

Strategies, Development and Applications of Polymer-Modified Electrodes for Stripping Analysis

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Abstract: Recent progress in polymer modified electrodes for stripping analysis is surveyed, mainly concerned with ion-exchange polymer and conducting polymer coatings on mercury thin film electrodes and other solid electrode substrates. Film preparation methods are discussed and applications involving different types of polymer film or polymer film composites illustrated, with emphasis on recent literature published in the last five years.

Keywords: Polymer coatings, Ion-exchange polymers, Conducting polymers, Stripping voltammetry.

1. INTRODUCTION

Electroanalytical techniques have been shown to be extremely powerful for measuring trace species, particularly using the pre-concentration technique of anodic stripping voltammetry due to its inherent sensitivity and the relatively compact and low cost of the instrumentation needed. In many cases there is no necessity for sample pre-treatment or digestion, which is a great advantage compared to other techniques such as atomic absorption spectrometry, neutron activation analysis and plasma emission spectrometry where the time taken for results to be obtained is higher and where the speciation of the system is normally destroyed. This can be particularly important in the analysis of environmental samples in which the chemically labile fraction of the trace metal ions, i.e. that which is potentially toxic to living organisms, needs to be measured [1,2].

Natural samples are often complex matrices which can include significant amounts of organic matter. The irreversible adsorption on the surface of solid electrodes of various surface-active compounds, such as organic matter or inorganic colloids present in such natural media, leads to a decrease or even suppresses the stripping signal response. Reduction or elimination of the adsorption of these substances is therefore of crucial importance in the stripping analysis of heavy metals in environmental, clinical or biological media.

Polymer coating or modification of the electrode surface has been used with success for reducing adsorption phenomena, by selective exclusion of interfering species, and by protecting the electrode. Additionally, coating polymer films on electrodes sometimes also allows electrocatalytic effects to be achieved as well as pre-concentration of the analyte within the film which can be a very important added benefit considering the nanomolar concentrations of species such as trace metal ions present in natural media. The polymer films can either act as a new electrode material surface in themselves, i.e. films formed by conducting polymers or redox

polymers, or they can be semi-permeable, selected so as to allow the passage of the required analytes to the electrode surface whilst preventing that of other compounds which could adsorb on the surface or undergo electrode reactions.

In the literature there is a large number of publications concerning polymer-modified electrodes with different substrates and different polymers. In this review the more important of these will be surveyed in order to illustrate the strategies which have been employed, and will cover both formation of polymer film/electrode substrate assemblies and their application in stripping voltammetry, focussing particularly on recent developments.

2. POLYMERS FOR ELECTRODE MODIFICATION

Several types of polymer have been employed for electrode modification, mainly based on ion-exchange, size exclusion and conducting polymers, for which the basic preparation methods will be described in turn.

2.1 Ion-Exchange Polymers

The advantages associated with the pre-concentration capabilities of electrodes coated with a thin film of an ion-exchange polymer were first reported at the beginning of 1980s [3-5]. The choice of these ion-exchange polymers must be done taking into account the exchange characteristics needed and the ease with which a stable and reproducible film can be formed on the electrode surface [6]. Different types of polymers that are commercially available and are widely used for electrode surface modification possess important characteristics such as chemical inertness, non-electroactivity, hydrophilicity and insolubility in water [7].

The usual method used for modification of the electrode surface with ion-exchange polymers is solvent casting, in which a small volume of a solution of the polymer is applied directly onto the electrode surface, and the solvent is allowed to evaporate. The cationomeric polymers Nafion[®] and Eastman AQ55[®] [8,9], and the anionomeric Tosflex[®] [6], have received much attention because of the possibility to recast

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thin films on electrode surfaces for pre-concentrating and determining trace concentrations of redox ion analytes.

Nafion[®] is a perfluorosulphonate cation exchange polymer and is the most commonly employed ion-exchange polymer for the determination of heavy metals. Its chemical structure is shown in (Fig. 1a), and is characterised by a solvated structure with two types of domain [10,11]: one hydrophilic, associated with the sulphonate groups, where cations can be attracted and water is adsorbed, and the other hydrophobic responsible for adsorption on and stabilisation of hydrophobic-like electrode surfaces, such as glassy carbon. Nafion coatings are usually made by recasting from a solution by a drop-coating evaporation method [8,12] or by spin coating [13] of the polymer, the properties of the resulting film being dependent on many factors deriving from the degree of hydration of the Nafion film. Therefore, the concentration of water or other solvents in the casting solution, the relative humidity and temperature during drying are critical for film formation, stabilisation and operation [14]. Due to the negatively-charged sulphonate groups at each end of the fluoropolymer chain, Nafion can also be mixed with other sulphonate polymers to improve the cation-exchange characteristics and improve discrimination against interferents [15].

A different type of sulphonate polymer with some similar cation-exchange characteristics as Nafion is poly(ester sulphonic acid) also known as Eastman-AQ. This polymer can be obtained as AQ55 with equivalent mass of 1500 or AQ38 and AQ29 with equivalent masses of 2500 [16]. The full polymer structure is not known but in all cases the cation-exchange character is due to a sulphonate group in the 5-position on an aromatic ring, the polymer chain propagating through the 1- and 3- positions by links to ester (-CO₂-) groups, (Fig. 1b). It can be cast into films on electrode surfaces by simple evaporation of the solvent. The resulting coatings exhibit good adhesion to many substrates and it has been shown that Eastman-AQ presents permselective, ion-exchange, and antifouling properties [17].

