

Inamuddin • Mohammad Luqman  
Editors

# Ion Exchange Technology I

Theory and Materials

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*Editors*

Inamuddin  
Assistant Professor  
Department of Applied Chemistry  
Faculty of Engineering & Technology  
Aligarh Muslim University  
Aligarh, India

Mohammad Luqman  
Assistant Professor  
Chemical Engineering Department  
College of Engineering  
King Saud University  
Riyadh, Kingdom of Saudi Arabia

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# Chapter 11

## Ion Exchange Voltammetry

Paolo Ugo and Ligia M. Moretto

**Abstract** This chapter focuses on recent advances in the field of ion-exchanger-based voltammetric sensors, whose widespread use has given rise to a new electroanalytical technique named ion exchange voltammetry (IEV). The chapter starts with a brief historical overview and a short introduction to voltammetric methods of analysis, followed by the presentation of the fundamentals of ion exchange voltammetry. Analytical advantages and limits up to the most recent developments in the technique are then presented and discussed. Typical examples of application to determinations of trace concentrations of inorganic and organic electroactive molecules of interest for environmental and biomedical analysis are finally given along with future prospects.

### 11.1 Introduction

#### 11.1.1 Ion Exchange Voltammetry: A Brief History

Ion exchange voltammetry (IEV) is a new analytical technique which conjugates recent advances in the field of ion exchange in thin films with detection capabilities of modern dynamic electrochemical methods of analysis. The idea as well as fundamentals of IEV date back to the beginning of the 1980s, when pioneering studies carried out in Anson's, Bard's, Murray's, and other laboratories [1–4] showed the possibility and advantages of modifying the surface of electrodes by simply depositing a thin layer of an ion exchange polymer onto the electrode surface. The term ion exchange voltammetry was firstly used by Chuck Martin and coworkers in a paper

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P. Ugo (✉) • L.M. Moretto  
Department of Molecular Sciences and Nanosystems,  
University Ca' Foscari of Venice, Santa Marta 2137, 30123 Venice, Italy  
e-mail: ugo@unive.it

published in 1986 [5]. These and following studies opened the way to extended research efforts which brought rapidly to the development of a large arsenal of polymer-modified electrodes whose surface properties were tailored for specific analytical purposes [6–9]. Side by side with continuously growing application for analytical purposes, further recent advances in the field of IEV came from improvements of the techniques used for controlling the molecular structure of ultrathin ion-exchanger layers, thanks to the application to this aim of Langmuir-Blodgett techniques, of self-assembled monolayers and layer-by-layer techniques, whose principles can be found in references [10, 11]. This allowed one to obtain nanostructured electrode interfaces which represent, indeed, successful examples of the bottom-up nanotech approach, by which the careful and controlled assembly of different molecular bricks allows the fulfillment of specialized functions in an analytical device, in this case, an electroanalytical sensor.

The modification of electrode surfaces is presently finding a large impulse, thanks to the widespread interest for electrochemical sensors to be applied in different fields, for instance, in advanced biomedical devices [12, 13] or for environmental monitoring [7]. It can be noted that many of the early studies on polymer-coated electrodes employed a variety of Ru, Ir, Os, and Fe complexes as electroactive reversible probes which were used for understanding the fundamentals of charge transfer at electrode/polymer interfaces. At that time, the electrochemistry of such metal complexes was considered of almost no interest as far as practical applications were concerned; nowadays, many of such molecules are widely used as redox mediators in a variety of biosensors, including some of the most advanced DNA chips [14–16] and glucose sensors [17].

The present chapter deals mainly with electrodes functionalized by thin films of ion exchangers, deposited onto the surface of metal electrodes. It is divided into two parts. In the first, the principles of IEV as well as its analytical advantages and limits are presented and discussed. In the second, recent examples of application to determinations of inorganic and organic electroactive molecules of interest for environmental and biomedical analysis are given along with prospects for future developments. For the case of electrodes in which the ion exchanger is incorporated into the body of the electrode, such as carbon paste or screen-printed electrodes, the reader is invited to refer to the review article published recently by Svancara et al. on this specific topic [18].

### ***11.1.2 An Introduction to the Detection Technique: Voltammetry***

This section presents some short basic notions on electrochemical methods of analysis, useful for understanding the functioning and better appreciating most recent advancements in IEV, which constitutes the core of this chapter. Readers interested in a deeper insight on fundamentals and applications of electroanalytical techniques are addressed to specialized textbooks [19, 20].



The analytes detected by electrochemical methods are redox species, that is, molecules or ions which can release (or acquire) electrons to (from) proper reactants (molecules or metal surfaces) characterized by oxidizing (or reducing) properties.

From a classification viewpoint, electrochemical methods of analysis are divided in equilibrium methods (potentiometry) and dynamic ones (polarography, amperometry, voltammetry, coulometry, and others) [19, 20].

In the former, no current circulate through the electrochemical cell and the tendency of a certain redox reaction to occur is obtained by measuring the open-circuit electrochemical potential ( $E_{OC}$ ) of the cell; it is linked to the concentration of redox species in the electrolyte solution by the Nernst equation.

In dynamic (or transient) electrochemical techniques, a net current (or charge) is obtained as the result of an external excitation (generally, a voltage waveform) applied to the electrochemical cell; since such a current signal obeys Faraday's law, it is named *Faradaic current*. Experimental conditions are chosen so that the system operates under concentration polarization conditions and the Faradaic current (at proper applied potentials) is a function of the concentration in the electrolyte solution of the redox species (analyte) being reduced or oxidized at the electrode.

In voltammetry, the quantity being measured is the intensity of the electrical current which circulates through the circuit composed of the so-called working electrode (which is the "sensing" electrode), the electrolyte solution, and the counter electrode (a large area electrode, with polarity opposite to the working electrode). The excitation waveform is given as an electrical potential applied (and changed in a known manner) to the working electrode with respect to a third electrode, which acts as an unpolarized reference electrode (generally, a second species electrode, e.g., an Ag/AgCl electrode).

In linear sweep and in cyclic voltammetry (CV), the potential ( $E_{appl}$ ) applied to the working electrode changes linearly with time ( $t$ ) according to Eq. 11.1:

$$E_{appl} = E_i + vt \quad (11.1)$$

where  $E_i$  is the initial potential which is lower than the Nernst potential ( $E^0$ ) of the redox couple (i.e.,  $|E_i| < |E^0|$ );  $v$  is the scan rate (in  $V s^{-1}$  or  $mV s^{-1}$ )

In CV, the potential is scanned forward and backward (once or many times, depending on the measurement mode used) from  $E_i$  (where no Faradaic current is observed since  $|E_i| < |E^0|$ ) to move (with a certain scan rate) toward a vertex potential ( $E_v$  chosen so that  $|E_v| > |E^0|$ ) where a net current corresponding to the Faradaic reduction (or oxidation) of the analyte is observed. In the backward scan (from  $E_v$  to  $E_i$ ), the opposite electrode process occurs, which corresponds roughly to the return to the initial redox state of the product generated; if the forward process is a reduction, the process expected in the backward scan is the reoxidation of reduction products.

Transport of the analyte from the bulk solution to the electrode/solution interface can take place only by diffusion since convection and migration are inhibited by keeping the solution quiet, by avoiding thermal gradients (eventually by a thermostat),

and by making negligible migration by annulling the effect of the applied electric field using an excess supporting electrolyte (electrochemically inert).

With planar electrodes of dimensions larger than the thickness of the diffusion layer (see below), that is, in the millimeter size range, diffusion follows the so-called semi-infinite planar diffusion model. The CV obtained under this diffusion regime is characterized by two associated voltammetric peaks, one recorded during the forward scan and one in the backward scan. The two peaks are located at potential values symmetric with respect to a characteristic potential value named half-wave potential ( $E_{1/2}$ ). For reversible redox couples,  $E_{1/2} = (E_{p_f} + E_{p_b})/2$ , where  $E_{p_f}$  and  $E_{p_b}$  are the potentials of the forward and backward peak, respectively;  $E_{1/2}$  is strictly related to  $E^0$  [19, 20]. If the analyte is an oxidized species, then the forward peak corresponds to the direct process:



and the backward peak to the reverse process (from electrogenerated Red back again to Ox).

It would be worthy to note that in voltammetry, an electrochemical process is considered reversible when the charge-transfer process between the analyte and the electrode is faster than mass transport (diffusion). Therefore, under diffusion control and when  $|E_{\text{appl}}| \gg |E^0|$ , a concentration gradient is generated between the electrode surface (where the concentration of analyte is zero since all redox molecules which come or are on the electrode surface are reduced) and the bulk of the solution (where the concentration is the initial analyte concentration). The region where a concentration gradient exists is called diffusion layer. Under these conditions, the Faradaic current relevant to reaction 11.2 depends on the flux of the analyte which diffuses from the bulk solution to the electrode surface, this being inversely proportional to the thickness of the diffusion layer. This points out that voltammetric responses are time dependent since the thickness of the diffusion layer,  $\delta$ , depends on time according to Eq. 11.3:

$$\delta = (D t)^{1/2} \quad (11.3)$$

where  $D$  is the diffusion coefficient of the analyte (in  $\text{cm}^2 \text{s}^{-1}$ ) and  $t$  is the timescale of the experiment. Note that in voltammetry,  $t$  depends on the scan rate according to:

$$t = RT/Fv \quad (11.4)$$

Scan rates normally used in voltammetry are between  $0.020$  and  $1.000 \text{ V s}^{-1}$ , and diffusion coefficients for solution species are of the order of  $10^{-5}$ – $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , so that it is easily estimated that the thicknesses of diffusion layers are in the micrometer scale. This will be relevant when using electrodes with some peculiar dimensions (electrode diameter or thickness of electrode coatings) in such or even smaller dimension range.

The Faradaic current signal ( $S$ ) is not the only current being measured by voltammetric electrodes; an electrode dipped in an electrolyte solution behaves, in fact, also as a capacitor, and a certain amount of current (charging current) is consumed to build up the so-called electrical double layer [19, 20]. The double-layer charging current increases with the electrode area and the scan rate. Other small currents, named residual currents and related to the electroactivity of trace concentrations of redox impurities, can interfere with the recording of the Faradaic current of the analyte. In voltammetry, double-layer charging currents and residual currents constitute the main component of the noise ( $N$ ). The voltammetric  $S/N$  ratio can be improved by using the pulsed voltammetric techniques, such as differential pulse voltammetry (DPV) or Osteryoung's square wave voltammetry (SWV) [19, 20]. These electroanalytical techniques use excitation waveforms which are the combination of linear (or staircase) potential ramps with superimposed sequences of short potential pulses (10–50 mV for 10–50 ms). Proper sampling and combination of current values measured at fixed time lag with respect to the pulses application allow significant improvements in  $S/N$  ratios and consequent lowering of detection limit (DL) values. In fact, while with classical cyclic voltammetry (where no noise reduction is applied), DLs are typically in the  $10^{-4}$  M range, with pulsed techniques, DLs go down to the  $10^{-6}$ – $10^{-7}$  M range. Newly advanced pulsed techniques such as, for instance, multiple square wave voltammetry (MSWV) [21, 22] and double-differential MSWV [23, 24], allowed even further lowering of voltammetric DLs.

The already low DLs achievable by using these pulsed techniques can be improved by introducing a preconcentration step before the voltammetric detection. The preconcentration of the analyte is performed directly at the transducer (electrode) surface via Faradaic (for anodic, ASV, or cathodic, CSV, stripping voltammetry) [25] and/or non-Faradaic (adsorption, ion exchange, complexation, etc.) processes [26]; this allows one to reach DLs as low as  $10^{-9}$ – $10^{-11}$  M.

### ***11.1.3 Classical Electroanalysis with Mercury and Related Electrodes***

Transient electrochemical techniques are very sensitive, and they allow one to work rather easily at very low detection limits. In addition, they can give information on the redox state and complexation of the analyte in the sample [27]. They can be used in turbid or colored samples and do not suffer for interference from ambient light. However, in some cases, dissolved oxygen (which is electroactive) can constitute a problem and should be eliminated; indeed, some experimental tricks can allow one to shorten or even avoid the necessity to eliminate dissolved oxygen [28, 29]. All these characteristics make, in principle, electrochemical methods and sensors attractive for determining redox analytes at trace (micromolar) and ultratrace (submicromolar) concentration levels in complex samples such as those

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of interest, for instance, in environmental monitoring or for biomedical analyses. However, up to the recent time, some limits to the widespread use of dynamic electrochemical methods came from the fact that a great part of these methods were based on the use of mercury as electrode material. Mercury has some advantages in electroanalysis, and the very first dynamic electroanalytical method, polarography, for which Jaroslav Heyrowski was prized with the Nobel Prize in 1959, was based on the use of the dropping mercury electrode. However, because of the high toxicity of mercury, nowadays, there is an increasing interest in developing methods which employ different electrode materials. Note that, in addition to toxicity-related problems, the use of mercury electrodes suffers also from other limitations. Even the most recent mercury drop electrode systems are still rather expensive and cumbersome; they use relatively high amounts of mercury and are rather complicate for set up of unmanned automatic analyses. Recently, silver-mercury amalgam [30] and bismuth [31] have been proposed as alternatives for mercury. However, mercury as well as these alternative materials cannot be used at positive potential values because of their easy oxidation, so that all the world of oxidation processes is precluded to this kind of electrodes.

