Use of Ruthenium–(Ethylenedinitrito)-tetraacetic Acid Monohydrate Ion Immobilized on Zirconium(IV) Oxide Coated Silica Gel Surface as an Amperometric Sensor for Oxygen in Water

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[Ru(edta)H₂O]⁻ adsorbed on zirconium(IV) oxide coated on the surface of silica gel was used for the construction of an amperometric sensor for O₂ in water, using a carbon paste electrode. The adsorbed complex electrocatalyses the oxygen reduction reaction at −250 mV *versus* SCE. The cathodic current was linear for an oxygen concentration between 0.55 and 8.0 ppm, with a correlation coefficient of 0.998 and a relative standard deviation of 2.7%. The sensor response is constant within the solution pH values 2.0 and 6.5. The concentration of O₂ in a natural sample was also determined.

A precise and specific method for the determination of oxygen is a matter of great interest. The most used device for such purpose has been the membrane covered Clark-type electrode[1], in which oxygen diffuses through a gas-permeable membrane and is reduced on a platinum cathode polarized between −0.6 and −0.8 V *versus* Ag/AgCl as reference. The resultant current flow is linearly related to the partial pressure of the oxygen in the sample. However, changes in the membrane permeability or cathode surface area can cause a considerable decrease in the sensor response. These can be avoided by use of chemically modified electrodes which allow direct contact of the sensor with the species in solution. However, such kind of electrodes are relatively rare.[2–6]

The study of the immobilization and electrochemical properties of electroactive species on metal oxide coated on silica gel surfaces has been a subject of interest in our laboratory in recent years.[7,8] Carbon paste electrodes prepared with these materials have been used as chemical sensors.[9–11] The electroactive species strongly adhere to the modified surfaces with an additional advantage that silica gel has high chemical stability and mechanical resistance. Of particular interest is the [Ru-(edta)H₂O]⁻ complex immobilized on zirconium(IV) oxide coated on a silica gel surface which electrocatalyses oxygen reduction in aqueous solution.[12] Taking into account the potential use of this material for the development of a new sensor for oxygen determination, a study of its preparation and uilization as an amperometric sensor is described here.
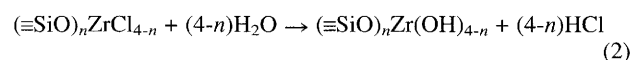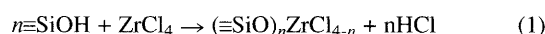
Experimental

Zirconium(IV) Oxide Coating on the Silica Gel Surface

Silica gel (Merck, Elmsford, NY, USA) with a specific surface area, S_{BET}, of 500 m² g⁻¹, an average pore diameter of 6 nm and a particle size between 0.025 and 0.2 mm, was dried at 423 K under vacuum (0.13 Pa) for 4 h. About 50 g of the activated

silica was added to a solution containing 11.6 g (0.05 mol) of pure $ZrCl_4$ dissolved in 300 cm³ of dry ethanol. The mixture was refluxed for 8 h, under a nitrogen atmosphere, and the resulting solid was washed by decantation and then heated at 400 K under vacuum (0.13 Pa). The material was carefully hydrolysed by immersion in demineralized water. The solid was washed with water to remove all chloride ions and then dried in an oven at 393 K for 5 h.

The following equations can be written to represent the reactions:

$$n{\equiv}SiOH + ZrCl_4 \rightarrow ({\equiv}SiO)_n ZrCl_{4-n} + nHCl \qquad (1)$$

$$({\equiv}SiO)_n ZrCl_{4-n} + (4-n)H_2O \rightarrow ({\equiv}SiO)_n Zr(OH)_{4-n} + (4-n)HCl \qquad (2)$$

where $\equiv$SiOH stands for silanol groups on the silica surface.

The amount of the attached Zr on the surface was 0.32×10^{-3} mol g⁻¹, as determined by X-ray fluorescence analysis.

Adsorption of [Ru(edta)(H₂O)]⁻ on the Matrix Surface

[Ru(edta)(H₂O)]⁻ was prepared as described in the literature.[13] About 0.2 g of the dry product $({\equiv}SiO)_n Zr(OH)_{4-n}$, hereafter denoted as SiO_2–ZrO_2, was immersed in 20 ml of 0.1 mol dm⁻³ [Ru(edta)(H₂O)]⁻ solution and shaken for 15 min. The complex is strongly adsorbed on the surface in slightly acidic solution (2 ≤ pH ≤ 6.5), forming the species represented as SiO_2–ZrO_2–[Ru(edta)H₂O]⁻.