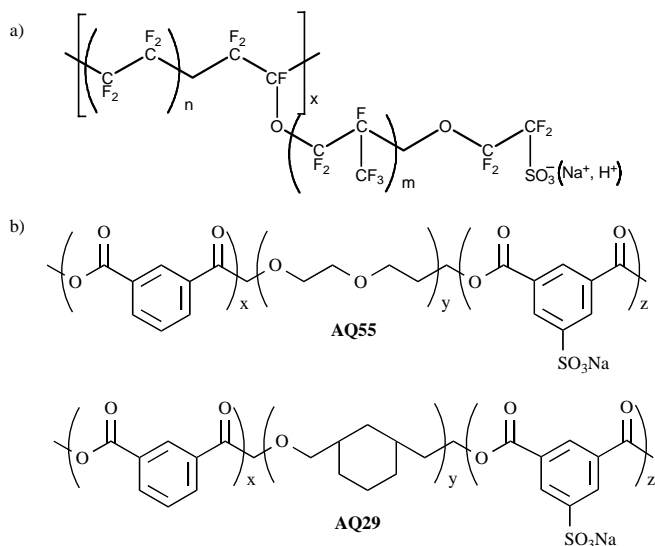


Fig. (1). Structural formulae of cation-exchange polymers (a) Nafion (b) Eastman AQ of different kinds, where the number refers to the glass transition temperature in °C.

Many species of analytical interest exist in the form of anions in sample solution, and anion-exchange polymers are necessary for developing methods for the determination of such analytes [18]. Protonated or quaternized polyvinylpyridine (PVP) was used as an anion-exchange polymer since the work of Oyama [3,4] for the immobilization of negatively charged electroactive species. However, some problems such as its non-ideal permselectivity [19,20], the need for chemical cross-linking to stabilize the polymer coating [21] and of a fairly acidic solution environment [18] makes PVP not so attractive as a modifier.

For anion exchange coatings, Tosflex[®], a perfluorinated anion exchanger is the most used. Its structural formula is shown in (Fig. 2), where *m* = 0-1, *n* = 1-5 and X = anion-exchange unit, including the counter anion. Since the polymer chains are perfluorinated it can be considered as the anion exchange analogue of Nafion, and is chemically inert, stable over a wide pH range, non-electroactive, hydrophilic and insoluble in water, and it is also easy to use [22]. Considering all these important and useful characteristics, Tosflex is a good alternative to PVP for modified electrode surfaces for electroanalysis of anionic species and, as for Nafion, due to the fact that Tosflex shows some solubility in lower alcohols it is possible to prepare a uniform film by spin-coating the electrode [23].

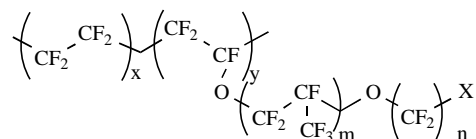


Fig. (2). Structural formula of the anion-exchange polymer Tosflex.

2.2. Size-Exclusion Polymer Coatings

Other types of polymer films for modifying electrode surfaces are thin permselective size-exclusion membranes used to prevent fouling of the electrode surface by discriminating against macromolecular species [24]. Size exclusion polymers such as cellulose acetate were first reported for use in electroanalytical determinations in the work of Sittampalam and Wilson [25]. However, recent evaluation of cellulose acetate film modified electrodes showed that they are not so robust for stripping analysis as would be desirable, owing to their fragility [15].

2.3. Conducting Polymer Coatings

Conducting polymer films have been widely used for electrode modification in electroanalysis, especially for trace metal detection due to their particular properties, the most important of which is electrocatalytic effects leading to a decrease of the overpotential, increasing the reaction rate and sensitivity [26]. Conducting polymers can show high electronic conductivity due to the delocalised electrons in the polymer chain and can usually be coated on any stable electrode surface by in situ electropolymerisation. The electrical conductivity can also be controlled by doping the polymer with non-redox dopants which also act as polymer counterions. They can function for pre-concentration purposes by immobilizing metal/ligand complexes or by mediating redox transport between metal centres. Among the conducting

polymers that are currently employed, polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANI), are those most chosen due to their ability to be electrodeposited on the electrode, the thickness of the film formed being controlled by the electrodeposition time and rate of nucleation of the cation radical deriving from monomer oxidation [27]. The basic structures of these conjugated polymers are shown in (Fig. 3). Such polymers and their derivatives are considered as multifunctional materials arising from the fact that their chemical structure consists of a polymer backbone that can have many possible substituents as well as from the many possible counterions (doping ions) or neutral molecules that can be trapped within the polymer matrix [28]. The properties and applications of conducting polymers as materials depends on the degree of oxidation (p-doping) or reduction (n-doping) of the conjugated polymer backbone, which can be controlled during the electropolymerisation of the monomer [29].

