

Review Article

Investigation of Electrochemical Behavior of Ferri/Ferrocyanide Redox on Carbon Paste Based Electrodes for Mercury (II) Electrochemical Sensor

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Abstract

The electrochemical characterisation of the materials used to make sensors is mostly based on the cyclic voltametry method. Cyclic voltametry is an electrical method for the dynamic study of electrochemical systems. Through a reversible potential sweep, the material is studied in contact with the ferri/ferrocyanide. Ferri/Ferrocyanide is one of the most studied chemical compounds in electrochemistry and photo-electrochemistry because of its singular known and controlled reactivity. The appearance of voltamograms and mathematical expressions make it possible to collect the information necessary for understanding the reaction. An electrode material is considered active if it shows a reversible peak in contact with the redox marker in cyclic voltametry. The mechanism of the reaction is also assessed using the peak potential difference ΔE_p . The nature of the mass transport is determined by the anodic and cathodic peak current ratio I_{pa}/I_{pc} . The aim of this work is to compare the electrochemical activity of the Ferri/Ferrocyanide couple achieved with carbon paste-based electrodes for application to the electrochemical sensor. The study of the peak potential difference ΔE_p showed that the composition of the electrode material influences the reaction mechanism at the interface. Material transport and electronic charge transfer are impacted by complex phenomena. By studying the electrical quantities potential difference ΔE_p , formal standard potential E° and current ratio I_{pa}/I_{pc} , the electrochemical sensors developed can be optimised.

Keywords

Ferri/Ferrocyanide, Cyclic Voltammetry, Modified Carbon Paste Electrode

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1. Introduction

A sensor is an electronic device capable of converting a physical, chemical or biological quantity, called the measurand, into a physically measurable signal, often a voltage or current [1]. The operating principle of a sensor includes a recognition layer (sensitive layer) and a physical component called the transducer [1]. The recognition layer interacts with the target analyte and the transformations resulting from this interaction are translated by the transduction element into usable signals. In the case of an electrochemical sensor, the signal produced (potential-current curve) is proportional to the concentration of the analyte [2]. The choice of the sensitive layer used in the (bio)receiver depends on several criteria, such as its specificity, stability and the nature of the chemical or biological substances to be analysed. The nature of the sensitive layer depends largely on the structure of the electrode material [3, 4]. Carbon paste or modified carbon paste electrodes have been of particular interest in recent decades [5-12].

Chemical modification of carbon paste electrodes is straightforward and can be classified according to three different criteria: the type of modification, the location of the modifier and the modification time. For the type of modification, a distinction can be made between intrinsic and extrinsic modification. When it is one of the components of the carbon paste that carries the functional groups, the modification is said to be intrinsic [13], whereas if the modifier is added to the carbon paste as an additional component, the modification is said to be extrinsic. With regard to the location of the modifier, a distinction can also be made between surface modification and volume modification, depending on the position of the modifying agent on or in the electrode. In the first case, the presence of chemically active components is limited to the surface of the electrode. The sensitive layer derived from these modifications must be able to target the pollutant in question. The aim of this study is to compare the electrochemical activity of the Ferri/Ferrocyanide couple on various working electrodes produced in the laboratory as part of the development of the electrochemical mercury (II) sensor.

2. Materials and Methods

2.1. Equipment

The electrochemical experiments were carried out using a PalmSens potentiostat (from Ecochemie Netherlands) controlled by pstrace software and driven by computer. The analytical method used is cyclic voltametry. The working electrode is a cylindrical glass tube open at both ends, in which the paste is compacted by mechanical and regular stress on clean, smooth paper. A copper rod connected to the potentiostat acts as a current collector. The Ag/AgCl/KCl sat electrode is used as the reference electrode (R) and the plat-

inum as the counter electrode (C). The curves are plotted using origine pro 8 software. The electrodes are in contact with the Ferri/Ferrocyanide couple prepared with distilled water from analytical grade potassium hexacyanoferrate (II) trihydrate $K_4[Fe(CN)_6]$ supplied by Sharlau.

2.2. Preparation of Working Electrodes

The electrodes used in this study are all obtained from bare or modified carbon paste. The modification is made by incorporating the modifier. The modifiers used are p-doped silicon, natural clay and Moringa Oleifera seed powder.

