

Electrochemical Analysis of Zirconium in Aqueous and Organic Media

Paul Mendy¹, Démo Koita¹, Theodore Tzedakis^{2*}, Cheikhou Kane¹, Codou Guèye Mar-Diop¹

¹Ecole Supérieure Polytechnique, Université Cheikh Anta DIOP, Dakar, Sénégal

²Laboratoire de Génie Chimique, Université de Toulouse III—Paul Sabatier, Toulouse, France

Email: paulsalvador.mendy@gmail.com, *tzedakis@chimie.ups-tlse.fr

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Abstract

For the challenging nature of the zirconium environment analysis, this study consists to analyze the electrochemical behavior of Zirconium in both aqueous and organic media. To that end first the electrolytic media was selected on the basis of the Pourbaix potential-pH diagram, which provides informations on the predominance of $Zr^{(IV)}$ ion and Zr in aqueous media. In aqueous media, analyzes were first carried out in acidic media then in basic media. Studies have thus revealed that the acidic environment is not favourable for the electrochemical analysis of zirconium. Voltammograms obtained in an acidic environment show no zirconium detection signal; this is due to the strong presence of H^+ ions in the solution. We have also observed in acidic media the phenomenon of passivation of the electrode surface. In aqueous alkaline media (pH = 13), we have drawn in reduction several Intensity-Potential curves by fixingsome technical parameterslike scanning speed, rotation speed of the electrode. The obtained voltammograms show cathodic waves, starting from -1.5 V/DHW and attributed to the reduction of $Zr^{(IV)}$ to Zr (0). The last phase of this study focused on the electrochemical analysis of zirconium in an organic media. In this media, several intensity-potential curves were plotted in reduction and in cyclic voltammetry with various parameters. Through several reduction analysis, the $Zr^{(IV)}$ was reduced to Zr (0) to the potential of -1.5 V/DHW. The electrochemical analysis of zirconium in organic media seems globally easier to achieve thanks to its large solvent window (*i.e.* dimethylformamide (DMF) solvent window > 6 V).

Keywords

Zirconium, Electrochemical, Reduction, Cyclic Voltammetry, Voltammogram, Dymethylformamide

1. Introduction

Because of its excellent physicochemical properties *i.e.* oxidation numbers +4, +3, +2, 0, -2, density in 20°C (g/cm³) 6.45, melting point 1852°C ± 10°C, boiling point 4409°C, thermal conductivity 22.7 W·m⁻¹·K⁻¹ and nuclear properties, *i.e.* thermal neutron absorption cross section 0.180 ± 0.004 barns/atm, emissivity coefficients 0.46(α)-0.50(β) (5410 Å), neutron capture cross-section 0.1 barns [1], the Zirconium metal is used in the nuclear industry, as a coating material of the tanks of fuels or even for the construction of elements at the heart of the nuclear reactors [2] [3].

Most of the authors having studied the electrochemical behavior of the Zirconium have chosen to operate on a molten salt medium because of its high ionic conductivities and diffusivity 2 to 9 Ω⁻¹·cm⁻¹ we can cite Yong YAN, Derek FRAY *et al.* [4], who have in their study related to the molten salt electrolysis for sustainable metal extraction and materials processing, determined the advantages of molten salt media in terms of ionic conductivities and diffusivity. Xiao Li XI *et al.* have also confirmed the same characteristics of molten salt media, through their study related to the applications of molten salt and progress of molten salt electrolysis in secondary metal resource recovery [5]. In addition molten salts possess, high solubility for electroactive species, electrochemical stability over a wide potential window (up to 6 V), and very fast electrochemical kinetics [6] [7] [8].

Supathorn Phongikaroon *et al.* [9] studied the electrochemistry of zirconium (Zr) in the eutectic salt LiCl-KCl. They showed that the temperature may be used as a tool for enhanced peak detection for any low concentration studies. Their works reveal that diffusion coefficients (D) of ZrCl₄ and ZrCl₂ as the function of temperature can be expressed as $D_{Zr^{IV}} = 0.0004 \exp\left(-\frac{3716}{T}\right)$ and

$$D_{Zr^{II}} = 0.027 \exp\left(-\frac{5617}{T}\right) \text{ respectively.}$$

They highlighted the need to work at a relatively high temperature in order to facilitate the electrochemical analysis of zirconium in molten salt.

