Original Research Article

Redox Characterization of the Ferri/Ferrocyanide System on the p-type Silicon Paste Electrode for Biosensor Application

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ABSTRACT

Silica-based materials generate the highly reactive silanol against metallic trace elements in contact with aqueous solutions. Their use in electroanalysis allows the creation of electrochemical sensors for the regular control of matrices. Silicon, a material derived from silica, is introduced into electroanalysis as an electrode material. This work deals with the study of the semiconductor/aqueous electrolyte junction in cyclic voltammetry. The study of the electrochemical behavior of ferri /ferrocyanide with the silicon paste electrode gives a frayed cyclic voltammogram whose anodic and cathodic redox peaks appear respectively at 0,38 V and 0,08 V vs Ag/AgCl/KCl_{sat}. The intensity of the anodic and cathodic peak current are respectively equal to 1,5 µA and – 0,5 µA. This low value shows that the PP junction is weakly conductive. The diffusion coefficients of ferri and ferrocyanide species are $1{,}15.10^{-4}$ and $6{,}68.10^{-5} cm^2.s^{-1}$.The oxidizing species diffuses faster than the reduced species. The voltammogramis influenced by the surface energy states of the semiconductor electrode. Its linearization makes it possible to obtain the slope of the curve which is the value of the differential capacitance of the state of surface $C_{es} = 1{,}45.10^{-9}$ F. The p-doped silicon paste electrode is weakly active in electrochemistry in the dark.

Keywords: juntion, silicon, cyclicvoltammetry, Ferri /Ferrocyanide, mass-transport

1. INTRODUCTION

In recent decades, pollution by metallic trace elements has increased sharply due to anthropogenic activities [1,2]. Conventional analysis methods for pre-concentrating them are becoming more and more precise. They are also becoming more and more expensive [3-5], making their acquisition uncertain by many structures responsible for regular monitoring of the quality of the environment. For a regular control of the quality of the living environment, it is necessary to develop increasingly precise and selective analytical methods. With this in mind, biosensors are undoubtedly a better alternative. A sensor is an analytical system combining different technologies from, for example, biology, microelectronics, optics and computer science [6,7]. The most essential part of the sensor is the working electrode material. Indeed the nature and the structure of the working electrode influences the performance of the sensor. In this work, the working material is p-doped silicon paste. This material is part of the large group of silicate materials, which, in contact with aqueous solutions, generate the silanol group, which is very complexing towards heavy metals [8]. Silicon in contact with an electrolytic solution constitutes a semiconductor/electrolyte junction.

The silicon paste electrode is characterized by cyclic voltammetry in contact with the ferri/ferrocyanide system to obtain information on the electrochemical activity of the new electrode. This characterization is done thanks to a negative potential difference E_{dep}= -1.1V delivered by the potentiostat. An excitation external is exerted on all the cell.

2. MATERIALS AND METHODS

2.1. Equipment

Electrochemical experiments are performed with a potentiostatPalmSens (from EcochemieNertherlands) controlled by pstrace software and driven by computer. The analytical method is cyclic voltammetry . The silicon paste electrode is used as the working electrode (W). The Ag/ AgCl / KClsat electrode is used as reference electrode (R) and platinum as counter electrode (C). The curves are drawn with the software origin pro 8. The body of the working electrode is made of a glass tube with a diameter of 3 mm, open on both sides, in which a metal rod is inserted which serves as a contact, the tube is packed each time with silicon paste.
It is cleaned whenever necessary by manual polishing on clean, smooth paper. The electrodes are immersed in solutions of Ferri/ferrocyanide (potassium hexacyanoferrate (II) trihydrate$K_4[Fe(CN)_6]$) from Sharlau , prepared with distilled water. The p-doped silicon is from Photowatt SA. All reagents are of analytical purity.

