Article

Electrochemical Behavior of Ruthenium-Hexacyanoferrate Modified Glassy Carbon Electrode and Catalytic Activity towards Ethanol Electrooxidation

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Eletrodo de carbono vítreo quimicamente modificado por filme fino de hexacianoferrato de rutênio (RuHCF) foi preparado pelo método da evaporação da gota. O eletrodo modificado RuHCF exibiu quatro processos redox em meio ácido forte (pH 1,5) atribuídos ao íon $Fe(CN)_6^{3-}$ e três formas de rutênio (Ru(II), Ru(III) e Ru(IV)), características do óxido de rutênio. O eletrodo modificado mostrou excelente atividade eletrocatalítica para oxidação de etanol na região de potenciais onde os processos eletroquímicos Ru(III)−O−Ru(IV) e Ru(IV)−O−Ru(VI) ocorrem. Dados de espectroscopia de impedância mostraram que a resistência de transferência de carga diminui com o aumento do potencial aplicado e da concentração de etanol, indicando o uso do eletrodo modificado RuHCF como sensor para etanol. Em condições otimizadas, este sensor respondeu linearmente e rapidamente para etanol na faixa de concentração entre 0,03 e 0,4 mol L^{-1} com um limite de detecção de 0,76 mmol L^{-1}, indicando uma sensibilidade adequada em análises de etanol.

Ruthenium-based hexacyanoferrate (RuHCF) thin film modified glassy carbon electrode was prepared by drop evaporation method. The RuHCF modified electrode exhibited four redox couples in strong acidic solution (pH 1.5) attributed to $Fe(CN)_6^{3-}$ ion and three ruthenium forms (Ru(II), Ru(III) and Ru(IV)), characteristic of ruthenium oxide compounds. The modified electrode displayed excellent electrocatalytic activity towards ethanol oxidation in the potential region where electrochemical processes Ru(III)−O−Ru(IV) and Ru(IV)−O−Ru(VI) occur. Impedance spectroscopy data indicated that the charge transfer resistance decreased with the increase of the applied potential and ethanol concentration, indicating the use of the RuHCF modified electrode as an ethanol sensor. Under optimized conditions, the sensor responded linearly and rapidly to ethanol concentration between 0.03 and 0.4 mol L^{-1} with a limit of detection of 0.76 mmol L^{-1}, suggesting an adequate sensitivity in ethanol analyses.

Keywords: ethanol sensor, ruthenium-hexacyanoferrate, cyclic voltammetry, chronoamperometry, electrochemical impedance

Introduction

The surface modification using different mediators for electrocatalytic oxidation of small organic molecules such as ethanol has been reported.[1-4] The modification with insoluble films of transition metal cyanide with general formula $M(I)_n[M(II)(CN)_6]_m$, where M(I) and M(II) are different transition metal ions, has attracted special attention because of their versatile oxidation states.[5,6] These compounds are mixed-valence complexes with a well-defined structure and stable electrochemical response.[7] Usually, these compounds are incorporated on the electrode surface to catalyze the electrooxication of several electroactive compounds[8-14] and to reduce their electrooxidation overpotential.[15,16] Among these compounds, ruthenium hexacyonate is of great importance.[17-20] The ruthenium hexacyanoferrate films can be deposited directly on the electrode surface by repetitive cyclic

voltammetry (several cycles in a given potential range) in aqueous solution containing Ru^{3+} ions and $Fe(CN)_6^{3-}$.[9] In the present work, glassy carbon electrode was modified with a thin film of ruthenium-based hexacyanoferrate (RuHCF) by a dripping method. Its catalytic activity towards ethanol oxidation was studied by cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS).

Experimental

Reagents and solutions

All reagents were of analytical grade purity and used without further purification. All solutions were prepared using deionized (DI) water (resistance ≥ 18 MΩ cm), purified through a Milli-Q system (Millipore Inc., USA).

Electrodes and electrochemical cell

All the experiments were carried out in a conventional three-electrode electrochemical cell. A glassy carbon (GC) disk electrode (A_{geom} = 0.065 cm^2), Ag|AgCl|KCl$_{sat}$ and a platinum wire were used as working, reference and auxiliary electrodes, respectively, and 0.1 mol L^{-1} Britton-Robinson buffer solution[21] at pH 1.5 was used as supporting electrolyte.

