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Electrochemical oxidation of oxalic acid and hydrazinium nitrate on platinum in nitric acid media

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ABSTRACT

Several studies in the literature have investigated the electrochemical effects of oxalic acid and hydrazine on various materials in neutral (pH buffered to 7), basic or weakly acidic media (pH 6). The present work proposes electrochemical techniques that allow for the study of the electrochemical behavior, on a Pt electrode, of oxalic acid and hydrazinium nitrate to better understand their oxidation mechanisms in a nitric acid medium at a pH below 1; in addition, some experiments were carried out to define an electrochemical method that would allow for the simultaneous detection of these species when present within process effluent in very acidic solutions. Some physical data regarding oxalic acid and hydrazinium nitrate were also determined: anodic oxidation of hydrazinium nitrate and oxalic acid were observed at 0.2 V and 0.7 V (vs. Ag/AgCl), respectively. The diffusion coefficients of hydrazinium nitrate and oxalic acid were found to be 5.2×10^{-6} and 2.9×10^{-7} cm^2 s^{-1}, respectively. An experimental design approach demonstrated the influence of nitric acid concentrations on the diffusion coefficients of these species.

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1. Introduction

Numerous papers have addressed the electrochemical behavior of oxalic acid and hydrazine [1–20], often with respect to biology. Oxalic acid and hydrazine are detected by electrochemical methods in aqueous solution for pH levels ranging from 6 to 7.

Works on the oxidation of oxalic acid have focused on designing an oxalate-specific sensor; they have studied the mechanism of degradation during anodic oxidation. Cyclic or linear voltammetry [1,2,4–7,9–11] and chronoamperometry [3–5,8] are the main electrochemical techniques that have been used. Various massive materials (Pt [1], glassy carbon [1,4], etc.) and modified metals (dimensionally stable anodes, DSA, Ti coated by Pt or IrO_2 or RuO_2 [1], boron-doped diamond [7], etc.) are used as anodes. Graphite modified by palladium nanoparticles [4,6] and rhodium [8,11] have also been examined as catalysts for the electrochemical oxidation of oxalic acid. The results show that the oxidation potential of oxalic acid is influenced by the type of electrode used as well as its surface and composition. Adsorption (especially on Pt), passivation and interaction phenomena can influence the rate of this reaction.

Cyclic voltammetry [12–18], amperometric detection and/or differential pulse voltammetry [12] have been used to study the oxidation of hydrazine on modified glassy carbon electrodes [12–16]. Zinc oxide [17] and carbon nanotubes [18] have also been used for the development of a hydrazine electrochemical sensor. As for oxalic acid, the oxidation of hydrazine may be influenced by the type of electrode used as well as its surface state and composition and solution pH.

A bibliographical review has revealed no studies investigating the development of a method for detecting both oxalic acid and hydrazine present in the same medium.

The purpose of the present work was to carry out voltammetric measurements on oxalic acid and hydrazinium nitrate on a platinum electrode in a concentrated nitric acid medium to obtain a better understanding of their oxidation mechanisms and to develop an electrochemical method for their simultaneous detection when present within process effluent in very acidic solutions. Some physical data regarding oxalic acid and hydrazinium nitrate were also obtained.

2. Experimental procedures

The chemicals used were of analytical grade (purity >98.5%). Solid oxalic acid was provided by Sigma Aldrich (CAS: 61353566). Nitric acid possessed a density $\rho = 1.42$ g cm^{-3} (purity 65%). Hydrazinium nitrate was a laboratory-prepared solution. Concentrated nitric acid was added to hydrazine hydrate (CAS: 78035378) until complete neutralization at pH 4.5, forming hydrazinium

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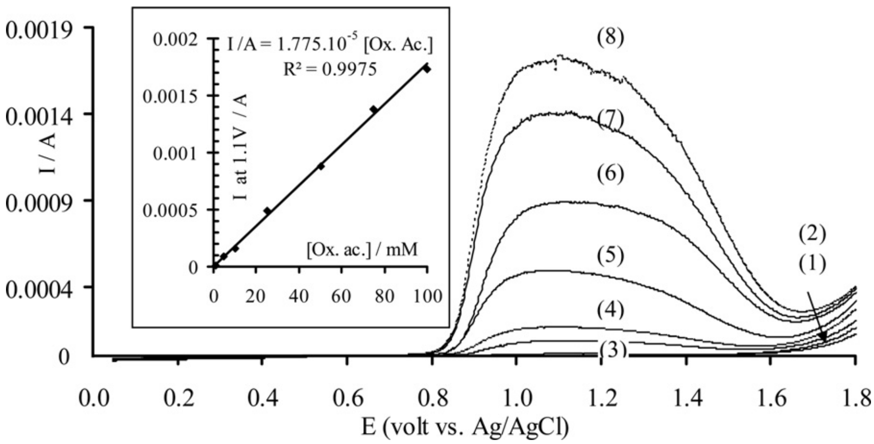

Fig. 1. [Ox. ac.] or oxalic acid's concentration dependence on the current–potential curves, obtained on Pt rotating disk. ω = 1000 RPM: supporting electrolyte 2 M HNO_3; (1) no oxalic acid; (2) 1 mM; (3) 5 mM; (4) 10 mM; (5) 25 mM; (6) 50 mM; (7) 75 mM; (8) 100 mM; potential scan rate: 0.005 V s^{-1}. Inset: the variation of anodic current at 1.1 V vs. the oxalic acid concentration.

nitrate; this reaction is highly exothermic and can be explosive. Particular caution is required when using hydrazine hydrate because it is a CMR (carcinogenic, mutagenic and reprotoxic) substance.