Development of the carbon paste electrode

The carbon paste working electrode is prepared from black graphite powder mixed with a few drops of paraffin oil (approximately 0.3 mL for 1g of graphite), a hydrophobic and inactive binder. The mixture is crushed in a mortar using a pestle to obtain a homogeneous paste. The mixed paste is placed in the electrode body. It is regenerated by regular wiping on clean, smooth paper.

Development of the silicon paste electrode

The silicon paste electrode is p-doped silicon powder (from PhotoWatt SA) obtained by pulverising and sieving polycrystalline silicon. The powder obtained is mixed with paraffin oil and ground in a mortar. The whole assembly is inserted into the body of the cylindrical electrode.

Development of the silicon-carbon paste electrode

The hybrid electrode is obtained by mixing carbon and silicon in a proportion of 10% of the mass of carbon. Paraffin oil (0.3 ml per gram of carbon) is added to this mixture. The mixture is crushed in a mortar to make a homogeneous paste.

Development of the Agban Bingerville clay-modified carbon paste electrode

The clay-modified carbon paste electrode is made by mixing 65% (0.65 g) graphite, 5% (0.05 g) of the extracted fine fraction and 30% (0.3 ml) paraffin oil. The whole mixture was mixed in an agate mortar until the paste was homogeneous. A portion of the paste obtained is then compacted under mechanical control in a glass cylinder and a copper wire is inserted into the carbon paste to ensure electrical contact.

Development of a carbon paste electrode modified with Moringa oleifera seed powder.

The Moringa-modified carbon paste electrode (EPC-MO) is prepared by carefully mixing 0.6 g of graphite powder, 0.1 g of the Moringa seed powder prepared previously and 0.3 ml of paraffin oil in an agate mortar until a homogeneous paste is obtained. Moringa seed powder is obtained from sun-dried seeds. The seeds are ground to a powder using a blender. The powder obtained is sieved with a 500 μ m sieve to obtain finer particles for easier mixing with the carbon powder.

3. Results

3.1. Cyclic Voltammetry Method

Cyclic voltammetry is a powerful means of characterisation in materials science and electrochemistry. It is an electrochemical method based on the measurement of current as a function of potential applied to an electrode. It is considered to be the most universal of electrochemical methods, and can be used both as a method of elucidating reaction mechanisms and as an analytical technique. The principle of the technique is to vary the potential of the working electrode by sweeping back and forth and to study the current obtained. This study is carried out through electrochemical behaviour. The current-potential curve, known as the voltamogram, gives a certain amount of information about the system under study. In the case of a reversible system, the peak current obeys the Randles-Sevcik equation (1) [14, 15]:

$$I_p = (2, 687 \cdot 10^5) n^{3/2} \cdot A \cdot D^{1/2} \nu^{1/2} \cdot C \quad (1)$$

where n is the number of electrons involved in the redox reaction; A is the surface area of the electrode in cm^2 , ν is the sweep rate in V/s ; C is the concentration of the active species in mol/cm^3 , D is the diffusion coefficient in cm^2/s .

The reaction mechanism is assessed using the peak potential deviation ΔE_p study (2) [16].

$$\Delta E_p = E_{pa} - E_{pc} \quad (\text{mV}) \quad (2)$$

With E_{pa} : anodic peak potential; E_{pc} : cathodic peak potential. The value of ΔE_p gives information about the reaction mechanism. Thus:

If $\Delta E_p = 60$ (mV), the system is rapidly reversible.

If $\Delta E_p > 60$ (mV), the system is slow quasi-reversible or slow quasi-irreversible.

From the peak potentials, the formal standard potential of the oxidizing/reducing couple E^0 is calculated from the relation (3) [17]:

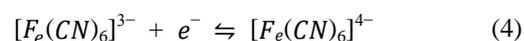
$$E^0 = (E_{pa} + E_{pc}) / 2 \quad (3)$$

The other parameter used to study the cyclic voltamogram is the ratio between the anodic and cathodic peak currents: $|I_{pa}/I_{pc}|$ [16]. This ratio provides information on transport phenomena and competing phenomena. Depending on the value taken by this ratio, the following interpretation is deduced.

- 1) if this ratio is equal in absolute value to 1, the reaction is reversible (slow kinetics);
- 2) if this ratio is different from 1, it means that a chemical reaction is coupled to the charge transfer or that complex phenomena are occurring at the electrode.

