

Preparation and properties of an electrode coated with a cerium poly(allyl ether *p*-benzenesulfonate) film for electroorganic reactions

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Abstract

New modified electrodes (ME) were prepared in coating carbon electrodes with cerium poly(allyl ether *p*-benzenesulfonate) that display reactivity for acetic aldehyde and benzylalcohol oxidation. Electrolysis of benzylalcohol gave benzaldehyde and benzoic acid. These electrodes have been proven to be very stable and resistant and they have the advantage to perform easily in function in the *para* position of the benzene ring that opens many possibilities for the use of ME of the ion exchange type. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Several modified electrodes (ME) coated with films of the ion-exchange type are known in literature and can be prepared by electropolymerization [1]. Electrochemical oxidation of aromatic phenols and amines produces non-conducting thin films and they can be made electroactive by subsequent incorporation of a transition metal ion. Others like vinyl substituted bipyridine and terpyridine complexes of ruthenium, osmium, iron and cobalt can be electropolymerized giving electroactive ME [2].

Polyvinylsulfonic acid and polystyrenesulfonic acid have been introduced into electrode surfaces as cation exchange films and protonated or quaternized aminopolymers were used as anion exchangers [3].

Nafion[®] is a remarkable commercially available material that can be easily applied to an electrode and can be used as an ion exchange film for the transformation of chemical compounds [4,5]. Ruthenium polypyridine complexes [6] and cerium salts [7] have already been incorporated in Nafion[®] films through ion exchange of their respective salts, leading to use-

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ful electrodes for the oxidation of organic substrates.

To continue the studies on the chemical and electrochemical properties of cerium derivatives in our laboratories [8–12], we have observed the polymerisation of phenyl allyl ethers in the chemical or electrochemical oxidation of the double allylic bond. The chemical oxidation was accomplished with either Ce^{III} nitrate or Ce^{III} methanesulfonate, which produced an amorphous brown compound identified as a substituted polyethylene. A film was electrochemically generated and it coated and electrically isolated the electrode. It is possible to suggest that electron transfer to the anode will generate a radical cation which will act as polymerisation initiator that would trigger a chain reaction in producing the polymer, as it is proposed for vinylic polymerisation [2]. The chemical and mechanical stabilities of this film were remarkable and they have led us to use it as a support for modifications that would introduce electroactivity into the coated electrode.

The presence of a phenyl group in the monomer allows its easy functionality in the *para* position. The ME produced with this film may function now as anion or cation exchanger, depending on the functional group that should be present in it.

In this work, we have used the monomer cerium allyl ether *p*-benzenesulfonate to prepare films on vitreous carbon E1 (cyclic voltammetry purpose) or reticulated carbon E2 (both voltam-

metric and preparative purposes) electrodes electrochemically. Such films are shown in Fig. 1.

These electrodes were electroactives in the oxidation of some of the organic substrates tested in this work.

2. Experimental

Most of the chemicals and solvents used were commercially available and purified when necessary. All the aqueous solutions were prepared with deionised water.

Cyclic voltammetry experiments were carried out in a cylindrical cell (10 ml) using vitreous carbon as the working electrode (3 mm diameter), saturated calomel electrode (SCE) as the reference and platinum wire as the auxiliary electrode.

The coated electrodes were either a vitreous carbon — E1 — (diameter = 3 mm) or a reticulated carbon electrode — E2 — (Electrosynthesis, model 80 PPI; surface area = 27.2 cm²). Cells of 10 or 50 ml were used for film deposition through scan or electrolysis.

Electrooxidations were carried out in a cylindrical cell (50 ml) using the film deposited on E2 as the working electrode, a platinum wire contained within a sintered glass tube as the auxiliary electrode and the reference was SCE.

The following equipment were used: a Potentiostat/Galvanostat PAR model 273A coupled to an Electrochemical Analysis software Model 270 and a Potentiostat MQPG-01 coupled to the program MGPQ.

Proton nuclear magnetic resonance (¹H NMR) spectra were obtained on a Bruker AC-80 (80 MHz) spectrometer. Infrared (IR) absorption spectra were recorded in a Perkin Elmer 1600 series FTIR spectrometer using KBr. Gas-liquid chromatography (g.l.c.) was carried out in an Intralab 3400 chromatograph containing an OV-17 column, coupled to an Intralab integrator. An ionisation flame detector was employed.

