

Sulfonated Polyaniline Coated Mercury Film Electrodes for Voltammetric Analysis of Metals in Water

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Abstract: The electrochemical polymerization of 2-aminobenzenesulfonic acid with and without aniline has been carried by cyclic potential sweep in sulfuric acid solution at the glassy carbon electrode. The polymer and copolymer formed have been characterized voltammetrically. The sulfonated polyaniline coated mercury thin-film electrodes have been evaluated for use with anodic stripping voltammetry. The electrodes were tested and compared with a conventional thin-film mercury electrode. Calibration plots showed linearity up to 10^{-7} mol L⁻¹. Detection limits for zinc, lead and cadmium test species are very similar at around 12 nmol L⁻¹. Applications to analysis of waters samples are demonstrated.

Keywords: Sulfonated polyaniline, Electropolymerization, Trace metal analysis.

Introduction

Sulfonated polyaniline (SPAN), a water soluble conducting polymer is interesting because of its unusual electroactive properties, improved processability and potential industrial applications [1-2]. Self-doped polyanilines have more stable and reproducible electrical properties and higher thermal stability than polyaniline (PANI) and showed a pH-independent conductivity from pH 0 to 14 [2].

Yue and Epstein [3] have synthesized the first protonic acid self-doped polyaniline by reaction of emeraldine base with fuming sulfuric acid to give a sulfonic acid ring-substituted polyaniline powder having a conductivity of about 0.1 S/cm and saturation of the polymer with sulfonate groups at a level of 50% with respect to the number of phenyl rings. Somewhat later, a modification of this treatment was proposed, leading to a self-doped polyaniline, containing up to 75% sulfonated monomer units [4]. Also, self-doped polyanilines with different sulfonation degree were obtained by treating aniline with sulfuric acid containing silver sulphate [5].

A different approach to obtain self-doped polyaniline employs electropolymerization of monomers containing anionic groups. From the applied point of view the electrochemical polymerization of cheap, simple aromatic benzoid or nonbenzoid and heterocyclic compounds is of utmost interest. Electrochemical polymerization is preferable than chemical oxidation if the polymeric product is intended to use as a polymer film electrode because the potential control is a precondition of the production of good-quality material and the polymer film is formed at the desirable spot that serves as an anode during the synthesis.

The course of an electropolymerization by potential cycling depends on the experimental conditions (composition of the solution; potential range, particularly the positive limit; potential scan rate; electrode material etc). Electrochemical oxidation of 2-, 3- and 4-aminobenzenesulfonic acids yielding a polymer films on electrode were reported [6-8]. These results contrast the unsuccessful attempts to forming of a film by other authors [9-11].

Sulfonated polyaniline has also been prepared electrochemically through the copolymerization of aniline with meta or orto-benzenesulfonic acid [9, 11-19].

Whereas many papers deal with the electropolymerization of aniline and the electrochemical and physical properties of polyaniline-modified electrodes, much less is known about the sulfonated polyaniline.

In this work, the electrochemical polymerization of sulfonated polyaniline has been carried out by cyclic potential sweep at the glassy carbon electrode. The SPAN possesses cation exchange properties due to the presence of the sulfonate substituents. The performance of SPAN-coated mercury film electrodes was investigated for trace metals analysis.

Experimental

Reagents and sample collection

All chemicals used were of analytical grade and the solutions were prepared using the system Millipore Milli-Q ultra-pure water. Experiments were carried out at 25 °C. Standard solutions of metals were prepared by dilution of a 1000 mg L⁻¹ stock solution. Aniline (AN) was distilled and stored under argon in a refrigerator in frozen form and 2-aminobenzenesulfonic acid (2 ABS) was used without purification.

The samples of river water were collected from São João da Boa Vista county (SP, Brazil). The rainwaters were collected from coal-fired power plant of Figueira area (PR, Brazil). Sample water from Mococa county (SP, Brazil) was collected after had passed through a water treatment plant. They were kept in polypropylene bottles. All samples were acidified to pH ≤ 1 with nitric acid and stored at 4 °C before analysis.

Equipament

Electrochemical experiments were carried out using a Autolab Basic PGSTAT 30 voltammetric analyzer. The cell assembly contained a magnetic stirrer, a 3 mm diameter glassy carbon electrode

employed as working electrode, a platinum wire, used as auxiliary electrode, and a Ag/AgCl/3 mol L⁻¹ KCl electrode as reference.

