

Electron Mediator Property of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ Immobilized on Zr(IV) Oxide Coated on a Silica Gel Surface

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Sílica possuindo um diâmetro médio de poros de 6nm e tamanho médio das partículas entre 0,063-0,20mm e uma área superficial específica de $500\text{m}^2\text{g}^{-1}$ foi recoberta com óxido de zircônio(IV). A sílica gel assim modificada foi utilizada para imobilizar o complexo aniônico de hexacianoferrato na superfície. O íon ligado à superfície foi capaz de mediar a transferência de elétrons entre o eletrodo e uma solução contendo ácido ascórbico. A magnitude do pico de corrente anódica mostrou uma correlação linear em função da concentração do ácido ascórbico. Esta propriedade foi utilizada para determinar ácido ascórbico em comprimidos de vitamina C e em sucos naturais e concentrados.

A silica gel having an average pore diameter of 6nm and particle size between 0,063-0,20mm and specific surface area of $500\text{m}^2\text{g}^{-1}$, was coated with Zr(IV) oxide. The resulting modified silica gel was used to immobilize a highly charged hexacyanoferrate anionic complex on the surface. The attached anion was able to mediate electron transfer between the electrode and the solution containing ascorbic acid. The magnitude of the anodic peak current showed a linear relationship against the ascorbic acid concentration. This property was used to determine the amount of ascorbic acid in tablets of vitamin C, in fresh and processed juices.

Key words: silica gel; zirconium(IV) oxide; ascorbic acid.

Introduction

In recent years, a great deal of attention has been paid to the development of chemically modified surface electrodes. Electrode materials used for modification include SnO_2 , RuO_2 , Pt/PtO, glassy carbon and pyrolytic graphite¹⁻⁵. The reason for working with such kinds of electrodes is the expectation that it should be possible to make use of catalytic and selective interactions between species in solution and on the electrode surface. In a method described by Murray, an electrode was coated with an ion exchange polymer film into which was partitioned a highly charged, redox active ion such as hexacyanoferrate⁶.

In our laboratory we have developed methods of preparing metal oxides highly dispersed on silica gel surface. The deposited substrate retained in most cases the ion exchange properties of the metal oxides obtained by precipitation methods^{7,8}. Of particular interest has been the property of zirconium(IV) oxide dispersed on silica gel surface which showed a high affinity for hexacyanoferrate anion, strongly entrapped on the surface by ion pairing interaction.

In this work is described the preparation, characterization and an attempt to use hexacyanoferrate anion immobilized on chemically modified silica gel surface with zirconium(IV) oxide as an electrochemical sensor for ascorbic

acid. The oxidation of ascorbic acid is known to be catalyzed by hexacyanoferrate(III)^{6,9}. The silica gel matrix despite its insulator nature showed good conductivity upon chemical modification and a great advantage in using such kind of material was the chemical stability of the electroactive species.

Experimental

In a reaction vessel, 50g of silica gel 60 Merck, particle size between 0.063-0.20mm and $500\text{m}^2\text{g}^{-1}$ of specific surface area, was immersed in 300ml of ZrOCl_2 0.17M and the mixture was stirred at 373K for 6h. The solid was filtered, washed with bidistilled water until negative test for chloride ion and then dried at 423K for 6h in an oven. The analysis of the attached Zr(IV) oxide on the silica surface was carried out by using the X-ray fluorescence technique.

Immobilization of $[\text{Fe}(\text{CN})_6]^{4-}$ on the surface

The silica gel modified with Zr(IV) oxide, hereafter denoted as SZ, was initially washed with 0.1M HNO_3 solution and shaken for 30 minutes. The solid was filtered, washed with water and dried at room temperature under vacuum (10^{-4} Torr).

The analysis of attached ferrocyanide on the surface was carried out following the procedure: 0.1g of the solid was treated with 10ml of concentrated HNO_3 and heated on a

water bath until reduction of the original volume to about 1ml. More HNO₃ was added to complete the original volume and the operation repeated. The solution was filtered and the amount of Fe³⁺ analyzed by atomic absorption spectroscopy.

Cyclovoltammetry study

A carbon paste electrode of the material was prepared to carry out the cyclovoltammetry (CV) studies. The electrochemical experiments were performed using a MRA-Cyclovoltamograph equipment coupled to a ECB RB400 X-Y recorder. A platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode was used.