2.2. Preparation of the working electrode.

The silicon paste electrode is p-doped silicon powder obtained by sputtering and sieving polycrystalline silicon. The powder obtained is mixed with paraffin oil and pounded in a mortar. The assembly is inserted into the body of the cylindrical electrode with a diameter d=3 mm and is connected to a metal rod which allows electrical contact with the potentiostat. The deposit potential is Edep = - 1,1V. The area of the active surface of the working electrode is equal to A = 0, 07 cm^2.

3. RESULTS AND DISCUSSIONS

3.1. Study of the semiconductor/electrolyte interface

Cyclic voltammetry is one of the analytical methods, which make it possible to specify the conditions under which an oxidation and reduction reaction can be carried out electrochemically and possibly to establish the mechanism [9]. The general principle of voltammetry is therefore to obtain a response (the current) of the system studied to the excitation (the potential) responsible for the desired electrochemical reaction. This operation is carried out by carrying out an exploration by imposition and progressive variation of the electrode potential (potential sweep). In order to be able to impose the electrode potential, to vary it and thus produce electrochemical reactions, it is necessary to operate in an electrolysis cell comprising three electrodes to which an external circuit is connected. The plot obtained is called a voltammogram .

The voltammetric curves can also be used to deduce kinetic parameters: either electrochemical kinetics or chemical kinetics when a chemical reaction is coupled to an electrochemical reaction. Similarly, the conditions under which a coulometry or a coulometric assay must be carried out can be determined using the tracing of the voltammograms .The current (1) measured is the sum of two contributions to the electrode-solution interface: the capacitive current linked to the existence of the electrochemical double layer and the faradic current associated with the oxidation-reduction processes [9]:

$$I = I_f + I_C \qquad (1)$$

with I the total current, $I_c$the capacitive and I_f and faradic currents
The faradic current takes on different more or less complex expressions depending on the system considered. Depending on the shape of its dependence on the sweep rate, it is possible to deduce certain characteristics of the reaction, such as its reversibility or the involvement of adsorbed species. The faradaic current also varies with the concentration of the electroactive species and the area of the electrode. Randles-Sevcik equation [10] gives the expression of the current peak at a temperature of 298.15° K (i.e. 25° C).

Taking into account the constant parameters, equation (2)

$$I_p = (2{,}687.10^5)\ n^{3/2}.A.D^{1/2}v^{1/2}.C(2)$$

Where n is the number of electrons involved in the redox reaction; A is the electrode area, v is the sweep rate; C is the concentration of the active species.

The global faradic current for a single-electron reversible system is given by (3):

$$I_0 = I_{0x} + I_{red} \qquad (3)$$

Where I_{ox} , the anodic peak, I_{red} the cathodic peak.

The resistance of the solution obtained from the current is given by Ohms law (4),

$$E = R_e.I_0 \qquad (4)$$

The capacitive current has several expressions but, in the case of the constant frequency electrolyte semiconductor interface, relation (5) gives it.

$$E = \frac{I}{C\omega} \qquad (5)$$

where E is the potential; C, is the differential capacitance; $\omega = 2\pi f$ is the angular pulsation, f the frequency (here f = 50 Hz).

A cyclic voltammogram makes it possible to study the reversibility or the reaction mechanism. Thus a redox process is said to be reversible if the following parameters are satisfied.

- A peak current ratio (I_{pa}/I_{pc}) equal to unity. When the ratio is different from 1, a chemical reaction or complex phenomena takes place at the interface.
- A peak potential separation (ΔE_p) at all scan rates should be about 59/n (mV), with n the number of electrons involved in reaction .

The kinetic parameters of the reaction are also deduced from the plots. The charge transfer resistance due to the faradaic process [9] is given by relation (6).

$$Rct = \frac{RT}{nFI_0} \qquad (6)$$

Where: R is the ideal gas constant; T: the absolute temperature (K); n: the number of electrons transferred;

