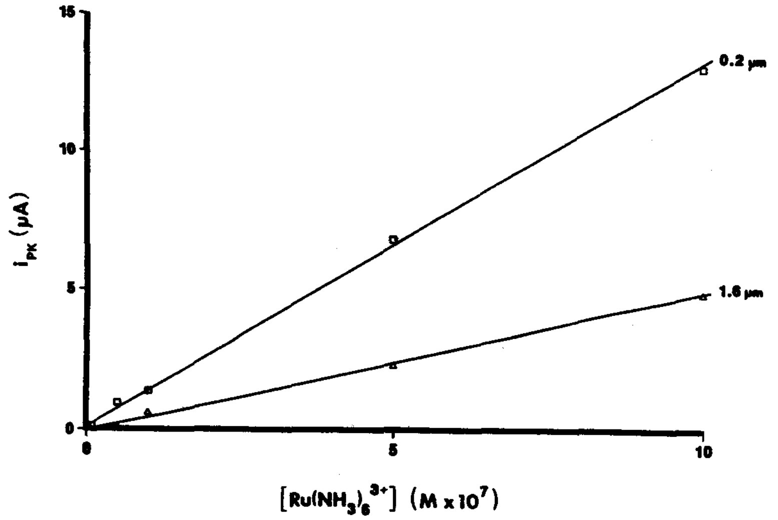

FIGURE 2 Effect of film thickness on sensitivity at the Nafion film-coated electrode. Analyte = $Ru(NH_3)_6^{3+}$; exposure time = 2 min; scan rate = 500 mV s^{-}. Data obtained as described in text. Error bars as per Figure 1.

The validity of the steady-state diffusion hypothesis can be checked by comparing the slopes of the thin and thick-film response curves (Figure 2). The volume of the thick film is eight times larger than the volume of the thin film. If steady-state diffusion obtains, the concentration in the thin film should be eight times that in the thick film. Because peak current is directly proportional to concentration, the slope of the thin-film curve should be eight times greater than the slope of the thick-film curve; in fact, the slope of the thin-film curve is only ca. 2.6 times greater (Figure 2). This means that the flux cannot be steady-state and that the average flux of analyte into the thin film is less than the average flux into the thick film.

The diminution of flux into the thin film is caused by accumulation of an appreciable concentration of analyte in the film; this decreases the concentration gradient from the maximal, steady-state value to smaller, time dependent values. While this non-steady-state flux means that the full sensitivity advantage is not realized, the thin-film electrode still has greater sensitivity than the thick-film device.

The second explanation for the enhanced sensitivity of the thin film electrode concerns finite vs. infinite diffusion during the electrochemical analysis. Figure 3 shows linear sweep voltammograms for $Ru(NH_3)_6^{3+}$, at 500 mV s^{-1}, in the 0.2 μm and 1.6 μm thick

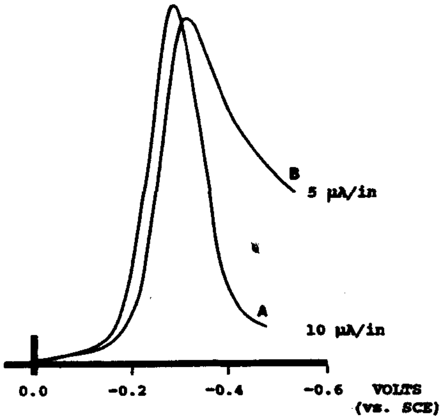

FIGURE 3 Linear sweep voltammograms for $Ru(NH_3)_6^{3+}$ in 0.2 (A) and 1.6 (B) µm Nafion films contacting a solution 1×10^{-6} M in $Ru(NH_3)_6^{3+}$. Scan rate = 500 mV s^-; exposure time = 8 min; supporting electrolyte = 0.1 M $NaClO_4$.