Methods

Prior to use, the working electrode was polished with alumina powder (Al₂O₃, 5 μm) on a polishing cloth and rinsed with Millipore water. Following this, it was held at a potential of +1.6 V in sulfuric acid electrolyte for 6 minutes and then cycled in the potential range - 0.5 V to +1.5 V at a sweep rate of 50 mV s⁻¹ for 15 minutes. After this treatment a reproducible voltammogram of the GCE was obtained showing much reduced background currents. Electrochemical polymerization of 2 ABS was carried out by cyclic potential sweep in 1.0 mol L⁻¹ sulfuric acid electrolyte solutions containing the 0.05 mol L⁻¹ monomer between - 0.3 V and +1.0 V at a scan rate of 50 mV s⁻¹. The copolymer (2ABS-AN) was electrodeposited from an initial solution of AN 0.001 mol L⁻¹ and 2 ABS 0,05 mol L⁻¹ in 0.1 mol L⁻¹ sulfuric by cyclic voltammetry in the potential range from - 0.5 to 0.9 V at a scan rate of 50 mV s⁻¹.

Preparation of the SPAN-coated mercury thin film electrode (SPANME)

The sulfonated polyaniline modified glassy carbon electrodes were immersed in a magnetically stirred solution containing 10⁻⁴ mol L⁻¹ Hg (II) in 0.1 mol L⁻¹ NaNO₃ / 5 mmol L⁻¹ HNO₃ and the mercury film was deposited applying a potential of -0.9 V for 5 minutes. Square wave anodic stripping voltammetry (SWASV) experiments were done by preconcentrating the metal ions with a potential of -1.3 V for 1 min. The square wave parameters were: frequency 100 Hz, potential increment 2 mV and square wave amplitude 25 mV.

Results and Discussion

Electrochemical behavior

The importance of deposition conditions on the ensuing structure and properties of conducting polymers has been demonstrated on numerous occasions [20]. It has been reported that a compact PANI film superimposed with a fibrillar structure can be obtained by cyclic potential sweep deposition from HClO₄ solutions. The compact layer is formed in the early stage of deposition and is resistant to polymer degradation. In H₂SO₄ electrolytes, however, a granular film of high porosity is produced instead [21]. The open structure allows the solution constituents to have better access of the polymer interior.

Electrosynthesis of polyaniline was performed by potential cycling between 0.0 V and 0.8 V vs. Ag/AgCl/ sat. KCl [22]. The higher anodic switching potential, the higher is the current and time and the higher amount of radical cation is generated. To oxidize the aminobenzenesulfonic acids, a slightly higher potential than that used to form polyaniline is necessary. Different positive potentials limits were used, it being found that a positive limit of between 0.9 V and 1.1 V gave the best results in terms of film formation with minimum degradation products.

In Fig.1 cyclic voltammograms (CVs) of films prepared from solutions of 2 ABS, and 2 ABS-AN after 100 cycles are presented.

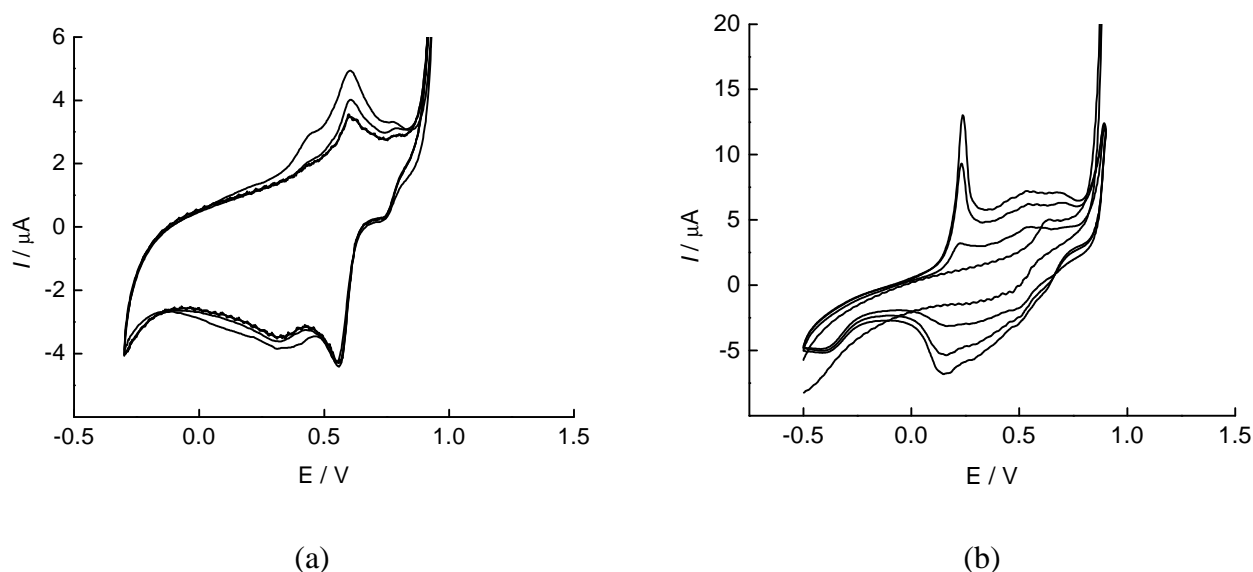


Figure 1. Cyclic voltammograms of polymer films formed on glassy carbon electrodes from: (a) 2 ABS in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (b) 2 ABS-AN in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Scan rate: 50 mVs^{-1} .

