

Electrodeposition of ruthenium N-pyrrole bipyridine films on carbon felt electrodes and application as catalysts in alcohol electrooxidation

Eletrodeposição de filmes N-pirrolbipiridínicos de rutênio em eletrodos de feltro de carbono e aplicação como catalisadores em eletrooxidações de álcoois

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Abstract

Research aimed at the use of sustainable technologies based on Green Chemistry principles is expanding in academic and industrial circles. The catalytic electrooxidation of alcohols is a crucial element in research on energy generation. In order to explore a selective catalytic system in a less environmentally aggressive chemical process, ruthenium N-pyrrole bipyridine poly-cis-[Ru(L)₂(OH₂)₂]²⁺ films (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) were prepared on carbon felt electrodes, through the anodic electropolymerization of cis-[Ru(L)₂Cl₂] monomer and subsequent electrochemical induction to the aqua complex. These carbon felt electrodes modified by deposition of these films were used as electrocatalysts in alcohol oxidation reactions at a constant potential of +1.15 V (vs SCE), in an aqueous medium at pH 6.8 and 8.1. The alcohols and their oxidation products were benzyl alcohol (benzaldehyde), cyclohexanol (cyclohexanone), 1-phenylethanol (acetophenone) and p-methoxybenzyl alcohol (p-methoxybenzaldehyde). The reactions took place with total selectivity of the products and provided satisfactory yields.

Keywords: Modified electrodes; Electrooxidation; Polypyrrole films; Ruthenium.

Resumo

Pesquisas visando o emprego de tecnologias sustentáveis alinhadas com os princípios da Química Verde estão sendo cada vez mais conduzidas nos meios acadêmicos e industriais. As eletrooxidações catalíticas de álcoois são processos importantes devido sua relação com pesquisas em geração de energia. Com o objetivo de explorar um sistema catalítico seletivo num processo químico menos agressivo ao meio ambiente, foram preparados filmes N-pirrolbipiridínicos de rutênio poli-cis-[Ru(L)₂(OH₂)₂]²⁺ (L=4-metil-4'-pirrol-1-il-butyl-2,2'-bipiridina), em eletrodos de feltro de carbono, por eletropolimerização

anódica do monômero cis-[Ru(L)₂Cl₂] e posterior indução eletroquímica ao aquacomplexo. Esses eletrodos de feltro de carbono modificados por deposição desses filmes foram utilizados como electrocatalisadores em oxidações de álcoois, a potencial constante de +1,15 V (vs ECS), em meio aquoso nos pHs 6,8 e 8,1. Os álcoois utilizados e seus produtos de oxidação foram: álcool benzílico (benzaldeído), cicloexanol (cicloexanona), 1-feniletanol (acetofenona) e álcool p-metoxibenzílico (p-metoxibenzaldeído). As reações ocorreram com total seletividade na obtenção dos produtos, com rendimentos satisfatórios.

Palavras-chave: Eletrodos modificados; Eletroxidação; Filmes polipirrólicos; Rutênio.

Introduction

Reports about the first investigations on electrodes with modified surfaces began to appear in the scientific literature about five decades ago [1]. Some authors consider that Moses et al. [2] were the first researchers to use the term “modified electrode” in the field of science. A chemically modified electrode takes on important characteristics of a conductor or semi-conductor, and it can be coated with a polymeric, ionic, monomolecular or multimolecular film [3]. Among the numerous possible applications of modified electrodes, their use as electrocatalysts in different reactions is especially attractive, particularly in the chemical industry [4-6]. This is due to their greater selectivity, efficiency, sensitivity and chemical and electrochemical stability compared to other oxidation methods [3,7-9], and because they involve processes that are in line with some of the principles of Green Chemistry [10,11].

Bipyridines and their superior derivatives have attracted the interest of chemists for the preparation of ruthenium complexes [12]. These ligands offer an interesting binding pattern, mainly due to their predictability in coordinating with a metal [13]. 2,2'-bipyridine is the first member of a series of superior oligopyridines. This 131-year-old ligand, whose synthetic preparation is usually simple, is undoubtedly the most common one in coordination chemistry. Its basic skeleton is simple; however, highly complex structural changes have been made [14,15]. Many reports in the literature highlight the stability of ruthenium complexes containing bipyridine ligands, whose stability surpasses even that exhibited by complexes linked to pyridine groups [16].

