

Full Research Paper

Electrochemical Oxidation and Determination of Oxalic Acid at an Exfoliated Graphite-Polystyrene Composite Electrode

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Abstract: An exfoliated graphite-polystyrene composite electrode was evaluated as an alternative electrode in the oxidation and the determination of oxalic acid in 0.1 M Na₂SO₄ supporting electrolyte. Using CV, LSV, CA procedures, linear dependences I vs. C were obtained in the concentrations range of oxalic acid between 0.5 to 3 mM, with LOD = 0.05 mM, and recovery degree of 98%, without need of surface renewing between successive runs. The accuracy of the methods was evaluated as excellent comparing the detection results with that obtained using conventional KMnO₄ titration method. In addition, the apparent diffusion coefficient of oxalic acid D was found to be around $2.89 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ by CA and CV.

Keywords: exfoliated graphite-polystyrene composite electrode, oxalic acid, electrochemical oxidation, electrochemical determination

1. Introduction

Oxalic acid naturally occurs in various organisms, including fungi, plants and animals. High levels of oxalic acid remove calcium from blood with severe disturbances in the activity of heart and neural

system. It also known that oxalic acid may cause digestive tract irritation and kidney damage, and increasing demand for its determination in urine appeared [1-3]. Oxalic acid is a metabolite of the advanced oxidation of phenol and its derivatives, and of other aromatic substrates of pesticides, herbicides, and fungicides, which are present in many industrial wastewaters. This compound is also known to be recalcitrant and resistant to further degradation [4-6]. Several methods for the determination of oxalic acid, for example, titration method [6], fluorimetric method [7], spectrophotometric [8], HPLC [9-13], chemiluminescence [14], HPLC-chemiluminescence [15], AAS [2], enzymatic method [16], electrochemical detection [17] were reported. Most of the methods require a preliminary separation of oxalic acid from its matrix, and exhibit lack of the sensitivity, efficiency or simplicity.

The electrochemistry of oxalic acid at some metal electrodes [6,18-19], Pd-modified GC [5], and BDD [17] has been studied.

Carbon electrodes are widely used in electroanalysis due to their low background current and wide potential window suitable for the investigation of an electrochemical oxidation process, chemical inertness, low-cost, and suitability for various sensing and detection application [20-37]. The use of a carbon-composite electrode, which consists of a carbon conductor phase mixed with an insulator phase, can be regarded as a randomly assembled carbon microelectrode array [23, 24, 33, 37]. The modifications of the carbon composite electrodes and applications to characterize various important electrochemical reactions were reported in the literature [28, 30-32]. Exfoliated graphite (EG) is a low dense, prepared by thermal exfoliation of intercalated natural graphite. Very few reports are available in the literature about its use for electroanalytical applications [31,32].

The electrochemical oxidation of oxalic acid at some electrode materials has been reported [5,6,17-19], but to the best of our knowledge there is no report on oxalic acid oxidation and determination using a graphite composite electrode.

The purpose of this work is to investigate the electrochemical oxidation and determination of oxalic acid on a 20% (w/w) exfoliated graphite-polystyrene composite electrode (EG-PS). This new composite electrode has been tested as an amperometric detector using cyclic voltammetry (CV), linear-scan voltammetry (LSV), chronoamperometry (CA). In addition, some characteristics of the electrochemical oxidation of oxalic acid were studied.

2. Results and Discussion

The prepared EG-PS electrode showed good mechanical strength and low electrical resistivity (3.2 Ω). Its main advantages versus simple graphite electrode are related to mechanical stability and rigidity, which allows the smoothing of the surface to obtain a fresh reproducible surface for new determination.

2.1. Surface characterization

SEM imaging has been used to provide qualitative information about structure, e.g., size and distribution of exfoliated graphite zones and some surface features of this composite electrode. Fig. 1 illustrates SEM image of the cross-section of EG-PS composite electrode and exhibits a closely spaced

exfoliated graphite zones with random distribution and orientation due to the irregular shapes of exfoliated graphite particles in polystyrene matrix [27, 37].

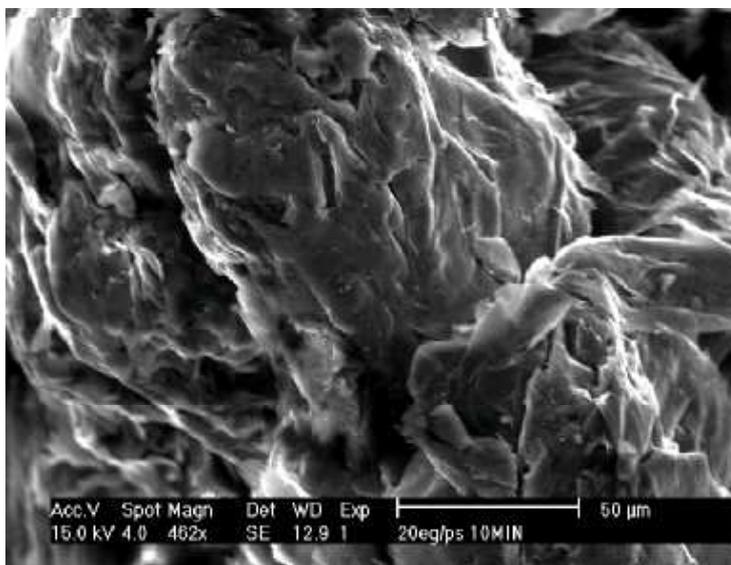


Figure 1. SEM image of the cross-section of the EG-PS film.