Nafion films (3 A and B, respectively). While the thick film voltammogram exhibits tailing, characteristic of semi-infinite diffusion, the thin film voltammogram shows the prompt current decay characteristic of finite diffusion.[24]

Peak current in the infinite and finite diffusion cases are given by equations 1, and 2, respectively.

$$i_{p,\mathrm{In}} = (2.69 \times 10^5) n^{3/2} A D_o^{1/2} v^{1/2} C_o^* \qquad (1)$$

$$i_{p,\mathrm{Fin}} = (9.39 \times 10^5) n^2 v V C_o^* \qquad (2)$$

where A is the electrode area, D is the diffusion coefficient, v is the scan rate, V is the film volume and C_o^* is the concentration of $Ru(NH_3)_6^{3+}$ in the Nafion film. If the known values of D,[6] v, A and V are inserted, equation 1 may be used to calculate i_p for the thin (0.2 µm) film and equation 2 may be used to calculate i_p for the thick (1.6 µm) film. Assuming first that the concentrations of $Ru(NH_3)_6^{3+}$ in the thin and thick films are the same, this analysis yields a ratio $i_{p,\mathrm{Fin}}/i_{p,\mathrm{In}} = 1.10$. Thus, on the basis of finite vs. infinite diffusion, the thin film electrode would be expected to show greater sensitivity. Furthermore, the ratio presented above assumed equal concentrations of analyte in the thin and thick films, yet, we have already established that the concentration in the thin film will be higher after any exposure, simply because the volume of the thin film is smaller.

The above data and discussion show that thinner films will yield sensors with greater sensitivity. There is, however, the usual caveat—the thin film device will become saturated at a lower analyte concentration and at shorter exposure times. Thus, a thin film sensor will have a shorter LRR than a thick film sensor (see Figure 6).

Effect of scan rate on sensitivity

The effect of scan rate on sensitivity for the LSV experiment at a Nafion film-coated electrode is shown in Figure 4. These data were obtained as follows: Each data point represents an average of peak currents at three electrodes. The first three electrodes were placed in 5 mL aliquots of the most dilute solution (1×10^{-7} M) and exposed for 2 min. LSV's at 50, 100 and 500 mV s^{-1} were obtained; these electrodes were then discarded. The second set of three electrodes was then exposed for 2 min to solutions of the next highest concentration (5×10^{-7} M). LSV's were obtained at 50, 100 and 500 mV s^{-1}. These electrodes were then discarded and this process was repeated for all of the analyte concentrations shown in Figure 4. Thus, Figure 4 represents data from 12 electrodes.

Figure 4 shows that sensitivity increases with scan rate. This is not surprising since peak current is proportional to either square root of

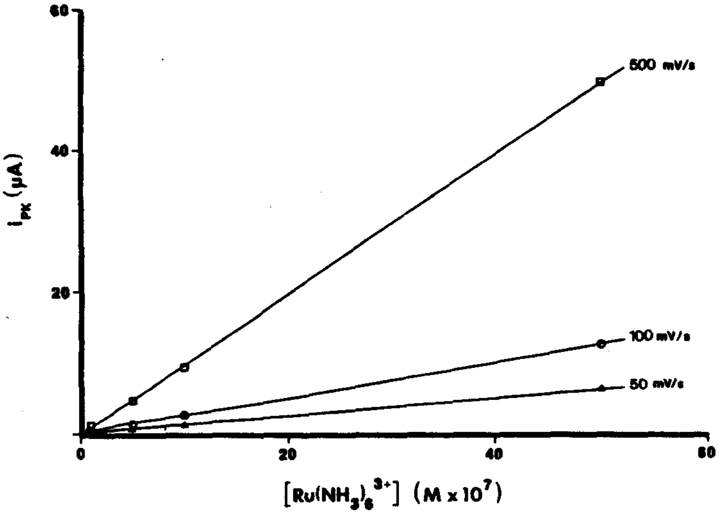

FIGURE 4 Effect of sweep rate on sensitivity at the Nafion film-coated electrode. Analyte = $Ru(NH_3)_6^{3+}$; film thickness = 0.4 µm; exposure time = 2 min. Data obtained as described in the text. Error bars as per Figure 1.

scan rate (Equation 1) or scan rate (Equation 2), depending on whether finite or infinite diffusion prevails. In either case, better sensitivity would be expected at higher scan rates.

As usual, however, there are several caveats. First, as scan rate increases, the diffusion layer thickness within the film decreases. This means that the diffusion layer will ultimately become thinner than the film and semi-infinite diffusion within the film will be obtained. Equation 1 shows that semi-infinite diffusion yields faradaic currents which increase with the square root of scan rate. In contrast, the capacitive current increases linearly with scan rate.[24] Thus, the background signal will ultimately increase faster with scan rate than the faradaic signal and this makes it increasingly more difficult to extract the faradaic signal. Furthermore, the higher currents associated with high scan rates cause uncompensated resistance distortion of the voltammogram which exacerbates the background subtraction problem. Finally, scan rates higher than ca. 1 V s^{-1} require an oscilloscope rather than a simple X-Y recorder and this increases the cost and complexity of the instrumentation.