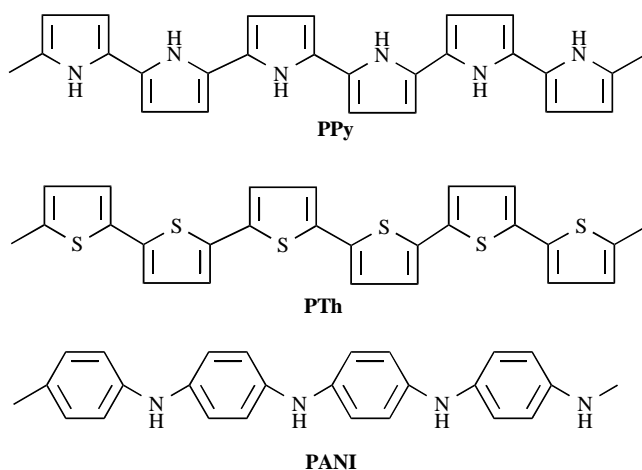


Fig. (3). Common conjugated polymers: PPy (polypyrrole), PTh (polythiophene) and PANI (polyaniline).

Complexing ligands can be incorporated within the conducting polymer film during its growth and subsequently used to capture metal cations, such as transition metal ions [30], at open circuit, followed by stripping analysis, in this way removing many of the possible interferents.

3. APPLICATIONS

In the literature there is a large number of publications devoted to polymer-modified electrodes for stripping analysis with different substrates and also with different polymers or mixtures of polymers. Ugo *et al.* reviewed the principles and analytical applications of ionomer-coated electrodes in 1995 [6] and in 2002 [9] with special emphasis on environmental monitoring. Applications using mercury-based thin films in stripping analysis of heavy metal ions, were reviewed in 2003 by Economou [31]. Therefore, this section will focus principally on more recent work, published since 2002.

Representative applications for each type of polymer film will be discussed with particular emphasis on work published in the last five years, which has been notable for developments in the use of conducting polymer films and molecular imprinting besides of ion-exchange coatings.

3.1. Ion-Exchange Coatings

3.1.1. Polymer-Coated Mercury Thin Film Electrodes

Nafion, as a perfluorosulphonated polymer, probably continues to be the most widely used cation-exchange polymer. Until recently, Nafion coatings were mostly used in combination with mercury thin films between the solid electrode substrate and the Nafion film [8,32,33]. These Nafion-coated mercury thin film electrodes (NCMTFE) can be prepared in two ways. The first is by directly electrodepositing mercury on the electrode, covering the thin mercury film formed with a Nafion membrane in air [34]. The alternative is to prepare the polymer film, by drop coating or by spin coating, and then deposit mercury through the Nafion film [35]. Although both strategies have been used, the second approach was found to be more convenient and lead to a more robust assembly, necessary for use with ultrasound-assisted stripping voltammetry [8] or in environmental analyses outside the laboratory by batch injection analysis (BIA) [15]. The preparation procedure is shown schematically in (Fig. 4), the film thickness being estimated from the known density of the polymer and the area covered, assuming uniform thickness. Additionally, coating the electrode with a Nafion film first and depositing the mercury afterwards offers more freedom for varying the curing procedure parameters (a warm flow of air) than in the presence of mercury, which may evaporate at higher temperatures. Characterization of the NCMTFE electrodes was done electrochemically and by optical microscopy: it was found that small closely spaced mercury microdroplets are formed on the glassy carbon substrate beneath the Nafion film, with the same behaviour as a continuous film owing to their close proximity [8,32].

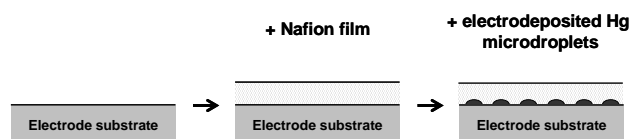


Fig. (4). Scheme showing the formation of a Nafion-coated mercury thin-film electrode (NCMTFE) by formation of a Nafion film (thickness typically 1 μm or less) followed by mercury electrodeposition in the form of microdroplets through the film.

Compared to other polymer modified electrodes [15,33], Nafion coatings are the easiest to prepare of those tested and give good discrimination against the passage of anions and large neutral molecules owing to reduced porosity, especially after curing. The NCMTFE was used in conjunction with BIA and square wave ASV for cadmium and lead determinations showing highly linear calibration plots with nanomolar detection limits and with no memory effects [32]. An interesting feature in these experiments is the shifting of the stripping peak by ~ 12 mV in the negative direction compared to the MTFE. This has been attributed to the cation exchanging behaviour of the Nafion coating favouring the oxidised state of the analysed species, since kinetic limitations due to the presence of the film were shown to be negligible. Electrochemical impedance spectroscopy was also used to probe this effect and demonstrated clearly that the electrolyte alters the impedance associated with the interfa-

cial region between Nafion film and solution, correlating well with the stripping signals obtained and with different values of peak potential [36]. The influence of organic surfactants was also analysed, showing a less pronounced peak depression compared with the uncoated electrode, in good agreement with previous reported work on Nafion [11,12,35,37].

The use of Nafion-coated electrodes in sono-electroanalysis for determination of heavy metal ions was first reported by Matysik *et al.* [8], and used extensively by Compton and co-workers [38-41] for the determination of trace metals in natural samples such as copper in beer, lead in saliva, zinc and cadmium in whole blood. The enhanced convective mass transport afforded by acoustic streaming during accumulation leads to fast analyses and the surface activation and cleaning due to insonation, in addition to the polymer protection, helps to prevent electrode fouling.