2.2. Voltammetric measurements

Cyclic voltammograms (CVs) obtained with the EG-PS electrode and various concentrations of oxalic acid in 0.1 M Na₂SO₄ are shown in Fig. 2.

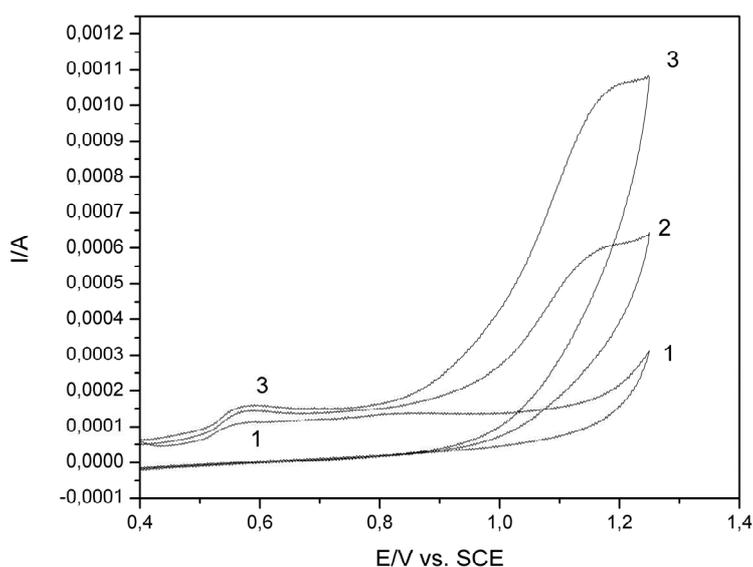


Figure 2. Cyclic voltammograms (3rd scan) of the EG-PS electrode in 0.1 M Na₂SO₄ solution (curve 1) and in the presence of 0.5 mM (curve 2) and 1 mM oxalic acid (curve 3); potential scan rate 0.05 V·s⁻¹.

The anodic process occurring at EG-PS electrode in 0.1 M Na₂SO₄ is based on the oxidation due to functional groups consisting from hydrogen and oxygen. A first anodic current peak, noticed on the CVs around 0.6 V vs. SCE, with a corresponding cathodic one (not shown), owing to graphite electrode material. Some interaction is possible between functional groups of the graphite surface and oxalic acid, which precede the oxidation process at more positive potential [17]. The current corresponding to the wave obtained at more positive potential range, owing to the oxidation of oxalic acid, increased progressively with its concentration. On the following reverse scan from 1.25 to 0.4 V vs. SCE, no corresponding reduction peak is observed, revealing that the electrode process on the EG-PS is totally irreversible.

The cyclic voltammetry of EG-PS at various scan rates (0.01-0.1 V·s⁻¹) in the presence of 1 mM oxalic acid was studied (Fig. 3). For the whole range of the scan rates studied, the peak shape that is sensitive to the scan rate shows irreversible characteristics and substantial hysteresis. Thus, under these circumstances, the random assembly behavior was exhibited. The anodic current wave at about 1.1–1.2 V vs. SCE increased linearly with the square root of the scan rate (inset *a* of Fig. 3) suggesting that the reaction is mass-transfer controlled. Moreover, the starting potential of the wave shifted towards positive potential when increasing v indicating that the electrooxidation process of oxalic acid is irreversible (inset *b* of Fig. 3).