Electrode preparation

The glassy carbon electrode surface was polished with 1.0 and 0.1 μm α-alumina suspensions on a microcloth polishing pad, rinsed with DI water and sonicated for a few minutes in DI water to remove traces of alumina particles. Then, 20 μL of 0.1 mol L^{-1} Britton-Robinson buffer solution at pH 1.5 containing 1.0 mmol L^{-1} [Fe(CN)$_6$]$^{3-}$ and 1.0 mmol L^{-1} RuCl$_3$ were added on the electrode surface. The solution was evaporated at room temperature under vacuum (1.3 × 10^{-5} Pa). After that, 10 μL of Nafion solution were added to the surface of Ru-Fe(CN) modified glassy carbon electrode by the drop evaporation method.

This modification method is similar to that usually used in fuel cell catalyst evaluation. The modified electrode was then subjected to electrochemical and electrocatalytic oxidation of ethanol.

Cyclic voltammetry and chronoamperometry measurements

Cyclic voltammetric measurements were performed using an electrochemical analyzer BAS CV-50W in a potential range between –0.4 and +1.2 V against an Ag|AgCl|KCl$_{sat}$ reference electrode, at a scan rate (ν) of 0.1 V s^{-1}. The chronoamperometric measurements were carried out at +0.9 V *vs.* Ag|AgCl|KCl$_{sat}$.

EIS measurements

For impedance measurements, a potentiostat/galvanostat (Autolab PGSTAT 30) with frequency response analysis system software (FRA2 modules) was used. For all modified electrodes, the impedance spectra were recorded in 0.1 mol L^{-1} Britton-Robinson buffer solution at pH 1.5. EIS measurements were performed by applying sine wave with amplitude of 10 mV rms in the 100 kHz-10 mHz frequency range at different potentials *vs.* Ag|AgCl|KCl$_{sat}$.

Results and Discussion

Electrochemical behavior of the modified electrode

The successful modification of the glassy carbon electrode surface with RuHCF was evidenced by the cyclic voltammogram, as shown in Figure 1. No electrochemical process is observed on the bare electrode surface (Figure 1 curve a), and for the RuHCF modified electrode, four pairs of anodic and cathodic peaks were well defined in the potential range of −0.4 to 1.2 V (Figure 1, curve b). These peaks with formal potentials of −0.08, 0.53, 0.86 and 1.01 V are marked as I, II, III and IV, respectively.
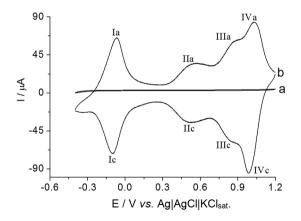

Figure 1. Cyclic voltammograms obtained at a (a) bare glassy carbon electrode and (b) glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate in 0.1 mol L^{-1} of Britton-Robinson buffer solution at pH 1.5, ν = 0.1 V s^{-1}.

According to the literature,[8,12,14] these peaks are assigned to the following redox processes: peak I at −0.08 V corresponds to Ru(II)O/Ru(III)O, formed in the RuHCF. Peak II at 0.53 V is assigned to the Fe(CN)$_6^{3-/4-}$ redox reaction from the ferrocyanide immobilized in the RuHCF complex.[11,22] Peaks III and IV at 0.86 and 1.01 V are attributed

to the electrochemical processes Ru(III)–O–Ru(IV) and Ru(IV)–O–Ru(VI), respectively. Cataldi *et al.*[22] characterized the ruthenium-containing cyanometallate film modified on a glassy carbon electrode by X-ray photoelectron spectroscopy (XPS) and found clear evidence demonstrating the existence of two oxidation states of ruthenium (Ru 3d region) attributed to oxo-ruthenium(IV) and dioxo-ruthenium(VI) in the framework of the RuHCF.

Figure 2 shows the effect of the scan rate on the electrochemical behavior of the RuHCF thin film. The anodic and cathodic peak currents of peak I, attributed to the Ru(II)O/Ru(III)O redox reaction, exhibited a linear relationship with scan rate in range of 0.01-0.1 V s⁻¹ (inset in Figure 2), which is expected for a surface-confined redox process. The peak separation increased with the increase of the scan rate. At 0.01 V s⁻¹, the peak separation was 5 mV, and at 0.08 V s⁻¹, it was 25 mV. However, this separation did not exceed 28 mV even at a scan rate of 0.1 V s⁻¹. This behavior indicates that the electron transfer in the RuHCF film is very fast.[23] As the scan rate increased, the anodic peak slightly shifted to a more positive direction and the cathodic peak moved towards a more negative direction, increasing the peak separation. The plot of ΔE_{peak} ($E_{anodic\ peak} - E_{cathodic\ peak}$) *vs.* ln ν showed a linear relationship with a slope of 10 (figure not shown). This also suggests that the Ru(II)O/Ru(III)O redox reaction rate is fast. One-electron reaction with a small ΔE_{peak} *vs.* ln ν slope indicates a fast electrochemical reaction.[22]
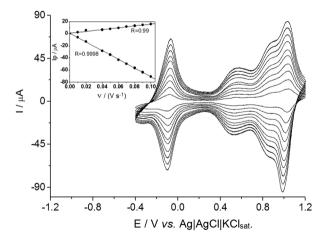