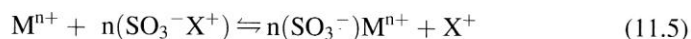
In order to widen the application field of electroanalytical methods, it is important to develop novel electrode systems characterized by high sensitivity, good reproducibility, wide usable potential window, and low cost and made of nontoxic materials. Moreover, they should be characterized by intrinsic molecular recognition properties so that they can give specific responses in complex real samples and can be used even for automatic continuous monitoring. Obviously, this is not an easy task, also because interferences and artifacts are always a possible important source of mistake; however, some significant steps in this direction have been taken recently, also thanks to the development of new electrode systems and IEV.

## 11.2 Films of Ion Exchangers on Metal Electrodes

### 11.2.1 Principles of Ion Exchange Voltammetry

For simplicity, principles of IEV are discussed here for the case of the preconcentration and electrochemical one-electron reduction of a cationic-oxidized analyte,  $M^{n+}$ , at an electrode coated with a polyanionic film containing, for instance, sulfonic groups as ion exchange sites. Analogue considerations can be obtained, with the proper easy corrections, for IEV of anionic oxidized species on a polycationic-coated electrode and for reduced cationic or anionic analytes as well.

The preconcentration capability of the coating is ruled by the ion exchange equilibrium between the electroactive counter ion (analyte) and non-electroactive counter ions present in the solution or already incorporated into the coating, according to the following reaction [32]:



where  $\text{SO}_3^-$  are the ion exchange sites in the polymer,  $\text{X}^+$  is an electrochemically inert counter ion (for simplicity, a cation of charge  $z = 1$ , as generally is the supporting electrolyte cation, e.g.,  $\text{Na}^+$ ), and  $\text{M}^{n+}$  is the multiply charged electroactive analyte.

The extent of such equilibrium reaction is expressed quantitatively by the selectivity coefficient  $K_X^M$ :

$$K_X^M = \frac{[\text{M}^{n+}]_p [\text{X}^+]_s^n}{[\text{M}^{n+}]_s [\text{X}^+]_p^n} \quad (11.6)$$

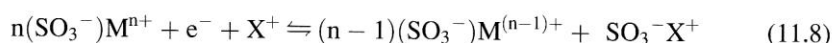
where subscripts p and s indicate concentrations in the polymer and solution phases, respectively, and square bracket indicates molar concentrations. With proper adaptations, ionic equivalent fractions can be used instead of molar concentrations. In some cases, a corrected selectivity coefficient is used, where activity coefficients of the solution species are used instead of concentrations. It is worth stressing that the selectivity coefficient is not strictly constant but can depend on experimental conditions [32].

When the ion-exchanged analyte is a trace species, the changes in  $[\text{X}^+]_s$  and  $[\text{X}^+]_p$  can be negligible and the selectivity coefficient can be conveniently substituted by the distribution coefficient,  $k_D$ , given as:

$$k_D(\text{M}^{n+}) = \frac{[\text{M}^{n+}]_p}{[\text{M}^{n+}]_s} \quad (11.7)$$

It is obvious that the analyte will be preconcentrated by coatings characterized by  $k_D > 1$ .

When a reducing electrochemical potential is applied (i.e.,  $E_{\text{appl}} < E^0$ ),  $\text{M}^{n+}$  is reduced at the polymer/electrode interface and a voltammetric peak is correspondingly recorded. If, as stated above, the reduction is a one-electron process (i.e., number of electrons exchanged,  $n = 1$ ), reaction 11.8 holds [33, 34]:



Under proper experimental conditions (three-electrode electrochemical cell; mass transport controlled by semi-infinite planar diffusion), the voltammetric reduction current is a function of the concentration of electroactive species incorporated into the coating. It is interesting to note that the open circuit electrochemical potential at the coated electrode ( $E(\text{OC})_{\text{CE}}$ ), obtained by applying the Nernst equation to reaction (11.8), is given by:

$$E(\text{OC})_{\text{CE}} = E^{0'} + \frac{RT}{F} \ln \frac{[\text{X}^+]_s}{[\text{X}^+]_p} + \frac{RT}{F} \ln \frac{[\text{M}^{n+}]_p}{[\text{M}^{(n-1)+}]_p} \quad (11.9)$$

where  $E^{0'}$  is the formal potential of the incorporated redox couple at the ionic strength of the coating; ionic activities have been approximated by their concentrations. Equation 11.9 can be easily rearranged for cases where  $n$  or  $z \neq 1$ .

It was shown [33, 35, 36] that, when differences in diffusion coefficients of oxidized and reduced species are negligible, the half-wave potential obtained by IEV at the coated electrode,  $(E_{1/2})_{IEV}$ , exhibited by the redox couple within the coating is given by:

$$(E_{1/2})_{IEV} = E^{0'} + \frac{RT}{F} \ln \frac{[X^+]_s}{[X^+]_p} \quad (11.10)$$

The partitioning of the oxidized and reduced species between the solution and the coating is ruled by relevant distribution coefficients; Eq. 11.7 for the oxidized analyte is complemented by Eq. 11.11 relevant to the reduced partner:

$$k_{D(M^{(n-1)+})} = \frac{[M^{(n-1)+}]_p}{[M^{(n-1)+}]_s} \quad (11.11)$$

By proper substitution, one gets:

$$E(OC)_{CE} = E^{0'} + \frac{RT}{F} \left\{ \ln \frac{[X^+]_s}{[X^+]_p} + \ln \frac{k_{D(M^{n+})}}{k_{D(M^{(n-1)+})}} + \ln \frac{[M^{n+}]_s}{[M^{(n-1)+}]_s} \right\} \quad (11.12)$$

This equation is important for cases where both redox partners  $M^{n+}$  and  $M^{(n-1)+}$  are present in the sample. In particular, when the concentration of electroactive analytes  $M^{n+}$  and  $M^{(n-1)+}$  is low, almost all the ion exchange sites are saturated by  $X^+$  so that changes in  $[X^+]_p$  are negligible [37], and Eq. 11.10 can be rearranged as:

$$E(OC)_{CE} = K + \frac{RT}{nF} \ln \frac{[M^{n+}]_s}{[M^{(n-1)+}]_s} \quad (11.13)$$

where

$$K = E^{0'} + \frac{RT}{nF} \ln \frac{k_{D(M^{n+})}}{k_{D(M^{(n-1)+})}} + \frac{RF}{F} \ln \frac{[X^+]_s}{[X^+]_p} \quad (11.14)$$

This means that open-circuit potential values,  $E(OC)_{CE}$ , measured by potentiometry [37] at the polymer-coated electrode, change linearly with  $\ln ([M^{n+}]_s/[M^{(n-1)+}]_s)$  with a slope equal to  $59/n$  mV (at  $25^\circ\text{C}$ ) and with an intercept given by Eq. 11.14. If all the other terms are independently known,  $E(OC)_{CE}$  values allow one to calculate the concentration ratio in the sample solution between the redox species  $M^{n+}$  and  $M^{(n-1)+}$ . Equation 11.13 is rather similar to the usual Nernst equation for a redox indicator electrode [20] with the advantage that the coated

electrode can preconcentrate the redox ions so, in principle, it can be used for trace analysis; moreover, the coating rejects interfering species of opposite ionic charge than the analyte.

These principles are the basis for performing redox state speciation of trace analytes of environmental interest, as for instance,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations [37], by using ionomer-coated electrodes. By combining ion exchange voltammetry and potentiometry (with both data sets obtained at the same polymer-coated electrode), it is possible to obtain quantitative information on speciation. IEV is used for quantifying total concentrations and for obtaining relevant  $k_D$  values (see below); potentiometry at the coated electrode is employed for obtaining the concentration ratio between chemical species characterized by different redox states.

### 11.2.2 Current Signals at Polymer-Coated Electrodes

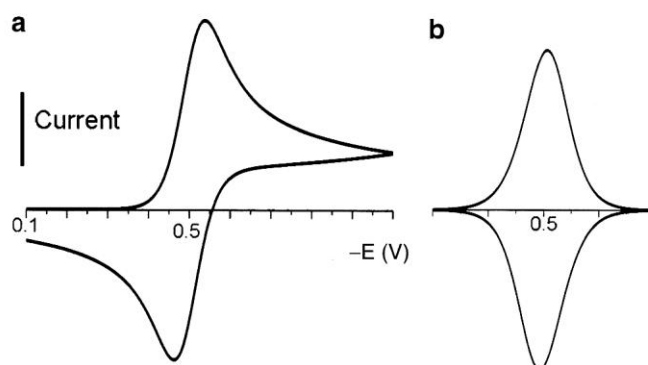
Many research papers have been devoted to study the mechanisms which rule mass and charge transport phenomena in polymeric matrices (see Ref. [38–40] for reviews). Depending on the experimental conditions involved (mainly, type of polymer, redox properties, and concentration of the ion-exchanged analyte), the overall transport process can be controlled by a variety of phenomena such as physical diffusion of redox species, electron hopping, segmental motion of polymer chains, polymer diffusion, counter ion migration, and ion pairing [38, 39]. Regardless of the microscopic mechanism, such transport phenomena obeys Fick's law of diffusion, and the rate of transport depends on an observable parameter characteristic for the analyte (and polymer layer) which is named apparent diffusion coefficient,  $D_{\text{app}}$ .

Analogously with voltammetric experiments performed at the electrode/solution interface, also at polymer-coated electrodes, peak currents are determined by the dimensions and time dependence of the diffusion layer which (for the polymer case) is the region of the electrode/polymer interface where an analyte concentration gradient is generated by the applied potential. Note that, at polymer-coated electrodes, the rate-limiting step which determines current responses is diffusion through the electrode/polymer interface. It is therefore important to distinguish whether the measurements are carried out in a timescale,  $t$ , for which the thickness of the diffusion layer,  $\delta$ , is smaller or larger than the thickness of the polymeric coating,  $\Phi$ . This determines the existence of two different kinds of voltammetric responses, typical of polymer-coated electrodes, which are [4]:

- (a) A linear diffusion controlled behavior, when  $\delta \ll \Phi$
- (b) A thin-layer-like behavior, when  $\delta \gg \Phi$

The passage from situation (a) to situation (b) depends on relevant values of the coating thickness and voltammetric scan rate. Under conditions (a), there is a pool outside the diffusion layer which furnishes fresh analyte able to diffuse to the electrode in the time course of the scan; for case (b), the analyte incorporated in





**Fig. 11.1** Typical CV patterns observed at electrodes coated with thin films of ion exchangers: (a) under semi-infinite linear diffusion (film thickness  $>$  diffusion layer thickness;  $I_p$  scales with  $v^{1/2}$ ); (b) under thin-layer-like conditions (film thickness  $\leq$  diffusion layer thickness;  $I_p$  scales with  $v$ )

the coating is reduced (or oxidized) exhaustively during the voltammetric scan. As illustrated in Fig. 11.1, the characteristics of the voltammograms recorded under the two conditions are very different:

- Under linear diffusion conditions (case a), the voltammetric peak shows the classical diffusive tail due to the Cottrellian current decay observed at potential values cathodic enough with respect to the peak potential (see Fig. 11.1a); the peak current depends on the square root of  $v$ , according to easy rearrangement [5] of the classical Randles-Sevcik equation, where  $D_{app}$  substitutes  $D$  and  $[M^{n+}]_p = k_D[M^{n+}]_s$  substitutes the bulk solution concentration.
- For a thin-layer-like behavior (case b), the voltammetric peak shows a characteristic symmetric Gaussian shape (see Fig. 11.1b); the peak current  $I_p$  depends linearly on the scan rate  $v$ , according to Eq. 11.15 [4]:

$$(I_p)_p = 9.39 \times 10^5 n^2 v V [M^{n+}]_p \quad (11.15)$$

where  $V$  is the volume of the polymer thin layer (electrode area  $\times$  film thickness).

Signals given by Eq. 11.15 are independent of  $D_{app}$  but depend on the film volume  $V$ . This means that the peak current in thin-layer-like conditions increases with the film volume, that is, film thickness.

Measurements under thin-layer-like conditions are useful for measuring voltammetrically the amount of analyte incorporated in the polymer layer after equilibration with a certain concentration of analyte in the sample solution; this quantity is obtained via coulometric integration of the voltammetric peak recorded in thin-layer-like conditions (low scan rate, generally 2–5 mV/s). The plots  $[M^{n+}]_p$  versus  $[M^{n+}]_s$  at constant temperature give the ion exchange distribution isotherms from which one can calculate relevant  $K_X^M$  or  $k_D$  values (see Eqs. 11.6, 11.7) [41, 42].