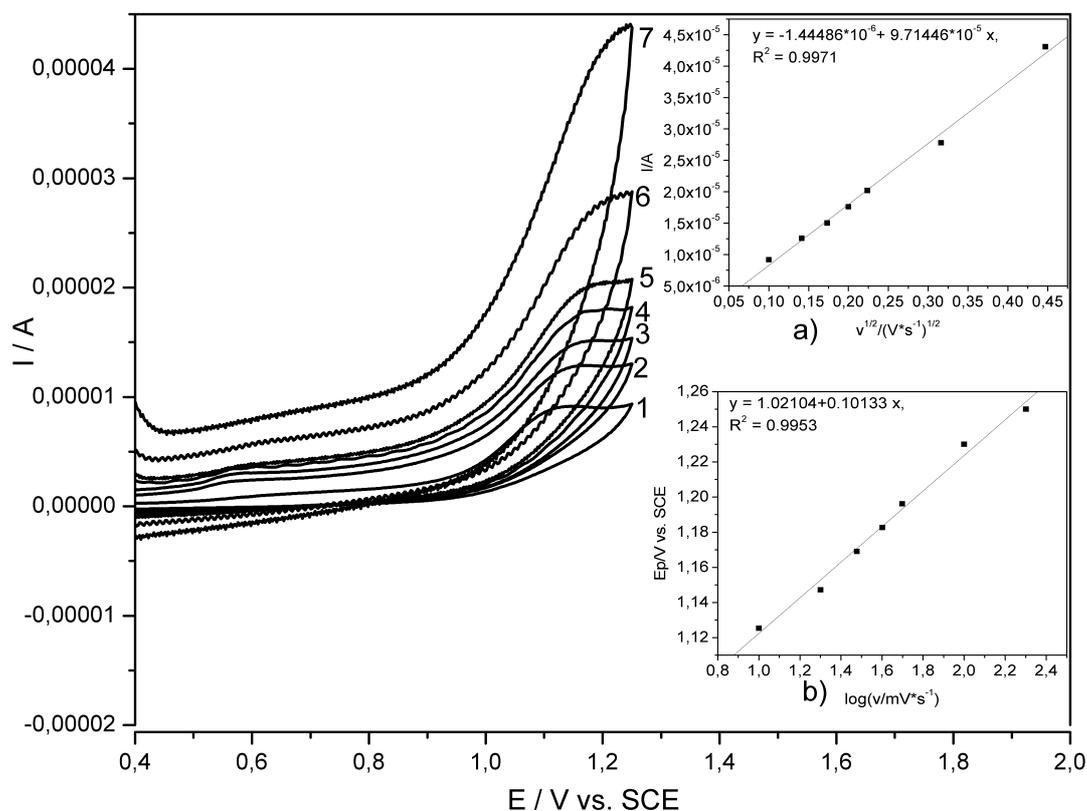


Figure 3. Cyclic voltammograms (3rd scan) of 1 mM oxalic acid at EG-PS with different scan rates in 0.1 M Na₂SO₄; 1-0.01 V s⁻¹; 2-0.02 V s⁻¹; 3-0.03 V s⁻¹; 4-0.04 V s⁻¹; 5-0.05 V s⁻¹; 6-0.1 V s⁻¹; 7-0.2 V s⁻¹; Inset a-The anodic peak current I_p vs. $v^{1/2}$; Inset b- Dependence of the potential of current peak, E_p to the $\log(v)$.

The anodic limiting current recorded at 1.15 V vs. SCE increases with increasing of oxalic acid in solution (Fig. 4). The inset of Fig. 4 shows that the anodic limiting current depends linearly on the oxalic acid concentration in the range 0.1-1.0 mM, with a correlation coefficient better than 0.999.

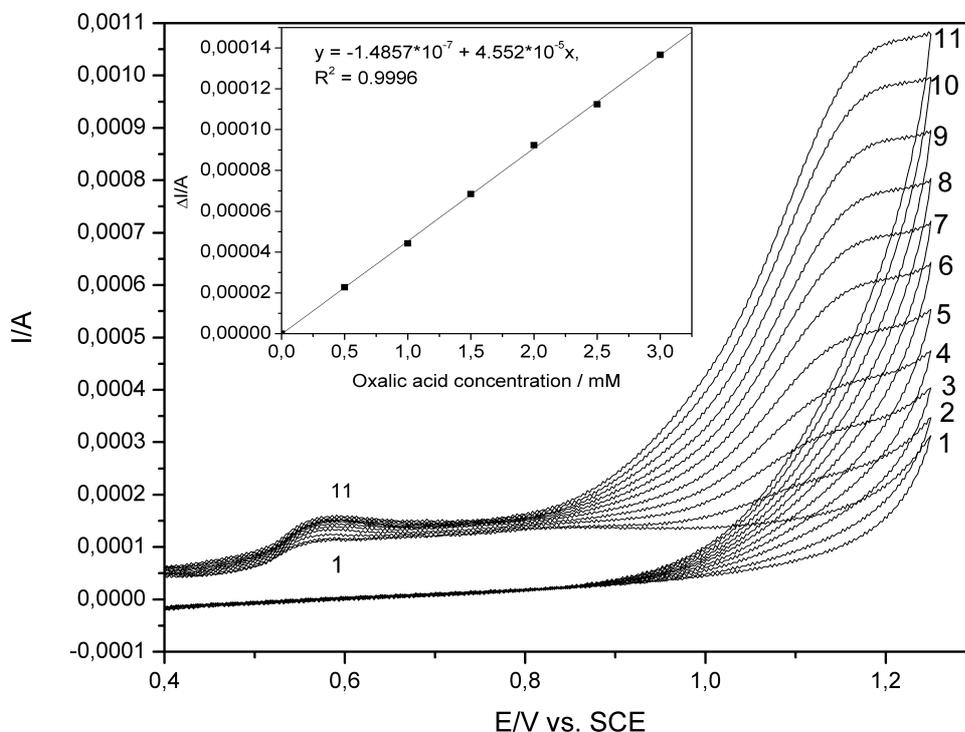


Figure 4. Cyclic voltammograms (3rd scan) of EG-PS in the presence of oxalic acid concentrations: 1-0 mM; 2-0.1 mM; 3-0.2 mM; 4-0.3 mM; 5-0.4 mM; 6-0.5 mM; 7-0.6 mM; 8-0.7 mM; 9-0.8 mM; 10-0.9 mM; 11-1 mM; potential scan rate 0.05 Vs⁻¹; supporting electrolyte 0.1 M Na₂SO₄. Inset: the variations of anodic limiting currents vs. oxalic acid concentrations.

In Fig. 5, linear scan voltammograms obtained under the same CV conditions are shown. The dependences of the current peaks vs. concentration, explored in the concentration range between 0.1 mM-1 mM, were linear, with the very good correlation coefficients, 0.998. The shapes of CVs at 0.6 V were conditioned by the previous successive scan in the extended potential range (cathodic branches at less positive potential are omitted in the above-presented figures).