The solid obtained was filtered, washed with demineralized water and dried for 2 h, at room temperature, under vacuum. The amount of adsorbed complex, determined by X-ray fluorescence analysis, was 12×10^{-6} mol g⁻¹.

Electrochemical Experiments

The electrochemical experiments were performed by using a PAR 273A potentiostat (EG&G Princeton, NJ, USA). A three-electrode system, consisting of a modified working electrode, a saturated calomel reference electrode (SCE) and a platinum wire as auxiliary electrode, was used. The working electrode was made by mixing 40 mg of the material with 30 mg of graphite powder (Fluka, Buchs, Switzerland) and a small amount of paraffin oil. All experiments were carried out in 1 mol dm⁻³ sodium chloride supporting electrolyte solution at pH 4.5.

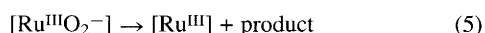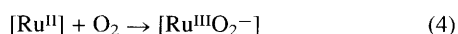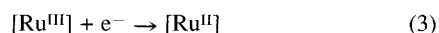The concentrations of O₂ in solution were determined by using a Fac 204 analyser with a Clark electrode.

Results and Discussion

Cyclic Voltammetry

Fig. 1 shows the cyclic voltammograms obtained when using the carbon paste electrodes. Fig. 1(c) shows the cyclic

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voltammogram obtained, under argon, for the electrode made with SiO_2–ZrO_2. No current is observed in this case. Fig. 1(a) shows the cyclic voltammogram using the carbon paste electrode made with SiO_2–ZrO_2–[Ru(edta)H$_2$O]$^-$, under argon. An enhancement of the current can be observed in this case and the cathodic peak potential corresponding to the reduction of Ru^{III}/Ru^{II} is observed at -300 mV. Saturation of the solution in the cell with pure oxygen causes an enhancement of the cathodic peak current [Fig. 1(b)] due to catalysis of the oxygen reduction reaction. The possible mechanism of this reaction can be represented as

$$[Ru^{III}] + e^- \rightarrow [Ru^{II}] \tag{3}$$

$$[Ru^{II}] + O_2 \rightarrow [Ru^{III}O_2^-] \tag{4}$$

$$[Ru^{III}O_2^-] \rightarrow [Ru^{III}] + \text{product} \tag{5}$$

where eqn. (3) represents the electrochemical reduction of [Ru(edta)H$_2$O]$^-$ complex on the electrode surface from Ru^{III} to Ru^{II}; eqn. (4) accounts for the coordination of the O$_2$ to the ruthenium atom and the electron transfer and eqn. (5) represents the formation of the product.

Because oxygen can also be reduced on the graphite surface, a cyclic voltammogram using an SiO_2–ZrO_2 electrode under an atmosphere of oxygen was obtained [Fig. 1(d)]. In this instance the cathodic current is observed at -500 mV. Comparing the peak potential in Fig. 1(b) with that of Fig. 1(d), in the electron mediated process (b) the potential is 200 mV more positive than in the absence of the electrocatalyst.

Chronoamperometry

Under stationary conditions, using chromoamperometry, for different applied potentials, it is observed that the catalytic current starts at -100 mV and achieves a constant value at -275 mV (Fig. 2). The cathodic potential of the present electrode is more positive than those observed for other chemically modified electrodes, *i.e.*, nearly -400 mV.[2,3,6] This minimizes the effect of interferent species which are normally reduced at lower potentials.

The sensor performance using chronoamperometry was tested at a constant potential of -250 mV while O$_2$ was bubbled into the cell in sucessive steps, at constant temperature. The catalytic current intensities generated on the surface of the working electrode were measured during the experiment and by using the Clark electrode immersed in the cell, the amounts of O$_2$ dissolved in the solution were measured simultaneously. Fig. 3 shows the current *versus* response time for one partial pressure of O$_2$. The response time is short: in this instance it is 10 s. On
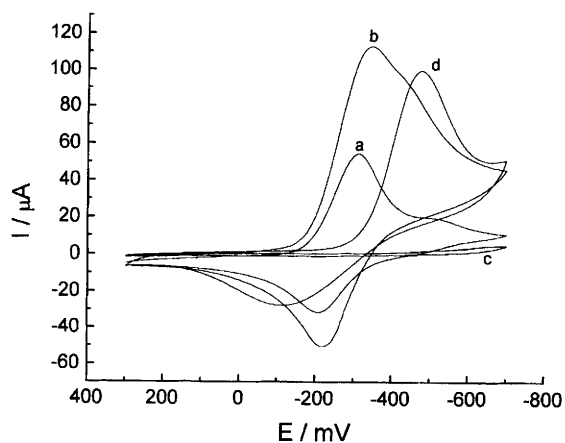
constructing the graph of cathodic current intensities against oxygen concentration in the solution, [O$_2$], a linear relationship is obtained and represented by the equation $I = 0.41[O_2] + 0.90$, with a linear correlation coefficient of 0.998 for oxygen concentrations between 0.55 and 8.0 ppm. The relative standard deviation for replicates of eight measurements was 2.7%.