Ion exchange voltammetric signals recorded under semi-infinite linear diffusion conditions are strongly influenced by  $D_{\text{app}}$  values. The ratio between peak currents recorded in the same experimental conditions at unmodified,  $(I_p)_s$ , and at polymer-coated electrodes,  $(I_p)_p$ , (of the same surface area  $A$  and with both electrodes operating under semi-infinite planar diffusion control) is given by Eq. 11.16 [5]:

$$\frac{(I_p)_p}{(I_p)_s} = \left( \frac{D_{\text{app}}}{D_s} \right)^{1/2} k_D \quad (11.16)$$

It shows that the factor  $(D_{\text{app}}/D_s)^{1/2} k_D$  plays the role of an amplification factor which quantifies the increase of voltammetric signals when polymer-coated electrodes are used instead of bare ones.  $D_{\text{app}}$  values are typically in the  $10^{-9}$ – $10^{-12}$   $\text{cm}^2 \text{s}^{-1}$  range [38–40]; they are two to three orders of magnitude lower than  $D_s$  values, usually in the  $10^{-5}$ – $10^{-6}$   $\text{cm}^2 \text{s}^{-1}$  range. Because of such a large difference in diffusion coefficient values, the ion exchange preconcentration results effective in increasing voltammetric signals for those analytes who are characterized by ion exchange distribution coefficient values  $k_D > 100$ – $1,000$ . In such cases, the increase in sensitivity can then be from one to several orders of magnitude.

Without entering into a detailed analysis of the dynamics of electron transport in ion-exchanger coatings, it is worth noting that the operativity of different microscopic charge-transfer mechanisms can have consequences also for the analytical application of IEV since it can cause the appearance of a dependence of  $D_{\text{app}}$  (and therefore of  $(I_p)_p$ ) on  $[M^{n+}]_p$ . Although such complications can be considered more exceptions than the rule, the possibility that  $D_{\text{app}}$  changes with  $[M^{n+}]_p$  cannot be neglected. If electron hopping between the redox centers incorporated into the polymeric coating is the rate-determining step [3, 43, 44], then  $D_{\text{app}}$  can increase with  $[M^{n+}]_p$  [45, 46]. According to the Dahms-Ruff electron hopping model [39, 47, 48],  $D_{\text{app}}$  is given as:

$$D_{\text{app}} = \frac{1}{6} k_{\text{ex}} d^2 [M^{n+}]_p \quad (11.17)$$

where  $k_{\text{ex}}$  = site to site electron exchange rate constant and  $d$  = distance of closest approach between two neighboring sites.

The incorporation of a multiply-charged analyte which can interact electrostatically with more than one polymeric chain can cause a sort of electrostatic cross-linking effect which reflects in a decrease of  $D_{\text{app}}$  with increasing  $[M^{n+}]_p$  [49–54]. With electrodes modified with perfluorosulfonate ionomers, the decrease of diffusion coefficients with increasing concentration was explained by a bottleneck effect caused by the narrow channels that interconnect ionic clusters in these polymers [49]. It was shown that changes in the microenvironment within the ionomeric coating can influence such a behavior [55].

### 11.3 Electrode Modifiers for Ion Exchange Voltammetry

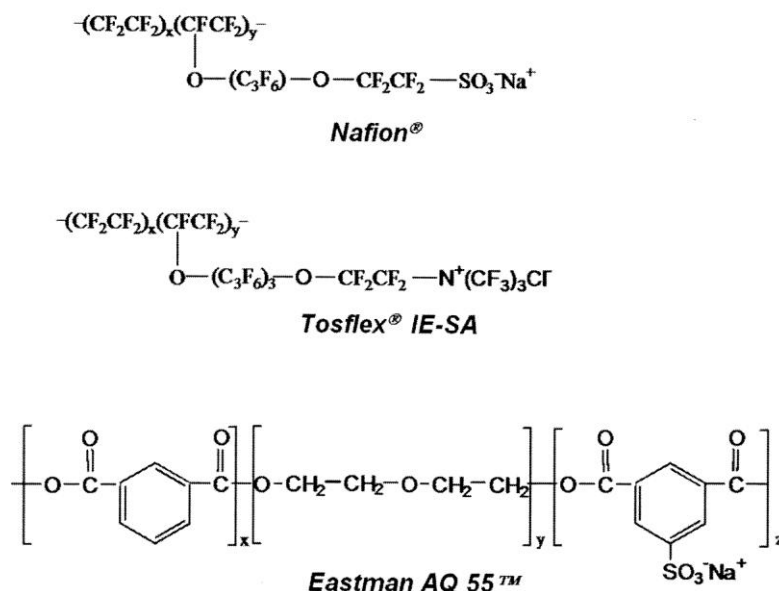
#### 11.3.1 Ion Exchangers and Coatings

The electrode coating most widely used in IEV of cationic analytes is probably Nafion<sup>®</sup>, followed by the sulfonated polyesters such those belonging to the Eastman AQ<sup>TM</sup> series. For anionic analytes, poly(4-vinylpyridine) and Tosflex<sup>®</sup> IE-SA 48 (produced by Tosoh Co., Japan) are the most used polymeric coatings. Nafion<sup>®</sup>, Tosflex<sup>®</sup>, and sulfonated polyesters (see Scheme 11.1) belong to the ionomer group that are ionic polymers characterized by a rather low content of ionic groups [56].

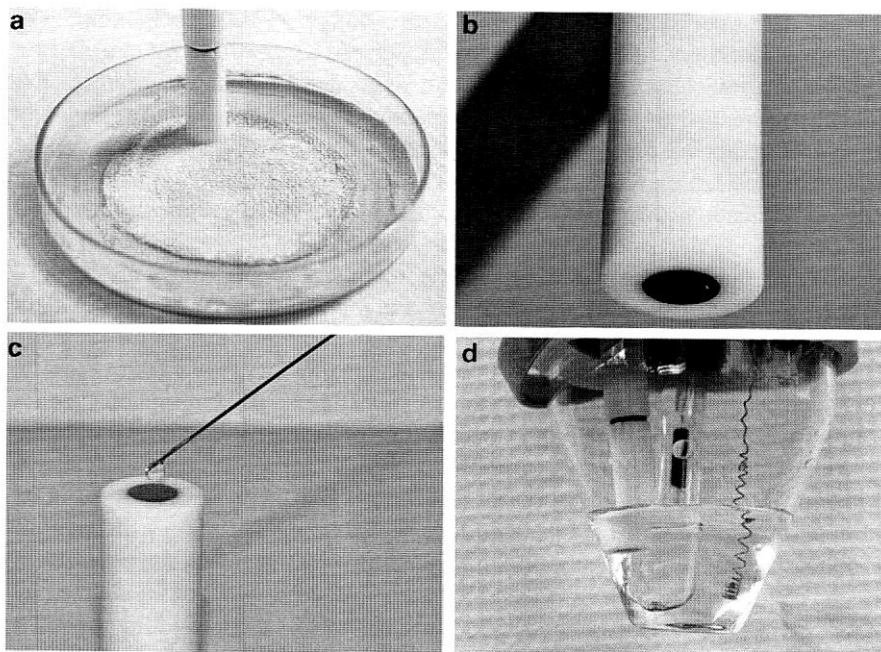
These ionic groups interact or associate to form ion-rich hydrophilic regions surrounded by hydrophobic domains [57], such a clustering being the basis of the high stability of ionomer films.

The easiness of modification of the electrode surface and mechanical and chemical stability of ionomer coatings explain their successful use in IEV. The physical properties of Nafion<sup>®</sup> such as density, ion exchange capacity, etc., which are relevant to the successful preparation and analytical application of coated electrodes have been the subject of careful studies by Leddy's group [58–60].

Apart from ionomers, also other ion exchangers were applied for ion exchange voltammetry such as, for instance, poly(4-vinylpyridine) [1], poly(2-vinylpyrazine) [35], and poly-L-lysine [61, 62]. However, because of the higher water solubility



Scheme 11.1 Structural formulas of some ionomers used in IEV



**Fig. 11.2** Sequence of the main steps used in the deposition of an ionomer by microvolume evaporation: (a) mirror polishing of a glassy carbon disk electrode on graded alumina powder (0.3 and, then, 0.05  $\mu\text{m}$  particle diameter), followed by rinsing in deionized water and ultrasonication; (b) a mirror-polished glassy carbon electrode with a disk diameter of 5 mm; (c) application of a microvolume (typically 3  $\mu\text{l}$ ) of 0.05% (w/v) Nafion solution in water/methanol/isopropanol (1/1/1); (d) after drying at room temperature for about 30 min, the modified electrode is dipped in the electrolyte in a three-electrode electrochemical cell; on the *left*: modified working electrode; in the *center*: Ag/AgCl reference electrode; on the *right*: Pt spiral counter electrode

of these polyelectrolytes which contain a large number of ion exchange sites, the preparation of stable coatings requires a chemical cross-linking stabilization procedure. Another class of electrode coatings of inorganic nature is based on the use of clays. Applications and recent trends on the promising use of these inorganic modifiers for IEV has been nicely reviewed by Walcarius [63, 64].

### 11.3.2 Classical Methods of Coating Depositions

Different ways of film deposition can be used, the simplest and more popular procedure being casting a microvolume of polymer solution onto the electrode surface, then allowing the solvent to evaporate slowly. The steps used for the modification of the electrode surface are summarized in Fig. 11.2. This procedure has been used successfully for modifying electrodes starting from alcohol-water

solutions of the perfluorinated cation-exchanger Nafion® [2, 65] or Tosflex® [66, 67]. Film uniformity can be improved by resorting to spin-coating [68, 69].

However, particular care must be devoted to avoid partial removing of the polymer solution by centrifugal force while spinning the electrode; otherwise, any information on the amount of deposited modifier will be lost. Droplet evaporation and/or spin coating has been used also for casting coatings of poly(estersulfonic acid) of the Eastman AQ series. However, in this case, stable films are obtained only after heating the deposited polymer at temperatures of about 60–80°C [70] or by dissolving the ionomer in a water-acetone mixture of proper composition [71].

Nafion®, Tosflex®, and Eastman AQ™ are characterized by high equivalent weights and by a low number of ion exchange sites interposed between long organic chains. This makes the structure of the solvated coating a cluster-like structure in which hydrophobic and hydrophilic domains exist [57], the hydrophobic zones being responsible for adsorption and stabilization of such coatings on hydrophobic electrode materials such as glassy carbon and pyrolytic graphite.

The influence of parameters such as composition of the polymer solution and drying temperature [72–75], humidity [76, 77], or other treatments such as RF-plasma treatment [78] on the structure, stability, and ion exchange behavior of recasted coatings is known.

Polymeric materials characterized by low equivalent weights and high number of ion exchange sites have been used to recast polymer films on electrode surfaces by microvolume evaporation, followed by stabilization via chemical cross-linking. A typical example is given by poly(4-vinylpyridine), which gives more stable and reproducible coatings when the polymer backbone is cross-linked by reacting with alkyl dihalides [79, 80]. This procedure was used also for other polymers containing heterocyclic nitrogen, such as poly(2-vinylpyrazine) [35]. Note that poly(4-vinylpyridine) behaves as an anion exchanger when the pyridinic nitrogen is in the pyridinium form, e.g., protonated by dipping the modified electrode in solution at  $\text{pH} < 5.2$  [1], or quaternized by reaction with alkyl halides [81]. Cross-linking of polyelectrolytes can be obtained also by irradiation methods, as for the case of poly(dimethyldiallylammonium chloride) [82].

Another popular and effective way of preparing ion exchange coatings is electropolymerization [4], this procedure being used for depositing films of electroactive polymers prepared by polymerization of electroactive monomeric precursors. They can be redox polymers (see, e.g., [83]), conducting polymers [84], or functionalized conducting polymers [85–89]. However, in principle, performing ion exchange voltammetry with electrodes coated with polymers which are electroactive themselves can suffer some limitations since the electroactivity window relevant to the polymer can overlap with the detection window of some analytes. On the other hand, the signal relevant to the electroactive moiety of the polymer can be used to good advantage as an internal standard to evaluate signals quantitatively [90].

As above mentioned, electrochemical oxidation is used to electropolymerize anionic or cationic derivatives of pyrrole [87–89], so obtaining coatings in which the potential dependent ion exchange properties typical of conducting polymers are enhanced and become independent on the applied potential. Moreover,

functionalization of polypyrrole with fixed ion exchange sites increases its ion exchange capacity about four times [88], compared with plain polypyrrole in its fully oxidized form. Electrochemical polymerization is used for the preparation of coatings which incorporate the electroactive mediators used in electrochemical biosensors. This approach has been introduced some years ago by Heller and coworkers [91], originating a class of electroactive polymeric materials tailored for the electrochemical “wiring” of redox enzymes and other biomacromolecules, successfully used for glucose sensors [92].