In order to study the electron mediator property of hexacyanoferrate adsorbed on SZ the response of the electrode, made with this material, against the concentration of H₂AA was studied. An electrochemical cell was filled with 20ml of NaCl 0.5M electrolyte solution the pH of which was adjusted to 4.5 and the electrode immersed in this solution. The solution in the cell was initially purged with purity grade nitrogen and then the electrode was allowed to condition for about ten minutes until a stable current vs potential signal was obtained. An aliquot of 0.200 ± 0.005ml of 0.100M standard ascorbic acid solution was added and the CV recorded between -0.3 to 0.7V. After each complete cycle this procedure was repeated by successively adding the same volume of the standard solution into the cell.

To determine the amount of H₂AA in a tablet of vitamin C, about 4g of the sample was dissolved in a bidistilled water and the volume completed to 50ml (solution A). The electrode used to obtain the calibration curve was rinsed in bidistilled water and immersed in 20ml of 0.5M NaCl electrolyte solution the pH of which was previously adjusted to 4.5. The cell was initially purged as described above and an aliquot of 0.300 ± 0.005ml of the solution A was added and the CV recorded. The analysis were carried out for three different trade name of vitamin C tablets.

The content of H₂AA was also determined in fresh orange and lemon juice and for processed juice. About 25ml of the juice was centrifuged when necessary, the acidity of the solution adjusted to pH=4.5 and the analysis of H₂AA carried out by CV technique as described above.

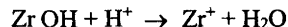
In order to check the reliability of the CV analysis, they were compared with results for determination of H₂AA obtained by standard procedures described in literature by using KIO₃ or 2,6-dichlorophenolindophenol as the titrant reagents¹⁰.

Table 1. CV parameters obtained for SZ-[Fe(CN)₆]^{3-/4-} in NaCl 0.5M.

Scan rate mVs ⁻¹	I _{pa} μA	I _{pc} μA	E _{pa} mV	E _{pc} mV	(E _{pa} +E _{pc})/2 V
1	11.0	14.5	235	208	0.22
2	22.5	31.0	240	180	0.21
5	49.0	66.0	265	133	0.20
10	77.0	100.0	298	95	0.20

Results and Discussion

Zirconium(IV) oxide is a weakly basic oxide at lower pH can dissociate according with the reaction described by the equation¹¹:



In the present case the Zr(IV) oxide grafted on the silica surface was able to adsorb the hexacyanoferrate anion at this pH giving rise to a chemical species immobilized on the surface. This material, which will hereafter be denoted as SZ-[Fe(CN)₆]^{3-/4-}, showed an amount of the electroactive species attached on the surface of 0.11x10⁻³mol g⁻¹.

The infrared spectrum of the disk obtained with the material SZ-[Fe(CN)₆]⁴⁻ showed a band at 2025cm⁻¹ due to the CN stretching mode. The position of this band is the same as that found for potassium hexacyanoferrate(II)¹², indicating that the interaction of the anion complex with the SZ surface is of electrostatic nature. A stronger interaction should shift the CN stretching frequency toward higher energy region^{13,14}.

Cyclovoltammetry study of SZ-[Fe(CN)₆]^{3-/4-}

The measurements were made using three electrodes prepared in all case following the same procedure in order to study the reproducibility characteristic. A typical CV figure, peak current, I_p, against the potential, E, is shown for a representative electrode in Fig. 1. The main parameters are listed in Table 1. The surface potential, E^o = (E_{pa} + E_{pc})/2 = 0.20 ± 0.03V, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, was obtained from the CV waves obtained at different scan rates. This potential is very close to that obtained for [Fe(CN)₆]^{3-/4-} in solution under similar conditions^{9,15}. The ratio between the anodic peak current, I_{pa}, and the cathodic peak current, I_{pc}, showed values very close to the reversibility condition at lower sweeping scan rate. Inset in the Fig. 1 shows the I_{pa} plotted against the square root of