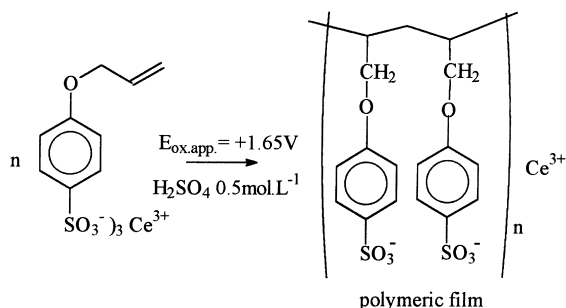


Fig. 1. Preparation of the cerium poly(allyl ether *p*-benzenesulfonate) films.

2.1. Electrochemical and chemical polymerisation of the allyl phenyl ether

By applying a +1.6 V vs. SCE potential, 0.75 mmol of cerium methanesulfonate or cerium nitrate in 30 ml of a 0.5 mol l⁻¹ of methanesulfonic or nitric acid solution were oxidised [8,10]. To this solution 1.5 mmol of allyl phenyl ether plus 26 mg of the phase transfer catalyst *N*-ketyl-*N,N,N*-trimethyl ammonium perchlorate in 10 ml of chloroform was added and a potential of +1.6 V was applied until a charge of 318 C was passed. Chloroform is necessary to avoid the coating of the electrode and its subsequent passivation. Extraction with chloroform, drying and evaporating the solvent, gave a brown amorphous solid (82 mg, 39% yield) that was identified as the correspondent polymer because the resemblance of the IR spectra but the absence of the allyl C=C double bond in 1646 cm⁻¹.

The above Ce^{IV} electrolysed solution was added dropwise to a stirring 10 ml chloroform solution of 1 mmol of allyl phenyl ether at room temperature. A brown and amorphous solid was obtained (20% yield) that shows to be the same product as in the “in cell” experiment.

2.2. Preparation of cerium allyl ether *p*-benzenesulfonate

Metallic sodium (1.61 g; 0.07 mol) was added to a round-bottomed flask containing methanol (23.5 ml), under stirring. Sodium 4-hydroxybenzenesulfonate [13] (11.7 g; 0.07 mol) was dissolved in methanol (100 ml) and such solution was added dropwise to the sodium methoxide solution. Then, allyl bromide (8.54 g; 0.07 mol) was added dropwise at room temperature and the mixture was allowed to reflux for 3 h. After cooling, the solvent was evaporated to the maximum extent possible and the quasi-solid mass was dissolved in a minimum amount of water at room temperature. When cooled to 0°C, a white solid separated and it was recrystallised from

water. 7.14 g (42.5% yield) of sodium allyl ether *p*-benzenesulfonate were obtained.

Analysis: ¹H NMR D₂O, δ (ppm) = 3.40 (4H, s)*, 4.50 (2H, d), 5.20 (1H, d), 5.40 (1H, d), 6.00 (1H, m), 6.90 (2H, d), 7.50 (2H, d). * relative to two water molecules. IR (KBr), ν (cm⁻¹) = 3066, 1646, 1138.

A concentrated aqueous solution (2.9 g; 0.012 mol) of this salt was introduced in a column containing Amberlite IR-120 resin activated with H₂SO₄ 0.01 mol l⁻¹. After water elution, the acid solution that left the column reacted with a suspension of Ce₂(CO₃)₃ · H₂O (2.0 g; 0.042 mol) in water (15 ml). CO₂ production was observed. The resulting solution was heated at 100° for 30 min, evaporated and the white solid obtained was washed with dry acetone. After this, 2.8 g (86% yield) of cerium allyl ether *p*-benzenesulfonate was obtained.

Analysis: ¹H NMR D₂O, δ (ppm) = 4.70 (4H, s)*, 4.65 (2H, d), 5.30 (1H, d), 5.40 (1H, d), 6.10 (1H, m), 7.05 (2H, d), 7.70 (2H, d). * relative to two water molecules. IR (KBr), ν (cm⁻¹) = 3060, 1650, 1051.