### ***11.3.3 Molecular Engineering of Ionomer Deposition***

Advances in the reliable use of polymer-coated electrodes for analytical purposes depend on improvements in the control and reproducibility of the deposition of the polymer layer. This allows the lowering of the film thickness and shortening of the response time. Moreover, molecular control of the coating structures allows the deliberate control of the hydrophobic/hydrophilic properties as well as clustering and surface exposures of the ion exchange sites.

Hoyer et al. [93] presented an electrostatic spray deposition method which allows the preparation of very uniform thin films (ca 0.3  $\mu\text{m}$ ), keeping unaltered the peculiar features of Nafion® as far as permselectivity and rejection of interferents are concerned.

New possibilities to built ordered structures of ionomer films on a smaller scale (nanometer) have been demonstrated by the application of layer-by-layer deposition techniques [12]. The layer-by-layer strategy allows the construction of supramolecular sandwiches, assembled by exploiting electrostatic interactions. It is based on the alternate deposition of molecular layers of cationic and anionic (poly)ions arranged in sandwiched ordered structures, thanks to favorable electrostatic interactions between the layers of opposite charge. Typical examples of application of the layer-by-layer strategy to the preparation of modified electrodes and sensors are found in the biosensors literature [94–101]; for instance, a thin film consisting of alternating layers of Nafion® and ferric ions was used to develop calcification-resistant implantable biosensors [102] or other nanolayered materials [103–105].

Other possibilities in the molecular engineering of ionomer films on electrodes surfaces were opened recently, by studying the preparation and characteristics of ionomer coatings prepared by using the Langmuir-Blodgett (LB) technique [10]. It is used to build up monolayers or multilayers of organic amphiphilic molecules in which the order and 2-D structure are controlled at the molecular level by controlling the compression extent in the LB trough of a monomolecular layer of amphiphilic molecules spread at the air/water interface. By this way, it is possible to obtain ultrathin films characterized by long-range order, which can provide new insights on electron transfer processes at molecularly ordered interfaces. The 2-D-ordered interfacial layer can be transferred on solid surfaces by controlled dipping through the interface. There are two ways of dipping the substrate: the classical

Langmuir-Blodgett technique (vertical transfer) and the Langmuir-Schaefer (LS) technique (horizontal transfer). The LS technique is usually employed for the transfer of rigid films of materials such as polymers. Although the LS technique showed to work well for Nafion® [106], it has the limitation to rely upon the manual ability and experience of the experimentalist. Recently, it was shown that successful transfer of Langmuir layers of ionomers [107] can be achieved also by optimizing the conditions for the classical LB technique which is a vertical dipping-lift deposition technique for which the rate and extent of the movement of the substrate through the interfacial film is controlled automatically by a mechanical dipper driven by suitable software.

It was shown that if proper electrolyte is dissolved in an aqueous subphase, Nafion® forms an interfacial film at the air/water interface, which can be compressed in a typical Langmuir-Blodgett experiment, giving a stable film transferable on the surface of a variety of materials, including electrode surfaces. The thickness of the Nafion film can be as thin as few nm and scales with the number of layers deposited, keeping its typical permselectivity [106].

Very recent advances showed the possibility to characterize the structure of these ultrathin coatings by using electroactive photoluminescent probes such as Ru(bpy)<sub>3</sub><sup>2+</sup> complexes [108] as well as to exploit electrochemically induced luminescence to detect suitable co-reactants (analytes) such as tertiary amines or oxalate [109, 110].

### ***11.3.4 Coating Regeneration and Electrochemical Control of Ion Exchange Voltammetry***

When considering the analytical application of IEV, it is important to assess the reusability of the modified surface. If the ion exchange selectivity coefficient for the analyte is not too large, regeneration can be achieved by simply exposing the film to a high concentration of non-electroactive salt solution so obtaining expulsion of the analyte from the ion-exchanger film. However, such a simple regeneration procedure cannot be successful for analytes characterized by very large ion exchange selectivity coefficients. For this reason, a number of studies were devoted to two alternative approaches which can overcome this problem; they are:

- Preparing single-use electrodes based on the preparation of cheap and disposable electrode systems such as screen-printed electrodes [111, 112]
- Developing coatings which can facilitate the regeneration of the ion exchange membranes

The modifiers used for the preparation of screen-printed electrodes are typically different from the polymeric membrane systems which are the subject of the present chapter, so we will not go into many details of this approach.



The regeneration of the coatings can be improved by developing polymer films whose net charge can be switched chemically and/or electrochemically from positive to neutral to negative. Pioneering studies in this direction were outlined already in the 1980s by researches performed in Anson's group where poly(4-vinylpyridine) [113] and poly(2-vinylpyrazine) [35], containing electroactive pendant groups such as  $[\text{Fe}(\text{CN})_5]^{3-/2-}$ , were used to this aim.

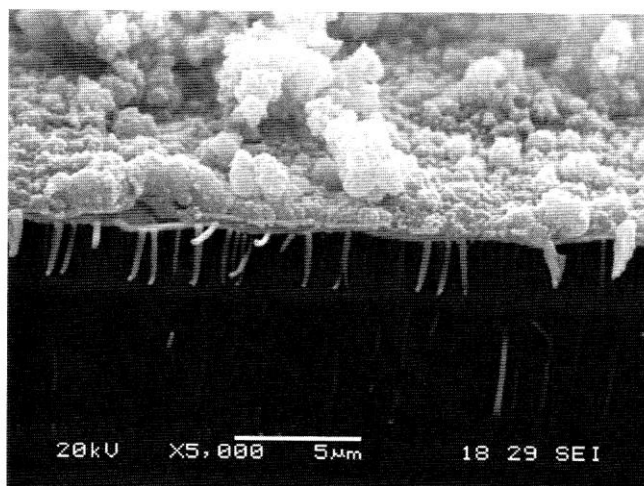
A similar approach, in which the ion exchange characteristics were modulated by electrochemical switching, implied terpolymers based on styrene (backbone), styrene sulfonate (unswitchable cation exchanger), and vinylferrocene (electrochemically switchable from neutral to anion exchanger) [114]. When the  $\text{Fc}/\text{Fc}^+$  couple in the film was reduced, the terpolymer acted as a cation exchanger. When  $\text{Fc}$  was oxidized, the electrogenerated  $\text{Fc}^+$  cation became the counter ion for the  $\text{SO}_3^-$  groups, thus allowing the release of the incorporated cations (analyte). A similar approach was extended recently to add electrochemical control to ion-permeation capabilities in templated nanotubes functionalized with 11-ferrocenyl-1-undecanethiol [115]. The switching from cation exchanger to neutral polymer was achieved also by using electrodes coated with conducting polymer and polyelectrolytes composites [116–125]. Typical examples of such an approach were the electrochemically controlled binding and release of cations at poly(*N*-methyl-pyrrole)/polystyrene sulfonate [123] or at polypyrrole/polyester sulfonate [125]. When the conducting polymer was reduced, cations such as protonated amines,  $\text{Ru}(\text{bpy})_3^{2+}$ , or methylviologen were incorporated into the film, while the release of these compounds was accomplished by simple reoxidation [113].

More recently, these principles were applied for developing solid-phase microextraction (SPME) electrodes in which the redox switching of the conducting polymer was exploited for performing the electrochemically controlled uptake and release of ionic analytes [126–129].

By taking advantage of the anion preconcentration capabilities of oxidized conducting polymers, Mark and coworkers [126] used a Pt microfiber coated with poly(3-methylthiophene) (PMeT) to perform the electrochemically controlled extraction and desorption of arsenate anions. The extension of this principle to cationic analytes was presented by Nyholm and coworkers [129], who used polypyrrole films doped with anions of low mobility in order to obtain a film which in the reduced state acts as a cation exchanger.

All these studies were performed using aqueous solution as the sample. However, both from a SPME viewpoint and when thinking to chromatographic applications of electrochemically switchable ion exchange devices [130], the development of electrochemically switchable polymer films usable in organic solvents is rather attractive; recently, a composite between poly(3-methylthiophene) and polyester sulfonate was developed to this aim [131]. The microscopic structure of this composite is shown in Fig. 11.3.

Note that, among the ionomers used as coatings on electrode surfaces, Eastman AQ55™ is the only one which is both stable and shows very good cation-exchange properties also in acetonitrile solutions [70, 71, 132].



**Fig. 11.3** SEM image of a cross-section of the bilayer composite Eastman AQ55™ (*lower* layer) and poly(3-methylthiophene) (*upper* granulated layer) for achieving electrochemical control of the ion exchange (Reproduced from Ref. [131] with kind permission of © Elsevier (2006))

The development of ionomer-based SPME devices can open the way to extended application of IEV for environmental electroanalysis and in electrochemically controllable separation methods.

#### 11.4 Recent Analytical Applications of Ion Exchange Voltammetry

Some of the earlier analytical applications of IEV have been reviewed previously [6–9]. In the following, Tables 11.1–11.3 are listed and briefly commented those examples which can be considered as typical for IEV, together with some very recent updates. These examples of analytical applications of IEV methods demonstrate the excellent capabilities of the technique; note that many of the methods listed are characterized by very low detection limits, typically in the  $10^{-9}$  M range or lower. In many cases, the use of ion-exchanger-coated electrodes can reduce drastically the effects of interferences and electrode poisoning and allows one to perform trace speciation analysis, that is, to identify and to measure the concentration of one or more individual chemical species of the same element. In the same cases, suitable electrocatalysts incorporated in the ion-exchanger film are used to sense a soluble analyte (substrate), generating an electrocatalytic current which scales with the analyte concentration. In Tables 11.1–11.3, we included only those examples of electrocatalysis at polymer-coated electrodes in which the ion exchange process plays a key role.



**Table 11.1** Organic cation exchangers

Exchanger	Analytes	Notes	Reference
Nafion Nafion + cellulose acetate	Dopa, epinephrine, norepinephrine	Amperometric detection in flow systems. Advantages of bifunctional coatings are described	[133, 134]
Nafion	Dopamine, serotonin	Carbon fiber electrodes for in vivo detection of the analytes in the nM range	[135–137]
Nafion	Yb <sup>3+</sup> , Eu <sup>3+</sup>	Determination of trace Yb <sup>3+</sup> and Eu <sup>3+</sup> . DL = 30 nM for Eu <sup>3+</sup> and 20 nM for Yb <sup>3+</sup>	[138, 139]
Nafion	Promethazine	Good exclusion of interfering anions and satisfactory results in flow analysis	[140]
Nafion	UO <sub>2</sub> <sup>2+</sup>	Effect of oxidation state on the partitioning of UO <sub>2</sub> <sup>2+</sup> is examined. Influence of local proton activity inside Nafion is studied	[42]
Nafion	4-Nitroso-N,N- diethylaniline	Study of the redox mechanism at the Nafion GC modified electrode. DL 3 nM	[141]
Nafion	Salbutamol, fenoterol, metaproterenol	Nafion is deposited on the surface of a CPE. DL $2.5 \times 10^{-8}$ M	[142]
Nafion	Pb(II)	Nafion/copper-mercury film electrode. DL 80 ng L <sup>-1</sup>	[143]
Nafion/1-(2-pyridylazo)- 2-naphthol	Pb(II)	The chelating agent in Nafion increases sensitivity and selectivity	[144]
Nafion and Nafion/poly (vinylsulfonic acid)	Cu(II), Cd(II), Pb(II), Zn(II)	Different kinds of coatings are compared for batch analysis of environmental samples such as river and run-off waters	[145]
Nafion	CH <sub>3</sub> Hg <sup>+</sup>	DPV and multiple square wave voltammetry (MSWV) allows ultratrace determination of CH <sub>3</sub> Hg <sup>+</sup> with Nafion	[23]
Nafion	Tl(I)	Square wave stripping, in the presence of EDTA. DL 0.01 ppb	[146]
Nafion	Parathion	DL 50 nM, linear range up to 15 μM	[147]
Nafion	Selenium(IV)	Nafion-coated mercury film electrode modified with 3,3'-diaminobenzidine. CSV, DL 0.48 μg L <sup>-1</sup>	[148]
Polyester sulfonate	Cu(II), Cd(II), Pb(II), Zn(II)	Electrodes coated with ionomer/mercury thin film for ASV of heavy metals	[149]
Nafion	Apomorphine	Ion exchange preconcentration, detection by SWV. DL 3 nM	[150]

(continued)