Chemical Stability

The electrode material, SiO_2–ZrO_2–[Ru(edta)H$_2$O]$^-$, was stored for 1 year after its peparation and no loss in the response capacity was detected. One electrode prepared as described in the experimental part, at continuous use, maintained the response for at least 240 h. These two experiments indicate that the electroactive species is chemically very stable.

Influence of pH

The carbon paste electrode can be used in supporting electrolyte solutions at a pH between 2 and 6.5 with no significant change in the current intensities. However, at solutions of pH lower than 2 the cyclic voltammograms change due to the protonation of the free carboxy group on the coordinated edta ligand. Fig. 4 shows the cyclic voltammograms obtained at pH 1.2 and 0.8. It can be observed that the mid-point potentials are at -250 and -220 mV, respectively. The reaction that occurs can be represented by the equation

$$[Ru(edta)H_2O]^- + H^+ \rightarrow [Ru(Hedta)H_2O] \tag{6}$$
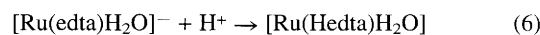
The pK_a of this reaction is 2.37.[14]

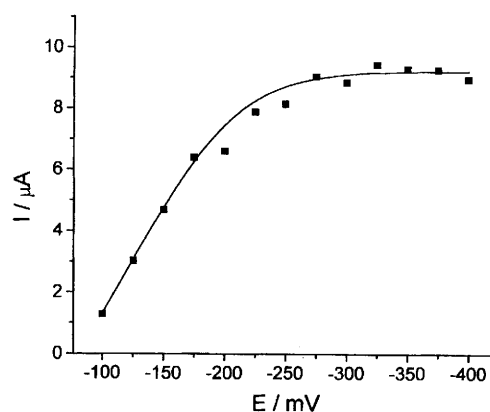**Fig. 2** Catalytic current of the electrode containing SiO_2–ZrO_2–[Ru(edta)H$_2$O]$^-$ as a function of potential (E), in an O$_2$ saturated supporting electrolyte solution

Fig. 1 Cyclic voltammograms of SiO_2–ZrO_2–[Ru(edta)H$_2$O]$^-$ in argon (a) and in oxygen (b), and of SiO_2–ZrO_2 in argon (c) and in oxygen (d) saturated solution. Scan rate, 5 mV s^{-1}

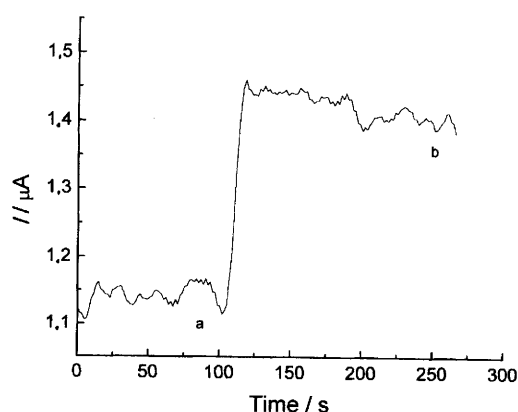**Fig. 3** Chronoamperogram of SiO_2–ZrO_2–[Ru(edta)H$_2$O]$^-$ with increasing oxygen concentration in solution: 0.6 (a) and 1.2 ppm (b). Applied potential, -250 mV

Lability of the Coordinated Water

It is known that the coordinated water molecule in the $[Ru(edta)H_2O]^-$ complex is kinetically labile in solution phase[15] as well as at the surface of the SiO_2–ZrO_2 matrix.[12] Replacement of the coordinated water molecule by nitrogen donor atom ligands such as pyridine and derivatives can deactivate the oxygen reduction reaction due to the reaction:

$$SiO_2\text{–}ZrO_2\text{–}[Ru(edta)H_2O]^- + L \rightarrow$$
$$SiO_2\text{–}ZrO_2\text{–}[Ru(edta)L]^- + H_2O \tag{7}$$
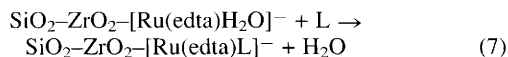
Since the mechanism of the electrocatalysis involves the coordination of the oxygen molecule to the ruthenium(II) atom as the first step of the reaction [eqn. (4)], and considering that the L-substituted surface complex is relatively inert, the reduction of the oxygen at this electrode surface is not observed.