F: Faraday's constant and I_0 : the exchange current density at equilibrium potential. This current density is directly related to the kinetic constant k^0 of electron transfer [9] by the following relation (7):

$$I_0 = nFSC_0k^0 \qquad (7)$$

S is the active surface of the electrode and C_0 the concentration of the redox couple in solution. For the reaction at the electrode, the active species diffuse from the solution to the surface of the electrode [9]. This diffusion phenomenon is characterized by the Warburg impedance (8):

$$W^*(\omega) = \frac{R_t \times y}{\sqrt{j\omega}}(8)$$

$$\text{Where } y = \frac{K_{red}}{\sqrt{D_{ox}}} + \frac{K_{ox}}{\sqrt{D_{red}}} \qquad (9)$$

The electrical parameters of chemical characterization are influenced by the nature of the electrode material in contact with the aqueous electrolyte [9].In the case of the semiconductor/electrolyte interface, Gerisher assigns to the oxidizing species the Eox potential a vacant level having the electron acceptor character and to the reduced species of Ered potential a full level having the donor character electron. The interface is therefore a junction analogous to a Schottky diode.

In open circuit, that is to say without external excitation, the bringing into contact of a solid phase (semiconductor) and a liquid phase (electrolyte) composed of electroactive species leads to an equalization of the Fermi levels. This shift in Fermi levels is accompanied by a potential difference (ddp) which ends up structuring the interface. The difference in potential causes the formation of layers of charged species on either side of the interface. The interface therefore has a structure. The differential capacitance of this interface includes the contribution due to the electrochemical double layer and that due to the surface states of the semiconductor material.

$$C = C_{dl} + C_{es}(10)$$

The impedance of such an interface is a function of frequency and is a complex quantity. It relates the resistance of the electrolyte Re, the impedance of the faradic current Z_f and the impedance linked to the capacitive current C. the overall impedance Z(ω) is given by relation (11).

$$Z(\omega) = R_e + \frac{Z_f}{1+i\,\omega\,C\quad Z_F}$$

(11)

This impedance is complex. It has a real part and an imaginary part. It is often used to plot impedance diagrams such as Bode, Black and Nyquist. Electrical circuits deriving from electrochemical systems are represented in the Nyquist impedance diagram generally to analyze their closed loop stability.

Achieving the parameters at the interface requires the linearization of the voltamogram. The slope of the curve gives the value of the overall differential capacitance at the interface. This capacity is influenced by the structural defects related to the surface condition at a constant frequency of 50 Hz.

3.2 Characterization with the couple Ferri /Ferrocyanide

3.2.1 Study of the Ferri / Ferrocyanide system.

Cyclic voltammetry is used for the electrochemical characterization of materials in contact with Ferri/ferrocyanide.This couple is called electrochemical marker. This couple is studied by cyclic voltammetry in contact with the working electrode to show the electrochemical activity.Based on its reaction in contact with the electrode, one can tell whether the electrode material is active.

The voltammogram of the ferri/ferrocyanide couple is known and listed [10]. The redox reactions at the electrodes are as follows: at the anode, oxidation of the ferrocyanide to the ferricyanide ion takes place mainly , equation (12).

$[Fe(CN)6]^{4-} \rightarrow [Fe(CN)6]^{3-} + e^{-}$(12)

at the cathode the reduction of ferricyanide to ferrocyanide ion takes place mainly, equation (13)

$[Fe(CN)6]^{3-} + e^{-} \rightarrow [Fe(CN)6]^{4-}$(13)

In the cell, there is conservation of the quantity of matter of the electro-active species since for each ferricyanide ion consumed at the cathode, there is a product at the anode and vice versa for the ferrocyanide ions. The limiting current is a function of the concentration. In this reactionferrocyanide is the reducing agent and ferricyanide is the oxidant.

The oxidant fixes or tears an electron from the working electrode to reduce itself. The couple Ox/Red is made up of the energy levels Eox and Ered[11]. The p-doped semiconductor is in contact with the ferricyanide which is of the P type. when they are brought into contact, the assembly forms the PPjunction . as we see, the two phases in contact are of the same nature. They are P-type. This junction is repulsive in nature. Bringing them into contact even without excitation leads to the alignment of the fermi levels. The studied electrochemical cell is subjected to a potential difference in the form of a cycle. The semiconductor/electrolyte junction is therefore subject to external excitation.