For all peaks the currents increase, indicating progressive polymerization and film forming. The anodic limit was not lowered after the initiation period. The polymerization process is more difficult than for aniline because polyaniline deposition is catalysed by polyaniline itself [23-24]. The stability of the radical-cation obtained by oxidation is affected by the substituents. The presence of the bulky electron-withdrawing $-\text{SO}_3\text{H}$ side-group greatly reduces nucleophilicity and increases steric hindrance.

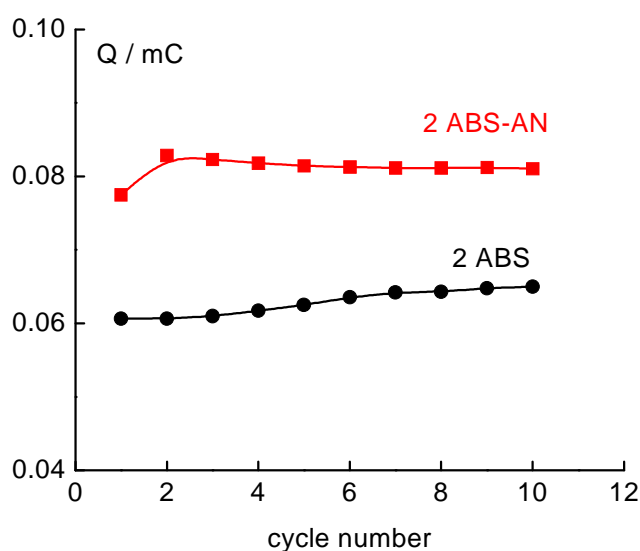


Figure 2. Dependence of the cathodic charge on the cycle number of SPAN films.

The CVs of SPAN recorded after 100 cycles differ from those recorded for polyaniline under the same conditions. SPAN has a higher potential for the first redox process and a lower potential for the second redox process. Such a phenomenon has been associated with the steric and electronic effects of the substituents and was already observed for several cases in polyaniline [1].

The growths of the polymers films were monitored as a function of potential cycle number by measurement of the charge under the cathodic portion of the CVs. The cathodic charge of the polymer is proportional to the thickness of the film. Fig. 2 shows the cathodic charge as a function of cycle number of SPAN films.

The degree of polymerization and growth of polymers are undoubtedly increased in the presence of AN. The influence of 2 ABS actually runs counter to the benefits reaped from AN addition.

Due to the electron-acceptor effect of the sulfonate group, the aromatic system of aminobenzenesulfonic acid is deactivated with respect to an electrophilic substitution reaction and retards the polymerization significantly. Besides this electronic effect, steric effects of this bulky pendant group could be a more significant factor. However, in the simultaneous electrooxidation of 2 ABS and AN copolymerisation can be initiated by the generation of radical cations by AN molecules, followed by a propagation based on attack on the growing chains by both AN and 2 ABS molecules.

SWASV response characteristics of SPANME

The characteristics of the SPAN-coated thin mercury film electrodes for use in ASV were examined. The SPAN would be a viable alternative to the use of ion-exchange polymers commercially available. Nafion and Eastman AQ are widely used, however, have a high price which hinders the increased commercial application of electro-membrane processes.

A procedure involving ten potential cycles was used in the electropolymerization of aminobenzenesulfonic acids. With thicker polymers, the ratio of mercury to polymer on the electrode surface decreased and the metal ions has less access to the dispersed mercury droplets. With thicker polymer coatings the background current also increased owing to the electroactive nature of the polymer. This increase in background current affects the determination of metals. Further, during deposition, degradation and film growth are reactions competing for a common intermediate from the oxidation of SPAN. The extent of degradation of SPAN was found to increase with increase in the number of deposition cycles.

The polymer-coated mercury electrodes were used for voltammetric stripping determinations of metal ions and the responses were compared with those obtained with the bare mercury thin film electrode (MTFE). The increases of peak current of the metals in SPANME in relation to MTFE are in the Table 1.

Table 1. Percentage change in the peak current of 10^{-7} mol L⁻¹ Cd²⁺, Pb²⁺, Zn²⁺ at SPANME.