Recent advances in the preparation of modified electrodes containing different ruthenium complexes and employed as electrocatalysts in several types of electrodes have been reported in the literature [17]. A case in point are carbon-based electrodes, which are widely used, partly because they are inexpensive, and some are made up of pores. Such is the case of the carbon felt electrodes used in this work, which provide greater contact surface, thereby increasing the amount of metallic complex deposited and enhancing the efficiency of the electron transfer process [18].

Prepared films containing ligands replaced by pyrrole groups have shown conduction characteristics without loss of stability [19]. Although several chemical groups can undergo polymer

electrodeposition, the pyrrole group stands out for the modification of electrode surfaces by not passivating them, especially when the pyrrole group (or substituted pyrrole) is coordinated with a transition metal [20]. Synthetic preparations of N-substituted pyrroles usually involve simpler steps than preparations of substituted pyrroles in positions 2 or 3. The combination of N-substituted pyrroles bound to 2,2'-bipyridines thus appears as an excellent alternative for the preparation of ruthenium complexes and their incorporation into electrodes.

Thus, seeking to combine the oxidizing properties of ruthenium pyrrole bipyridine aqua/oxo complex systems with the advantages offered by the modified electrodes, we prepared poly-cis-[Ru(L)₂(OH₂)₂]²⁺ (*L*=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) films (Figure 1) on carbon felt electrodes for application as possible electrocatalysts in aqueous-phase alcohol oxidation reactions.

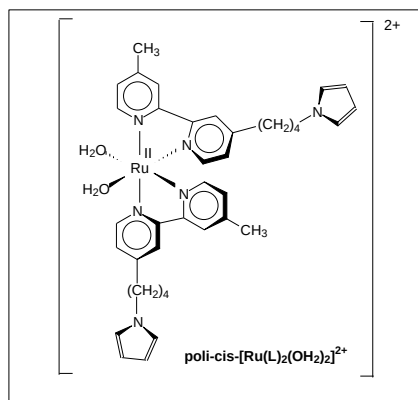


Figure 1: Chemical structure of ruthenium N-pyrrole bipyridine poly-cis-[Ru(L)₂(OH₂)₂]²⁺ films (*L*=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine).

Experimental

Materials and reagents

Bi-distilled water was prepared by treating distilled water with an alkaline solution of potassium permanganate (KMnO₄) and then distilling it [21]. Diethyl ether was predistilled in sulfuric acid in order to remove impurities [21]. Dichloromethane was dried on an aluminum trioxide column (Al₂O₃) for the cyclic voltammetry experiments. All the other reagents and solvents, from Merck, Aldrich, Mallinckrodt and Sigma, were used in their commercial p.a. grade without further purification. Solutions were prepared with pH levels of 6.8 and 8.1, using a mixture of NaH₂PO₄/Na₂HPO₄·H₂O salts, with ionic strength of 0.25 mol.L⁻¹ (phosphate buffers), in a solution of 70:30 mL of bidistilled water: t-butanol. The aforementioned pH levels of the phosphate buffer: t-butanol solutions were determined by reading a

pH meter and are therefore apparent pH values. Tetrabutylammonium perchlorate (Bu_4NClO_4) was prepared from tetrabutylammonium bromide, following a procedure described in the literature [22].

Preparation of modified electrodes and equipment

Carbon felt electrodes modified with the diaqua poly-cis- $[\text{Ru}(\text{L})_2(\text{OH}_2)_2]^{2+}$ ($\text{L}=4\text{-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine}$) complex were prepared in an EG&G Princeton Applied Research 273A potentiostat/galvanostat coupled to a Houston Instruments XY 100 recorder, in an electrochemical cell containing saturated calomel electrode as reference and two platinum plates (1.00 cm^2 area, 0.20 cm thickness) as an auxiliary electrode, placed on either side of the working electrode. Carbon felts with an area of 1.00 cm^2 ($1.00\text{ cm} \times 1.00\text{ cm}$) and 0.40 cm thickness were used, making 35 successive electropolymerization sweeps.

Electrooxidation experiments were carried out at atmospheric temperature and pressure, in a FAC-200 A potentiostat/galvanostat coupled to an Intralab current data logger. A two-compartment electrochemical cell was used, containing saturated calomel as the reference electrode and a platinum plate (1.00 cm^2 area, 0.20 cm thickness) as the auxiliary electrode inside a sintered glass tube. Carbon felt modified with the electrodeposited poly-cis- $[\text{Ru}(\text{L})_2(\text{OH}_2)_2]^{2+}$ complex was used as the working electrode.