3.2.2. The semiconductor/ Ferri /Ferrocyanide junction after external excitation

Fig. 1 shows the voltammogram obtained following the external excitation of the activity of the ferri /ferrocyanide pair in aqueous solution on a silicon paste electrode. The curve is explicit of an electrochemical activity. The voltammogram appears to be symmetrical around an axis of revolution. It looks like a reversible system. The limiting anode current intensity is a maximum of 1,50 µA and the limiting cathodic current is - 0,5 µA. This very low current confirms the blocking nature of silicon in the dark. The current peaks therefore exist despite the frayed structure of the voltammogram .The reduction and oxidation peaks appear respectively at the potentials of 0,08V and 0,38V. It can be seen that despite the scanning speed of 40 mV/s, the maximum peak oxidation current of the ferri /ferrocyanide couple with the silicon paste electrode remains less than 2µA. The material seems weakly conductive**.** The electrical parameters deduced from Fig.1 are presented in Table 1.

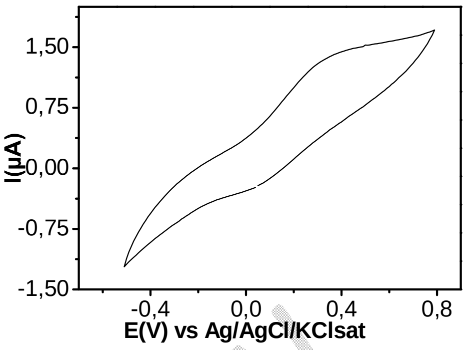

Fig. 1. Cyclic voltammogram of the couple ferri/ferrocyanide of concentration 30 mM on silicon paste electrode at pH =7, sweep rate = 40 mV/s,Edep = -1.1V

The peak current ratio Ipa / Ipc is greater than 1 in absolute value. This means that a chemical reaction is coupled to the charge transfer or that complex phenomena occur at the electrode [12].

Table 1. Characteristic values of the electrochemical parameters of the couple ferri /ferrocyanide

Epa (V)	Epc (V)	Ipa (µA)	Ipc (µA)	ΔEp (V)	Ipa / Ipc
0.38	0,08	1,5	-0,5	0,30	3

The difference between the peak potentials of the Ox species and the Red species makes it possible to specify the rapidity for a reversible system. In this study ΔEp = 300 mV >59 mV, the kinetics are very slow [13].

The diffusion of redox species from the boundary to the surface of the electrode is not sufficiently influenced by the supporting electrolyte and the concentration of ferri /ferrocyanide.

The reduced species has almost the same kinetic constant in neutral medium and in KCl supporting electrolyte. The oxidized species diffuses more in a neutral medium than in a KCl medium. The experimental electronic transfer rate constants k^0 of the Red and Ox species obtained from relation (4) are proportional to 10^{-5} for the activated electrodes.

The existence of the charge transfer rate constant confirms what the cyclic voltamogram in Fig.1 shows Ferri /ferrocyanide reacts on the working electrode at the negative deposition potential of -1.1 V in the dark. The charge transfer kinetics is faster in line with that of indigo carmine [9].

The charge transfer resistances are respectively 17178 Ω and 51906 Ω for the Ox species and for the Red species. These values are higher than those obtained in the case of the oxidation of fibrinogen which vary from 6500 Ω to 11000 Ω [15]

Table 2. Kinetic parameters of the reaction

Sizes	Value	Value of Literature
D_Ox	1,15.10 $^{-4}$	0.726(±0.011). 10 $^{-5}$ [10]
D_{Red}	6,66.10 $^{-5}$	0.667(±0.014).10 $^{-5}$ [10]
R_{ctO}	17178.	6500 - 11000[15]
R_{ctR}	51906	
k_{Red}	2.47.10 $^{-5}$	1, 7.10 $^{-5}$ [9]
k_{Ox}	7.41.10 $^{-5}$	
W(Ox)	223	
W(Red)	674	

Where

D_{Ox} : diffusion coefficient of the oxidizing species (cm^2.s^{-1})