2.3. Chronoamperometric measurements

Chronoamperometry was employed as the detection method and for the investigation of the electrode process as well. Fig. 6 shows chronoamperometric measurements of oxalic acid with EG-PS. This figure presents the current-time profiles obtained by setting the working electrode at 1.1 V vs. SCE for various concentrations of oxalic acid. The useful net current signals recorded at 50 seconds are linearly dependent on oxalic acid concentration in the explored concentration range between 0.5 mM and 3 mM (Inset of Fig. 6).

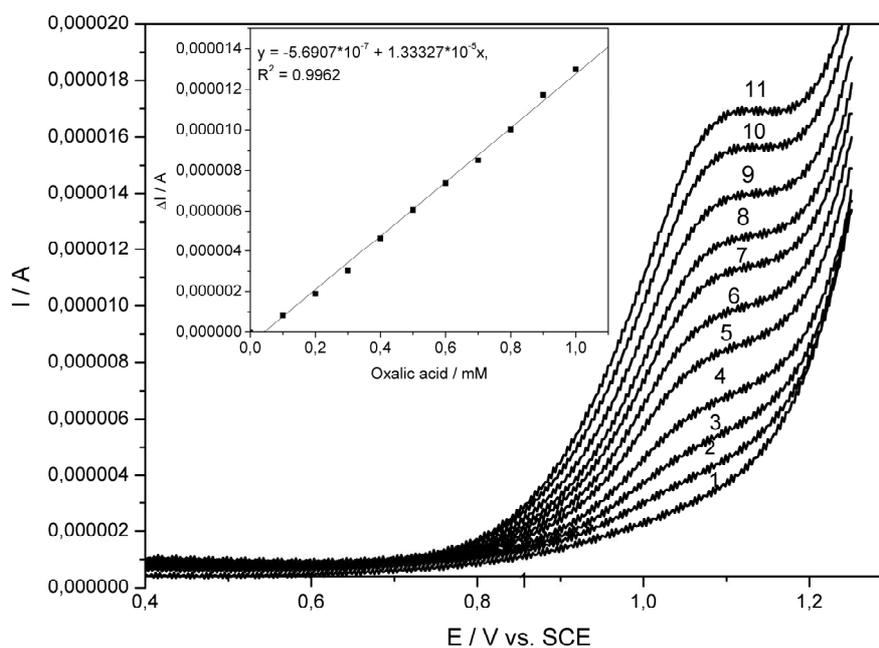


Figure 5. Linear voltammograms of EG-PS in the presence of oxalic acid concentrations: 1-0 mM; 2-0.1 mM; 3-0.2 mM; 4-0.3 mM; 5-0.4 mM; 6-0.5 mM; 7-0.6 mM; 8-0.7 mM; 9-0.8 mM; 10-0.9 mM; 11-1 mM; potential scan rate 0.05 Vs^{-1} ; supporting electrolyte $0.1 \text{ M Na}_2\text{SO}_4$. Inset: the variations of anodic limiting currents vs. oxalic acid concentrations.

The current corresponding to the electrochemical reaction (under mass transport control) of an electroactive material with a diffusion coefficient, is described by Cottrell's equation (Fig. 7) [38]:

$$I_{(t)} = nFAC^* (D/\pi t)^{1/2}, \quad [1]$$

where D is diffusion coefficient (cm^2s^{-1}), C^* -bulk concentration ($\text{mol}\cdot\text{cm}^{-3}$), n -number of electrons, F -Faraday's constant, and A -electrode area. The plot of I vs. $t^{-1/2}$ is linear (Fig.7) and from the slope the value of D can be obtained. According to the Cottrell equation, a diffusion coefficient of oxalic acid D was found to be $2.99 \cdot 10^{-8} \text{ cm}^2\cdot\text{s}^{-1}$. Also, this diffusion coefficient was determined based on the equation that characterizes an irreversible process investigated by cyclic voltammetry [39]:

$$i_p = (2.99 \cdot 10^5) n(\alpha n_a)^{1/2} ACD^{1/2} v^{1/2}, \quad [2]$$

where α is the transfer coefficient, n_a is the number of electrons involved in the charge transfer step. Assuming $\alpha=0.5$ and $n=2$, D was found to be $2.89 \cdot 10^{-8} \text{ cm}^2\cdot\text{s}^{-1}$. These very closed values of diffusion coefficient are smaller compared to the diffusion coefficient data reported by Casella on palladium-based modified glassy carbon electrode in acidic medium [5]. The diffusion coefficient must be regarded as an apparent value. This aspect could be correlated with a real electroactive surface area different from the geometric one in the exfoliated graphite composite systems.