Palchetti *et al.* [7] used Nafion, Eastman AQ29 and Methocel (a cellulose derivative) to modify mercury-coated screen-printed electrodes and use them in stripping analysis of heavy metals in the field. Each coating was prepared by mixing the same amount of mercury acetate in the polymer solution in a ratio of 30 % mercury-70 % polymer solution (v/v). Characterisation of polymer modified electrodes was done in 0.1 M HCl by potentiometric stripping analysis. It was found that Methocel-coated mercury electrodes showed best performance in HCl solutions of different concentrations where perfluorosulphonate polymers (such as Nafion) cannot be used due to changes in the morphology and geometrical parameters of the polymeric microstructure with increasing ionic strength of the solution [12]. Good sensitivity and well-shaped peaks were found for SWASV of lead and cadmium ions with detection limits of $0.8 \mu\text{g L}^{-1}$ and $1 \mu\text{g L}^{-1}$ for those metal ions, respectively. Methocel modified electrodes were used in the determination of lead and cadmium by SWASV in wastewater samples and in herbal samples giving good correlation with ICP spectrometry. In [42], an optimised SWASV sensor based on Methocel modified mercury coated screen-printed electrodes for lead, cadmium and copper, is reported.

Alternatives to the Nafion polymer with cation exchange behaviour, poly(ester sulphonic acid) (PESA) [33] and poly(sodium 4-styrenesulfonate) (PSS) [43] have been studied. Brett and Fungaro [33] used a mercury-thin film modified glassy carbon electrode coated with a thin film of PESA to study trace heavy metals by square wave anodic stripping voltammetry using BIA and SWASV. A limitation of the PESA polymer is that it can only be obtained in dispersion, [17], although attempts have been made to create a proper solution [37] - mixtures of water and acetone with PESA were studied, since the identity and ratio of the solvents can influence the morphology of the film obtained and the reformation of the crystalline phases of the polymer. The overall thickness of the thin film was $1 \mu\text{m}$. The influence of electrolyte anion as well as of model surfactants (Triton X100, SDS and protein standard) on polymer film properties and on ASV signals was studied and acetate buffer was found to be the best electrolyte solution. The reduction in stripping signal of 30% in the case of cadmium and 70% in the case of lead with PESA-modified electrodes was attrib-

uted partly to variations of film thickness and to a greater extent to the variable porosity of the film which is very difficult to control, an effect that has been noted previously for various different polymer coatings [11].

The use of poly(sodium 4-styrenesulphonate) coated mercury thin film electrodes (PSS-MTFE) for the determination of metal ions in estuarine water by SWASV was described by Monterroso *et al.* [43,44]. The PSS was recast from a PSS solution, followed by electrodeposition of a mercury film. The PSS-MTFE showed an 82 % and ca. 43-49 % increase in sensitivity compared to the uncoated MTFE and to the Nafion-coated MTFE, respectively. The PSS coatings showed good antifouling properties against surfactants, their permselectivity based on electrostatic interactions and molecular size (the cut-off molecular weight was ca. 190 with a film thickness of ca. $18 \mu\text{m}$).

Mixtures of other ion-exchange polymers with Nafion have also been investigated, such as of Nafion-poly(vinyl sulphonic acid) and Nafion-poly(styrene sulphonic acid) [15], or Nafion-PSS [45]. The overall effect of such mixing is to compensate limitations of single polymer coatings, improving the cation-exchange ability of Nafion films by combination with a polymer having a higher degree of sulphonation [45], although film preparation may be harder and film integrity lost after use, owing to partial dissolution of the polymer film components.

In [15], polymer film formation on glassy carbon electrodes was carried out by using a mixture of 80% Nafion and of 5% - 20% polymer: PVSA, poly(vinyl sulphonic acid); PVSA-MA, poly(vinyl sulphonic acid-co-maleic anhydride); PVSA-S, poly(vinyl sulphonic acid-co-styrene) or PSSA, poly(styrene sulphonic acid). In this case the mixture improves the cation-exchange ability of the Nafion coatings the limitation being the high solubility of these polymer additives in water so that they cannot be used alone. Optimization of the polymer-coated MTFEs showed that electrodes coated with a film containing 95% Nafion and 5% PVSA gave the best performance in minimizing the influence of surfactants such as Triton-X-100 on the response of metal ions.

Rocha *et al.* [45] used a mixture of Nafion with poly(sodium 4-styrenesulfonate) (PSS) to modify a glassy carbon electrode followed by electrodeposition of a thin mercury film in order to improve the sensitivity, reproducibility as well as stability of the coatings and their antifouling properties. The two sulphonated cation-exchange polymers have dissimilar characteristics so that the coating was produced by solvent evaporation in an optimized mass ratio of 5:3 Nafion/PSS. The sensitivity of Nafion/PSS-MTFE to lead ions with SWASV increased 24 % compared to that of the Nafion-MTFE, the detection limit being 5.5 nM for both modified electrodes.