3.2. Study of the Electrochemical Behaviour of Ferri/Ferrocyanide

Cyclic voltametry of the Ferri/Ferrocyanide pair reveals a reversible mechanism with an anodic peak and a cathodic peak. This redox reaction obeys Nernst's law. The balance equation is equation (4):



By convention, the peak above the $I = 0$ line is the peak of an oxidation and the peak below this line is the peak of a reduction.

Figure 1 shows the cyclic voltamogram obtained with the carbon paste electrode (EPC).

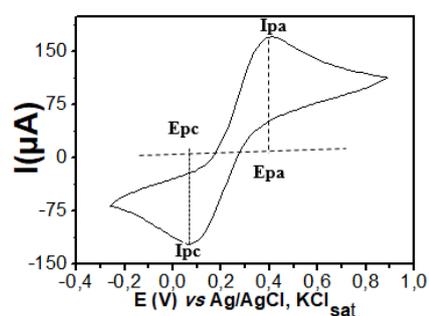


Figure 1. Cyclic voltamogram of the ferri/ferrocyanide pair at 30 mM concentration on a carbon paste electrode at pH = 7, sweep rate 30 mV/s.

The voltamogram shows an anodic current peak (I_{pa}) and a cathodic current peak (I_{pc}) separated by the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. The redox reaction is correctly carried out in contact with this electrode material. The carbon paste electrode is an active material. All electrode materials in contact with the Ferri/Ferrocyanide couple should show this curve if they are active. The materials in this comparative study were studied using cyclic voltammetry at deposition potential $E_{dep} = -1.1$ V in contact with the Ferri/Ferrocyanide couple. The electrical parameters current and potential were processed to obtain the peak potential and current ratio. Table 1 shows the results obtained.

Table 1. Electrical values of the working electrode in the presence of the Ferro/Ferrocyanide couple in cyclic voltametry (CV).

W	ΔE_p (V)	$ I_{pa}/I_{pc} $	E^0 (V)
EPC [18]	0.19	1.05	0,205
EPSi [20]	0,30	3.00	0,23
EPC-Si [20]	0,29	1,51	0,245
EPC-MO [18]	0.17	0.96	0,205

W	ΔE_p (V)	$ I_{pa}/I_{pc} $	E^0 (V)
EPC- AG [19]	0.10	1.59	0,505

Analysis of the table shows different values for E^0 , ΔE_p and the ratio of $|I_{pa}/I_{pc}|$ ratio. This first observation suggests that the electrode materials influence the electrochemical activity of the Ferri/Ferrocyanide couple. Their different values indicate the position of the parameters I_{pa} , I_{pc} , E_{pa} , and E_{pc} are influenced by the electrode material during the reaction.

4. Discussion

4.1. Study of the Peak Potential Difference

The study of the potential difference ΔE_p obtained with all reactions is greater than 60 mV [16]. This suggests that the Ferri/ Ferrocyanide reaction is slow, quasi-reversible or quasi-irreversible. The slow reaction obtained suggests that the resistance to current flow is large in the electrode material. The value of ΔE_p makes it possible to compare the reaction mechanism obtained with each electrode. The lower the ΔE_p , the more conductive the electrode material. This suggests that there is better cohesion within the material, and therefore a more conductive material. Analysis of the table reveals that it is the carbon paste electrodes modified by clay and Moringa seed powder that show better cohesion, while the silicon-based materials show greater resistivity. The reactivity of Moringa is closer to that of bare carbon paste. The reaction with the clay-modified electrode appears to be faster. Electrodes modified with inorganic materials produce a higher anode current. The nature of the current influences the nature of the anodic and cathodic reactions [12].

4.2. Current Ratio Study

The current ratios $|I_{pa}/I_{pc}|$ obtained are different and different from unity. This difference in values indicates that the electronic transfers do not operate in the same way with the electrode materials. It also shows the importance of the anodic and cathodic currents. When the two currents have the same value, the two peaks are in equal proportions. When the ratio is greater than 1, the anode current is greater than the cathode current in absolute value. Otherwise, the cathodic current is higher. Analysis of the table shows high peak ratios with the inorganic materials silicon and clay. With *Moringa oleifera*, the ratio is less than 1, showing that the reduction reaction produces a larger peak than the oxidation reaction. The fact that this ratio is different from unity suggests that the electron transfer linked to the reaction is coupled to the phenomenon of matter transport.