LSV calibration experiments

Calibration curves for 0.4 μm thick Nafion film-coated electrodes at two different exposure times are shown in Figure 5. These calibration curves illustrate a number of important points concerning the effect of exposure time on sensitivity, DL and LRR. Note first that, in agreement with the above discussion, the long-time calibration curve (Curve A in Figure 5) has greater sensitivity than the short time curve. Furthermore, the long-time curve shows a lower DL than the short-time curve (see Table I for a compilation of DL's). In agreement with our previous investigations, the DL for the long exposure time experiment (10^{-8} M) is three orders of magnitude lower than DL's observed for LSV at the uncoated electrode.[6]

While prolonged exposure extends the low concentration end of the calibration curve, it shortens the high concentration end. Note that in Curve A, current becomes independent of concentration at concentrations above ca. 3×10^{-6} M. This is due to saturation of the film by the analyte cation.[4] Because lower quantities of analyte are partitioned into the film during the short exposure experiment, saturation effects are not observed until the analyte concentration is above ca. 3×10^{-5} M (Curve B). Finally, note that the short exposure time experiment yields a longer LRR than the long time experiment.

The above discussion can be summarized as follows; if the ultimate

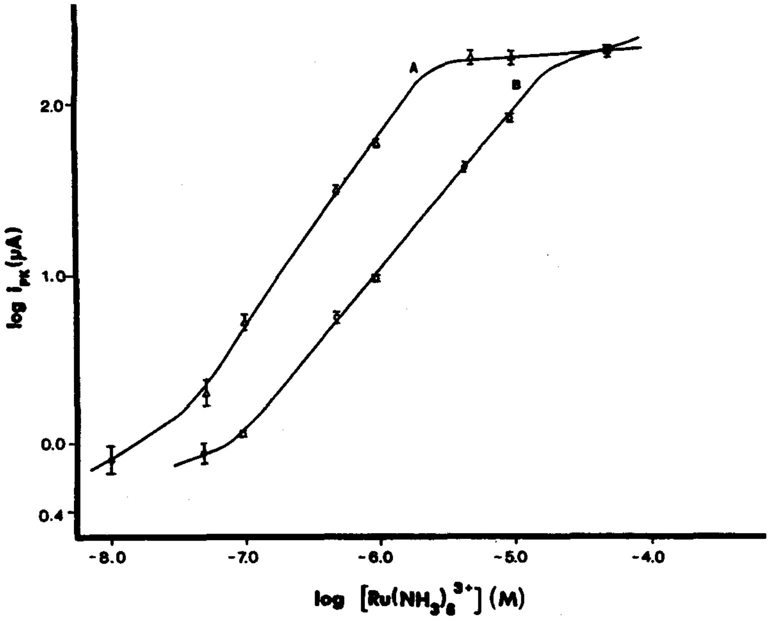

FIGURE 5 LSV calibration curves for $Ru(NH_3)_6^{3+}$ at Nafion film (0.4 μm thick) coated electrodes. Scan rate = 500 mV s^{-1}. Exposure time = 14 min (A) and 2 min (B). Peak currents are averages for three different electrodes.

DL is desired, a long exposure time should be used; however, this sacrifices sample throughout and LRR. In contrast, if it is known that the sample contains relatively high concentrations of analyte, shorter exposure times can be used; this will increase sample throughput and dynamic range.

Figure 6 shows calibration curves for electrodes coated with 1.6 and 0.4 μm thick Nafion films (exposure time = 2 min). These curves illustrate the point made earlier concerning the effect of film thickness on LRR; the thinner film becomes saturated at lower concentrations and thus has a shorter LRR. However, while it is not obvious from the log-log format used in Figure 6, the slope of the thinner film calibration curve (1.1 μA M^{-1}) is greater than the slope for the thick film curve (0.4 μA M^{-1}); this amplifies the conclusions reached earlier concerning the effect of film thickness on sensitivity.