The films were analyzed by gas chromatography with flame ionization detector (GC-FID) in a Varian 3400 gas chromatograph, using OV-17 W-HP (3% in Chromosorb W, 80-100 mesh) and Carbowax 20M (10% in Chromosorb W, 80-100 mesh), metal packed columns, both 2.00 m long and 3.00 mm in diameter, and the values obtained were compared with commercially obtained standards.

General electrooxidation method

A single carbon felt electrode modified with the poly-cis- $[\text{Ru}(\text{L})_2(\text{OH}_2)_2]^{2+}$ complex was used as the working electrode in each electrooxidation experiment. Before each oxidation, the prepared electrode was kept immersed for one night in an aqueous solution of 0.10 mol.L^{-1} trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$), without stirring, at room temperature. The stability of each prepared electrode was examined by cyclic voltammetry before and after each experiment, also in an acidic environment. It was found that the films did not lose their characteristics after use, and were thus reusable for other investigations, including electrocatalytic studies.

Fifty mmol.L^{-1} of each alcohol substrate was used In each electrooxidation reaction. The applied potential was $+1.15\text{ V}$ vs SCE, a potential that is close to or above where ruthenium is presumably in its

highest oxidation state. Initially, the modified electrode charge was measured, while cycling at 0.05 V.s^{-1} between 0.00 and +1.00 V in an oxidation cycle, in an aqueous solution of $0.10 \text{ mol.L}^{-1} \text{ CF}_3\text{SO}_3\text{H}$. The substrate was then added while the solution was stirred and a given number of Coulombs were allowed to pass through, represented in Tables 1 and 2 as a percentage of charge. At the end of each electrooxidation, the electrode charge was measured, as mentioned earlier for the initial charge.

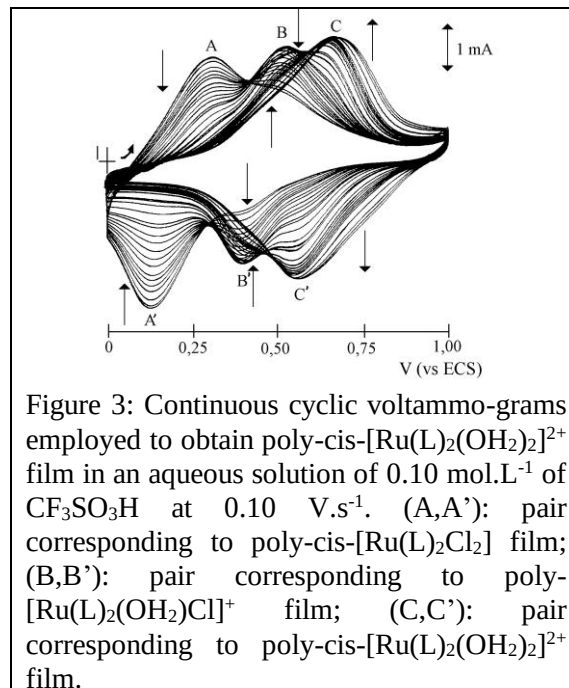
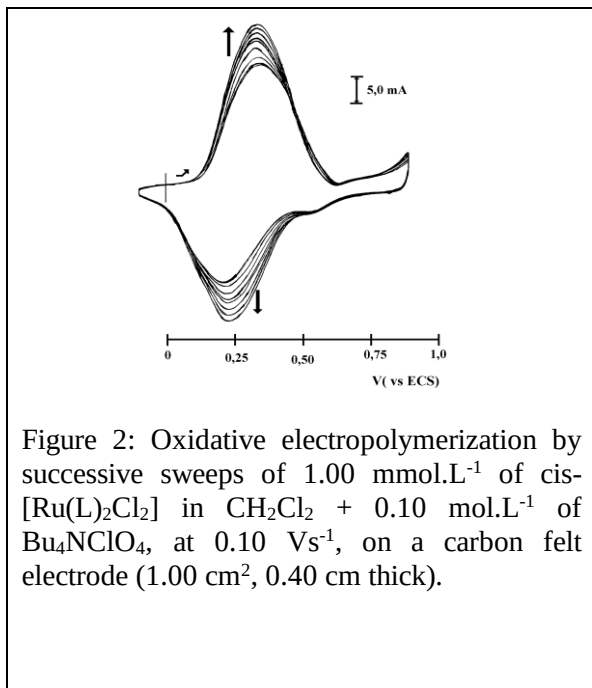
The organic phase extraction procedure was repeated five times using portions of 5 mL of diethyl ether, and the resulting ether extracts were combined and dried with MgSO_4 . The extractions of the products of electrolysis of cyclohexanol and 1-phenylethanol were carried out in the same reaction medium as the experiments, while the extractions of the products of electrolysis of benzyl alcohol and p-methoxybenzyl alcohol were first carried out at a pH level of about 10 (by adding a solution of 1.00 mol.L^{-1} of NaOH). Using fuming hydrochloric acid, the remaining aqueous phases were then acidified to a pH of around 2.0 to investigate the possible presence of benzoic acid and p-methoxybenzoic acid in the process.