D_{Red}: diffusion coefficient of the reduced species (cm^2.s^{-1})

R_{ctO} :Charge transfer resistance of the oxidizing species (Ω)

R_{ctR}:Charge transfer resistance of the reduced species(Ω)

W(Ox): Warburg impedance of the oxidizing species($j^{-0,5(}$Ωcm^2)

W(Red): Warburg impedance of the reduced species ($j^{-0,5(}$Ωcm^2)

k_{Red} : Charge transfer kinetic constantof the reduced species (cm/s)

k_{Ox}: : Charge transfer kinetic constantof theoxidizing species(cm/s)

These strong values show to tear off the electron it is necessary to deploy a great energy. Electronic cash transfer Ox is done faster compared to the Red species. The repulsive electric field allows the separation of the electron more easily at the level of the oxidant. The warburg impedance characteristic of the ion movements at the interface gives respective values of 223 and 674 $j^{-0,5}$(Ωcm^2). The high value obtained shows the ionic motion at the interface is important for both ionic species

These compared values show the ionic movement is three times greater at the level of the Red species. The red species reaches the surface of the electrode faster. There is a phenomenon of attraction due to the electric field [9]. The study of the semiconductor junction reveals a PP type junction before the external excitation. The existence of a current peak shows that the junction is conductive.

The reduction reaction of ferricyanide to ferrocyanide takes place, this shows that during the forced reaction an electron from the doped semiconductor, already deficient in electrons, is removed. The weakness of the current shows that the reaction as fast as it is is quickly slowed down. This could be due to the fact that the reducing species is hindered in its propagation by the many holes present on the surface of the active area of the working electrode.

3.2.3. Study of transport phenomena at the interface

In cyclic voltammetry, the study according to the number of cycles makes it possible to study the nature of mass-transport at the interface. When the peaks grow, the phenomenon at the interface is diffusion and when the peaks stagnate, the transport phenomenon is adsorption.

The study according to the number of cycles (Fig. 2), shows that the currents of anodic peaks increase weakly with a shift of potential of peaks and while the cathodic peaks do not change. The slight increase in the anodic peaks suggests a phenomenon of transport by diffusion of the oxidant. The deposition of the ferrocyanide film becomes important. The stagnation of the cathodic peak as noted by Coulibaly and coll.[16] suggests that there is adsorption of iron on the surface of the electrode.

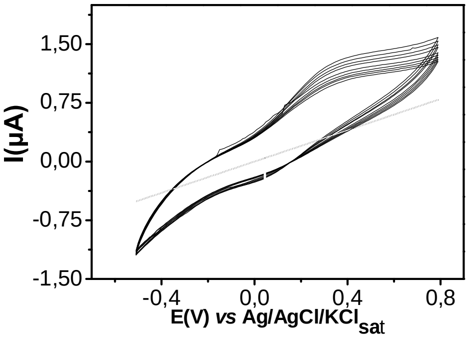

Fig. 2. Cyclic voltammogram of the ferri /ferrocyanide couple on a silicon paste electrode at pH = 7, sweep rate of 40 mV/s, 10 cycles

Surface states of a capacitive nature influence the reaction, so it is important to study their contribution. To evaluate their contribution the linearization of the voltammogram is necessary. The axis of symmetry obtained from the voltammogramis shown in Fig. 3.

From this graph is deduced the potential of the global faradic current $I_0 = I_{0x} + I_{red}$= 1µA equal to 0.4 V. The resistance of the solution found from (4) is then equal to 4.10^5 Ω. It is very high because the measurements are made in aqueous electrolyte [9]. A slow kinetics punctuated by a high resistance of the suggests a high viscosity of the solution.