Figure 2. Cyclic voltammograms obtained at a glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate at different scan rates (0.01 to 0.1 V s⁻¹) in aqueous solution containing 0.1 mol L⁻¹ of Britton-Robinson buffer solution at pH 1.5. Inset figure: plot of anodic and cathodic peak currents *vs.* scan rate.

The Faradic charge involved in this process is determined by integrating the anodic peak and the value was found to be 29.5 μC. The surface coverage (Γ) is obtained according to the following equation:[23]

$$\Gamma = \frac{Q}{nFA} \tag{1}$$

where Q is the charge under the first oxidation wave (peak I), A is the electrode surface geometric area (0.065 cm²) and n is the number of electrons transferred during the redox reaction (one electron). The surface coverage was estimated to be 4.7×10^{-9} mol cm⁻², suggesting the adsorption of one monolayer on the electrode surface.

The effect of the pH value on the electrochemical behavior of the RuHCF thin film was studied by cyclic voltammetry at pH range of 1.5 to 7.0, as shown in Figure 3. For all the 4 peaks, as pH value increased, the peak currents decreased, while the peak potential shifted to negative values, especially for peaks II, III and IV. Also, the shape of the peaks changed as the pH value increased. This behavior suggests that the film is only stable in strong acid solution (pH 1.5). It has been reported that the RuHCF film could not be produced in alkaline solution because it decomposes.[20] The plot of the formal potential of peak IV (E°') (redox process Ru(IV)–O–Ru(VI)) *vs.* pH value (inset in Figure 3) gave a linear relationship with a slope of –73.1 mV pH⁻¹, indicating fractional values of e⁻ and H⁺ (or OH⁻) involved in the redox process.[24,25] Similar phenomenon was observed for the Ru⁴⁺/⁶⁺ redox transitions in a ruthenium oxide paste electrode.[25,26]
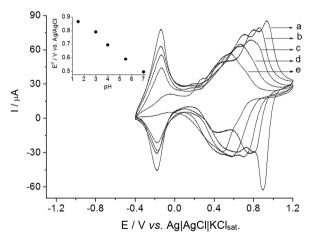

Figure 3. Cyclic voltammograms obtained at a glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate at different pH values of 0.1 mol L⁻¹ Britton-Robinson buffer solution: (a) 1.5, (b) 3.0, (c) 4.0, (d) 5.5 and (e) 7.0, ν = 0.1 V s⁻¹. Inset figure: plot of E°' *vs.* pH.

Electrocatalytic activity of the RuHCF modified electrode towards ethanol oxidation

Figure 4 shows CVs obtained at the bare glassy carbon electrode and at the RuHCF modified GC electrode in the absence or presence of ethanol at pH 1.5. No observable

electrocatalytic activity towards ethanol oxidation was noticed on the bare GC electrode when it was cycled in Britton-Robinson buffer electrolyte containing 0.1 mol L^{-1} ethanol (Figure 4, curve a). However, a significant oxidation process was observed on the RuHCF modified electrode (Figure 4, curve c). For comparison, the CV curves of RuHCF modified electrode in blank electrolyte were also shown (Figure 4, curve b). The oxidation of ethanol started at 0.8 V *vs.* Ag|AgCl|KCl$_{sat}$. The anodic current was considerably enhanced while the cathodic current decreased. This behavior is consistent with a very strong electrocatalytic process.
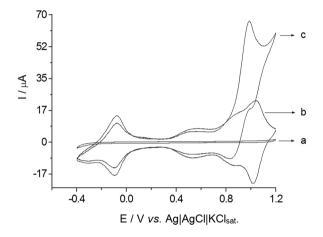

Figure 4. Cyclic voltammograms obtained at the bare glassy carbon electrode in the presence of ethanol (a), and at glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate in Britton-Robinson buffer solution at pH 1.5 (b) in the absence and (c) presence of 0.1 mol L^{-1} ethanol, ν = 0.02 V s^{-1}.