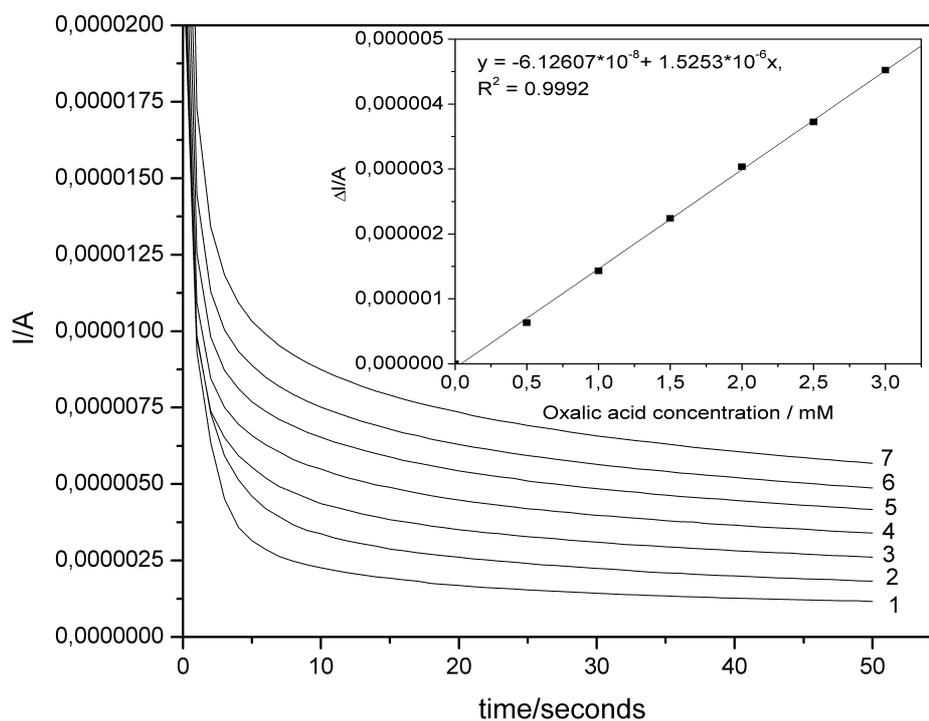


Figure 6. Chronoamperograms obtained at EG-PS in the absence (1) and the presence of (2) 0.5 mM, (3) 1 mM, (4) 1.5 mM, (5) 2 mM, (6) 2.5 mM, (7) 3 mM; 0.1 M Na_2SO_4 supporting electrolyte; electrode potential 1.1 V vs. SCE; Inset: the calibration plots of current, read at 50 seconds, vs. oxalic concentration.

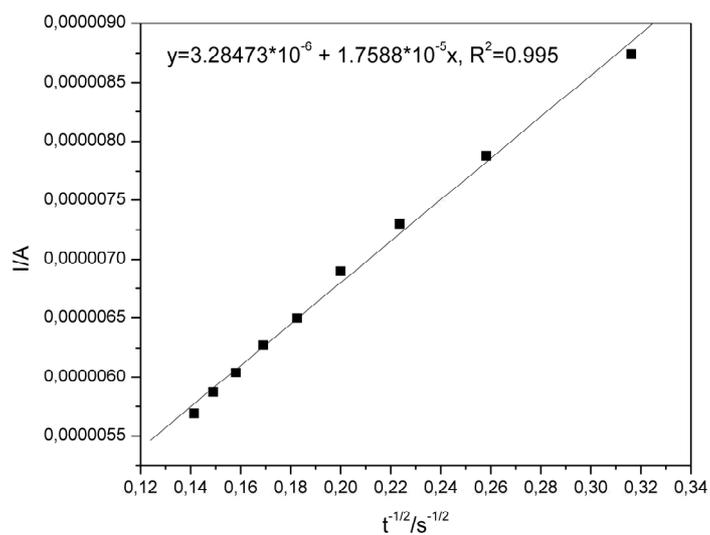


Figure 7. Cottrell's plot for potential step chronoamperometry of EG-PS in 0.1 M Na_2SO_4 in the presence of 1 mM oxalic acid

The amperometric response of the EG-PS electrode obtained for successive and continuous addition of 0.5 mM oxalic acid to 0.1 M Na₂SO₄ solution (batch system analysis -BSA) at an applied potential of 1.1 V vs. SCE is shown in Fig. 8. The response of the electrode is linear in the concentration range of 0.5 mM to 2.5 mM (Inset of Fig. 8).