Differential pulse voltammetry at the Nafion film-coated electrode

Because of the capacitive current problem, LSV shows relatively poor detection limits. A variety of techniques, which discriminate against

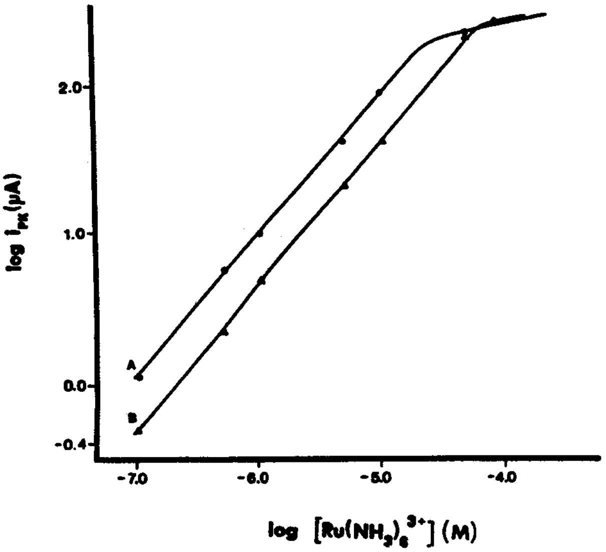

FIGURE 6 LSV calibration curves for $Ru(NH_3)_6^{3+}$ at Nafion film coated electrodes. Film thickness = 0.4 μm (A) and 1.6 μm (B). Exposure time = 2 min; scan rate = 500 mV s^-.

capacitive current, have been developed; differential pulse voltammetry (DPV) is the most sensitive of these techniques.[27] Thus, it seemed likely DPV would yield lower DL's than LSV in the ion exchange voltammetry experiment.

In LSV, sensitivity is affected by essentially only one scan parameter, scan rate. In contrast, sensitivity in DPV is affected by scan rate, modulation amplitude and clock time.[25,26] As is frequently observed at the uncoated electrode,[25,28] sensitivity increases with increasing modulation amplitude and decreasing scan rate. Sensitivity also increases as the clock time decreases, as observed at the uncoated electrode.[28] The optimum current response was found at a modulation amplitude of 100 mV, a scan rate of 2 mV/s, and a clock time of 0.5 s.

Figure 7 compares DPV's for 10^{-6} M $Ru(NH_3)_6^{3+}$ at naked and Nafion-coated electrodes. While the faradaic signal at the uncoated electrode is barely perceptible, a clearly discernable signal is obtained at the Nafion-coated electrode. The enormous differences between the coated and uncoated electrode responses (note current sensitivity change) illustrates the tremendous sensitivity of the ion exchange voltammetric method with DPV detection.

Figure 8 shows a calibration curve for $Ru(NH_3)_6^{3+}$ at the Nafion

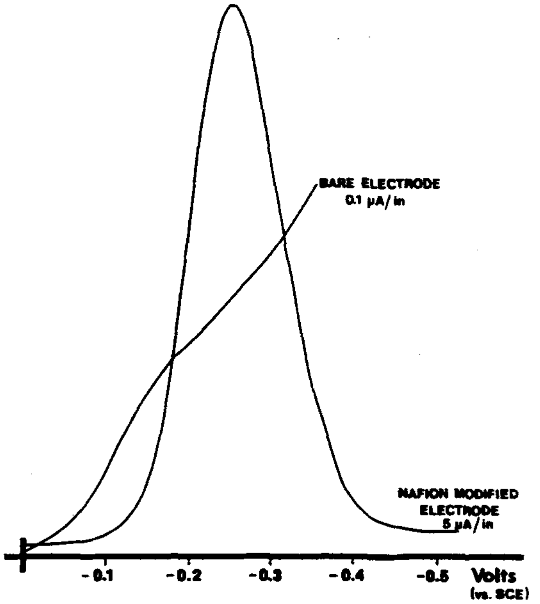

FIGURE 7 DPV's for 0.4 μm thick Nafion film-modified electrode and naked electrode contacting solutions 1×10^{-6} M in $Ru(NH_3)_6^{3+}$. Modulation amplitude = 100 mV; clock time = 0.5 s; scan rate = 2 mV s^{-1}.

film-coated electrode using DPV detection. The DL for this curve is ca. 10^{-9} M, three orders of magnitude lower than the DPV DL at an uncoated electrode and an order of magnitude lower than the best DL observed for LSV detection at the coated electrode (see Table I). Furthermore, the best LSV DL (Figure 5) was obtained using an exposure time of 14 minutes, greater than twice the exposure time used in the DPV experiment (Figure 8). These data show, as anticipated, that DPV yields lower DL's than LSV. Furthermore, these data show that ion exchange voltammetry using DPV detection is one of the most sensitive electroanalytical techniques known.