4.3. Study of Formal Standard Potential

The analysis in Table 1 shows different values for the apparent standard potential. The differences in the apparent standard potential suggest that the electrode material has an influence on the apparent standard potential. The electrode material is subject to the stable potential provided by the reference electrode. This suggests that the reaction environment has an impact on this parameter. The values presented are close to those of the bare carbon paste electrode apart from that of the clay-modified carbon paste electrode. The values for the silicon-based electrodes are slightly higher than those for the bare carbon paste electrode. The high value obtained with clay is thought to be due to the influence of the complex structure of natural clay. The structure of the electrode modifier influences the formal standard potential.

5. Conclusions

The electrochemical behaviour of Ferri/Ferrocyanide at the working electrode in cyclic voltammetry is a powerful means of characterising materials. The shape of the voltammograms and the mathematical expressions for the potential difference ΔE_p , the formal standard potential E^0 and the peak current ratio I_{pa}/I_{pc} provide information about the reaction mechanism and the nature of the mass transport. Analysis of these parameters shows that all the electrodes exhibit a reaction with slow kinetics in contact with the redox marker. Mass transport is influenced by complex phenomena. The effect of these phenomena is greatest for the carbon paste electrode modified with natural clay. The standard formal potential of this electrode shows a large overvoltage at the electrode. The complex composition of this material is thought to be the cause. The difference in values for the parameters studied shows that the reactivity is different. To understand and identify the phenomena interacting during the reactions, we need to consider the physical characterisation of these materials.

Abbreviations

W	Working Electrode
EPC	Carbon Paste Electrode
EPSi	Silicon Paste Electrode
EPC-Si	Carbon Paste Electrode Modified with 10% p-doped Silicon
EPC-MO	Carbon Paste Electrode Modified with 10% Moringa Oleifera Seed Powder
EPC-AG	Carbon Paste Electrode Modified with 5% Natural Agban Clay

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The authors respected scientific integrity during the writing

of the review article. All material used was properly cited. This article is not published anywhere. The article will undergo all stages of publication before deciding otherwise. Furthermore, generative AI was not used during the writing.

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The authors have respected the codes of ethics in writing this article. The journal used has been correctly cited. There is no plagiarism or self-plagiarism.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