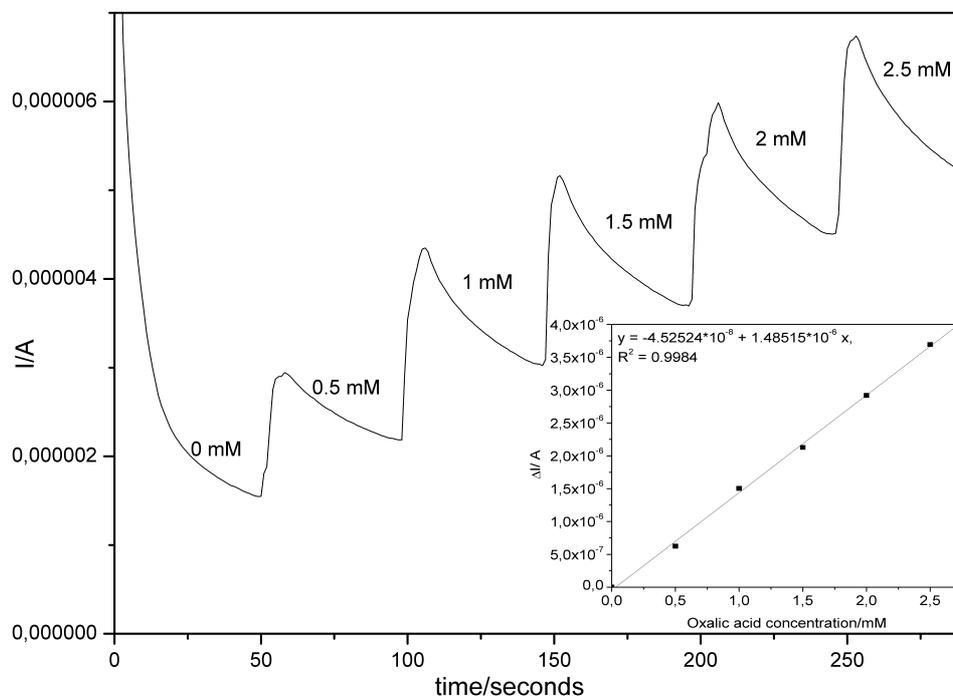


Figure 8. Amperometric response (BSA) of the EG-PS electrode for the successive and continuous addition of 0.5 mM oxalic acid. Applied potential: 1.1 V vs. SCE. Inset: calibration plots of useful signal vs. oxalic acid.

At the potential value of 1.1 V vs. SCE, a linear relationship between the amperometric signal and oxalic acid concentration was obtained in the range 0.1 to 1 mM using cyclic voltammetry and linear scan voltammetry and between 0.5 and 2.5 mM using chronoamperometry and batch system analysis (BSA). Under these experimental conditions, no cleaning or pretreatment of the electrode after each addition of oxalic acid was required. The analytical parameters are presented in Table 1. The lowest limit of detection (LOD) was evaluated based on $S/N \geq 3$. The reproducibility of the EG-PS electrode using the above-mentioned techniques was evaluated for five replicates measurements of oxalic acid detection. The relative standard deviations (RSD) gathered in table 1 shows the good reproducibility of the electrode.

Table 1. The analytical parameters of amperometric detection of oxalic acid at an EG-PS electrode using different techniques.

Technique used	Concentration range(mM)	Calibration plots*	Correlation coefficient (R^2)	LOD (mM)	RSD (%)
CV	0.1-1	$y = -3.07 \cdot 10^{-8} + 2.22 \cdot 10^{-5} x$	0.9992	0.05	2.5
LSV	0.1-1	$y = -5.69 \cdot 10^{-8} + 1.33 \cdot 10^{-5} x$	0.9962	0.08	2.7
CA	0.5-3	$y = -6.13 \cdot 10^{-8} + 1.52 \cdot 10^{-6} x$	0.9992	0.5	3.1
BSA-CA	0.5-3	$y = -4.52 \cdot 10^{-8} + 1.48 \cdot 10^{-6} x$	0.9984	0.8	3.5

*-y- ΔI amperometric useful signal obtained by subtraction of background current (A) and x-oxalic acid concentration (mM)

A recovery test was also performed by analyzing five parallel tap water samples, which contain 90 mg·dm⁻³ oxalic acid. This test was run in 0.1 M Na₂SO₄ as supporting electrolyte and a recovery of 98% was found with a RSD of 2.8 % using LSV. Finally, the results obtained by this method were compared with that obtained by means of a conventional KMnO₄ titration method. Using a titration with 0.1 N KMnO₄ solution to evaluate the precision of this method, it can be concluded that the results obtained by the two methods are very closely and the accuracy of the proposed voltammetric method is excellent.

3. Experimental Section

The composite electrode was obtained by film casting from polystyrene pellets by type PS N2000 dissolved in toluene and addition of exfoliated graphite powder (SGL Carbon) with constant stirring. The ratio between the components was chosen to reach 20 weight percent (w/w) content of exfoliated graphite. The film obtained was pressed to a thickness of 1 mm, at a temperature of 250 ° C for 30 minutes and cooled to the room temperature in the open air. After drying for 14 h at room temperature, the plate with a geometric surface area of 81 mm² was put on a glass substrate and electrical contacts were made through silver contacts. The matrix PS N2000 is a commercial grade delivered by Shell. The prepared EG-PS electrode showed good mechanical strength and low electrical resistivity (3.2 Ω). Prior to use, this working electrode was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.3 μm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes and rinsing with distilled water.

The electrochemical performances of this electrode were studied by cyclic voltammetry (CV), linear-scan voltammetry (LSV), and chronoamperometry (CA). Subsequently, an electrochemical pretreatment by three repetitive cyclings between -0.5 V to 1.25 V vs. SCE in 0.1 M Na₂SO₄ supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode and EG-PS working electrode.

A Scanning Electron Microscope (Philips CM30T) was used to observe the working electrode surface.

Oxalic acid and sodium sulphate were analytical grade from Merck, and freshly prepared with double-distilled water.

Conclusions

The EG-PS composite electrode with 20 % (w/w) exfoliated graphite contains the clusters of graphite gathered in random areas due to the random distribution and orientation of graphite particles in the polystyrene.

This electrode exhibited useful features for the oxidation and amperometric determination of oxalic acid with respect to its mechanical resistance, very low cost, simple preparation and easy renewal of the active electrode surface.

Using CA based on Cottrell's equation and equation that characterize irreversible process using cyclic voltammetry, the apparent diffusion coefficient of oxalic acid D was found to be around $2.89 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ and respective, $2.99 \cdot 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$. This value is apparent and smaller than reported in the literature [5]. The difference is due to the fact that in this study the geometric area was calculated, which differs from the electroactive one.