There are at least two caveats associated with the use of DPV detection. First, because lower scan rates are used, DPV requires longer analysis times than LSV. This caveat would be particularly significant for in vivo studies where temporal data are usually desired.[5] Second, DPV requires more sophisticated and, at this time, expensive instrumentation than LSV. There is, however, no reason why lower cost DPV equipment could not be produced. Other methods such as square wave voltammetry[29] might also be useful for detecting analyte cations partitioned into the film.

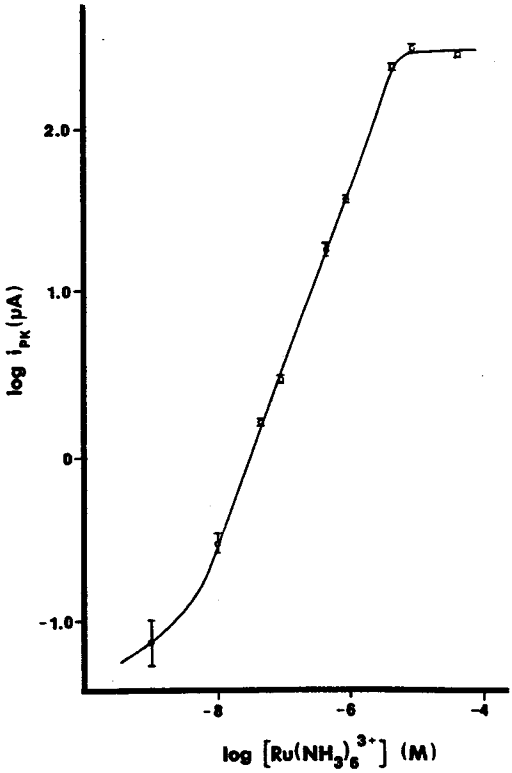

FIGURE 8 DPV calibration curve for $Ru(NH_3)_6^{3+}$ at Nafion coated electrodes. Film thickness = 0.4 µm; equilibration time = 6 min; other conditions as per Figure 7.

Expelling the analyte cation from the Nafion film

While the above data suggest that ionomer-coated electrodes can be useful electroanalytical sensors, methodology employing these electrodes must be developed. As suggested in this paper, this methodology might be similar to that of anodic stripping voltammetry where a preconcentration period is followed by an electrochemical analysis step. In anodic stripping voltammetry, the electrochemical step purges the analyte from the sensor and thus readies the sensor for the next sample. In contrast, there is no à priori reason to expect that oxidation or reduction of an analyte cation within an ionomer film would cause this ion to be expelled from the film. Thus, some method for regenerating the film between analysis and/or calibration steps must be devised.[2,8,9,30,31]

There are several possible ways to accomplish film regeneration. The first is simply to reverse the ion exchange reaction by soaking the analyte-loaded film in a high salt content solution.[9] However, because aqueous ion exchange selectivity coefficients can be enormous, the rate of this ion exchange-based leaching reaction may be prohibitively low. For example, Figure 9 shows that a 10 min exposure to 1 N $NaClO_4$ will not purge all of the $Ru(bpy)_3^{2+}$ from a Nafion film.

Our chromatographic studies of Nafion have shown that addition of a polar organic solvent to the leach solution greatly accelerates the rate of the leaching reaction.[19] This acceleration occurs because