The ethanol oxidation potential lied exactly in the region where electrochemical processes of the Ru(III)−O−Ru(IV) and Ru(IV)−O−Ru(VI) occur, indicating that ruthenium metallic centers are responsible for the electrocatalytic effect, as observed in previous works.[17,19]

Figure 5 shows cyclic voltammograms of the RuHCF modified electrode in Britton-Robinson buffer solution at pH 1.5 containing 0.1 mol L^{-1} ethanol at different potential scan rates. The anodic peak potential for ethanol oxidation slightly shifted to positive direction with the increase of the scan rate. As shown in the inset in Figure 5, the plot of the anodic peak current *vs.* the square root of the scan rate was linear between 0.04 and 0.15 V s^{-1} with an equation of I$_{pa}$ (μA) = (1.67 ± 1.48) + (198 ± 3.68) $\nu^{1/2}$ (V s^{-1})$^{1/2}$ (r = 0.998), expected for a diffusion-controlled reaction.[24]

Table 1 summarized the effect of the scan rate on the anodic peak current for the electrocatalytic oxidation of ethanol between 40 and 500 mV s^{-1}. The current function I$_{pa}$ $\nu^{-1/2}$ almost did not change with the scan rate,
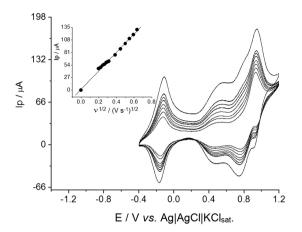

Figure 5. Cyclic voltammograms obtained at a glassy carbon electrode modified with a thin film of ruthenium-based hexacyanoferrate in Britton-Robinson buffer solution at pH 1.5 in the presence of 0.1 mol L^{-1} ethanol at different scan rates (0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1 and 0.15 V s^{-1}). Inset figure: plot of I$_{pa}$ *vs.* $\nu^{1/2}$.

Table 1. Dependence of the electrocatalytic anodic peak current and the current function (I$_{pa}$ $\nu^{-1/2}$) on the scan rate for ethanol oxidation

ν / (mV s^{-1})	I$_{pa}$ / μA	I$_{pa}$ $\nu^{-1/2}$ / (μA mV$^{-1/2}$ s$^{1/2}$)
40	46.43	7.34
50	49.28	6.97
60	53.26	6.88
70	55.62	6.65
80	58.82	6.58
90	60.38	6.36
100	61.80	6.18
150	75.34	6.15
200	88.18	6.24
300	110.20	6.36
500	149.60	6.69

corroborating with an anodic peak current controlled by ethanol diffusion to the electrode surface.

EIS technique is a powerful tool to investigate charge transport processes of chemically modified electrodes. It provides information on the impedance of the electrode surface/electrolyte interface during an electrochemical process.[27,28] Figure 6 shows Nyquist plots (imaginary impedance *vs.* real impedance) for the RuHCF film catalyzed ethanol electrooxidation between 0.82-0.98 V *vs.* Ag|AgCl|KCl$_{sat}$. All the impedance spectra showed a depressed semicircle, which is related to ethanol oxidation reaction on the electrode surface. The diameter of the semicircle represents the charge transfer resistance (R$_{ct}$).[29] The inset in Figure 6 shows EIS curve of the RuHCF modified glassy carbon electrode in blank electrolyte, in which only the diffusion type impedance was observed. It is known that the magnitude of R$_{ct}$ is related to the ethanol electrocatalytic oxidation kinetics.[27] R$_{ct}$ decreased with the

increase of the potential because the reaction kinetics was significantly improved at higher potentials. This is in good agreement with the voltammetric results (Figure 4, curve c), in which the maximum anodic current peak occurred around 0.98 V *vs.* Ag|AgCl|KCl$_{sat}$.
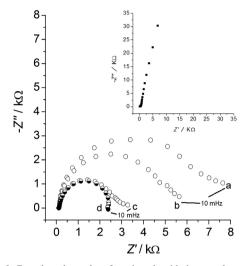

Figure 6. Complex-plane plots for ethanol oxidation on glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate in Britton-Robinson buffer solution at pH 1.5 in the presence of 1.0 mol L^{-1} ethanol at different applied potential: (a) 0.82, (b) 0.84, (c) 0.88 and (d) 0.98 V *vs.* Ag|AgCl|KCl$_{sat}$. Inset figure: signal for modified electrode in supporting electrolyte in the absence of ethanol.