For the determination of oxalic acid using CV, LSV, CA procedures, linear plots of current vs. concentration were obtained in the concentration range of oxalic acid between 0.5 to 3 mM, with LOD = 0.05 mM, without the need of a renewed surface between successive runs, and with a recovery degree of 98 %. The accuracy of the applied methods was excellent as compared to the detection results obtained using the conventional KMnO_4 titration method.

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References and Notes

1. Health Council of the Netherlands: Committee on Updating of Occupational Exposure Limits. Oxalic acid; Health-based Reassessment of Administrative Occupational Exposure Limits. The Hague: *Health Council of the Netherlands*, **2004**; 2000/15OSH/106.
2. Menache, R. Routine Micromethod for Determination of Oxalic Acid in Urine by Atomic Absorption Spectrophotometry. *Clin. Chem.* 1974, 20, 1444-1445.
3. Powers, H. H.; Levatin, P. A Method for the Determination of Oxalic Acid in Urine. *J. Biol. Chem.* **1944**, 154, 207-213.
4. Quisepe, C.; Villasenor, J.; Pecchi, G.; Reyes, P. Catalytic ozonation of Oxalic Acid with $\text{MnO}_2/\text{TiO}_2$ and Rh/TiO_2 . *J. Chil. Chi. Soc.* **2006**, 51, 1049-1051.
5. Casella, I.G. Electrocatalytic Oxidation of Oxalic Acid on Palladium-Based Modified Glassy Carbon Electrode in Acidic Medium. *Electrochim. Acta.* **1999**, 44, 3353-3360.

6. Martinez-Huitle, C. A.; Ferro, S.; De Batisti, A. Electrochemical Incineration of Oxalic Acid. Role of Electrode Material. *Electrochim. Acta.* **2004**, *49*, 4027-4034.
7. Zarembski, P. M.; Hodgkinson, A. The Fluorimetric Determination of Oxalic Acid in Blood Biological Materials. *Biochem. J.* **1965**, *96*, 717-721.
8. Ensafi, A. A.; Emadi, M. Spectrophotometric Reaction Rate Method for Determination of Oxalic Acid in Food Based on its Enhancing Effect on the Oxidation of Pyrocatechol Violet by Dichromate. *Anal. Lett.* **2004**, *37*, 321-332.
9. Wilson, Ch. W.; Shaw, Ph.E.; Knight, R. J. Analysis of Oxalic Acid in Carambola (*Averrhoa carambola* L.) and Spinach by High-Performance Liquid Chromatography. *J. Agric. Food Chem.* **1982**, *30*, 1106-1108.
10. Gancedo, M. C.; Luh, B.S. HPLC Analysis of Organic Acids and Sugars in Tomato Juice. *J. Food Sci.* **1986**, *51*, 571-573.
11. Oderiz, V.; Blanco, V.; Hernandez, L.; Lozano, S.; Rodriguez, R. Simultaneous Determination of Organic Acids and Vitamin C in Green Beans by Liquid Chromatography. *J. AOAC Int.* **1994**, *77*, 1056-1059.
12. Khaskhali, M. H.; Bhangar, M. I.; Khand, F. D. Simultaneous Determination of Oxalic Acid and Citric Acids in Urine by High-Performance Liquid Chromatography. *J. Chromatogr. B. Biomed. Appl.* **1996**, *675*, 147-151.
13. Zhanguo, C.; Jiuru, L. Simultaneous and Direct Determination of Oxalic Acid, Tartaric Acid, Malic Acid, Vitamin C, Citric Acid, and Succinic Acid in Fructus Mume by Reversed-Phase High-Performance Liquid Chromatography. *J. Chromatogr. Sci.* **2002**, *40*, 35-39.
14. He, Z.; Yuan, L.; Luo, Q.; Zeng, Y. Simultaneous Determination of Oxalic and Tartaric Acid with Chemiluminescence Detection. *Analyst.* **1997**, *122*, 1343-1345.
15. Wu, F.; He, Z.; Luo, Q.; Zeng, Y. High-Performance Liquid Chromatographic Determination of Oxalic Acid in Tea using Tris (1,10-phenanthroline)-ruthenium (II) Chemiluminescence. *Anal. Sci.* **1998**, *14*, 971-973.
16. Hong, F.; Nilvebrant, N.-O.; Jonsson, L. J. Rapid and Convenient Determination of Oxalic Acid Employing a Novel Oxalate Biosensor Based on Oxalate Oxidase and SIRE Technology. *Biosens. Bioelectron.* **2003**, *18*, 1173-1181.
17. Ivandini, T. A.; Rao, T. N.; Fujishima, A.; Einaga, Y. Electrochemical Oxidation of Oxalic Acid at Highly Boron-Doped Diamond Electrode. *Anal. Chem.* **2006**, *78*, 3467-3471.
18. Berna, A.; Rodes, A.; Feliu, J. M. Oxalic Acid Adsorption and Oxidation at Platinum Single Crystal Electrodes. *J. Electroanal. Chem.* **2004**, *563*, 49-62.
19. Pron'kin, S. N.; Petrii, O. A.; Tsirlina, G. A.; Schiffrin, D. J. Size Effects on the Electrochemical Oxidation of Oxalic Acid on Nanocrystalline Platinum. *J. Electroanal. Chem.* **2000**, *480*, 112-119.
20. Sun, D.; Zhu, L.; Zhu, G. Glassy Carbon Ceramic Composite Electrodes. *Anal. Chim. Acta* **2006**, *564*, 243-247.
21. Mendes, R. K.; Cervini, P.; Cavalheiro, E. T. G. The Use of a Graphite-Castor Oil Polyurethane Composite Electrode for the Determination of Hydroquinone in Photographic Developers. *Talanta.* **2006**, *68*, 708-712.