An interesting application of NCMTFEs on a glassy carbon electrode substrate together with BIA has been described [46]. The tip of the $100 \mu\text{l}$ electronic micropipette used for injection was filled with the chelating resin Chelex-100. Environmental samples were aspirated into the micropipette, the metal ions being concentrated on the resin. After washing the sorbent, eluent was aspirated and the metal ion-

containing eluent injected over the NCMTFE detector where it was measured by SWASV. This enabled a 10-fold additional pre-concentration besides reducing the effect of high concentrations of interfering species, which would influence the signal obtained with Nafion coatings.

3.1.2. Polymer Coatings on Other Electrode Materials

With the recent move away from the use of mercury thin film electrodes owing to concerns with pollution [47], there have been investigations of replacement materials in stripping analysis. Even though the use of polymer-protected mercury thin films prevents mercury from being released to the local environment, and mercury ions are used only when the mercury film is formed, complete removal is perceived to be preferable. Thus, new polymer-coated electrode materials have been investigated in recent years for this purpose, particularly on carbon film electrodes, bismuth film electrodes, and carbon nanotubes on appropriate electrode substrates.

Carbon Film Electrodes

Carbon film electrodes fabricated from carbon film electrical resistors have been developed and evaluated [48,49], and show a sufficiently wide potential window to be used for the ASV of several metal cations without the need for a mercury thin film. The influence of coating the carbon film electrode with Nafion was studied, it being found that the Nafion coating does not alter the potential window in acetate buffer solution [50]. Changes in electrode characteristics due to the coating were evaluated by electrochemical impedance spectroscopy (EIS). In particular, impedance spectra recorded with lead and cadmium ions in solution before and after applying -1.0 V vs SCE (the potential used in the ASV deposition step of lead and cadmium) demonstrated irreversible changes to the polymer coating due to physical distortion of the Nafion film, attributed to the formation of tiny metal deposits within the Nafion pores close to the electrode substrate surface.

In [51], these Nafion-coated carbon film electrodes were investigated in solution containing Triton-X-100 surfactant, its influence most noted for cadmium, with a decrease of almost 90 % in the stripping peak current for 5 mg L^{-1} of Triton (a much higher surfactant concentration than normally observed in environmental matrices), being $\sim 80\%$ in the case of lead. Although the lead and/or cadmium ion containing system normally recovers completely from the adsorption of surfactant in terms of results of ASV determinations, after being exposed to higher concentrations (500 mg L^{-1} of Triton) a similar memory effect in the polymer was observed as mentioned above. Fig. (5a) shows the effect of surfactant on the position of the stripping peaks as well as on the reduction in height, and (Fig. 5b) demonstrates that the impedance spectra do not return to their original form once an SWASV experiment has been conducted, although further changes on repeating SWASV experiments are not seen.

Bismuth Film Electrodes

Bismuth-coated carbon electrodes for ASV were first described by Wang *et al.* [52,53]. Bismuth is an environmentally friendly element, with very low toxicity, has the ability to form alloy with many metals, and has a wide potential window. Bismuth films can be deposited by applying a con-

stant potential ex-situ or in-situ (simultaneous deposition of bismuth and the target heavy metals, in a manner analogous to in situ plated mercury film electrodes), by potential cycling or galvanostatically [54].

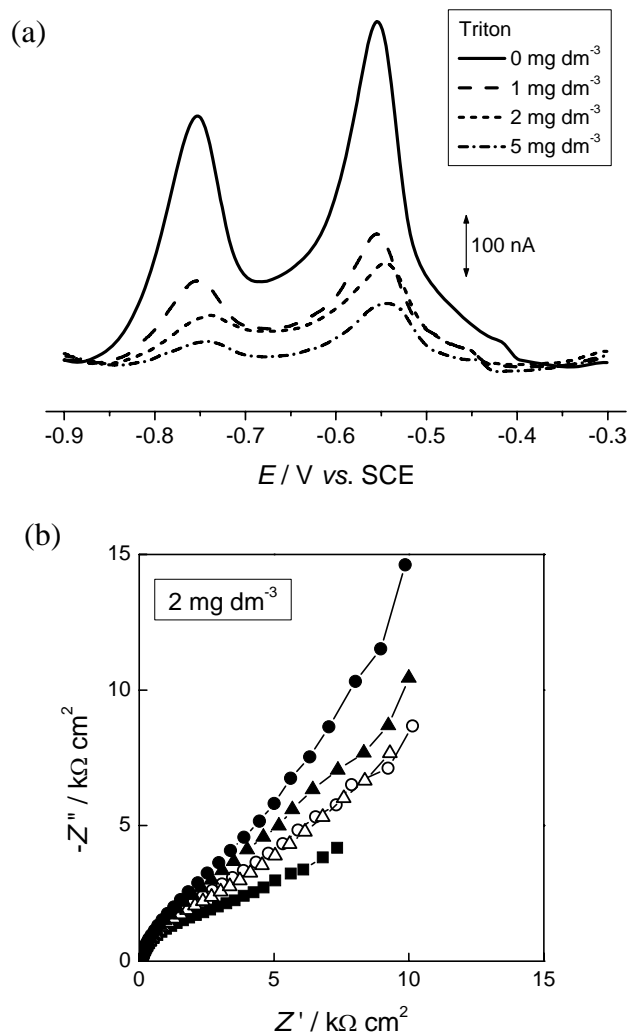


Fig. (5). SWASV of Cd and Pb at a Nafion-coated C film electrode in pH 4.3 0.1 M acetate buffer. (a) Stripping signals of Cd (~ -0.76 V and Pb (~ -0.57 V) in the presence of Triton-X-100 surfactant (deposition 120 s at -1.0 V vs. SCE). (b) Sequential complex plane impedance spectra (\blacksquare) buffer electrolyte; (\bullet) after deposition of Pb^{2+} and Cd^{2+} ; (\circ) after SWASV; (\blacktriangle) with Triton and (Δ) after electrochemical cleaning. From [51] with permission of Elsevier.