SPANME	ρ_{i_p} (%)		
	Zn	Cd	Pb
2 ABS	200	62	232
2 ABS-AN	- 65	6	11

$$\rho_{i_p} = [(I_p - I_{MTFE}) / I_{MTFE}] \times 100; I_p \text{ and } I_{MTFE} \text{ are stripping peak currents with SPANME and MTFE.}$$

The electrodeposition of metal onto polymeric films take place in the open pores of the film. It was showed that thin films are more porous than thick films [25]. The amount of deposited metal decreased with increases of the thickness of film. The poly(2 ABS-AN) electrode exhibited a lower sensitivity to metal ions than the poly(2 ABS) electrode mainly for zinc, the metal ion with higher ionic size.

The poly(2-amonibenzenesulfonic acid)-coated mercury thin-film electrode showed the best sensitivity and was used in study of the analytical SWASV characteristics.

If the polymer film is to be reused, ease of removal of the preconcentrated analyte is highly desirable. The removal of the accumulate 10^{-7} mol L⁻¹ Cd²⁺ was studied by holding at 0 V at the end of the stripping step for 10 min and exchange stripping medium. The removal of the analyte was essentially complete. The complete removal of the cadmium was impossible without use a separate solution in reduction and anodic stripping steps.

The results of linear regression of the zinc, cadmium and lead are shown in Table 2.

Table 2. Determination of zinc, lead and cadmium ions by SWASV at the poly(2 ABS).

Metal	Slope ($\mu\text{A nmol L}^{-1}$)	Intercept (μA)	Correlation coefficient (n = 6) (%)
Cd	0.067	-0.03	99.3
Pb	0.033	0.03	99.3
Zn	0.048	0.13	99.5

Detection limits for the zinc, cadmium and the lead were of 12.3, 12.0 and 10.8 nmolL⁻¹, respectively. This sensibility is comparable with that obtained using Nafion-coated thin mercury film electrode (NCMTFE) prepared under the same conditions [26]. Calibration graphs for the stripping voltammetric responses of the cadmium, lead and zinc are linear up to 10^{-6} , 0.8×10^{-7} and 1.5×10^{-7} mol L⁻¹, respectively. The precision of the results at the coated electrode was estimated from a series of six successive measurements of 1.0×10^{-7} mol L⁻¹ of cadmium, zinc and lead resulted in relative standard deviations of the peak currents of 3.1%, 2.0% and 1.7%, respectively.

The effect of surface-active organic compounds (Triton X-100, gelatin, agar and n-octanol) with concentrations ranging 1 mg L⁻¹ to 20 mg L⁻¹ on the SWAVS at the poly(2 ABS) was examined by using 2.0×10^{-7} mol L⁻¹ of cadmium as test analyte. A fresh electrode was used for each surfactant and this same electrode was used for increasing amounts of the surfactant in question. The results were compared to those obtained using MTFE. In the presence of surfactants the poly(2 ABS) behaved only slightly better than the MTFE. The poly(2 ABS) was less susceptible to peak depression than MTFE in the presence of surfactants up to 5 mg L⁻¹. For higher concentrations, it is necessary to reduce electrode contamination using the batch-injection analysis with anodic stripping voltammetry [27- 28].

Analysis of environmental samples

The suitability of the sulfonated polyaniline coated mercury film electrode for real analysis was demonstrated by using it for the determination of zinc, cadmium and lead in water samples. The results are summarized in Table 3.

Table 3. Determination of trace metals ($\mu\text{g L}^{-1}$) in water samples^a.

Analyte	Samples		
	river water	drinking water	rain water
Zn	nd	$1.2 \pm 3.7 \%$	$20.7 \pm 1.9 \%$
Cd	nd	nd	$18.1 \pm 3.6 \%$
Pb	$132.0 \pm 3.1 \%$	$5.7 \pm 2.9 \%$	$96.0 \pm 2.7 \%$

^an = 3; nd = not detected

The concentrations of Zn, Pb and Cd were lower than the Brazilian standards for drinking water. The high level of colloidal particles of Fe_2O_3 interfered with Zn and Cd signal in river water. The high concentrations of metals in rainwater are because the samples were collected in a coal-fired power plant area.

Conclusions

The electrooxidation of 2-aminobenzenesulfonic acid yielded conducting polymer films characterized voltammetrically even in the absence of aniline as a co-monomer. When aniline was used as co-monomer, the resulting films showed properties that are characteristic both for poly(aminobenzenesulfonic acid) and polyaniline. The rate of film growth increased in presence of aniline. This means that the polymerization rate depends on the slowest reaction taking place, e.g. the oxidation of the aminobenzenesulfonic acid monomer, and mirror the active part the aminobenzenesulfonic acid monomers play in the formation of the polymers.

It has been demonstrated that sulfonated polyaniline-coated mercury thin-film electrodes can be used successfully in the analysis of trace metals by square wave anodic stripping voltammetry. Of the films tested, best results were obtained with poly (2-aminobenzenesulfonic acid). The sensitivity using polymer modified electrode for the detection of metal ions was better than that observed with conventional mercury film electrode.

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Sample Availability: Available from the author.

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