22. O'Hare, D.; Macpherson, J. V.; Wilson, A. On the Microelectrode Behaviour of Graphite-Epoxy Composite Electrodes. *Electrochem. Commun.* **2002**, *4*, 245-250.
23. F. Marken, M. L. Gerrard, I. M. Mellor, R. J. Mortimer, C. E. Madden, S. Fletcher, K. Holt, J. S. Foord, R. H. Dahm, F. Voltammetry at carbon nanofiber electrodes. *Electrochem. Commun.* **2001**, *3*, 177-180.
24. Tu, Y.; Lin, Y.; Yantasee, W.; Ren, Z. Carbon Nanotubes based Nanoelectrode Arrays: Fabrication, Evaluation, and Application in Voltammetric Analysis. *Electroanalysis.* **2005**, *17*, 79-84.
25. Luque, M.; Rios, A.; Valcarcel, M. A Poly(vinyl chloride) Graphite Electrode for Flow-Injection Amperometric Determination of Antioxidants. *Anal. Chim. Acta.* **1999**, *395*, 217-223.
26. Fernandez, C.; Reviejo, A. J.; Polo, L. M.; Pingarron, J. M. HPLC-Electrochemical Detection with Graphite-poly (tetrafluoroethylene) Electrode Determination of the Fungicides Thiram and Disulfiram. *Talanta.* **1996**, *43*, 1341-1348.
27. Moreno-Baron, L.; Merkoci, A.; Alegret, S. Graphite-epoxy Composite as an Alternative Material to Design Mercury Free Working Electrodes for Stripping Voltammetry. *Electrochim. Acta.* **2003**, *48*, 2599-2605.
28. Sun, D.; Zhang, H. Electrochemical Determination of 2-chlorophenol Using an Acetylene Black Film Modified Glassy Carbon Electrode. *Wat. Res.* **2006**, *40*, 3069-3074.
29. Pumera, M.; Merkoci, A.; Alegret, S. Carbon-Nanotube-Epoxy Composites for Electrochemical Sensing. *Sens. Actuators B.* **2006**, *113*, 617-622.
30. Mailley, P.; Cummings, E. A.; Mailley, S.; Cosnier, S.; Eggins, B. R.; McAdams, E. Amperometric Detection of Phenolic Compounds by Polypyrrole-Based Composite Carbon Paste Electrodes. *Bioelectrochem.* **2004**, *63*, 291-296.
31. Ramesh, P.; Sivakumar, P.; Sampath, S. Renewable Surface Electrodes based on Dopamine Functionalized Exfoliated Graphite: NADH Oxidation and Ethanol Biosensing. *J. Electroanal. Chem.* **2002**, *528*, 82-92.
32. Somashekarappa, M. P.; Sampath, S. Sol-gel Derived, Silicate-Phtalocyanine Functionalized Exfoliated Graphite Based Composite Electrodes. *Anal. Chim. Acta.* **2004**, *503*, 195-201.
33. Shankaran, D. R.; Uehara, N.; Kato, T. Sol-gel Derived Metal Dispersed Ceramic-Graphite Composite Electrode for Amperometric Determination of Dopamine. *Anal. Chim. Acta.* **2003**, *478*, 321-327.
34. Cervini, P.; Ramos, A.; Cavalheiro, E. T. G. Determination of Atenolol at a Graphite-Polyurethane Composite Electrode. *Talanta.* **2007**, *72*, 206-209.
35. Salimi, A.; MamKhezri, H.; Hallaj, R. Simultaneous Determination of Ascorbic Acid, Uric Acid and Neurotransmitters with a Carbon Ceramic Electrode Prepared by Sol-Gel Technique. *Talanta.* **2006**, *70*, 823-832.
36. Kirgoz, U. A.; Odaci, D.; Timur, S.; Merkoci, A.; Alegret, S.; Besun, N.; Telefoncu, A. A Biosensor Based on Graphite Epoxy Composite Electrode for Aspartame and Ethanol Detection. *Anal. Chim. Acta.* **2006**, *570*, 165-169.
37. Ramirez-Garcia, S.; Alegret, S.; Cespedes, F.; Forster, R. J. Carbon Composite Electrodes: Surface and Electrochemical Properties. *Analyst* **2002**, *127*, 1512-1519.

38. Ardakani, M. M.; Akrami, Z.; Kazemian, H.; Zare, H. R. Electrocatalytic Characteristics of Uric Acid Oxidation at Graphite-Zeolite-Modified Electrode Doped with Iron (III). *J. Electroanal. Chem.* **2006**, *586*, 31-38.
39. Wang, J. In *Analytical Electrochemistry*; VCH Publishers: *New York*, **1994**; *Chapter 6*, p.163.

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