After the solvent evaporated, the reaction yield was calculated by means of gas chromatography, using a known amount of cyclohexanol as an internal standard for all the electrolysis, except for that of cyclohexanol, for which benzyl alcohol was used. An OV-17 W-HP column was used to determine the products of electrolysis of benzyl alcohol and cyclohexanol, while a Carbowax 20M column was used to determine the products of electrolysis of 1-phenylethanol and p-methoxybenzyl alcohol.

Results and Discussion

Preparation of diaqua poly-cis-[Ru(L)₂(OH₂)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine):

The cis-[Ru(L)₂Cl₂] (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) complex, whose synthesis is described in the literature [23], was supplied by the Laboratoire d'Electrochimie Organique et Photochimie Rédox, Université Joseph Fourier in Grenoble, France. Starting from this dichloro complex, the cis-[Ru(L)₂Cl₂] film was initially produced on a carbon felt electrode by anodic electropolymerization in CH_2Cl_2 [23], by cycling between -0.15 and +0.90 V under an atmosphere of N_2 ($E_{1/2} = +0.30 \text{ V}$, corresponding to the $\text{Ru}^{\text{III/II}}$ pair) (Figure 2). The film showed continuous growth on the electrode. To obtain the desired diaqua poly-cis-[Ru(L)₂(OH₂)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) film (C,C' pair, $E_{1/2} = +0.65 \text{ V}$, corresponding to the $\text{Ru}^{\text{III/II}}$ pair), the electrode previously prepared with the dichloro complex was subjected to cycling between 0.00 and +1.00 V for 6 hours in an aqueous solution of 0.10 mol.L^{-1} of $\text{CF}_3\text{SO}_3\text{H}$, passing through the formation of poly-[Ru(L)₂(OH₂)Cl]⁺ film (B,B' pair, $E_{1/2} = +0.45 \text{ V}$, corresponding to the $\text{Ru}^{\text{III/II}}$ pair) (Figure 3).



Qualitative investigation into the catalytic activity of diaqua poly-cis-[Ru(L)₂(OH₂)₂]²⁺ films (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) film:

A qualitative assessment was made of the catalytic activity of the diaqua poly-cis-[Ru(L)₂(OH₂)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) film against the cyclohexanol substrate in a cyclic voltammetry experiment (Figure 4). The oxidation current showed a substantial increase, starting at around +1.00 V. Compared to studies involving homogeneous phase with an analogous complex, cis-[Ru(bpy)₂(OH₂)₂]²⁺ [24], at this potential it is assumed that high metal oxidation states are achieved in the electrodeposited complex (Ru^V or Ru^{VI}), generating the oxo complex responsible for oxidation of the substrate [25-27].

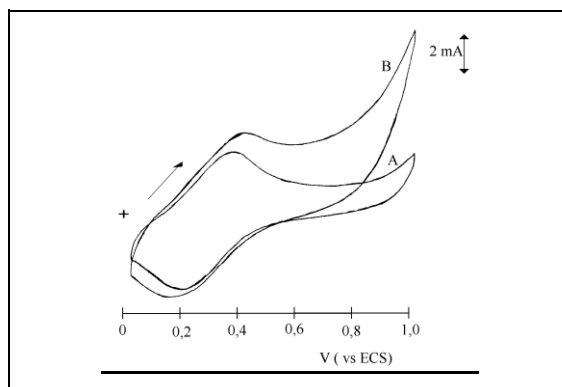


Figure 4: Cyclic voltammograms providing qualitative information about the catalytic activity of a modified carbon felt electrode, poly-cis-[Ru(L)₂(OH₂)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) film.

bipyridine) in phosphate buffer at pH 6.8: (A) in the absence, and (B) in the presence of 50.00 mmol.L⁻¹ of cyclohexanol.