**Table 11.1** (continued)

Exchanger	Analytes	Notes	Reference
Nafion	Eu <sup>3+</sup>	MSWV for ultratrace determination, DL 10 pM, application to nuclear plants cooling waters	[24]
Nafion	Phenol	Adsorptive stripping in the presence of ethyltrimethylammonium which favors the analysis. DL 1 nM	[151]
Sulfopolyester (Eastek)	N-nitrosamines	Study on the effect of the degree of sulfonation; comparison with Nafion, cellulose acetate, and butyrate. DL 0.1 nM	[152]
Eastman AQ55™	Cyt c	GCE modified with AQ55™. Incorporation of cyt c; electrocatalytic activity is observed	[153]
Eastman AQ55™/silica composite	Oxalate, TPA, chlorpromazine	Ru(bpy) <sub>3</sub> <sup>2+</sup> immobilized in AQ55™/silica film. ECL detection	[154]
Polydiphenylamine/Na-dodecylsulfate	Electro-inactive cations	Gold electrode modified with ion exchanger	[155]
PDMDAAC	Cations	Amperometric detector for IEC Sol-gel preparation of CPE with ion exchanger incorporated. Preconcentration by IE, detection by SWV	[156]
Poly(sodium 4-styrene sulfonate)	Trace heavy metals	Application for heavy metal analysis in estuarine waters	[157]
Nafion Eastman AQ55™	Cytochrome <i>c</i> / ascorbate	Nafion or AQ55™ film deposited by LB technique incorporating cyt c. Electrocatalytic detection of ascorbate	[158]
Eastman AQ55™	Ethyl 4-iodobenzoate Di-bromocyclohexane	Incorporation of nickel complexes by ion exchange, as detecting electrocatalyst	[159]
Polylysine/polystyrene sulfonate	Pb(II), Cu(II), Cd(II)	GC/TMFE, preconcentration by IEV and detection by SW-ASV	[160]
2,5-Bis(2-thienyl)- <i>N</i> -(3-phosphorylpropyl) pyrrole	DNA	Electropolymerization of PPy, target 27- and 18-mer DNA incorporated in the film by IE. Detection of 0.16-fmol DNA	[161]
Hexacyanoferrate nanocomposite	Radioactive caesium	Incorporation of Cs by ion exchange in the reduction of nickel hexacyanoferrate	[162]
Nafion	TPA	Immobilization of Ru(bpy) <sub>3</sub> <sup>2+</sup> in Nafion LB film for ECL, detection of tertiary amines	[109, 163]

(continued)

**Table 11.1** (continued)

Exchanger	Analytes	Notes	Reference
Nafion/CNT	NADH	Ion exchange immobilization of thionine, electrocatalyst for NADH detection	[164]
Nafion/PSS	TPA	Immobilization of Ru(bpy) <sub>3</sub> <sup>2+</sup> on ITO/Nafion/PSS electrode	[165]
Poly (sodium-4-styrene sulfonate) (PSS)	Pb(II)	ECL detection. DL 3 nM GC/TMFE, preconcentration by IEV and detection by SW-ASV	[166]
Polyvinyl ferrocenium	Hg <sup>2+</sup>	DL 5 × 10 <sup>-10</sup> M	[167]
Nafion/nano-Au/thionine multilayer	Thrombin (TB)	Au electrode coated LBL by ion exchange with Nafion, thionine, and nano-Au. DL 40 pM	[168]
Nafion	Cr(VI)	Preparation of silver nanoparticles in GCE/Nafion film. Electrocatalysis of Cr (VI)	[169]
Nafion	Phenolic compounds	Electrospun Ru(bpy) <sub>3</sub> <sup>2+</sup> -doped Nafion nanofibers. ECL detection. DL 1.0 nM	[170]
Phosphonic acids bearing pyridinium groups	Cations	Phosphonic acids bearing pyridinium groups grafted on mesoporous TiO <sub>2</sub> . Cations are incorporated by ion exchange	[171]
Nafion	NO <sub>2</sub> <sup>-</sup>	Fe(bpy) <sub>3</sub> <sup>2+</sup> immobilized in Nafion by IE. Amperometric sensor	[172]

**Table 11.2** Organic anion exchangers

Exchanger	Analytes	Notes	Reference
Protonated poly (4-vinylpyridine)	Cr(VI)	Detection by reduction to Cr (III). Linear range: 10 <sup>-6</sup> –10 <sup>-8</sup> M	[173]
Quaternized poly (4-vinylpyridine)	Cu/Cl <sup>-</sup>	Copper preconcentrated as electrogenerated anionic cuprous complexes	[174]
Tosflex	Cu/Cl <sup>-</sup>	Copper preconcentrated as electrogenerated anionic cuprous complexes. DL 3 × 10 <sup>-6</sup> M. Influence of amino acids is examined	[66]
Tosflex	Hg/Cl <sup>-</sup>	Trace determination of Hg(II) in chloride-containing media. DL 4 × 10 <sup>-11</sup> M. Application to seawater analysis	[175]

(continued)

**Table 11.2** (continued)

Exchanger	Analytes	Notes	Reference
Poly(4-vinylpyridine)	Bi(III)	Square wave stripping of anionic complexes of Bi (III) with chloride	[176]
Tosflex	HgCl <sub>4</sub> <sup>2-</sup>	The mechanism of IEV preconcentration/detection is examined	[177]
Tosflex/8-quinolinol	Te(IV)	Cathodic stripping of anion TeCl <sub>6</sub> <sup>2-</sup> . DL 0.1 µg/L	[178]
Quaternized poly(4-vinylpyridine) (QPVP)	Pb(II)	Anionic complexes generated in the coating are preconcentrated; application to groundwater analyses	[179]
Tosflex	Bi(III)	Preconcentration of the analyte by IE. DL 0.58 ppb	[180]
PDMDAAC	Anions	Cross-linking of the modifier by µ-irradiation. Application to Fe(CN) <sub>6</sub> <sup>3-</sup> analysis	[181]
Tosflex	Zn <sup>2+</sup>	TMFE modified with Tosflex DL 0.1 ng/mL	[182]
Tosflex	Diethyldithiophosphoric acid	DL 0.4 ppb	[183]
Poly(N-chloranil N,N,N',N'-tetramethylethylene diammonium dichloride)	β-Lactam antibiotics	DL 2.12 nM	[184]
Poly(vinylsulfonic acid) (PVSA)	Anions Fe(CN) <sub>6</sub> <sup>4-</sup>	Sol-gel preparation of the modified electrode. SWV detection	[185]
Poly-L-lysine	Iodide	DL 0.017 µg/mL	[62]
Tosflex	Idoxuridine S <sup>2-</sup>	SPE modified with Tosflex/Fe(CN) <sub>6</sub> <sup>3-</sup> . Electrocatalytic detection. DL 8.9 nM	[186]
Cationic poly(allylamine hydrochloride) (PAH)	Pb(II)	Anionic complexes of Pb are detected DL 6 nM	[187]
Tosflex	2-Naphthol	DL 0.2 × 10 <sup>-7</sup> M	[188]
Poly(allylamine) + poly(acrylic acid)	PdCl <sub>4</sub> <sup>2-</sup>	Ion exchange loading of PdCl <sub>4</sub> <sup>2-</sup> for application as nanocatalyst	[189]

**Table 11.3** Clays, zeolites, and silica and organosilica modifiers

Exchanger	Analyte	Notes	Reference
Zeolite-Y	MV <sup>2+</sup>	Study of ion exchange/charge transfer mechanism	[190]
Zeolite-Y	Cl <sup>-</sup> , Br <sup>-</sup>	Ag-modified zeolite	[191]
Zeolite-Y + anionic surfactant	MV cation radical	Preconcentration by ion exchange, detection by double potential step chronocoulometry	[192]
Montmorillonite/cellulose acetate (NCA)	Cu(II)	NCA-modified GCE; preconcentration by IE. DL 1.73 ppb	[193]
Zeolite (nano)	Ag <sup>+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	GCE modified by nanoscale zeolites building blocks via layer-by-layer technology	[194]
Clays and organoclays	Cations or anions	Grafting of amine groups and protonating with HCl. It is not better than Nafion	[195]
Na-montmorillonite nanoparticles + anthraquinone	Cd(II), Pb(II)	Preconcentration by ion exchange, detection by DP-ASV DL 3-nM Cd <sup>2+</sup> ; 1-nM Pb <sup>2+</sup>	[196]
Clay	TPA, oxalate	Ru(bpy) <sub>3</sub> <sup>2+</sup> immobilized in clay multilayer films. Detection by ECL	[197]
Silica	Anions	Sol-gel preparation of quaternary amine functionalized silicon alkoxide	[198]
Polysiloxane-immobilized amine or thiol ligands	Hg(II)	Selective accumulation of anionic chloro-complexes of Hg(II). Speciation analysis	[199]
Porous silica sphere functionalized with ammonium quaternary groups	Anions	Silica microspheres obtained by the surfactant template route	[200]
Kaolinite/dimethylsulfoxide triethanolamine	CN <sup>-</sup>	GCE modified with triethanolamine grafted kaolinite. Electrochemical preconcentration of cyanide	[201]
Mesoporous silica functionalized	Cations or anions	CPE modified with solid ion exchanger	[202]
Nanomontmorillonite	Methyl jasmonate	DL 5 × 10 <sup>-7</sup> M	[203]
Clay + p-phenylene dimethylene bis-dodecyl N,N-dimethylammonium	Methyl parathion	DL 70 nM	[204]

## 11.5 Conclusion and Prospects

The functionalization of voltammetric electrodes by depositing on their surface thin films of ion exchangers has contributed significantly to develop a new class of tailored electrochemical sensors characterized by very high sensitivity and very low detection limit, both characteristics being improved dramatically with respect to conventional electrodes.

Ion exchange voltammetry at ionomer-coated electrodes has grown progressively up to reaching nowadays the rank of a widespread powerful electroanalytical technique. It is suitable for trace and ultratrace analyses and can be used as a valuable tool in speciation analysis for environmental studies and biomedicine. The ion-exchanger coating gives to the electrode high sensitivity and selectivity and protects it from surfactant and organic interferences. Further efforts should be devoted in the near future to continue improving the reproducibility and control of the coating deposition procedure and to shorten the analysis time. The application of molecular engineering procedures such as LB, electrostatic spray, layer-by-layer deposition, or other bottom-up approaches can play a crucial role in this issue.

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## References

1. Oyama N, Anson FC (1980) Electrostatic binding of metal complexes to electrode surfaces coated with highly charged polymeric films. *J Electrochem Soc* 127:247–250
2. Rubinstein I, Bard AJ (1980) Polymer films on electrodes. 4. Nafion-coated electrodes and electrogenerated chemiluminescence of surface-attached tris(2,2'-bipyridine)ruthenium(2+). *J Am Chem Soc* 102:6641–6642
3. Murray RW (1981) Modified electrodes. Chemically modified electrodes for electrocatalysis. *Philos Trans R Soc Lond A* 302:253–265
4. Murray RW (1984) Chemically modified electrodes. In: Bard AJ (ed) *Electroanalytical chemistry*, vol 13. Marcel Dekker, New York, pp 191–368
5. Espenscheid MW, Ghatak-Roy AR et al (1986) Sensors from polymer modified electrodes. *J Chem Soc Faraday Trans I* 82:1051–1070
6. Ugo P, Moretto LM (1995) Ion-exchange voltammetry at polymer modified electrodes: principles and analytical prospects. *Electroanalysis* 7:1105–1113
7. (a) Ugo P, Moretto LM, Vezzà F (2002) Ionomer-coated electrodes and nanoelectrode ensembles as electrochemical environmental sensors: recent advances and prospects. *Chem Phys Chem* 3:917–925; (b) Ugo P, Moretto LM, Vezzà F (2003) Ionomer-coated electrodes and nanoelectrode ensembles as electrochemical environmental sensors: recent advances and prospects. In: Baltes H, Fedder GK, Korvink JG (eds) *Sensors update*, vol 12. Wiley-VCH, Weinheim, pp 121–140
8. Zen JM, Kumar AS, Tsai DM (2003) Recent updates of chemically modified electrodes in analytical chemistry. *Electroanalysis* 15:1073–1087