Quian Xu *et al.* have also approached in this direction through studies carried out on the redox behavior of zirconium in *eutectic LiF-NaF bath* [10].

Through several expediences they showed that zirconium has the advantage to diffuse in molten salt and the diffusion coefficient is function of the temperature.

The estimations of Zr^(IV) diffusion coefficient in the LiF-NaF eutectic melt at 750°C through cyclic voltammetry and chronopotentiometry are in fair agreement, as to be approximately 1.13E⁻⁵ and 2.42E⁻⁵ cm²/s respectively.

With regard to ionic liquids, it should be noted that although there are studies of the electrochemical behavior of the cation in these solvents, their number is very small, compared to that carried out in the organic medium.

K.A. Venkatesan *et al.* [11], have examined the electrochemical behavior of

Zr^(IV) in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, ionic liquid, by transient electrochemical techniques such as cyclic voltammetry, chronoamperometry, and chronopotentiometry. Since the mass transport of the analyte to the electrode surface occurs by diffusion. They have determined the “apparent diffusion coefficient” of Zr^(IV). It can be seen that the apparent diffusion coefficient increases with increase of temperature due to the enhance diffusion of Zr^(IV) in C₄ mimNTf₂ with increase of temperature.

The Arrhenius relation between the apparent diffusion coefficient and temperature is given by $\ln D = \ln(A - E_{a/RT})$, where A is the pre-exponential factor and E_a is the energy of activation. Despite the numerous electrochemical studies carried out on zirconium, a very small number of them have been carried out in aqueous and organic media. We can cite E. GOBER *et al.* who studied the electrochemical behavior of zirconium in various acidic or neutral media [12]. In addition, we note that the temperature is widely used during the various studies carried out in the organic media but also the ionic liquid media.

In order to try to define an analytical method, simple and rapid, for the challenging nature of the zirconium environment analysis, this study consists to analyse the electrochemical behaviour of Zirconium in both aqueous and organic media. To that end first the electrolytic media was selected on the basis first of the Pourbaix potential-pH diagram, presented through **Figure 1** below, which provides information on the predominance of Zr^(IV) ion and Zr in aqueous media.

The species of Zr^(IV) predominates in acidic medium (pH < 1.7; E < -1.5 V), while the alkaline one indicates the predominance of the HZrO₃⁻ ion. Consequently, to reduce Zr^(IV) to metallic Zr, it is necessary to reach potential lower than -1.5 V without reduction of the solvent nor the electrolyte, which is very difficult in acidic conditions [15] [16].

We were interested therefore in the present study on the reduction of the Zr^(IV) on cathodic materials exhibiting important overvoltage for the water reduction such as Boron doped diamond (BDD) or lead or even carbon. Then, in order to extend that solvent window, an organic solvent (DMF) was used in a

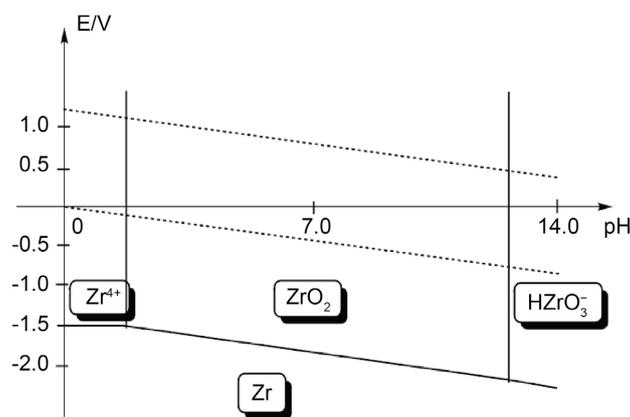


Figure 1. Pourbaix Potential-pH Diagram of Zirconium at 298 K in aqueous media [13] [14].

HCl/HNO₃ supporting electrolyte.

2. Experimental Part

2.1. Chemical Products

All chemicals and reagents used in this study were of analytical quality. The products were purchased from Sigma Aldrich. The electrolytes were:

- Hydrofluoric acid (HF 48%).
- Nitric acid (HNO₃ 68%).
- Hydrochloric acid (HCl 37%).
- Commercial zirconium solutions (10⁻¹ M and 10⁻² M).