2.3. Preparation of the cerium poly(allyl ether *p*-benzenesulfonate)

195 mg (0.25 mmol) of the cerium allyl ether *p*-benzenesulfonate were dissolved in an H₂SO₄ solution (10 ml; 0.5 mol l⁻¹). Scans in the range of +1.0 to +2.0 V, at 50 mV s⁻¹, were carried out on E1. When the film was prepared with E2 electrode, the volume of the H₂SO₄ solution was 30 ml and the scan rate was 5 mV s⁻¹.

The same procedure was repeated for five scans in the range of +1.0 to +1.5 V, at 50 mV s⁻¹ in the case of E1 and +1.0 to +1.3 V and +1.0 to +1.65 V, at 5 mV s⁻¹ in the case of E2.

Film deposition was also done by electrolysis on E2. A constant potential of either +1.3 or +1.65 V was applied, in the same concentrations described above, until a total charge of

2 C (more than enough for film formation) had been passed through the solution.

2.4. Electroactivity concerning acetic aldehyde and benzylalcohol oxidation

Cerium poly(allyl ether *p*-benzenesulfonate) prepared with E1 was fitted into an electrolytic cell containing an H_2SO_4 solution (10 ml; 0.5 mol l^{-1}). Scans were carried out from +1.0 to +2.0 V, at 50 mV s^{-1} , by adding different volumes (0.2 to 1.0 ml) of a 0.5 mol l^{-1} acetic aldehyde or benzylalcohol in an H_2SO_4 solution 0.5 mol l^{-1} . Comparison with uncoated E1 was done by using 0.6 ml of the substrate solutions.

2.5. Use of benzylalcohol as probe

In several experiments for the preparation of the ME on E2, benzylalcohol was used as a probe to register current values for its discharge at +1.6 V, in the scans in which the experimental conditions were tested. Such registers were done at different benzylalcohol concentrations (0 to 90 mmol l^{-1}).

2.6. Benzylalcohol electrolysis

Benzylalcohol (108 mg; 1.0 mmol) was added to an H_2SO_4 solution (30 ml; 0.5 mol l^{-1}). Using cerium poly(allyl ether *p*-benzenesulfonate) deposited on E2, a potential of +1.65 V was applied until the passage of 193C (2 F mol^{-1}). Extraction with CH_2Cl_2 led to benzaldehyde (16 mg; 15.6% yield) and extraction with diethyl ether produced benzoic acid (52 mg; 42.7% yield), which were both identified by conventional methods.

3. Results and discussion

Cyclic voltammograms of cerium allyl ether *p*-benzenesulfonate were carried out up to +2.0 and +1.65 V on the vitreous carbon electrode E1 and on the reticulated carbon electrode E2, respectively. In both cases, two irreversible oxida-

tion discharges were observed: on E1, such discharges occurred at +1.68 and +1.23 V (Fig. 2), and on E2 at +1.47 and +1.23 V (Fig. 3). These discharges decreased throughout the scans until these currents fell to residual values. The discharges at higher potentials were assigned to $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ monomer oxidation and those at lower potentials to allylic oxidation. In our laboratories, we have prepared and studied cerium methanesulfonate [8–11], *p*-toluenesulfonate and *p*-metoxibenzenesulfonate [12] and we have assigned an approximately +1.7 V vs. SCE discharge as been the $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ oxidation (irreversible). The allyl phenyl ether presents a +1.35 V allyl function discharge that disappear as the film is formed [12].

One can observe in Figs. 2 and 3 that there is an increase of the current in the highest potentials at +2.0 and +1.65 V, respectively, due to the oxidation of the fixed Ce^{III} in the film (formed here by chain reaction), as Morita et al. [7] have already remarked for cerium salts incorporated in Nafion[®] films (no increase in the current was observed at +1.5 and +1.3 V). The lower cerium oxidation potential on E2 is due, probably, to the higher surface of the electrode. The electrodes became electrically isolated (Ce^{IV} is stable and cyclic voltammetry of various salts also present an irreversible oxidation discharge) [8,12] and the formation of sta-