9. Arrigan DWM (1994) Voltammetric determination of trace metals and organics after accumulation at modified electrodes. *Analyst* 119:1953–1966
10. Ulman A (1991) Ultrathin organic films. Academic, San Diego
11. Decher G (1997) Toward layered polymeric multicomposites. *Science* 277:1232–1237
12. Marquette CA, Bouteille F, Corgier BP et al (2009) Disposable screen-printed chemiluminescent biochips for the simultaneous determination of four point-of-care relevant proteins. *Anal Bioanal Chem* 393:1191–1198
13. Willner I, Katz E (eds) (2005) *Bioelectronics*. Wiley VCH, Weinheim
14. Thorp HH, Loomis CR, Napier ME (1999) Polymer-electrodes for detecting nucleic acid hybridization and method of use thereof. US Patent 5,968,745
15. Drummond TG, Hill MG, Barton JK (2003) Electrochemical DNA sensors. *Nat Biotechnol* 21:1192–1199
16. Dill K, Montgomery DD, Ghindilis AL et al (2004) Immunoassays and sequence-specific DNA detection on a microchip using enzyme amplified electrochemical detection. *J Biochem Biophys Methods* 59:181–187
17. Heller A, Feldman B (2010) Electrochemistry in diabetes management. *Acc Chem Res* 43:963–973
18. Svancara I, Vytras K, Kalcher K et al (2009) Carbon paste electrodes in facts, numbers, and notes: a review on the occasion of the 50-years jubilee of carbon paste in electrochemistry and electroanalysis. *Electroanalysis* 21:7–28
19. Bard AJ, Faulkner L (2000) *Electrochemical methods*, 2nd edn. Wiley, New York
20. Wang J (2000) *Analytical electrochemistry*, 2nd edn. VCH, Weinheim
21. Fatouros N, Simonin JP, Chevalet J et al (1986) Theory of multiple square wave voltammetry. *J Electroanal Chem* 213:1–16
22. Krulic D, Fatouros N, Chevalet J (1990) Multiple square wave voltammetry: experimental verification of the theory. *J Electroanal Chem* 287:215–227
23. Moretto LM, Ugo P, Lacasse R et al (1999) Determination of methylmercury at Nafion® coated electrodes by single and multiple pulse voltammetric techniques. *J Electroanal Chem* 467:193–202
24. Moretto LM, Chevalet J, Mazzocchin GA et al (2001) Advances in multiple square wave techniques for ion-exchange voltammetry at ultratrace levels: the europium(III) case. *J Electroanal Chem* 498:117–126
25. Brainina Kh, Neyman E (1993) *Electroanalytical stripping methods in chemical analysis*. Wiley, New York
26. Wang J (1989) Voltammetry following nonelectrolytic preconcentration. In: Bard AJ (ed) *Electroanalytical chemistry*, vol 16. Marcel Dekker, New York, pp 1–88
27. Buffle J (1988) *Complexation reactions in aquatic systems – an analytical approach*. Ellis Horwood, Chichester
28. Wojciechowski M, Go W, Osteryoung J (1985) Square-wave anodic stripping analysis in the presence of dissolved oxygen. *Anal Chem* 57:155–158
29. Colombo C, van den Berg C (1988) In-line deoxygenation for flow analysis with voltammetric detection. *Anal Chim Acta* 377:229–240
30. Mikkelsen Ø, Schröder KH (2000) Dental amalgam in voltammetry – some preliminary results. *Anal Lett* 33:3253–3269
31. Wang J, Lu J, Kirgoz UA et al (2001) Insights into the anodic stripping voltammetric behavior of bismuth film electrodes. *Anal Chim Acta* 434:29–34
32. Helfferich F (1962) *Ion-exchange*. McGraw-Hill, New York
33. Naegeli R, Redepenning J, Anson FC (1986) Influence of supporting electrolyte concentration and composition on formal potentials and entropies of redox couples incorporated in Nafion coatings on electrodes. *J Phys Chem* 90:6227–6232
34. Redepenning J, Anson FC (1987) Permselectivities of polyelectrolyte electrode coatings as inferred from measurements with incorporated redox probes or concentration cells. *J Phys Chem* 91:4549–4553

35. Ugo P, Anson FC (1989) Poly(2-vinylpyrazine) as a soluble polymeric ligand and as an electrode coating. Reactions with pentacyanoferrate(II). *Anal Chem* 61:1799–1805
36. Toniolo R, Comisso N, Bontempelli G et al (1994) Potential shifts at electrodes coated with ion-exchange polymeric films. *Talanta* 41:473–478
37. Ugo P, Moretto LM, De Boni A et al (2002) Iron(II) and iron(III) determination by potentiometry and ion-exchange voltammetry at ionomer-coated electrodes. *Anal Chim Acta* 474:147–160
38. Hillman AR (1987) Reactions and applications of polymer modified electrodes. In: Linford RG (ed) *Electrochemical science and technology of polymers*, vol 1. Elsevier Applied Science, London, Chap 5
39. Majda M (1992) Dynamics of electron transport in polymeric assemblies of redox centers. In: Murray R (ed) *Molecular design of electrode surfaces*. Wiley, New York, pp 159–206
40. Oyama N, Ohsaka T (1992) Voltammetric diagnosis of charge transport on polymer coated electrodes. In: Murray R (ed) *Molecular design of electrode surfaces*. Wiley, New York
41. Szentirmay MN, Martin CR (1984) Ion-exchange selectivity of Nafion films on electrode surfaces. *Anal Chem* 56:1898–1902
42. Ugo P, Ballarin B, Daniele S et al (1992) Electrochemical behaviour and preconcentration of uranyl(VI) at Nafion-coated glassy carbon electrodes. *J Electroanal Chem* 324:145–159
43. Kaufman FB, Engler EM (1979) Solid-state spectroelectrochemistry of crosslinked donor bound polymer films. *J Am Chem Soc* 101:547–549
44. Facci J, Murray RW (1981) Charge transport by electron exchange cross reaction in cyclic voltammetry of  $\text{IrCl}_6^{3-}$ - $\text{Fe}(\text{CN})_6^{3-}$  mixtures trapped in polycationic films on electrodes. *J Phys Chem* 85:2870–2873
45. Buttry DA, Anson FC (1983) Effects of electron exchange and single-file diffusion on charge propagation in Nafion films containing redox couples. *J Am Chem Soc* 105:685–689
46. Anson FC, Blauch DN, Saveant JM et al (1991) Ion association and electric field effects on electron hopping in redox polymers. Application to the tris(2,2'-bipyridine)osmium(3+)/tris(2,2'-bipyridine)osmium(2+) couple in Nafion. *J Am Chem Soc* 113:1922–1932
47. Dahms HI (1968) Electronic conduction in aqueous solution. *J Phys Chem* 72:362–364
48. Ruff I, Friedrich VJ (1971) Transfer diffusion. I. Theoretical. *J Phys Chem* 75:3297–3302
49. Whiteley LD, Martin CR (1989) Fresh look at transport in perfluorosulfonate ionomers: ultramicroelectrode investigations of Nafion and the Dow ionomers. *J Phys Chem* 93:4650–4658
50. Kuo K-N, Murray RW (1982) Electrocatalysis with ferrocyanide electrostatically trapped in an alkylaminesiloxane polymer film on a Pt electrode. *J Electroanal Chem* 131:37–60
51. Majda M, Faulkner LR (1984) Electrochemical behaviour of tris(2,2'-bipyridine)ruthenium complexes in films of poly(styrenesulfonate) on electrodes. *J Electroanal Chem* 169:77–95
52. Martin CR, Rubinstein I, Bard AJ (1982) Polymer films on electrodes. 9. Electron and mass transfer in Nafion films containing tris(2,2'-bipyridine)ruthenium(2+). *J Am Chem Soc* 104:4817–4824
53. Shi M, Anson FC (1997) Some consequences of the significantly different mobilities of hydrophilic and hydrophobic metal complexes in perfluorosulfonated ionomer coatings on electrodes. *Anal Chem* 69:2653–2660
54. Daniele S, Ugo P, Bragato C et al (1996) Use of Nafion® coated carbon disk microelectrodes in solution without and with different concentrations of supporting electrolyte. *J Electroanal Chem* 418:29–34
55. Amatore C, Sella C, Thouin L (2003) Effects of chemical environment on diffusivities within thin Nafion® films as monitored from chronoamperometric responses of generator–collector double microband assemblies. *J Electroanal Chem* 547:151–161
56. Kroschwitz JI (1990) *Concise encyclopedia of polymer science and engineering*. Wiley, New York
57. Yeo RS, Yeager HL (1985) Structural and transport properties of perfluorinated ion-exchange membranes. In: Conway BE, White RE, Bockris JO'M (eds) *Modern aspects of electrochemistry*, vol 16. Plenum, New York, pp 437–504



58. Zook LA, Leddy J (1996) Density and solubility of Nafion: recast, annealed, and commercial films. *Anal Chem* 68:3793–3796
59. Chen T-Y, Leddy J (2000) Ion exchange capacity of Nafion and Nafion composites. *Langmuir* 16:2866–2871
60. Oberbroeckling KJ, Dunwoody DC, Minter SD et al (2002) Density of Nafion exchanged with transition metal complexes and tetramethyl ammonium, ferrous, and hydrogen ions: commercial and recast films. *Anal Chem* 74:4794–4799
61. Pereira FC, Fogg AG, Ugo P et al (2005) Determination of iodide and idoxuridine at a glutaraldehyde-cross-linked poly-L-lysine modified glassy carbon electrode. *Electroanalysis* 17:1309–1316
62. Anson FC, Saveant JM, Shigehara K (1983) New model for the interior of polyelectrolyte coatings on electrode surfaces. Mechanisms of charge transport through protonated poly (L-lysine) films containing  $\text{FeIII}(\text{edta})^-$  and  $\text{FeII}(\text{edta})^{2-}$  as counter ions. *J Am Chem Soc* 105:1096–1106
63. Walcarius A (2008) Electroanalytical applications of microporous zeolites and mesoporous (organo)silicas: recent trends. *Electroanalysis* 20:711–738
64. Walcarius A (2001) Electroanalysis with pure, chemically modified and sol-gel-derived silica-based materials. *Electroanalysis* 13:701–718
65. Buttry DA, Anson FC (1981) Electron hopping vs. molecular diffusion as charge transfer mechanism in redox polymer films. *J Electroanal Chem* 130:333–338
66. Ugo P, Moretto LM, Mazzocchin GA (1993) Voltammetric determination of trace mercury in chloride media at glassy carbon electrodes modified with polycationic ionomers. *Anal Chim Acta* 273:229–236
67. Dunsch L, Kavan L, Weber J (1990) Perfluoro anion-exchange polymeric films on glassy carbon electrodes. *J Electroanal Chem* 280:313–325
68. Kaufman FB, Schroeder AH, Engler EM et al (1980) Ion and electron transport in stable, electroactive tetrathiafulvalene polymer coated electrodes. *J Am Chem Soc* 102:483–488
69. Schroeder AH, Kaufman FB (1980) The influence of polymer morphology on polymer film electrochemistry. *J Electroanal Chem* 113:209–224
70. Gennett T, Purdy WC (1990) Voltammetric determination of the ion-exchange behaviour of AQ polymers [poly(ester sulfonic acid) anionomers] in acetonitrile. *Anal Chem* 62:2155–2158
71. Brunetti B, Ugo P (1999) Factors influencing the ion-exchange preconcentration and voltammetric behaviour of redox cations at polyestersulfonated ionomer coated electrodes in acetonitrile solutions. *J Electroanal Chem* 460:38–45
72. Weber J, Janda P, Kavan L et al (1986) Study of Nafion film on electrodes prepared from dimethylacetamide solution. *J Electroanal Chem* 200:379–381
73. Moore RB III, Martin CR (1988) Chemical and morphological properties of solution-cast perfluorosulfonate ionomers. *Macromolecules* 21:1334–1339
74. Goebel G, Aldebert P, Pineri M (1987) Structure and related properties of solution-cast perfluorosulfonated ionomer films. *Macromolecules* 20:1425–1428
75. Hoyer B, Jensen N (1994) Signal stability of Nafion-coated thin mercury film electrodes for stripping voltammetry. *Talanta* 41:449–453
76. Stribel KA, Scherer GG, Haas O (1991) Effect of curing-humidity on recast-Nafion films. *J Electroanal Chem* 304:289–296
77. Shi M, Anson FC (1996) Effects of hydration on the resistances and electrochemical responses of nafion coatings on electrodes. *J Electroanal Chem* 415:41–46
78. Shimazu K, Kita H, Kuwana T (1989) RF-plasma treatment of Nafion film electrodes. *J Electroanal Chem* 258:49–59
79. Nishide H, Deguchi J, Tsuchida E (1977) Adsorption of metal ions on cross-linked poly (4-vinylpyridine) resins prepared with a metal ion as template. *J Polym Sci* 15:3023–3029
80. Lindholm B, Sharp M (1986) Simple preparation and characteristics of stabilized, protonated poly-4-vinylpyridine films containing electroactive anions on glassy carbon electrode surfaces. *J Electroanal Chem* 198:37–52