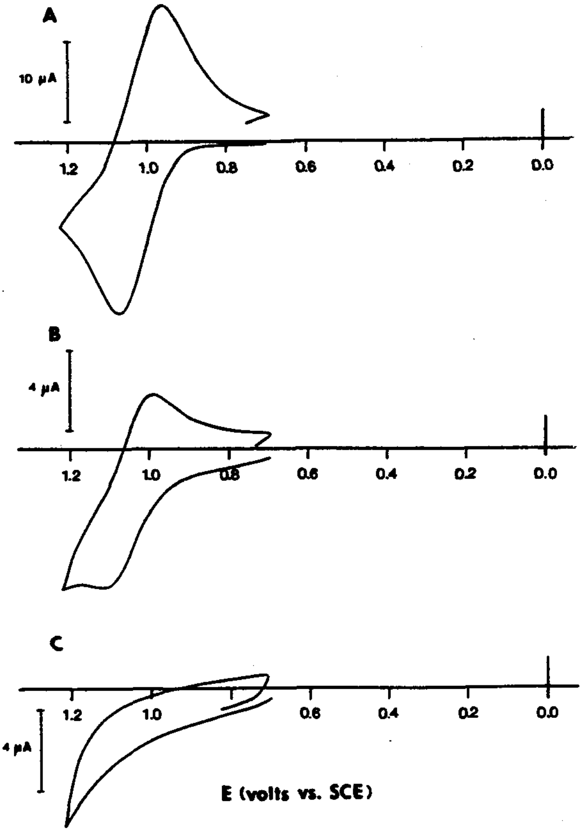

FIGURE 9 Removal of $Ru(bpy)_3^{2+}$ from Nafion films at electrode surfaces. (A.) Voltammogram for $Ru(bpy)_3^{2+}$ within a Nafion film. (B.) As per A but after 10 min exposure of the film to 1.0 M aqueous $NaClO_4$. (C.) As per A but after 30 s exposure to 1 M $NaClO_4$ in 50-50 CH_3CN-H_2O.

the ion exchange selectivity coefficient for organic cations are much smaller when organic solvents are present in the solution phase and because the organic solvent swells the polymer, thus enhancing the dynamics of the exchange process (19). Note, for example, that all of the $Ru(bpy)_3^{2+}$ is leached from a Nafion film after only 30 sec exposure to an aqueous/CH_3CN solution of $NaClO_4$ (Figure 9). Thus, aqueous/CH_3CN salt solutions are good media for regeneration of Nafion film-coated electrode sensors.

We have recently described the electrochemical and ion exchange characteristics of a new class of ion exchange polymers called electroactive ionomers.[8,32] We have shown that electroactive ionomers preconcentrate organic cations and thus can be used for ion exchange voltammetric analyses.[32] Furthermore, electroactive ionomers are electroreleasing polymers in that counterions present in the polymer phase can be expelled electrochemically into a contacting solution phase. Thus, sensors based on electroactive ionomers have the advantage of being electrochemically regenerable; this could prove useful in situations where exposure of the film to a leach solution is inconvenient (e.g. in in vivo applications).

CONCLUSIONS

Detection limits for $Ru(NH_3)_6^{3+}$ at the uncoated and Nafion-coated glassy carbon electrode are summarized in Table I. The detection limit of 1×10^{-9} M observed for differential pulse detection at the Nafion film-coated electrode is one of the lowest detection limits ever reported for an electrochemical method of analysis.[20] Furthermore, it seems likely that even lower detection limits would be possible with thinner films and/or longer exposure times.

It is important to point out that the detection limit at the Nafion-coated electrode will be dependent on both the Nafion/water partition coefficient for the analyte ion and on the diffusion coefficient for this ion in the polymer phase. It is now well established that the partition coefficient increases as the hydrophobicity of the ion increases.[6,19] The diffusion coefficient in the polymer phase will, in general, decrease as the size of the analyte ion increases. Thus, larger analyte ions will require longer exposure times.

While the data obtained here have provided insight into a variety of fundamental issues concerning the use of ionomer-modified electrodes as chemical sensors, a number of questions regarding practical applications of these sensors to "real world" analytical problems re-

TABLE I

Detection limits for $Ru(NH_3)_6^{3+}$ at uncoated and Nafion-coated electrodes

Electrode	Conditions	Detection Method	Detection Limit (M)
Uncoated	—	LSV[a]	1×10^{-5}
Coated[b]	14 min exposure	LSV	1×10^{-8}
Coated[b]	2 min exposure	LSV	5×10^{-7}
Uncoated	—	DPV[c]	2×10^{-6}
Coated[b]	6 min exposure	DPV	1×10^{-9}

[a] Linear sweep voltammetry at 500 mV s^{-1}.

[b] 0.4 μm thick Nafion film

[c] Differential pulse voltammetry. Scan rate = 2 mV s^{-1}; modulation amplitude = 100 mV; clock timie = 0.5 s.

main to be answered. For example, questions concerning the selectivity and the lifetime of these sensors have yet to be addressed. We are currently investigating these and other issues and will report the results of these studies soon.