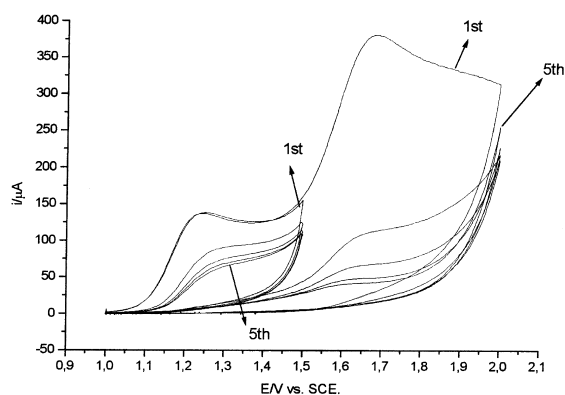


Fig. 2. Cyclic voltammograms for the film on E1. Scan intervals from +1.0 to +1.5 V and +1.0 to +2.0 V. Scan rate 25 mV s^{-1} and H_2SO_4 0.5 mol l^{-1} solution.

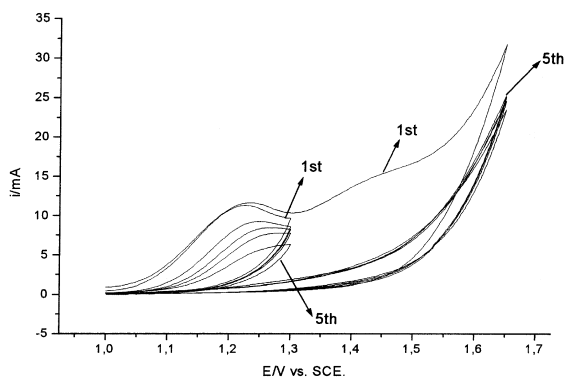


Fig. 3. Cyclic voltammograms for the film on E2. Scan intervals from +1.0 to +1.3 V and +1.0 to +1.65 V. Scan rate 5 mV s^{-1} and H_2SO_4 0.5 mol l^{-1} solution.

ble films on their surfaces could be observed. The blue colour film on E1 was resistant to mechanical and chemical handling and could only be removed when the electrode was polished with alumina. Oxidised film immobilised on E2 presented a golden colour due to the presence of Ce^{IV} and the latter was stable for at least 24 h in the solution where it had been prepared.

When scans up to +1.5 V for E1 and +1.3 V for E2 (below Ce^{III} oxidation) were carried out, films with the same characteristics and properties described above were formed. However, the decrease in the allylic function current discharge was slower than in the previous cases (Figs. 2 and 3) This phenomenon may be attributed to the fact that immobilised Ce^{IV} in the film may oxidise the allylic function of the monomer in solution as had been stated above (Section 2.1), and thus contribute to a more efficient polymer formation. This in turn isolates the electrode after fewer scans.

The activity of ME with the film immobilised on E1 was tested for two substrates: acetic aldehyde and benzylalcohol. Figs. 4 and 5 show the catalytic oxidation currents obtained for scans up to +2.0 V that correspond to $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ oxidation and its increase with substrate concentration. The cyclic voltammetry record assigned as g in these figures scanned with an uncoated E1 electrode, shows the occurring cat-

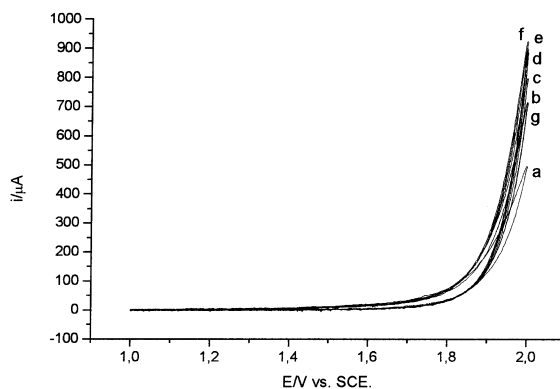


Fig. 4. Cyclic voltammograms for film on E1: (a) 0.0 ml, (b) 0.2 ml, (c) 0.4 ml, (d) 0.6 ml, (e) 0.8 ml, (f) 1.0 ml, 10% v/v acetic aldehyde solution in H_2SO_4 0.5 mol l^{-1} , at 50 mV s^{-1} . (g) 0.6 ml of the same solution carried out at uncoated E1.

alytic current for the other scans for both substrates studied.