The organic solvent used (Di-methylformamideDMF, HCO-N (CH₃)₂), is miscible with the water and most of organic solvents.

The zirconium ore sample is extracted from the titaniferous sand mines of Senegal, operated by GCO (Grande Côte Operations), a subsidiary of the ERAMET group.

2.2. Experimental Device

Equipment used for electrochemical analyses included a three electrodes electrochemical cell Metrohm type, having 100 cm³ a volume capacity; Various materials were used as working electrodes: Zinc (Zn); lead (Pb), boron-doped diamond (BDD), platinum (Pt), vitreous carbon and stain steel electrodes. Some of them are screwed onto a rotating system at controlled angular velocity.

The disk of the glassy carbon electrode, was polished before each analysis using a high-end mechanical polisher, model MECATECH 234 REF. 67100 with plates with a diameter of between 200 and 250 mm, combined with TC10, TI10 and TCI10 polishing heads, thus achieving a better polishing result [17].

- The reference electrode used (saturated calomel electrode) was inserted into Ionic bridge in order to avoid eventual reciprocal contaminations.
- A Pt wire was used as counter electrode.
- A Magnetic stirrer.
- The experimental device was connected to an origastat-potentiostat OGS100 manufactured by Origalys and connected with a computer with the ORIGA MASTER software for plotting the voltammograms.

2.3. Dissolution of Zirconium

The zirconium ore sample was previously analysed by XRF (see **Table 1**).

Table 1. Zircon powder composition obtained by X ray fluorescence (XRF).

XRF ANALYSES OF ZIRCON						
(Values expressed in %)						
oxide	TiO ₂	ZrO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
%	0.11	67.01	0.03	0.07	0.26	32.52

The dissolution of the zircon powder was obtained by its immersion into an alkaline solution, followed by an exposure to aqua regia.

To achieve the complete dissolution of the powder, the suspension was heated under reflux for 15 minutes (**Figure 2**). The solution was then cooled to ambient temperature to about 25 °C and then analyzed by electrochemistry.

2.4. Procedure for Electrochemical Analysis of Zirconium (IV)

We carried out the first part of our study in an alkaline medium and the second part in an organic medium. The procedures for the analysis of Zr in alkaline and organic medium are described below. First it's important to stress that the experimental procedures for studying electrochemical behavior of zirconium (IV) in both alkaline and organic media are similar.

A certain volume of the zirconium solution obtained initially by dissolving the zircon powder in aqua regia, is introduced into 10 cm³ of the appropriated solvent/electrolyte and introduced into an electrochemical cell of 20 cm³ of capacity, into which three electrodes connected to a potentiostat were immersed.

For aqueous alkaline media studies, the pH of the mixture was fixed by gradually adding a saturated NaOH solution. The pH was always fixed at 13, and the volume of the final solution to be analyzed was fixed to being equal to 15 ml. The study consisted to plot current potential curves at the steady state as well as at the transient state (*i.e.* cyclic voltammetry) for various concentration of the zirconium, and the idea is to evaluate the ability of the chosen material (see above) for the working electrode to properly analyze the zirconium.

Note that the boron-doped diamond electrode (BDD) appears to exhibit the higher electro-activity window [18] [19] [20]; however, because of its relatively low conductivity, BDD can induce an important ohmic drop [21], and it is

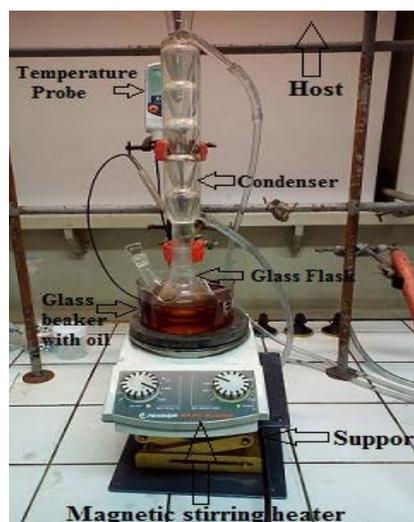


Figure 2. Set-up used to dissolve the zircon powder. Glass flask (50 cm³), connected to a refrigerant. Heating of the flask was performed by an oil bath herself heated at 300 °C via a MR Hei-TEC heating plate with magnetic stirrer.