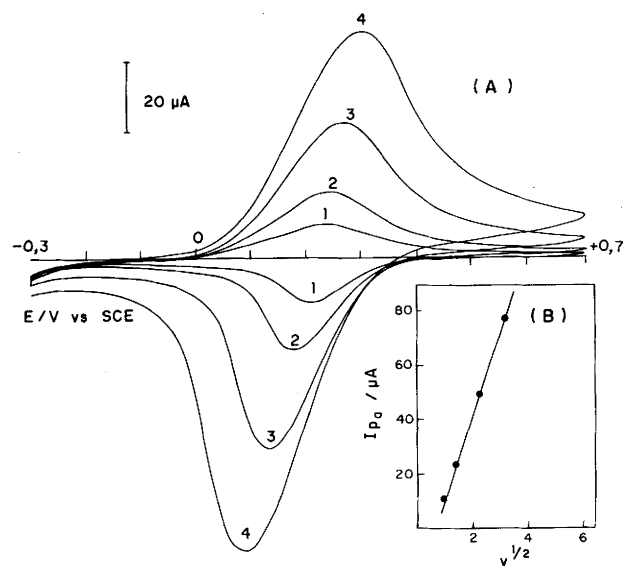


Figure 1. (A) CV waves for SZ-[Fe(CN)₆]^{3-/4-} carbon paste electrode (0.13cm²) in 0.5M NaCl solution. 1) 1mVs⁻¹ 2) 2mVs⁻¹ 3) 5mVs⁻¹ 4) 10mVs⁻¹.

(A) Anodic peak current, I_{pa}, against the square root of the scan rate.

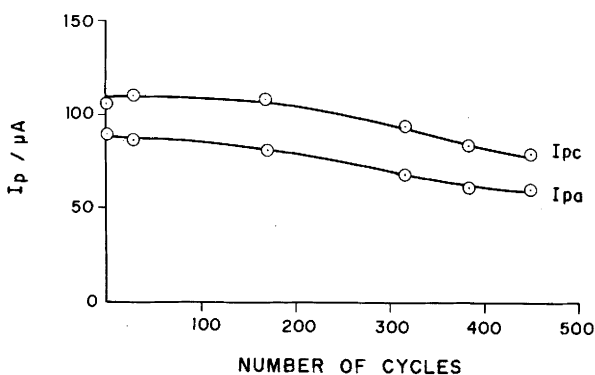


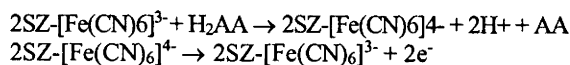
Figure 2. Peak currents vs number of redox cycles of SZ-[Fe(CN)₆]^{3-/4-} carbon paste electrode in 0.5M NaCl solution and scan rate of 20mVs⁻¹.

the scan rate. A linear relationship was obtained in this case.

The system is electrochemically very stable as can be observed in Fig. 2, where both, the I_{pa} and I_{pc} are plotted against the number of redox cycles. The small decrease observed in I_{pa} and I_{pc} is indicating that leaching or decomposition of the electroactive species from the surface is very small after 450 redox cycles.

Electron mediator property of SZ-[Fe(CN)₆]^{3-/4-}

The hexacyanoferrate(II) ion attached on SZ surface was able to mediate electron transfer between the electrode and the solution containing ascorbic acid, H₂AA. Comparing the CV waves scanned in absence and presence of H₂AA (Figs. 1 and 3), the enhancement of I_{pa} in the latter case, is an indication of the following reactions at the solid-solution interface:



where AA is the dehydroascorbic acid.

The magnitude of the I_{pa}, subtracted for the anodic peak current in absence of H₂AA, is plotted against the concen-

Table 2. Comparison of amount of ascorbic acid determined in a vitamin C tablet and in fruit juices.

Samples	CV (g)	Titration (g)	Declared amount (g)
A	1.03 ± 0.02 ^a	1.00 ± 0.01 ^c	1.0
B	0.99 ± 0.02 ^a	1.01 ± 0.01 ^c	1.0
C	1.09 ± 0.02 ^a	1.10 ± 0.01 ^c	1.0
lemon juice	0.26 ± 0.01 ^b	0.25 ± 0.01 ^d	
orange juice	0.28 ± 0.01 ^b	0.29 ± 0.01 ^d	
proc. juice	0.22 ± 0.01 ^b	0.21 ± 0.01 ^d	

^a content per tablet of 4g; ^b mg per ml of juice; ^c titration with standard KIO₃ solution; ^d titration with standard 2,6-dichlorophenolindophenol solution.