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References

1. N. Oyama and F. C. Anson, *J. Am. Chem. Soc.*, **101**, 3450–3456 (1979).
2. J. A. Cox and P. J. Kulasza, *Anal. Chim. Acta*, **154**, 71–78 (1983).
3. J. Wang, B. Greene and C. Morgan, *Anal. Chim. Acta*, **158**, 15–22 (1984).
4. A. R. Guadalupe and H. D. Abruna, *Anal. Chem.*, **57**, 142–149 (1984).
5. G. A. Gerhardt, A. F. Oke, G. Nagy, B. Moghaddam and R. N. Adams, *Brain Res.* **290**, 390–395 (1984).
6. M. N. Szentirmay and C. R. Martin, *Anal. Chem.*, **56**, 1898–1902 (1984).
7. G. Nagy, G. A. Gerhardt, A. F. Oke, M. E. Rice, R. N. Adams, R. B. Moore, III, M. N. Szentirmay and C. R. Martin, *J. Electroanal. Chem.*, **188**, 85–94 (1985).
8. M. W. Espenscheid, A. R. Ghatak-Roy, R. B. Moore, III, R. M. Penner, M. N. Szentirmay and C. R. Martin, *J. Chem. Soc.*, Faraday Trans. 1, **82**, 1051–1070 (1986).
9. K. Kalcher, *Analyst*, **111**, 625–630 (1986).
10. M. C. Pham, G. Tourillon, P. C. Lacaze and P. C. Dubois, *J. Electroanal. Chem.*, **111**, 385–390 (1980).
11. D. M. T. O'Riordan and G. G. Wallace, *Anal. Proc.*, **23**, 14–15 (1986).
12. M. J. Gehron and A. Brajter-Toth, *Anal. Chem.*, **58**, 1488–1492 (1986).
13. K. W. Willman and R. W. Murray, *J. Electroanal. Chem.*, **133**, 211–231 (1986).
14. D. J. Turk, S. A. McClintock and W. C. Purdy, *Anal. Lett.*, **18**(B20), 2605–2618 (1985).

15. N. Oyama, T. Shimomura, K. Shigehara and F. C. Anson, *J. Electroanal. Chem.*, **112**, 271–280 (1980).
16. C. R. Martin, I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4817–4824 (1982).
17. T. Ohsaka, T. Okajima and N. Oyama, *J. Electroanal. Chem.*, **200**, 159–178 (1986).
18. A. Eisenberg and H. L. Yeager, *ACS Symposium Series, Perfluorosulfonated Ionomer Membranes*; American Chemical Society: Washington, D.C., 1982; Vol. 180.
19. R. B. Moore, III, J. E. Wilkerson and C. R. Martin, *Anal. Chem.*, **56**, 2572–2575 (1984).
20. R. N. Adams and C. A. Marsden, In *Handbook of Psychopharmacology*; Plenum: New York, 1982; Vol. 15.
21. R. M. Wightman, Indiana University, personal communication, 1986.
22. C. R. Martin, T. A. Rhodes and J. A. Ferguson, *Anal. Chem.*, **54**, 1639–1641 (1982).
23. C. R. Martin and K. J. Dollard, *Electroanal. Chem.*, **159**, 127–135 (1983).
24. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p. 221.
25. S. C. Rifkin and D. H. Evans, *Anal. Chem.*, **48**, 2174–2180 (1976).
26. T. B. Jarbawi, W. R. Heineman and G. J. Patriarche, *Anal. Chim. Acta*, **126**, 57–64 (1981).
27. J. Wang and B. A. Freiha, *Talanta*, **30**, 317–322 (1983).
28. EG&G Princeton Applied Research *Model 174A Polarographic Analyzer, Operating and Service Manual*; 1982, p V-9.
29. S. P. Kouvaves, J. J. O'Dea, P. Chandresekhar and J. Osteryoung, *Anal. Chem.*, **58**, 3199–3202 (1986).
30. D. J. Harrison, K. A. Daube and M. S. Wrighton, *J. Electroanal. Chem.*, **163**, 93–115 (1984).
31. L. M. Wier, A. R. Guadalupe and H. D. Abruna, *Anal. Chem.*, **57** 2009–2011 (1985).
32. M. W. Esphenscheid and C. R. Martin, *J. Electroanal. Chem.*, **188**, 73–84 (1985).