81. Oyama N, Shimomura T, Shigehara K et al (1980) Electrochemical responses of multiply-charged transition metal complexes bound electrostatically to graphite electrode surfaces coated with polyelectrolytes. *J Electroanal Chem* 112:271–280
82. De Castro ES, Huber EW, Villaroel D et al (1987) Electrodes with polymer network films formed by  $\gamma$ -irradiation cross-linking. *Anal Chem* 59:134–139
83. Denisevich P, Abruna HD, Leidner CR et al (1982) Electropolymerization of vinylpyridine and vinylbipyridine complexes of iron and ruthenium: homopolymers, copolymers, reactive polymers. *Inorg Chem* 21:2153–2161
84. Kaner RB (1990) Preparations and properties of electrochemically synthesized polymers. In: Linford RG (ed) *Electrochemical science and technology of polymers*, vol 2. Elsevier, London, pp 97–148
85. Ugo P, Sporni L, Moretto LM (1997) Ion-exchange voltammetry of trace mercury(II) at glassy carbon electrodes coated with a cationic polypyrrole derivative. Application to porewaters analysis. *Electroanalysis* 9:1153–1158
86. Mao H, Pickup PG (1989) Electronically conductive anion exchange polymers based on polypyrrole. Preparation, characterization, electrostatic binding of ferrocyanide and electrocatalysis of ascorbic acid oxidation. *J Electroanal Chem* 265:127–142
87. Pickup PG (1987) Poly-(3-methylpyrrole-4-carboxylic acid): an electronically conducting ion-exchange polymer. *J Electroanal Chem* 225:273–280
88. Basak S, Rajeshwar K, Kaneko M (1990) Ion binding by poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} thin films. *Anal Chem* 62:1407–1413
89. Cosnier S, Deronzier A, Moutet J-C et al (1989) Alkylammonium and pyridinium group-containing polypyrroles, a new class of electronically conducting anion-exchange polymers. *J Electroanal Chem* 271:69–81
90. Guadalupe AR, Abruna HD (1985) Electroanalysis with chemically modified electrodes. *Anal Chem* 57:142–149
91. Degani Y, Heller A (1989) Electrical communication between redox centres of glucose oxidase and electrodes via electrostatically and covalently bound redox polymers. *J Am Chem Soc* 111:2357–2358
92. Heller A, Feldman B (2008) Electrochemical glucose sensors and their applications in diabetes management. *Chem Rev* 108:2482–2505
93. Hoyer B, Jensen N, Busch LP (2001) Effect of the pretreatment of recast Nafion membranes on their rejection of the albumin interference in anodic stripping voltammetry. *Electroanalysis* 13:843–848
94. Wilner I, Katz E (2000) Integration of layered redox proteins and conductive supports for bioelectronic applications. *Angew Chem Int Ed* 39:1180–1218
95. Mano N, Kuhn A (2002) Affinity assembled multilayers for new dehydrogenase biosensors. *Bioelectrochemistry* 56:123–126
96. Mano N, Kuhn A (2001) Electrodes modified with nitrofluorenone derivatives as a basis for new biosensors. *Biosens Bioelectron* 16:653–660
97. Anicet N, Bourdillon C, Moiroux J et al (1998) Simple electrochemical procedure for measuring the rates of electron transfer across liquid/liquid interfaces formed by coating graphite electrodes with thin layers of nitrobenzene. *J Phys Chem B* 102:9845–9854
98. Hodak J, Etchenique R, Calvo EJ et al (1997) Layer-by-layer self-assembly of glucose oxidase with a poly(allylamine)ferrocene redox mediator. *Langmuir* 13:2708–2716
99. Ma H, Hu N, Rusling J (2000) Electroactive myoglobin films grown layer-by-layer with poly(styrenesulfonate) on pyrolytic graphite electrodes. *Langmuir* 16:4969–4975
100. Lojou E, Bianco P (2003) Quartz crystal microbalance and voltammetry monitoring for layer-by-layer assembly of cytochrome  $c_3$  and poly(ester sulfonic acid) films on gold and silver electrodes. *J Electroanal Chem* 557:37–47
101. Lojou E, Bianco P (2004) Buildup of polyelectrolyte–protein multilayer assemblies on gold electrodes. Role of the hydrophobic effect. *Langmuir* 20:748–755
102. Galeska I, Chattopadhyay D, Moussy F et al (2000) Calcification-resistant Nafion/ $\text{Fe}^{3+}$  assemblies for implantable biosensors. *Biomacromolecules* 1:202–207

103. Harris JJ, Stair JL, Bruening ML (2000) Layered polyelectrolyte films as selective, ultrathin barriers for anion transport. *Chem Mater* 12:1941–1946
104. Calvo EJ, Wolosiuk A (2002) Donnan permselectivity in layer-by-layer self-assembled redox polyelectrolyte thin films. *J Am Chem Soc* 124:8490–8497
105. De Longchamp DM, Hammond PT (2003) Fast ion conduction in layer-by-layer polymer films. *Chem Mater* 15:1165–1173
106. Bertoncello P, Ram MK, Notargiacomo A et al (2002) Fabrication and physico-chemical properties of Nafion Langmuir-Schaefer films. *Phys Chem Chem Phys* 4:4036–4043
107. Bertoncello P, Ugo P (2003) Preparation and voltammetric characterization of electrodes coated with Langmuir-Schaefer ultrathin films of Nafion®. *J Braz Chem Soc* 14:517–522
108. Moretto LM, Kohls T, Chauvin A et al (2008) Epifluorescence imaging of electrochemically switchable Langmuir-Blodgett films of Nafion. *Langmuir* 24:6367–6374
109. Moretto LM, Kohls T, Badocco D et al (2010) Electrochemiluminescence of Ru(bpy)<sub>2</sub><sup>3+</sup> loaded in Nafion Langmuir-Blodgett films: role of the interfacial ultrathin film. *J Electroanal Chem* 640:35–41
110. Bertoncello P, Dennany L (2007) Nafion-tris(2-2'-bipyridyl)ruthenium(II) ultrathin Langmuir-Schaefer films: redox catalysis and electrochemiluminescent properties. *Anal Chem* 79:7549–7553
111. Wring SA, Hart JP (1992) Chemically modified, carbon-based electrodes and their application as electrochemical sensors for the analysis of biologically important compounds. A review. *Analyst* 117:1215–1229
112. Ugo P, Moretto LM, Bertoncello P et al (1998) Determination of trace mercury in saltwaters at screen-printed electrodes modified with Sumichelate Q10R. *Electroanalysis* 10:1017–1021
113. Zumbrennen HR, Anson FC (1983) Electrostatic binding of anions and cations to graphite electrodes coated with a polyelectrolyte containing both positive and negative fixed charges. *J Electroanal Chem* 152:111–124
114. Espenscheid MW, Martin CR (1985) Electroactive ion exchange polymers. *J Electroanal Chem* 188:73–84
115. Buyukserin F, Kohli P, Wirtz MC et al (2007) Electroactive nanotube membranes and redox-gating. *Small* 3:266–270
116. Fan FF, Bard AJ (1986) Polymer films on electrodes. *J Electrochem Soc* 133:301–304
117. Penner RM, Martin CR (1986) Electronically conductive composite polymer membranes. *J Electrochem Soc* 133:310–315
118. Nagasubramanian G, Di Stefano S, Moacanin J (1986) Electrochemical incorporation of poly(pyrrole) into Nafion and comparison of the electrochemical properties of Nafion-poly(pyrrole) and poly(pyrrole) films. *J Phys Chem* 90:4447–4451
119. Orata D, Buttry DA (1988) Virtues of composite structures in electrode modification. Preparation and properties of poly(aniline)/Nafion composite films. *J Electroanal Chem* 257:71–82
120. Hirai T, Kuwabata S, Yonegani H (1988) Electrochemical behaviours of polypyrrole, poly-3-methylthiophene, and polyaniline deposited on Nafion-coated electrodes. *J Electrochem Soc* 135:1132–1137
121. Shimidzu T, Ohtani A, Iyoda T et al (1987) Charge-controllable polypyrrole/polyelectrolyte composite membranes. Part II. Effect of incorporated anion size on the electrochemical oxidation-reduction process. *J Electroanal Chem* 224:123–135
122. Shimidzu T, Ohtani A, Iyoda T et al (1988) Charge-controllable polypyrrole/polyelectrolyte composite membranes. Part III. Electrochemical deionization system constructed by anion-exchangeable and cation-exchangeable polypyrrole electrodes. *J Electroanal Chem* 251:323–337
123. Zhou QX, Miller LL, Valentine JR (1989) Electrochemically controlled binding and release of protonated dimethyldopamine and other cations from poly(N-methyl-pyrrole)/polyanion composite redox polymers. *J Electroanal Chem* 261:147–164
124. Elliot CM, Kopelove AB, Alberty WJ et al (1991) Nonaqueous electrochemistry of polypyrrole/polystyrenesulfonate composite films: voltammetric, coulometric, EPR, and a.c. impedance studies. *J Phys Chem* 95:1743–1747

125. Wang J, Sun Z, Lu Z (1991) Electrochemical behaviour of polypyrrole/Kodak AQ composite polymeric films. *J Electroanal Chem* 310:269–279
126. Gbatu TP, Ceylan O, Sutton KL et al (1999) Electrochemical control of solid phase micro-extraction using unique conducting polymer coated fibers. *Anal Commun* 36:203–205
127. Wu J, Yu X, Lord H et al (2000) Solid phase microextraction of inorganic anions based on polypyrrole film. *Analyst* 125:391–394
128. Wu J, Pawliszyn J (2001) Preparation and applications of polypyrrole films in solid-phase microextraction. *J Chromatogr A* 909:37–52
129. Liljgren G, Petterson J, Markides KE et al (2002) Electrochemical solid-phase microextraction of anions and cations using polypyrrole coatings and an integrated three-electrode device. *Analyst* 127:591–597
130. Deinhammer RS, Porter MD, Shimazu K (1995) Retention characteristics of polypyrrole as a stationary phase for the electrochemically modulated liquid chromatographic (EMLC) separations of dansyl amino acids. *J Electroanal Chem* 387:35–46
131. Scopece P, Moretto LM, Polizzi S et al (2006) Composite films of poly-(ester-sulphonated) and poly-(3-methylthiophene) for ion-exchange voltammetry in acetonitrile solutions. *Electrochim Acta* 51:2153–2160
132. Hanzlik J, Ugo P, Daniele S et al (1996) Ion-exchange voltammetry of tris(2,2'-bipyridyl) ruthenium(II), iron(II), osmium(II) and tris(2,2'-bipyrazyl) ruthenium(II) in acetonitrile solutions at poly(ester-sulphonate) coated electrodes. *J Electroanal Chem* 404:89–97
133. Wang J, Tuzhi P (1986) Selectivity and sensitivity improvements at perfluorinated ionomer/cellulose acetate bilayer electrodes. *Anal Chem* 58:3257–3261
134. Wang J, Tuzhi P, Golden T (1987) Amperometric detection of cationic neurotransmitters at Nafion-coated glassy carbon electrodes in flow streams. *Anal Chim Acta* 194:129–138
135. Brazell MP, Kasser RJ, Renner KJ et al (1987) Electrocoating carbon fiber microelectrodes with Nafion improves selectivity for electroactive neurotransmitters. *J Neurosci Methods* 22:167–172
136. Kristensen EW, Kuhr WG, Wightman RM (1987) Temporal characterization of perfluorinated ion exchange coated microvoltammetric electrodes for in vivo use. *Anal Chem* 59:1752–1757
137. Crespi F, Martin KF, Marsden CA (1988) Measurement of extracellular basal levels of serotonin in vivo using Nafion-coated carbon fibre electrodes combined with differential pulse voltammetry. *Neuroscience* 27:885–896
138. Ugo P, Ballarin B, Daniele S et al (1991) Determination of trace amounts of  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  ions at Nafion-coated thin mercury film electrodes. *Anal Chim Acta* 244:29–38
139. Ugo P, Ballarin B, Daniele S et al (1990) Electrochemistry of  $\text{Yb}^{3+}$  and  $\text{Eu}^{3+}$  at Nafion modified electrodes. *J Electroanal Chem* 291:187–199
140. Zhou J, Wang E (1991) Ion exchange of cationic drugs at a Nafion-coated electrode in flow-through analysis. *Anal Chim Acta* 249:489–494
141. Gorski W, Cox JA (1992) Stripping voltammetry with preconcentration through chemical reactions coupled to charge transfer in an ionomer-coated electrode: application to the determination of a nitrosoamine. *Anal Chem* 64:2706–2710
142. Boyd D, Barreira Rodriguez JR, Miranda Ordieres AJ et al (1994) Voltammetric study of salbutamol, fenoterol and metaproterenol at unmodified and Nafion-modified carbon paste electrodes. *Analyst* 119:1979–1984
143. Zen J-M, Ting Y-S (1996) Square-wave voltammetric stripping analysis of lead(II) at a Nafion®/copper-mercury film electrode. *Anal Chim Acta* 332:59–65
144. Hu Z, Seliskar CJ, Heineman WR (1998) PAN-incorporated Nafion-modified spectroscopic graphite electrodes for voltammetric stripping determination of lead. *Anal Chim Acta* 369:93–101
145. Brett CMA, Fungaro DA, Morgado JM et al (1999) Novel polymer-modified electrodes for batch injection sensors and application to environmental analysis. *J Electroanal Chem* 468:26–33
146. Lu T-H, Yang H-Y, Sun I-W (1999) Square-wave anodic stripping voltammetric determination of thallium(I) at a Nafion/mercury film modified electrode. *Talanta* 49:59–68