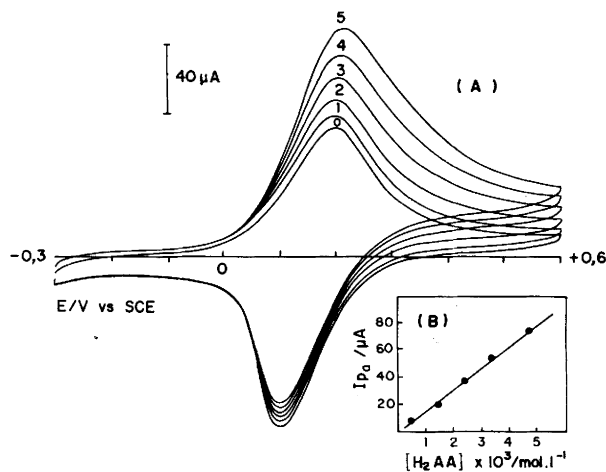


Figure 3. (A) CV waves scanned at 10mVs⁻¹ in 0.5M NaCl solution, in absence of ascorbic acid (curve 0), and in presence of ascorbic acid (curves 1-5). (B) Anodic peak current, I_{pa}, against the concentration of ascorbic acid.

tration of ascorbic acid (Inset of Fig. 3). The correlation coefficient of the straight line was 0.997.

Determination of ascorbic acid

The measurement were carried out in a solution pH=4.5 and the concentration of the H₂AA between 0.5×10⁻³ and 5×10⁻³ M. The electrochemical response, I_{pa}, in this region was linear and from the calibration straight line, the concentrations of H₂AA in the vitamin C tablets and in the juices were obtained. The results are listed in Tab. 2 and compared with those obtained from chemical analysis using KIO₃ or 2,6-dichlorophenolindophenol as titrants. The declared amount of the H₂AA in each tablet according to each industry certificate was 1.0g of ascorbic acid per tablet.

Conclusions

The electrode fabricated using silica gel matrix coated with zirconium(IV) oxide strongly retained the hexacyanoferrate anion complex on the substrate surface, and was able to mediate the electrocatalytic oxidation of ascorbic acid. The results of the chemical analysis showed a mean value with a relative standard deviation of 4%. The main advantage in using such kind of electrode was the facility of its preparation and the relative high stability of the attached electroactive species which showed small loss of activity after various redox cycles.

Acknowledgements

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References

1. M. Peterson, *Anal. Chim. Acta* **147**, 350 (1983).
2. M. Peterson, *Anal. Chim. Acta* **187**, 333 (1986).
3. H.D. Abruna, *Cood. Chem. Rev.* **86** 135 (1988).

4. B.R. Shaw, and K.E. Creasy, *J. Electroanal. Chem.* **243**, 209 (1988).
5. K.K. Kasem, and H.D. Abruna, *J. Electroanal. Chem.* **242**, 87 (1988).
6. K. Kuo, and R.W. Murray, *J. Electroanal. Chem.* **131**, 37 (1982).
7. L.T. Kubota, Y. Gushikem, and J.C. Moreira, *Analyst* **116**, 281 (1991).
8. S. Denofre, Y. Gushikem, and C.U. Davnzo, *European J. Sol. State Inorg. Chem.* **28**, 1295 (1991).
9. P.W. Geno, K. Ravichandran, and R.P. Baldwin, *J. Electroanal. Chem.* **183**, 155 (1985).
10. M. Freed, *Methods of Vitamin Assay*, (Interscience. New York; 1966) 3th ed.
11. V.V. Strelko, S.A. Khainakov, A.P. Kvashenko, V.N. Belyakov, and A.I. Bortun, *J. Appl. Chem. USSR* **61**, 1922 (1988).
12. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley Interscience. New York; 1970).
13. D.F. Shriver, *J. Am. Chem. Soc.* **85**, 1405 (1963).
14. M. Lamanche, *Electrochim. Acta* **24**, 79 (1979).
15. D. Belanger, *J. Electroanal. Chem.* **251**, 55 (1988).