Chemical Analysis

An experiment to compare the response of the chemically modified electrode with that obtained using a Clark electrode was also carried out. Plotting the concentration of oxygen in a water sample obtained simultaneously using both electrodes, a linear relationship represented by the equation $[O_2]_{Ru(edta)} = 0.023 + 0.99 [O_2]_{Clark}$ and a correlation coefficient of 0.997 was obtained, in a concentration range between 0.6 and 7 ppm.

To test the electrode response for a natural sample, water from the lake on the University campus was collected, analysed and compared with the result obtained using the Clark electrode.
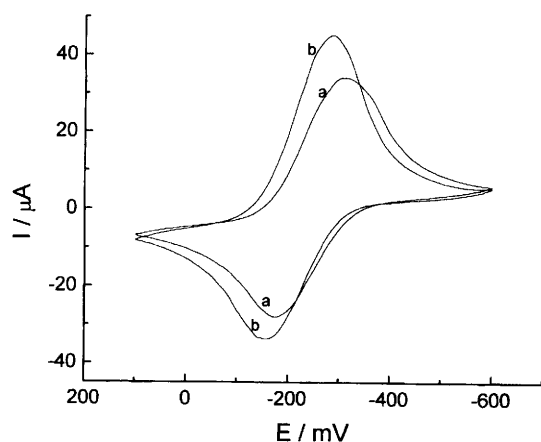

Fig. 4   Cyclic voltammogram of SiO_2–ZrO_2–$[Ru(edta)H_2O]^-$, under an argon atmosphere, at pH 1.2 (a) and 0.8 (b). Scan rate, 10 mV s^{-1}

The results were (in ppm) 2.10 ± 0.09 and 2.10 ± 0.06, respectively. The results are in excellent agreement, indicating that the SiO_2–ZrO_2–$[Ru(edta)H_2O]^-$ carbon paste electrode can be employed for the determination of O_2 in water.

Conclusions

The performance of the SiO_2–ZrO_2–$[Ru(edta)H_2O]^-$ carbon paste electrode is similar to that shown by the Clark electrode. However, the advantage in the present work is that the electrode is specific for dissolved oxygen. Another advantage is that the use of a semi-permeable membrane, the main function of which is to avoid diffusion of interferent species which could also be reduced at the electrode surface, is not necessary for the present electrode because the reduction potential is -250 mV against -500 mV for the Clark electrode.

References

1   Clark, L. C., Jr., *Trans. Am. Soc. Ant. Int. Organs*, 1956, **2**, 41.
2   Zen, J. M., and Wang, C. B., *J. Electroanal. Chem.*, 1994, **368**, 251.
3   Litong, J., Ping, J., Jiannong, Y., and Yuzhi, F., *Talanta*, 1992, **39**, 145.
4   Yim, H. S., and Meyerhoff, M. E., *Anal. Chem.*, 1992, **64**, 1777.
5   Dong, S., and Kuwana, T., *Electrochim. Acta*, 1988, **33**, 667.
6   Oyama, N., Oki, N., Ohno, H., Ohnuki, Y., Matsuda, H., and Tsuchida, E., *J. Phys. Chem.*, 1983, **87**, 3642.
7   Zaldivar, G. A. P., Gushikem, Y., Benvenutti, E. V., de Castro, S. C. and Vasquez, A., *Electrochim. Acta*, 1994, **39**, 33.
8   Kubota, L. T., and Gushikem, Y., *J. Electroanal. Chem.*, 1993, **362**, 219.
9   Lorencetti, L. L., and Gushikem, Y., *J. Braz. Chem. Soc.*, 1993, **4**, 88.
10   Kubota, L. T., Gushikem, Y., Perez, J., and Tanaka, A. A., *Langmuir*, 1995, **11**, 1009.
11   Milagres, B. G., Kubota, L. T., and de Oliveira Neto, G., *Electroanalysis*, in the press.
12   Peixoto, C. R. M., Rodrigues Filho, U. P., Stadler, E., Kubota, L. T., and Gushikem, Y., *Vth Iberoamerican Meeting of Inorganic Chemistry*, Mexican Inorganic Chemistry Academy, Mexico City 1995, p. 321.
13   Mukaida, M., Okuno, H., and Ishimori, T., *Nippon Kagaku Zasshi*, 1965, **86**, 589.
14   Shimizu, K., Matsubara, T., and Satô, G. P., *Bull. Chem. Soc. Japan*, 1974, **47**, 1651.
15   Matsubara, T., and Creutz, C., *Inorg. Chem.*, 1979, **18**, 1956.