Electric isolation of the electrode promoted by the film and the irreversible character of the cerium oxidation called for an indirect method that would allow one to follow the various experiments that were necessary to optimise the preparation of this ME. Since a remarkable Ce^{IV} catalytic current is observed for a discharge at +1.6 V for benzylalcohol oxidation when it was used the reticulated electrode E2, this substrate was chosen as a probe and its discharge currents were plotted against its concentrations.

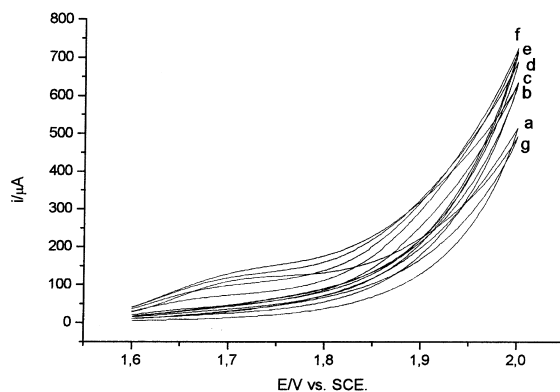


Fig. 5. Cyclic voltammograms for film on E1: (a) 0.0 ml, (b) 0.2 ml, (c) 0.4 ml, (d) 0.6 ml, (e) 0.8 ml, (f) 1.0 ml, 10% v/v benzylalcohol solution in H_2SO_4 0.5 mol l^{-1} at 50 mV s^{-1} . (g) 0.6 ml of the same solution carried out at uncoated E1.

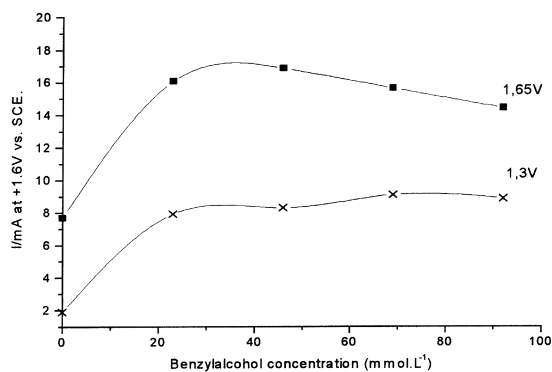


Fig. 6. Benzylalcohol current oxidation for films on E2 coated with scan intervals from +1.0 to +1.3 V and +1.0 to +1.65 V. Scan rate 5 mV s^{-1} and H_2SO_4 0.5 mol l^{-1} solution.

The higher values of these currents reflect the better efficiencies of the electrodes prepared under different experimental conditions where number of cycles, scan rates, concentration of monomer, scan intervals and film deposition through electrolysis were tested. The experimental conditions described for the preparation of the ME were the ideal ones and were estimated by this indirect method.

Fig. 6 shows the discharges for benzylalcohol as a probe, using films immobilised on E2. The latter were prepared through scans up to +1.3 V (allylic oxidation) and +1.65 V (Ce^{III} film oxidation). Here it was possible to see again that immobilised Ce^{IV} may oxidise the allylic function in solution, as had been stated above. The oxidation current at +1.65 V is twice bigger than that at +1.3 V, probably due to a greater number of active centres and, thus, higher electrochemical efficiency. When the film was formed by constant potential application, the same result was obtained. It has given an oxidation current at +1.65 V. This was 35% bigger than that at +1.3 V. By comparing the two procedures, it can be seen on the other side that the scan method is more efficient than the constant potential application.

This ME was used for benzylic alcohol electrolysis and led to the production of benzoic aldehyde and benzoic acid, with predominance of the latter.

4. Conclusions

It is possible to demonstrate that the preparation of ME with cerium poly(allyl ether *p*-benzenesulfonate) films leads to an electroactive electrode for some organic substrates oxidation. The easy functionality in the *para* position of the benzene ring opens many possibilities for the use of these ME of the ion exchange type, which has been proven to be very stable and resistant.

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