147. Zen J-M, Jou J-J, Kumar AS (1999) A sensitive voltammetric method for the determination of parathion insecticide. *Anal Chim Acta* 396:39–44
148. Yang H-Y, Sun I-W (2000) Cathodic stripping voltammetric determination of selenium(IV) at a Nafion coated mercury film electrode modified with 3,3'-diaminobenzidine. *Electroanalysis* 12:1476–1480
149. Brett CMA, Fungaro DA (2000) Poly(ester sulphonic acid) coated mercury thin film electrodes: characterization and application in batch injection analysis stripping voltammetry of heavy metal ions. *Talanta* 50:1223–1231
150. Cheng HL, Sun IW (2001) Square-wave voltammetric detection of apomorphine on a Nafion film modified glassy carbon electrode. *Electroanalysis* 13:1544–1546
151. Yi H, Wu K, Hu S et al (2001) Adsorption stripping voltammetry of phenol at Nafion-modified glassy carbon electrode in the presence of surfactants. *Talanta* 55:1205–1210
152. Collyer SD, Bradbury SE, Hatfield JV et al (2001) A study of factors affecting the enhanced voltammetric stripping analysis of N-nitrosamines at sulfopolyester modified electrodes. *Electroanalysis* 13:332–337
153. Ugo P, Zangrando V, Moretto LM et al (2002) Ion-exchange voltammetry and electrocatalytic sensing capabilities of cytochrome *c* at polyestersulfonated ionomer coated glassy carbon electrodes. *Biosens Bioelectron* 17:479–487
154. Wang HY, Xu GB, Dong SJ (2003) Electrochemiluminescence sensor using tris(2,2'-bipyridyl)ruthenium(II) immobilized in Eastman-AQ55D-silica composite thin-films. *Anal Chim Acta* 480:285–290
155. Xu Q, Xu C, Wang Q et al (2003) Application of a single electrode, modified with polydiphenylamine and dodecyl sulfate, for the simultaneous amperometric determination of electro-inactive anions and cations in ion chromatography. *J Chromatogr A* 997:65–71
156. Rodríguez Gutiérrez JA, Petit Domínguez MD, Pinilla Macías JM (2004) Development of ionoselective electrochemical sensors by using the sol-gel process. *Anal Chim Acta* 524:339–346
157. Monterroso SCC, Carapuça HM, Duarte AC (2005) Ion-exchange and permselectivity properties of poly(sodium 4-styrenesulfonate) coatings on glassy carbon: application in the modification of mercury film electrodes for the direct voltammetric analysis of trace metals in estuarine waters. *Talanta* 65:644–653
158. Moretto LM, Bertoncello P, Vezzà P et al (2005) Electrochemistry of cytochrome *c* incorporated in Langmuir-Blodgett films of Nafion and Eastman AQ 55. *Bioelectrochemistry* 66:29–34
159. Buriez O, Moretto LM, Ugo P (2006) Ion-exchange voltammetry of tris-(2,2'-bipyridine) nickel(II), cobalt(II), and Co(salen) at polyestersulfonated ionomer coated electrodes in acetonitrile: reactivity of the electrogenerated low-valent complexes. *Electrochim Acta* 52:958–964
160. Monterroso SCC, Carapuça HM, Duarte AC (2006) Mixed polyelectrolyte coatings on glassy carbon electrodes: ion-exchange, permselectivity properties and analytical application of poly-L-lysine-poly(sodium 4-styrenesulfonate)-coated mercury film electrodes for the detection of trace metals. *Talanta* 68:1655–1662
161. Riccardi CD, Yamanaka H, Josowicz M et al (2006) Label-free DNA detection based on modified conducting polypyrrole films at microelectrodes. *Anal Chem* 78:1139–1145
162. Lin YH, Cui XL (2006) Electrosynthesis, characterization, and application of novel hybrid materials based on carbon nanotube-polyaniline-nickel hexacyanoferrate nanocomposites. *J Mater Chem* 16:585–592
163. Bertoncello P, Dennany L, Forster RJ et al (2007) Nafion-Tris(2-2'-bipyridyl)ruthenium(II) Ultrathin Langmuir-Schaefer films: redox catalysis and electrochemiluminescent properties. *Anal Chem* 79:7549–7553
164. Huang M, Jiang H, Zhai J et al (2007) A simple route to incorporate redox mediator into carbon nanotubes/Nafion composite film and its application to determine NADH at low potential. *Talanta* 74:132–139

165. Zhang LB, Li J, Xu YH et al (2009) Solid-state electrochemiluminescence sensor based on the Nafion/poly(sodium 4-styrene sulfonate) composite film. *Talanta* 79:454–459
166. Silva CP, Carapuça HM, Rocha LS et al (2009) Evaluation of poly(sodium 4-styrenesulfonate) film coating in thin mercury film electrodes for lead determination. *J Electroanal Chem* 626:192–196
167. Çelebi MS, Özyörük H, Yıldız A et al (2009) Determination of  $\text{Hg}^{2+}$  on poly(vinylferrocenium) (PVF<sup>+</sup>)-modified platinum electrode. *Talanta* 78:405–409
168. Yuan Y, Yuan X, Chai Y et al (2010) A novel label-free electrochemical aptasensor for thrombin based on the {nano-Au/thionine}<sub>n</sub> multilayer films as redox probes. *Anal Chim Acta* 668:171–176
169. Xub H, Chenc J, Shia G, Jina L (2010) Nafion stabilized silver nanoparticles modified electrode and its application to Cr(VI) detection. *J Electroanal Chem* 652:60–65
170. Zhou C, Liu Z, Dai J et al (2010) Electrospun Ru(bpy)<sub>3</sub><sup>2+</sup>-doped Nafion nanofibers for electrochemiluminescence sensing. *Analyst* 135:1004–1009
171. Taffa DH, Kathiresan M, Walder L et al (2010) Pore size and surface charge control in mesoporous TiO<sub>2</sub> using post-grafted SAMs. *Phys Chem Chem Phys* 12:1473–1482
172. Azad UP, Ganesan V (2010) Efficient sensing of nitrite by Fe(bpy)<sub>3</sub><sup>2+</sup> immobilized Nafion modified electrodes. *Chem Commun* 46:6156–6158
173. Cox JA, Kulesza PJ (1983) Stripping voltammetry of chromium(VI) at a poly(4-vinylpyridine)-coated platinum electrode. *Anal Chim Acta* 154:71–78
174. Cassidy JF, Tokuda K (1990) Preconcentration and voltammetric determination of copper ions in aqueous chloride solutions at a cross-linked poly(4-vinylpyridine)-coated electrode. *J Electroanal Chem* 285:287–294
175. Ugo P, Moretto LM, Mazzocchin GA (1995) Voltammetric determination of trace mercury in chloride media at glassy carbon electrodes modified with polycationic ionomers. *Anal Chim Acta* 305:74–82
176. Zen J-M, Chung M-J (1996) Square-wave voltammetric stripping analysis of bismuth(III) at a poly(4-vinylpyridine)/mercury film electrode. *Anal Chim Acta* 320:43–51
177. Moretto LM, Mazzocchin GA, Ugo P (1997) Electrochemical study on the ion-exchange voltammetric behaviour of Hg(II) at Tosflex<sup>®</sup>-coated glassy carbon electrode. *J Electroanal Chem* 427:113–121
178. Lu T-H, Sun I-W (1998) Anodic stripping voltammetric determination of thallium(III) using a Tosflex/mercury film electrode. *Electroanalysis* 10:1052–1056
179. Zen J-M, Chung H-G, Ilagovan G (1999) Selective voltammetric determination of lead(II) on partially quaternized poly(4-vinylpyridine)/mercury film electrodes. *Electroanalysis* 11:108–113
180. Yang H-Y, Chen W-Y, Sun I-W (1999) Anodic stripping voltammetric determination of bismuth(III) using a Tosflex-coated mercury film electrode. *Talanta* 50:977–984
181. Maizels M, Heineman WR, Seliskar CJ (2000) Graphite electrodes coated with poly(dimethyldiallylammonium)chloride network films cross-linked by gamma-irradiation. *Electroanalysis* 12:241–247
182. Lu T-H, Huang J-F, Sun I-W (2001) Perfluorinated anion-exchange polymer mercury film electrode for anodic stripping voltammetric determination of zinc(II): effect of model organic compounds. *Anal Chim Acta* 454:93–100
183. Cheng H-L, Kuei C-H, Sun I-W (2002) Electrochemical detection of O, O-diethylthiophosphoric acid at a Tosflex film modified glassy carbon electrode. *Electroanalysis* 14:767–772
184. Prasad BB, Arora B (2003) Application of polymer-modified hanging mercury drop electrode in the indirect determination of certain  $\beta$ -lactam antibiotics by differential pulse, ion-exchange voltammetry. *Electroanalysis* 15:1212–1218
185. Rodríguez Gutiérrez JA, Petit Domínguez MD, Pinilla Macías JM (2004) Development of ionoselective electrochemical sensors by using the sol-gel process. *Anal Chim Acta* 524:339–346



186. Tsai DM, Kumar AS, Zen JM (2006) A highly stable and sensitive chemically modified screen-printed electrode for sulfide analysis. *Anal Chim Acta* 556:145–150
187. Silva CP, Carapuça HM (2006) Glassy carbon electrodes coated with poly(allylamine hydrochloride), PAH: characterization studies and application to ion-exchange voltammetry of trace lead(II) at combined PAH/mercury film electrodes. *Electrochim Acta* 52:1182–1190
188. Tsai M-C, Chen P-Y (2007) Electrochemical detection of 2-naphthol at a glassy carbon electrode modified with Tosflex film. *Electroanalysis* 19:1315–1321
189. Vago M, Tagliazucchi M, Williams FJ et al (2008) Electrodeposition of a palladium nanocatalyst by ion confinement in polyelectrolyte multilayers. *Chem Commun* 5746–5748
190. Hui T-W, Baker MD (2001) Ion exchange and electron transport at methyl viologen Y modified electrodes. *J Phys Chem B* 105:3204–3210
191. Li Y-J, Liu C-Y (2001) Silver-exchanged zeolite Y-modified electrodes: size selectivity for anions. *J Electroanal Chem* 517:117–120
192. Hui T-W, Baker MD (2002) Redox processes of methyl viologen cation radicals at zeolite Y-modified electrodes. *J Phys Chem B* 106:827–832
193. Zen JM, Wang HF, Kumar AS et al (2002) Preconcentration and electroanalysis of copper(II) in ammoniacal medium on nontronite/cellulose acetate modified electrodes. *Electroanalysis* 14:99–105
194. Zhang Y, Chen F, Shan W et al (2003) Fabrication of ultrathin nanozeolite film modified electrodes and their electrochemical behavior. *Micropor Mesopor Mat* 65:277–285
195. Tonle IK, Ngameni E, Walcarius A (2004) From clay – to organoclay-film modified electrodes: tuning charge selectivity in ion exchange voltammetry. *Electrochim Acta* 49:3435–3443
196. Yuan S, Chen W, Hu S (2004) Simultaneous determination of cadmium (II) and lead (II) with clay nanoparticles and anthraquinone complexly modified glassy carbon electrode. *Talanta* 64:922–928
197. Guo Z, Shen Y, Zhao F et al (2004) Electrochemical and electrogenerated chemiluminescence of clay nanoparticles/Ru(bpy)<sub>3</sub><sup>2+</sup> multilayer films on ITO electrodes. *Analyst* 129:657–663
198. Lin C-L, Tien P, Chau L-K (2004) Electrochemical behavior of an anion-exchanger modified electrode prepared by sol-gel processing of an organofunctional silicon alkoxide. *Electrochim Acta* 49:573–580
199. Walcarius A, Etienne M, Delacote C (2004) Uptake of inorganic Hg<sup>II</sup> by organically modified silicates: influence of pH and chloride concentration on the binding pathways and electrochemical monitoring of the processes. *Anal Chim Acta* 508:87–98
200. Walcarius A, Ganesan V (2006) Ion-exchange properties and electrochemical characterization of quaternary ammonium-functionalized silica microspheres obtained by the surfactant template route. *Langmuir* 22:469–477
201. Letaief S, Tonle IK, Diaco T et al (2008) Nanohybrid materials from interlayer functionalization of kaolinite. Application to the electrochemical preconcentration of cyanide. *Appl Clay Sci* 42:95–101
202. Ganesan V, Walcarius A (2008) Ion exchange and ion exchange voltammetry with functionalized mesoporous silica materials. *Mat Sci Eng B* 149:123–132
203. Gan T, Hu C, Chen Z et al (2010) Direct electrochemical determination of methyl jasmonate in wheat spikelet at a nano-montmorillonite film modified electrode by derivative square wave voltammetry. *J Agric Food Chem* 58:8942–8947
204. Tcheumi HL, Tonle IK, Ngameni E et al (2010) Electrochemical analysis of methylparathion pesticide by a gemini surfactant-intercalated clay-modified electrode. *Talanta* 81:972–979