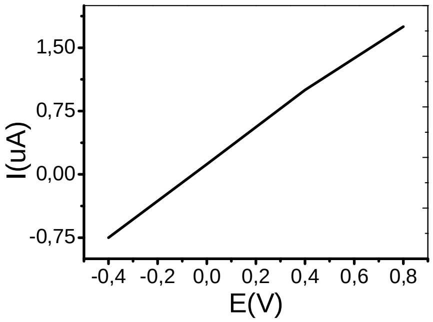

Fig. 3. Axis of symmetry deduced from the linearization of the voltamogram

Fig. 3 is a straight line linking the current I and the potential E.The ohms law describing this curve is given by relation (5). The slope which is the capacitance of the surface states of the interface at a constant frequency of 50 Hz is determined. The calculations give the value of the differential capacitance Ces = $1,45.10^{-9}$ F. The overall capacitance is the action of the surface states and of the electrochemical double layer expressed by relation (10). The contribution of the double layer is calculated at the global faradic intensity of 1µA. The value obtained is $7,96.10^{-9}$ F.

This value is greater than that of the capacitances of the surface states. The property of the electrochemical double layer due to adsorption is predominant before those of the surface states.

The overall capacity is $9,41.10^{-9}$ F. This differential capacitance interferes with the redox reaction. The silicon paste/ferri/ferrocyanide interface is characterized by two important physico-chemical processes:

- the oxidation-reduction reaction of ferri /ferrocyanide and
- by capacitive phenomena due to the surface condition and the double layer.

The oxidation reaction is translated by the equivalent electric circuit of Randles and Sevich[9,17,18]taking into account the faradic impedance and the capacitive impedance is presented in Fig. 4.

The surface states are described by a differential capacitance C_{es}.Surface energy states interfere with the redox reaction of ferri /ferrocyanide. The differential capacitance $C_{es}$is therefore placed in parallel with the double-layer capacitance C_{dl}. The semiconductor/electrolyte interface produced with the ferri/ferrocyanide system is expressed by the following electrical circuit shown in the Fig. 4.

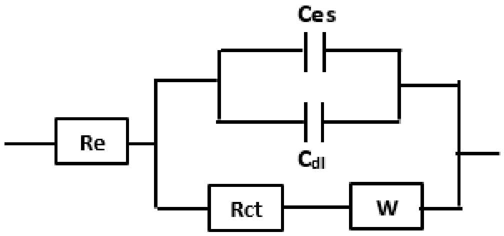

Fig. 4. Equivalent electrical assembly of the silicon/ ferri /ferrocyanide junction

In fig.4, the charge transfer resistance is that of the Ferri/Ferrocyanide couple. It is calculated from Rct = (Rcto+RctR)/2 = (17178+51906)/2 = 34542 Ω. The search for the equivalent differential capacitance of the electric circuit of fig.4 leads to the global capacitance C.

Its introduction tightens the circuit. The new form of the electrical circuit is shown in fig.5. This circuit is named Randles[9,17,18]

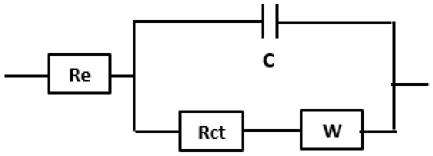

Fig. 5 .Randles equivalent electric circuit

The Nyquist digraph of the Randles circuit is listed in the literature [19]. Not having direct measurements by electrochemical impedance spectroscopy (EIS). We will put in the conditions of ideal electrochemical system. In an ideal electrochemical system, in the presence of semi-infinite diffusion, the Warburg impedance is characterized by a 45° slope for low frequencies. The Nyquist diagram is given by Tribolletand .al. its representation is given in fig.6 [19]

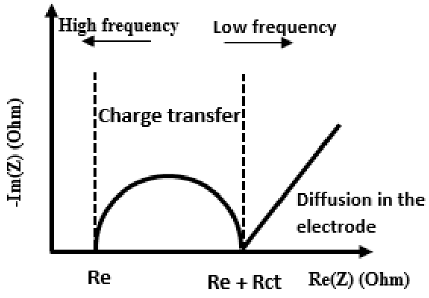

Fig. 6. Nyquist diagram of an ideal electrode/electrolyte interface for low frequencies

The capacitive current parameters contained in Table 3 are discussed with those of the available literature.