Nafion-coated bismuth film electrodes in the determination of trace metals by ASV were first carried out by Kefala *et al.* on glassy carbon substrates [55], assessing various fabrication and operational parameters that could affect the ASV signals of modified bismuth electrodes. Nanomolar limits of detection were obtained for Cd, Pb and Zn. They were then successfully applied in systems using sequential injection analysis and SWASV for samples containing all three metal ions [56].

Carbon films were also found to be excellent substrates for bismuth and showed an analytical sensitivity similar to or better than Bi films deposited on other carbon substrates

[54]. Nafion coated bismuth film modified carbon film electrodes were studied in [57] for Zn, Cd and Pb analysis by SWASV. Consecutive additions of Triton-X-100 surfactant to a maximum of 20 mg L⁻¹ showed good discrimination.

Bismuth film electrodes coated with a mixture of Nafion/PSS have been employed [58]. PSS in the mixture increases the reproducibility as well as the sensitivity towards lead and cadmium ions. The influence of surface active compounds, at the nanomolar concentration level, such as cetyltrimethylammonium bromide (CTAB), Triton X-100, bovine serum albumin (BSA) and SDS was also studied leading to different conclusions: the CTAB gave a moderate decrease in the current signal, Triton X-100 and BSA a big decrease and SDS had least influence. The reason was related to the charge of the active compounds.

Carbon Nanotubes

The metal deposition and stripping processes at carbon nanotube/Nafion modified electrodes have been investigated as a viable alternative to mercury-based procedures [59]. The performance of a thin film of multiwalled carbon nanotubes (MWCNT) functionalised in Nafion, was evaluated as a MWCNT/Nafion-modified glassy carbon electrode for the electroanalytical detection of Cd²⁺ and Pb²⁺ in the presence of surface active interferents such as SDS, Triton-X-100, DPC, and BSA [60]. ASV for lead and cadmium ions with an accumulation potential of -0.9 V during 240 s, led to detection limits of ~50 nM for both ions. The stripping peak current of cadmium decreased with the addition of Triton X-100, but that of lead increased. This behaviour was observed in [11] and in other studies, explained by complexation between lead ions and the surfactant, being equivalent to an extra pre-concentration effect. An increase in both stripping peaks led to the conclusion that SDS can probably be used as an anti-fouling additive in stripping analysis at MWCNT/Nafion electrodes.

Single-walled carbon nanotubes (SWCNT) were also used in the ASV determination of cadmium ions [61]. SWCNT were dispersed into ethanol via ultrasonication, leading to a stable and uniform SWCNT/Nafion suspension, which was then used to modify a glassy carbon electrode by drop coating. ASV of cadmium showed a well-defined stripping peak with a nanomolar detection limit. However, due to the high cation-exchange capacity of Nafion and strong adsorptive ability of SWCNT, Cd²⁺ was difficult to clean from the SWCNT/Nafion film, so that the films could only be used once, although the reproducibility between electrode assembly preparations was 6.1% for 10 SWCNT/Nafion modified glassy carbon electrodes, suggesting potential use in diagnostic measurements.

Other Electrode Substrate Materials

In a recent report, a Nafion-modified glassy carbon electrode was used to pre-concentrate sulphamethazine from milk, after clean-up, in its protonated form at low pH, followed by electrooxidation in the determination step, with nanomolar detection limits [62]. Nafion-modified platinum microelectrodes on silicon substrates were used to measure trace lead and cadmium ions in environmental water samples without pre-treatment by SWASV [63].

Finally, in what seems to be the only recent example of the use of Tosflex for pre-concentration in electroanalysis, a Tosflex-modified glassy carbon electrode was employed to pre-concentrate 2-naphthol, in its anionic form at high pH, prior to determination by differential pulse oxidation [64].

3.2. Conducting Polymer-Coated Electrodes

Modification of the electrode surface with conducting polymers can be also a useful strategy for stripping voltammetry of heavy metals with mercury free electrodes. The counterions can be used to confer extra selectivity and specificity and permit complexation accumulation.

Polypyrrole-based coatings are probably currently those most employed. This is partly due to the wide pH range over which they can be prepared by electropolymerisation and then used, whilst retaining their conducting properties.

3.2.1. Polypyrrole-Based Coatings

Overoxidised polypyrrole (OPPy) has been used as polymer matrix. In one study it was doped with 2-(2-pyridylazo)chromotropic acid anion (PACH²⁻) as chelating agent and counterion to modify glassy carbon electrodes for the quantitative electrochemical detection of lead using differential pulse anodic stripping voltammetry (DPASV), with a submicromolar detection limit [30]. Using a similar strategy, 4,5-dihydroxy-3-(*p*-sulphophenylazo)-2,7-naphthalene disulphonic acid (SPADNS) was incorporated in the film on a platinum substrate and used successfully for the measurement of copper down to nanomolar concentrations by DPASV, with little interference from other heavy metal ions [65], see (Fig. 6).