Figure 7 shows the effect of the ethanol concentration on the impedance response on a RuHCF modified glassy carbon electrode obtained at 0.98 V *vs.* Ag|AgCl|KCl$_{sat}$. It was found that the charge transfer resistance decreased as ethanol concentration increased. This behavior was possibly due to the fast reaction kinetics promoted by the adsorption of ethanol on the RuHCF modified electrode surface.[30] The charge transfer resistance for the RuHCF catalyzed ethanol oxidation depends on kinetic parameters.[27,29-31]
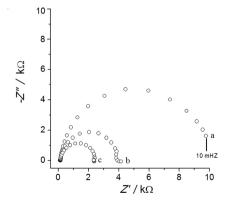

Figure 7. Nyquist plots for ethanol oxidation on glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate in Britton-Robinson buffer solution at pH 1.5 with different concentrations of ethanol: (a) 0.1, (b) 0.5 and (c) 1.0 mol L^{-1} at applied potential 0.98 V *vs.* Ag|AgCl|KCl$_{sat}$.

The possibility of using this modified electrode as an electrochemical sensor was verified through chronoamperometric studies of the RuHCF modified glassy carbon electrode in ethanol solutions. Preliminary experiments were performed in order to determine the optimal potential in which the highest limiting current can be obtained at a given ethanol concentration (0.1 mol L^{-1}). The optimal potential was found to be +0.9 V *vs.* Ag|AgCl|KCl$_{sat}$. Figure 8 shows chronoamperometric responses of the RuHCF modified glassy carbon electrode at different ethanol concentrations. The limiting current increased as the ethanol concentration increased.
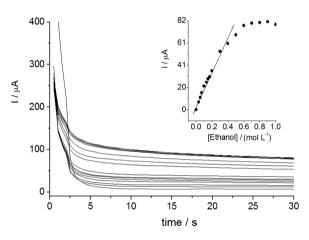

Figure 8. Chronoamperometric responses of the glassy carbon electrode modified with a mixed film of ruthenium-based hexacyanoferrate in Britton-Robinson buffer solution at pH 1.5 at different ethanol concentrations. Inset figure: Plot of I$_a$ *vs.* [ethanol].

The plot of limiting current *vs.* ethanol concentration showed a linear relationship (r = 0.996, n = 10) between 0.03 and 0.4 mol L^{-1} (inset in Figure 8), following the equation: I$_a$ (μA) = (2.20 ± 0.76) + (171 ± 5.14) [ethanol]. For ethanol concentration higher than 0.4 mol L^{-1}, the limiting current did not increase any more, indicating that electrode surface saturation occurred.

The limit of detection (LOD) was calculated using the equation LOD = 3.3 *s*/m (*s*: relative standard deviation of the intercept; *m*: slope of the linear current *vs.* the ethanol concentration).[32] LOD and sensitivity were found to be: 0.76 mmol L^{-1} and 0.21 μA mmol L^{-1}, respectively. These values are considered adequate for the application of the proposed sensor in the detection of ethanol in many commercially available samples.

The response is fast. In about 5 s, the limiting current is observed, making it suitable for an electrochemical sensor.

The oxidation current of ethanol catalyzed by the RuHCF modified GC electrode did not decrease substantially. The electrode was found stable even after 25 cyclic voltammetric scans in ethanol solution, indicating

that the RuHCF modified GC electrode exhibited a good stability for applications as an electrochemical sensor.

Conclusions

A RuHCF modified GC electrode was prepared by dripping a mixed solution of Ru^{3+} and $Fe(CN)_6]^{3-}$ followed by coating it with a thin layer of Nafion. The RuHCF modified electrode showed good catalytic activity towards ethanol electrooxidation, under strong acidic conditions (pH 1.5). The catalytic ethanol oxidation started at about 0.8 V and reached maximum at 0.98 V *vs.* Ag|AgCl|KCl$_{sat}$, exactly in the region where electrochemical processes Ru(III)−O−Ru(IV) and Ru(IV)−O−Ru(VI) occur. The electrochemical impedance spectroscopy studies showed that the charge transfer resistance of the RuHCF catalyzed ethanol electrooxidation decreased as the applied potential or ethanol concentration increased, suggesting that the reactions kinetics were promoted by high oxidation potential and by the adsorption of ethanol on the modified electrode surface. This modified electrode presented good sensitivity with a fast response time. The catalytic oxidation current was proportional to ethanol concentration over a wide ethanol concentration range. These characteristics make it possible to serve as a sensor probe for ethanol amperometric analysis.

Acknowledgments

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