The solution resistance value is about three times greater for the same type of solvent. The resistivity of the semiconductor increases with the aqueous solution unlike the carbon paste [9] which is a conductive material.

The capacitances at the level of the silicon paste are lower than that of the silicon carbon composite paste electrode. This increase in the composite electrode is related to the structure of each material in the aggregate. It istherefore the contribution of eachmaterial

Table 3. Electrical quantities of the capacitive current

Sizes	**Values**	
	From the study	**Literature**
Resistance of solution: Re (Ω.)	4.10^{5}	17062 [13]
OverallCapacitance: C (F)	$9,41.10^{-9}$	$2,93.10^{-2}$ [9]
Capacitance of surface states Ces (F)	$1,45.10^{-9}$	
Double Layer Capability: Cdl (F)	$7,96.10^{-9}$	$1,87.10^{-5}$ [9]

4. CONCLUSIONS

The p-doped silicon paste electrode is weakly active in electrochemistry in contact with the electrochemical marker. The nature of the electrode greatly influences electronic transfers. Since silicon is used in the dark, these electrical properties are reduced. To improve its properties it is necessary to consider illuminating it or exciting it with a positive deposition potential or incorporating it into graphite carbon.

5. REFERENCES

1. Gendron A.; and Burelle S. Residual Materials Service. ing.M.Sc. **2007,** Quebec 41 p.
2. RYTUBA, J., J., Geogenic and mining sources of mercury to the environment *Mercury*: Sources, Measurements. *Cycles and Effects.***2005**, 34, 21 - 41
3. Bruzzoniti, M. C., De Carlo, R. M and Sarzanini, C., *Chromatographia.***2011**, Vol. 73(1) , 15 - 28
4. Zhang, R. and Chen, W., *Biosensors and Bioelectronics*. **2014**, 55, 83 - 90
5. Almeida I.. L. S; Oliveira, M.. D. .R..; Silva, J. B. B.; and Coelho, N. M. M., *Microchemical Journal.***2016**. 124, 326 – 330
7. Gao, C. ;Huan, X., J. , Voltammetric determination of mercury (II). *TrAC Trends in Analytical Chemistry*. **2013**, 51, 1-12.,
8. Despas, C., PHD thesis. 1998, University Henri Poincaré, Nancy I, France
9. N'dri,S., R.; Coulibaly, M.; Yao, N., A.; Bamba, D.; Zoro, E.,G. *Int.J.Sci.Res*. **2016**, 5(1), pp 1300-1305,
(10) Konopka,S., J. , McDuffie, B. *Analytical Chemistry*. **1970,** 42(14), pp 1741-1746
11. *Gerischer*, *H*.: In: *Physical chemistry* (*Eyring*, *Henderson*, *Jost*, eds.), *Vol*. *IXA*, p. 463. *New York*: *Academic Press 1970*.
12. Bigot, J.-P., PHD thesis, **1987**, Ecole Normale Supérieure des mines de saint-Etienne,,
13. N'Dri,S., .R. ;Coulibal, M. ; Yao, N., A. ; Diby, K., .A.; Bamba, D. ; Zoro, G., .E.,*AfriqueScience*.**2017,**13(2) ,384 – 395
14. Maquere , F.; Frappart, C., *Bulletin of the Union of physicist's flight*..**2002,** 96
15. Mama El Rhazi , PhD Thesis . **1996**, University Mohamed IV of Morocco,
16. Coulibaly, M. ,PHD thesis**. 2008**, University of Cocody , Côte d'Ivoire
17. Randles,J. E.; A cathode ray polarograph. Part II, The current-voltage curves. *Transactions of the Faraday Society*.**1948**.44, 327-338
18. Ševčik, A.; Oscillographic polarography with periodical triangular voltage. *Collection of Czechoslovak Chemical Communications*.**1948**. 13, 349-377.,
19. Tribollet,B.; Orazem M.; .B., Electrical Circuits. Electrochemical Impedance Spectroscopy. 1st ed. ed, ed. I. John Wiley & Sons, Publication. 2008.

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