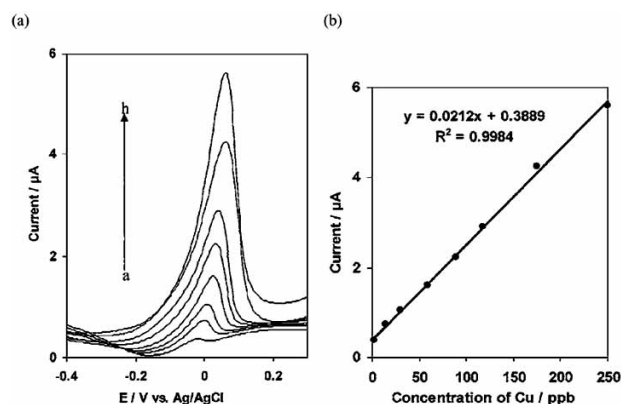


Fig. (6). (a) DPASV of Cu(II) at OPpy/SPADNS modified electrode; 15 min deposition at -0.4 V in pH 8 electrolyte; [Cu²⁺]: 2, 15, 30, 59, 89, 118, 175 and 250 ng ml⁻¹ (b) related calibration plot. From [65] with permission of the Japan Society for Analytical Chemistry.

Pyrrole was electropolymerised in the presence of Eriochrome Blue-Black B as counter anion on glassy carbon. Modified electrodes were then subjected to several oxidation/reduction potential steps in silver nitrate solution to accumulate and then strip silver species, generating templated selective recognition sites in the EBB/PPy film for silver ions. Apart from potentiometric detection, the EBB/PPy modified electrode was also used for DPASV with a sub-

nanomolar detection limit and little interference from other heavy metal ions [66].

Heitzmann *et al.* [67] developed a one step procedure for synthesis of complexing polymer film modified glassy carbon electrodes by oxidative electropolymerisation of (3-pyrrol-1-ylpropyl)malonic acid monomer, then employed them for the ASV of copper, lead, cadmium and mercury ions after complexation, with detection limits varying from subnanomolar to micromolar for Pb(II), Cu(II), Hg(II) and Cd(II), these differences being due to different stability constants for complex formation.

In another study, a pyrrole derivative monomer [3-(pyrrol-1-yl)propylamine] was mixed with EDTA (ethylenediaminetetraacetic acid) in DMF [68], then electropolymerised it in acetonitrile solution on a carbon disk electrode or in an imprinted electrode prepared by the electropolymerisation of the complex with Cd(II). These modified electrodes were used for the ASV determination of copper, lead and cadmium ions. The modified carbon electrode showed greater affinity towards Cu(II) ions and was almost insensitive to Cd(II), but the imprinted electrode allowed the selective sensing of Cd(II).

Electropolymerisation of anthranilic acid and pyrrole at platinum, gold, or glassy carbon electrodes gave stable polymer-coated electrodes that were then employed to prepare an improved functionalized PPY-modified gold electrode to collect and measure Cu(I) species by DPASV down to 5 nM levels [69].

3.2.2. Polythiophene-Based Coatings

Polythiophene modified electrodes have also been employed in stripping voltammetry. In [70], polythiophene was formed by potential cycling on glassy carbon, gold and platinum electrodes and then used for the detection of several heavy metal ions, best results being obtained with glassy carbon substrates, leading to nanomolar detection limits. Formation of polythiophene-quinoline films on glassy carbon substrates led to a film which was selective for trace mercury determination by DPASV down to 2 nM concentration and was applied to measurements in wastewaters [71].

Substituted thiophenes have also found application. Poly(3-methylthiophene)-modified sonogel-carbon electrodes were used for trace mercury determination [72]. Sonogels are sol-gel polymers prepared from oxysilane precursors under ultrasound conditions, and mixed with graphite under insonation to form a sonogel-carbon electrode, on top of which 3-methyl thiophene was polymerised. DPASV was then used to pre-concentrate and determine mercury in natural samples of waters. Secondly, a highly substituted thiophene, i.e. 3',4'-diamino-2,2'; 5',2''-terthiophene, was polymerised together with EDTA for preconcentrating a number of metal ions which were then stripped by SWV under different conditions of pH and electrolyte, in order to obtain the necessary selectivity at trace levels [73].

3.2.3. Polyaniline-Based Coatings

Polyaniline (PANI) has been less used as a conducting polymer matrix, probably owing to the fact that its conductivity can decrease significantly in weakly acidic or alkaline

solutions. Nevertheless, there are several recent reports worthy of mention which use polyaniline, or substituted polyaniline, in combination with another modifying species.

In the first, the use of PANI/carbon nanoparticle-modified electrodes for the ASV of lead and copper was described by Zimer *et al.* [74]. A mixture of template carbon (produced by pyrolysis) and polyaniline was cast on an indium tin oxide electrode surface, and it was shown that the interconversion reactions of polyaniline were facilitated in the presence of the carbon nanoparticles.

