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# Ion Exchange Technology I

Theory and Materials

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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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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.

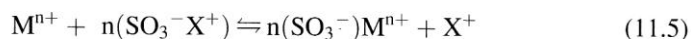
In order to widen the application field of electroanalytical methods, it is important to develop novel electrode systems characterized by high sensitivity, good reproducibility, wide usable potential window, and low cost and made of nontoxic materials. Moreover, they should be characterized by intrinsic 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  $K_X^M$ :

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

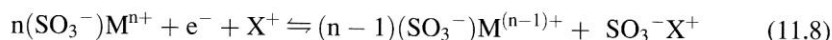
where subscripts p and s indicate concentrations in the polymer and solution phases, respectively, and square bracket indicates molar concentrations. With proper adaptations, ionic equivalent fractions can be used instead of molar concentrations. In some cases, a corrected selectivity coefficient is 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

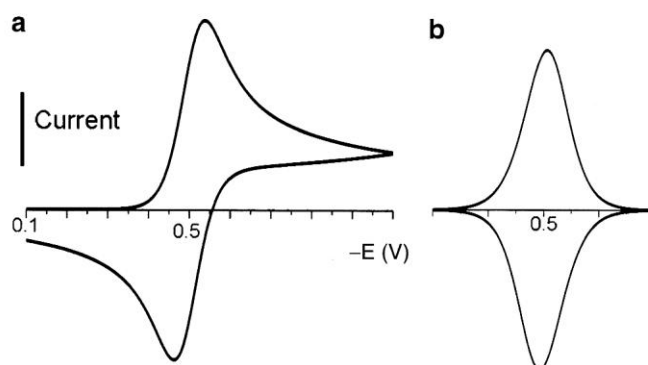
Many research papers have been devoted to study the mechanisms which rule mass and charge transport phenomena in polymeric matrices (see Ref. [38–40] for reviews). Depending on the experimental conditions involved (mainly, type of polymer, redox properties, and concentration of the ion-exchanged analyte), 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

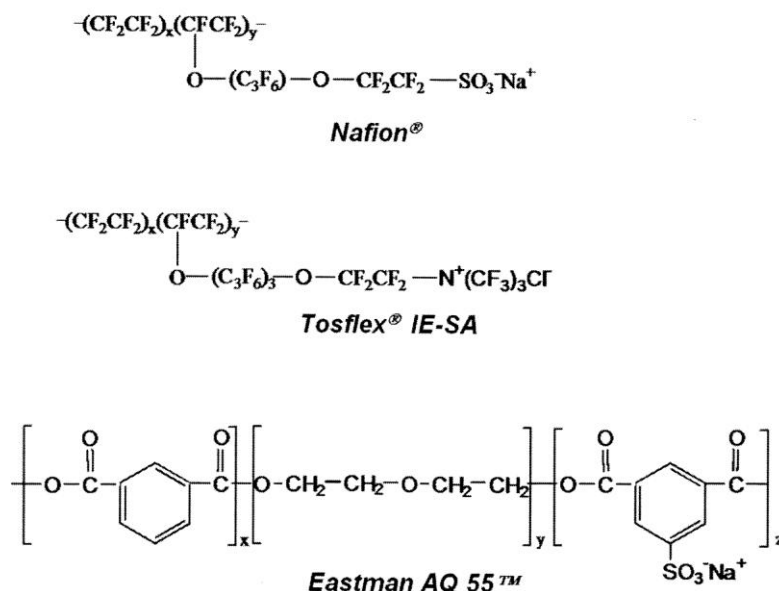
#### 11.3.1 Ion Exchangers and Coatings

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>™</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].

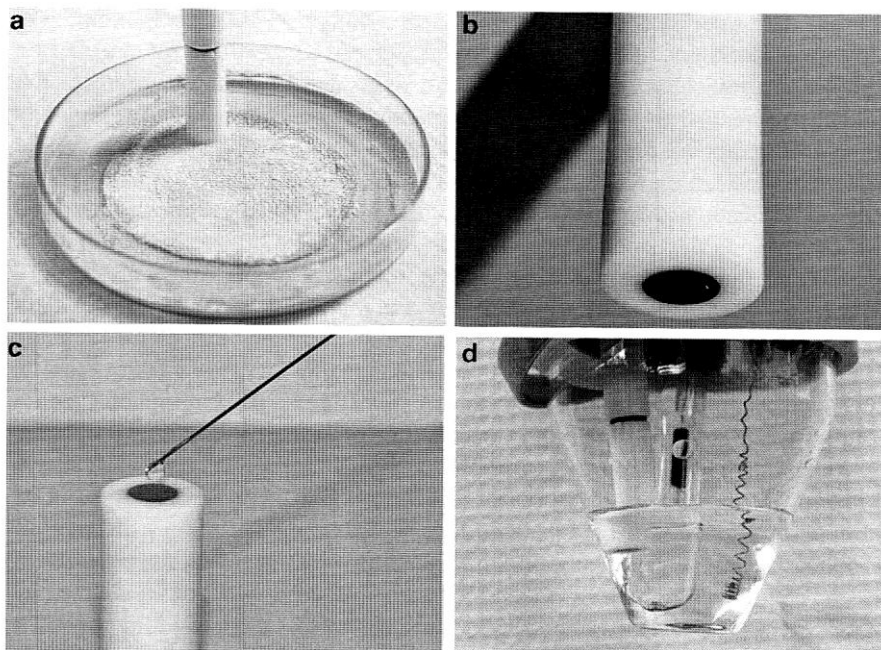
These ionic groups interact or associate to form ion-rich hydrophilic regions surrounded by hydrophobic domains [57], such a clustering being the basis of the high stability of ionomer films.

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.

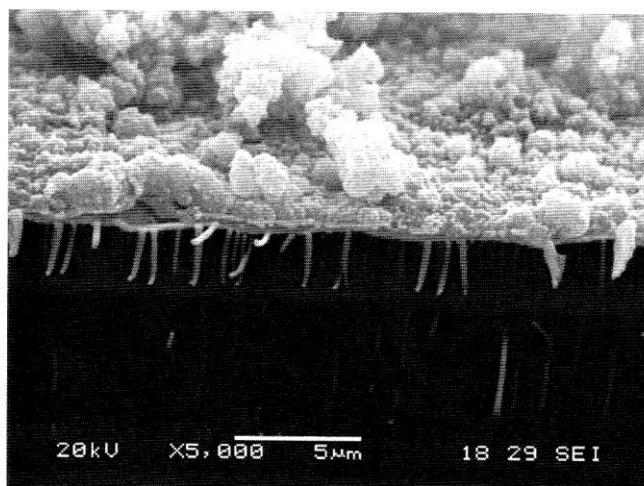
A similar approach, in which the ion exchange characteristics were modulated by electrochemical switching, implied terpolymers based on styrene (backbone), styrene sulfonate (unswitchable cation exchanger), and vinylferrocene (electrochemically switchable from neutral to anion exchanger) [114]. When 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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