- [1] Asch, G. Desgoutte, P. Les capteurs en instrumentation industrielle - 8th edition. Dunod. 2017, p28. <https://doi.org/10.3917/dunod.asch.2017.01.0469>
- [2] Luo, P., Zhang, F., and Baldwin, R. P. Constant-potential amperometric detection of underivatized amino acids and peptides at a copper electrode. *Analytical Chemistry*. 1991, 63(17), 1702-1707. <https://doi.org/10.1021/ac00017a010>
- [3] Chen, S., Liu, Y., & Chen, J. Heterogeneous electron transfer at nanoscopic electrodes: importance of electronic structures and electric double layers. *Chemical Society Reviews*. 2014, 43(15), 5372-5386. <https://doi.org/10.1039/c4cs00087k>
- [4] Parsons, R. The kinetics of electrode reactions and the electrode material. *Surface Science*. 1964, 2, 418-435. [https://doi.org/10.1016/0039-6028\(64\)90083-4](https://doi.org/10.1016/0039-6028(64)90083-4)
- [5] Coulibaly, M., El Rhazi, M. Determination of Traces of Copper by Anodic Stripping Voltammetry at a Rotating Carbon Paste Disk Electrode Modified with Poly (1,8 Diaminonaphthalene), *Journal of Analytical Chemistry* 2009, 64(6), 632-636. <https://doi.org/10.1134/s1061934809060161>
- [6] Yan, L., Niu, X., Wang, W., Li, X., Sun, X., Zheng, C.,... & Sun, W. Electrochemical sensor for rutin detection with graphene oxide and multi-walled carbon nanotube nanocomposite modified electrode. *International Journal of Electrochemical Science*. 2016, 11(2), 1738-1750. [https://doi.org/10.1016/s1452-3981\(23\)15957-8](https://doi.org/10.1016/s1452-3981(23)15957-8)
- [7] Sapountzi, E., Braiek, M., Chateaux, J-F., Jaffrezic-Renault, N., and Lagarde, F. Recent Advances in Electrospun Nanofiber Interfaces for Biosensing Devices, *Sensors*. 2017, 17(8), 1887. <https://doi.org/10.3390/s17081887>
- [8] Murray, R. W. Chemically modified electrodes, *Acc. Chem. Res*. 1980, 13(5), 135 -141. <https://doi.org/10.1021/ar50149a002>
- [9] Murray, R. W., Ewing A. G., and Durst R. A.. Chemically modified electrodes. Molecular design for electroanalysis, *Anal. Chem*. 1987, 59(5), 379A-390A. <https://doi.org/10.1021/ac00132a001>
- [10] Wang, J. Voltammetry following nonelectrolytic preconcentration. In *Electroanalytical chemistry*, CRC Press. 2021, 1-88. <https://doi.org/10.1201/9781003210078-1>
- [11] Kuwana, T., and French, W. G. Electrooxidation or Reduction of Organic Compounds into Aqueous Solutions Using Carbon Paste Electrode, *Anal. Chem*. 1964, 36(1), 241-242. <https://doi.org/10.1021/ac60207a006>
- [12] Svancara, I., Kalcher, K., Walcarius, A., and Vytras, K. *Electroanalysis with Carbon Paste Electrodes*, CRC Press. 2012. <https://doi.org/10.1201/b11478>
- [13] Cai, X., Kalcher, K., Neuhold, C., and Ogorevc, B. An improved voltammetric method for the determination of trace amounts of uric acid with electrochemically pretreated carbon paste electrodes, *Talanta*. 1994, 41(3), 407-413. [https://doi.org/10.1016/0039-9140\(94\)80146-0](https://doi.org/10.1016/0039-9140(94)80146-0)
- [14] Randles. J. E. A cathode ray polarograph. Part II, The current-voltage curves. *Transactions of the Faraday Society*. 1948, 44, 327-338. <https://doi.org/10.1039/tf9484400327>
- [15] Ševčík, A. Oscillographic polarography with periodical triangular voltage. *Collection of Czechoslovak Chemical Communications*. 1948, 13, 349-377. <https://doi.org/10.1135/cccc19480349>
- [16] Sanou, A., Coulibaly, M., N'dri, S. R., Tămaş, T. L., Bizo, L., Frentiu, T.,... & Turdean, G. L. Raw clay material-based modified carbon paste electrodes for sensitive heavy metal detection in drinking water. *Journal of Materials Science*. 2024, 1-17. <https://doi.org/10.1007/s10853-024-09945-2>
- [17] Belqat, B., & Belcadi, S., Electrochemical behaviour of ferrocene, perylene and tetracene in an electrolytically bound carbon paste electrode in water-phosphoric acid mixtures. *Comptes Rendus de l'Académie des Sciences-Series IIC-Chemistry*. 2001, 4(12), 933-939. [https://doi.org/10.1016/s1387-1609\(01\)01314-7](https://doi.org/10.1016/s1387-1609(01)01314-7)

- [18] N'Guessan, K. J. M., N'Dri S. R., Yapo YHA, Gauly, L. P., Sanou, A., Soro, S. B., Coulibaly, M., Bamba, D., and Yao, N. A. Characterization and Application of Carbon Paste Electrode Modified by Moringa Oleifera Seed Powder to the Electrochemical Detection of Mercury. *Chemical Science International Journal*. 2024, 33(1): 36-46. <https://doi.org/10.9734/CSJI/2024/v33i1883>
- [19] Bakary Soro, S. B., Coulibaly, M., Gauly, L. P., N'dri, S. R., Sanou, A., and Trokourey, A. Characterization of clay materials from Côte d'Ivoire: possible application for the electrochemical analysis. *Journal of Materials Science Research*. 202312(1): 51-64. <https://doi.org/10.5539/jmsr.v12n1p51>
- [20] N'dri, S. R., Coulibaly M., Yao N. A, Bamba D, & Zoro G E., Redox Characterization of the Ferri/Ferrocyanide System on the P-type Silicon Paste Electrode for Biosensor Application. *Journal of Materials Science Research and Reviews*. 2022, 5(3), 366-374.

Research Field

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