All electrochemical measurements were carried out using an Autolab PGSTAT 30 potentiostat/galvanostat controlled with GPES 4.9 software and a three-electrode setup with a saturated silver reference electrode (Ag/AgCl, 3 M KCl), a platinum wire counter-electrode and a platinum-disk working electrode.

3. Results and discussion

3.1. Electrochemical kinetics on Pt rotating disk electrode

3.1.1. Oxalic acid

Linear voltammograms, obtained at the steady state (5 mV s^{-1}) with a Pt rotating-disk electrode (ω = 1000 RPM) and various concentrations of oxalic acid in 2 M HNO_3, are shown in Fig. 1. A signal indicating the oxidation of oxalic acid to carbon dioxide on Pt according to equation (3.1.1.1) was observed for potentials higher than 0.7 V; simultaneously, bubbles appeared at the electrode surface. For low concentrations (curves (1)–(3)), the obtained signal shows a practically constant 'limiting current', with a slight decrease for potentials higher than 1.4 V. For concentrations above 10 mM, a peak-shaped curve was obtained and the magnitude of the current decreased nearly to zero for potentials higher than ~1.2 V; partial and reversible passivation of the platinum electrode caused by the gaseous carbon dioxide produced on the electrode surface could explain this decrease. Indeed, all of the curves obtained can be reproduced without mechanical treatment. The oxidation reaction can be written as follows:

$$\text{HCOO—COOH} \rightarrow 2CO_2 + 2H^+ + 2e^- \qquad (3.1.1.1)$$

A linear dependence of the anodic current ($I_{\max}$ recorded at 1.1 V) vs. the oxalic acid concentration observed in the range 1–100 mM (inset, Fig. 1) reflects a mass-transfer limitation, even if the magnitude of the current decreases for higher potentials:

$$I_{\max\ \text{at}\ 1.1\,\text{V(A)}} = 1.77 \times 10^{-5}[\text{Ox. Ac.}]_{(\text{mmol L}^{-1})},$$

$$\text{where} \quad R^2 = 0.9975.$$

Tafel plots ($\ln i = \ln i_0 + \alpha nF\eta/RT$) for curves obtained in 1 mM oxalic acid were used to determine the exchange-current density i_0, the electron-transfer coefficient α and the intrinsic heterogeneous electron-transfer coefficient k^0 (cm s^{-1}). The exchange-current density ($i_0 = nFk^0C^0$) was found to be 2×10^{-7} A cm^2. Assuming $n = 2$, α and k^0 were found to be 0.3 and 10^{-6} cm s^{-1}, respectively. The value of k^0 indicates that oxalic acid can be considered an irreversible system.

3.1.2. Hydrazinium nitrate

Linear voltammograms obtained at the steady state with a Pt rotating-disk electrode and various concentrations of hydrazinium nitrate in 2 M HNO_3 are shown in Fig. 2(a).

Considering that the final oxidation product is N_2, the overall oxidation reaction of hydrazinium nitrate can be written as follows:

$$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^- \qquad (3.1.2.1)$$

The following results were obtained:

- For hydrazinium nitrate concentrations lower than 10 mM, classically shape curves were obtained, containing one wave beginning at ~0.2–0.4 V. The wave "plateau" with a limiting current clearly indicates a mass-transfer limitation (diffusion limitation). The magnitude of its limiting current increases linearly with the hydrazinium nitrate concentrations according to the relationship (3.1.2.2).

$$I/A = 7.37 \times 10^{-5} \cdot [\text{H}\quad\text{Nitrate}] \quad R^2 = 0.9991 \qquad (3.1.2.2)$$

- For higher concentrations of hydrazinium nitrate (50–75 mM), the curves indicate three important modifications:
  - The beginning of the I/E curve for hydrazinium nitrate oxidation shifts to lower potentials when the concentration increases, meaning that the corresponding electroactive species is oxidized more easily.
  - Increasing the hydrazinium nitrate concentration causes two signals to appear, at 0.2–0.6 V and 0.7–1.2 V.
  - After the potential of the second signal was reached, the magnitude of the current decrease indicates the passivation of the platinum electrode. Nevertheless, the curves obtained can be reproduced without mechanical treatment, which suggests that this passivation is reversible. The final oxidation product of hydrazinium nitrate is gaseous nitrogen and the presence of a gaseous layer at the interface could explain the decrease in the magnitude of the current.

Two possible explanations could justify this behavior:

Assuming that one electron was exchanged through an elementary step, for hydrazinium nitrate oxidation, the global reaction

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