Alcohol electrooxidation reactions using diaqua poly-cis-[Ru(L)₂(OH)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) films

Tables 1 and 2 contain data pertaining to the electrooxidation experiments of the four alcohols, carried out at pH 6.8 and 8.1, respectively, under catalysis of the modified poly-cis-[Ru(L)₂(OH)₂]²⁺ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) carbon felt electrodes.

Table 1: Alcohol electrooxidation reactions in phosphate buffer solution, pH 6.8, using as electrocatalyst a carbon felt electrode (1.00 cm², 0.40 cm thick) modified by the cis-[Ru(L)₂(OH)₂](PF₆)₂ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) complex.

Alcohols	I _i / I _f (mA)	Time (h)	% Charge passed ¹	Product	Yield (%) ²
benzyl alcohol	10/0.8	20.5	35.5	benzaldehyde	45
p-methoxybenzyl alcohol	9/0.7	16.0	21.0	p-methoxybenzaldehyde	50
cyclohexanol	6/2.2	19.5	55.7	cyclohexanone	57
1-phenylethanol	12/0.8	45.0	30.1	acetophenone	62

¹ Percentage of Coulombs for a process involving two electrons.

² Yield calculated based on the number of Coulombs passed through (electrical yield).

Table 2: Alcohol electrooxidation reactions in phosphate buffer solution, pH 8.1, using as electrocatalyst a carbon felt electrode (1.00 cm², 0.40 cm thick) modified by the cis-[Ru(L)₂(OH)₂](PF₆)₂ (L=4-methyl-4'-pyrrole-1-il-butyl-2,2'-bipyridine) complex.

Alcohols	I _i / I _f (mA)	Time (h)	% Charge passed ¹	Product	Yield (%) ²
benzyl alcohol	16/0.9	16.0	24.5	benzaldehyde	28
p-methoxybenzyl alcohol	7/0.7	18.5	41.4	p-methoxybenzaldehyde	60
cyclohexanol	9/2.3	16.0	63.2	cyclohexanone	53
1-phenylethanol	9/0.8	22.0	33.0	acetophenone	66

¹ Percentage of Coulombs for a process involving two electrons.

² Yield calculated based on the number of Coulombs passed through (electrical yield).

The products of all the experiments described in Tables 1 and 2 were formed selectively, with the electrooxidation of the primary alcohols benzyl and p-methoxybenzyl into their respective aldehydes, and complete absence of carboxylic acid products. The secondary alcohols cyclohexanol and 1-phenylethanol were transformed into their respective ketones.

The electrooxidation reactions analyzed in this study produced moderate to fairly high yields. In previous studies, the electrooxidation of secondary alcohols with other aqua complexes of ruthenium in a homogeneous aqueous medium have produced low yields [28], unlike the yields obtained in this work using a heterogeneous aqueous phase. Therefore, it was found that the heterogeneous catalytic system involving the effective transfer of two electrons ensures this selectivity, which is why this type of process is in high demand in the chemical industry and important in synthetic chemistry [29-31].

Conclusions

One of the advantages of immobilizing $\text{cis-}[\text{Ru}(\text{L})_2(\text{OH}_2)_2]^{2+}$ complexes on carbon electrodes was the stability the polymeric films exhibited even after successive potential scans, without ligand loss. This has been observed in some cases in homogeneous aqueous phase with the $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ complex, with loss of bipyridine ligand [24], as well as in ruthenium oxo complexes [32,33]. Another advantage is that this method of confining and concentrating these catalysts in the vicinity of the electron source requires considerably smaller amounts of catalyst than that required for electrocatalysis in a homogeneous medium.

In all the electrooxidation experiments carried out with films, selectivity was a constant in the different organic reactions, leading to a single product. This finding underscores the importance of these mediators incorporated in electrodes when they are used as electrocatalysts in the transformation of organic substances in an electrochemical process in line with some of the principles of Green Chemistry.

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