Secondly, a bismuth/PANI modified glassy carbon electrode was investigated [75]. After electropolymerisation of aniline on glassy carbon to form the PANI film, a bismuth film was deposited in situ with cadmium and lead ions for ASV. The optimised parameters led to nanomolar detection limits for lead and cadmium and a higher sensitivity compared with bismuth film or PANI-modified electrodes separately.

Thirdly, nanogold particles were deposited into previously formed polyaniline films grown on glassy carbon electrodes. This assembly was then used to measure As(III) in hydrochloric acid solution in the presence of iodide ions by SWASV down to 5 nM concentrations [76].

Regarding PANI with substituents, Gao *et al.* [77] simultaneously deposited MWCNT and formed poly(1,2-diaminobenzene) (DAB) on a glassy carbon electrode by multipulse potentiostatic electropolymerisation, leading to a nanoporous structure, with excellent stability and conductivity. It was successfully applied to the SWASV determination of cadmium and copper ions with detection limits of 2 and 5 nM, respectively. Fig. (7) shows the significant current enhancement in the stripping signal due to the MWCNT as well as due to the polymer film. This coated electrode was then used to analyse metallurgical wastewater samples.

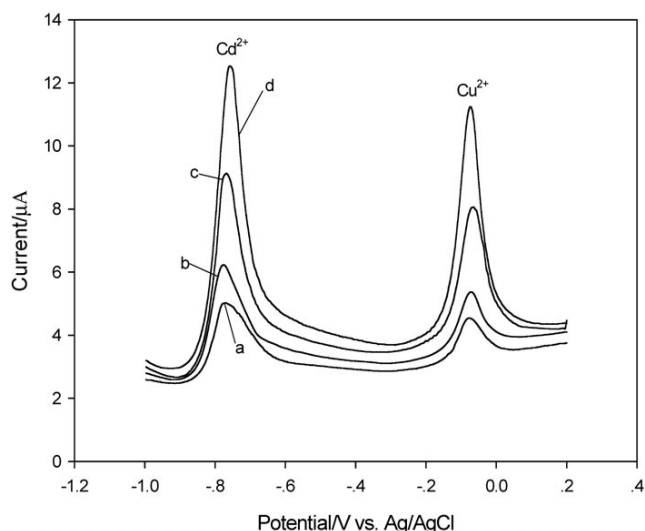


Fig. (7). SWASV of 100 ppb Cd²⁺ and Cu²⁺ in pH 4.4 0.1 M acetate buffer solution on a) Bare GCE, b) poly(1,2-DAB)/GCE, c) MWCNT/GCE, and d) MWCNT/poly(1,2-DAB)/GCE. Deposition potential: -1.0 V for 180 s. From [77] with permission of Wiley-VCH Verlag GmbH & Co. KGaA.

3.2.4. Other Conducting Polymer-Based Coatings

Two recent articles employing other conducting polymer coatings are of interest. The first of these used a glassy carbon electrode coated with poly(vinylferrocene) for the ASV determination of gold at micromolar levels [78]. The Au(III) was chemically reduced by, and accumulated within, the polymer film, without the interference of Cu(II): a response to Cu(II) was a drawback of previous methodologies, although they achieved lower detection limits.

The second concerns the determination of trace lead ions at poly(*N,N'*-(*o*-phenylene)-bis-benzenesulfonamide) coatings [79]. This modified electrode showed a high selectivity towards Pb²⁺ over interfering cations, with a nanomolar detection limit, and was applied to the analysis of samples from pond water.

3.3. Miscellaneous Polymer Materials

In an attempt to increase the selectivity of the polymer coatings, modified polymers have been prepared. In one of these approaches, styrene copolymers were made from styrene monomer together with acrylic acid, acetamide, acetamide acrylic acid, itaconic acid or vinylpyridine [80,81]. It was found that these polymers successfully retained lead ions and that these could be stripped, although the detection limits are still high. Nevertheless, it can be expected that this co-polymer approach will be exploited in the future.

In the second, hanging mercury drop electrodes were modified with molecularly imprinted polymers (MIP) for increased selectivity and specificity in the analysis of diquat herbicide [82], creatinine [83] and creatine [84]. No reports of modification of solid electrode substrates by MIP for stripping voltammetry have been found.

4. CONCLUDING REMARKS

Polymer-coated electrodes for stripping voltammetry continues to constitute an active field of research. The reason is clear – the need to be able to analyse electroactive species at trace concentrations in complex matrices, whether they be environmental, food or clinical, efficiently and rapidly. Such matrices, sometimes of unknown composition, can contain many interferents which can influence the results of stripping voltammetric experiments directly or by blocking/fouling the electrode surface. Polymer coatings seek to address both these issues.

Besides the more widely used ion exchange coatings, which are evolving with new electrode materials and composite films, strategies based on conducting polymer film electrodes have been described which can have great potential if exploited in the correct way, particularly by incorporating nanoparticles which can introduce beneficial electrocatalytic effects. Molecularly imprinted polymers is another avenue which can be expected to open up further in the future.

To find wide application, these electrodes must be easy to calibrate and use over the required time period with the necessary selectivity and minimum of sample pre-treatment, and also be sufficiently physically robust. All the research

being undertaken in the area of polymer-coated electrodes for stripping analysis is with these goals in mind.

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