necessary to ensure a good connectivity with any conductive connection paste. Some authors like A. DEKANSKI *et al.* have shown some electrochemical properties of glassy carbon electrodes which are interesting for zirconium studies, such as the electrode impedance, the pH sensitivity and the polarization characteristic [22]. In addition we can also cite K. MUND, C. CORTES, J. MANTILLA *et al.* who have shown through their studies of the electrochemical properties of platinum, glassy carbon, and pyrographite as stimulating electrodes, the advantage of using glassy carbon as stimulating electrode because of its sensing behavior, polarization, body compatibility and energy consumption [23] [24]. To avoid disturbances on the curve $I = f(E)$ by the dissolved oxygen reduction, gaseous argon was used to maintain inert atmosphere into the electrochemical cell.

This technique was developed by some authors, in particular, G. Luyckx and J. Ceulemans who worked on techniques for the elimination of gases in liquids but also Z. Gao *et al.* who have worked in the “*Effects of deaeration methods on dissolution testing in aqueous media*”.

They have studied varieties of desaturation methods and underline the importance of reducing the amount of gases in liquid solutions in order to avoid disturbing main chemical and electrochemical reactions [25]. **Figure 3** presents the overall setup used for the electrochemical analyses of Zirconium.

3. Results and Discussion

In this section, we present the different electrochemical results obtained during the electrochemical analyses of zirconium in aqueous medium and in organic medium, under different operating conditions.

3.1. Electrochemical Study of Zirconium in an Aqueous Medium

In this section, emphasis is placed on the electrochemical study of zirconium in

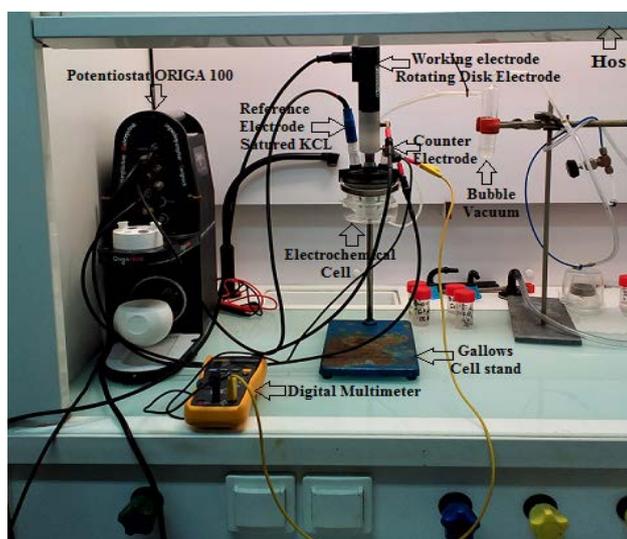


Figure 3. Experimental set-up used for the electrochemical analyses of the zirconium solutions.

an aqueous medium; in the first part we will present the results of the various electrochemical analyses of zirconium in **acidic medium**; the second one will be consecrated to **alkaline medium**.

3.1.1. Electrochemical Studies of Zirconium in Acidic Medium

In this section we initially worked with three solutions of commercial zirconium of known concentration then we have in the second part of our studies worked with a zirconium sample which is produced at the mine. It is important to note that studies carried out in an acidic medium have revealed difficulties related to the phenomenon of passivation of Zr observed through the formation of a thin layer of ZrO_2 solid, rendering electronic exchanges almost impossible. We could also highlight the phenomenon of complexation observed with chloride and fluoride ions.

Nevertheless, we are going to present some results of our various electrochemical studies of zirconium in an acid medium.

a) Reduction of commercial zirconium solutions: effect of Nitrogen bubbling

$I = f(E)$ curves were plotted in reduction on a rotating glassy carbon disk in a strongly acid medium, $pH \leq 1$, on three commercial zirconium solutions S' , S'' , and S''' , of respective concentrations $C' = 0.001$ M, $C'' = 0.003$ M and $C''' = 0.005$ M.

In the first step of our study, nitrogen was used as bubbling gas in order to reduce significantly the amount of oxygen dissolved in solution. The results are presented in **Figure 4** below.

Zirconium reduction was not observed; no zirconium signal. The observed waves correspond to the reduction of the remaining dissolved oxygen in solution

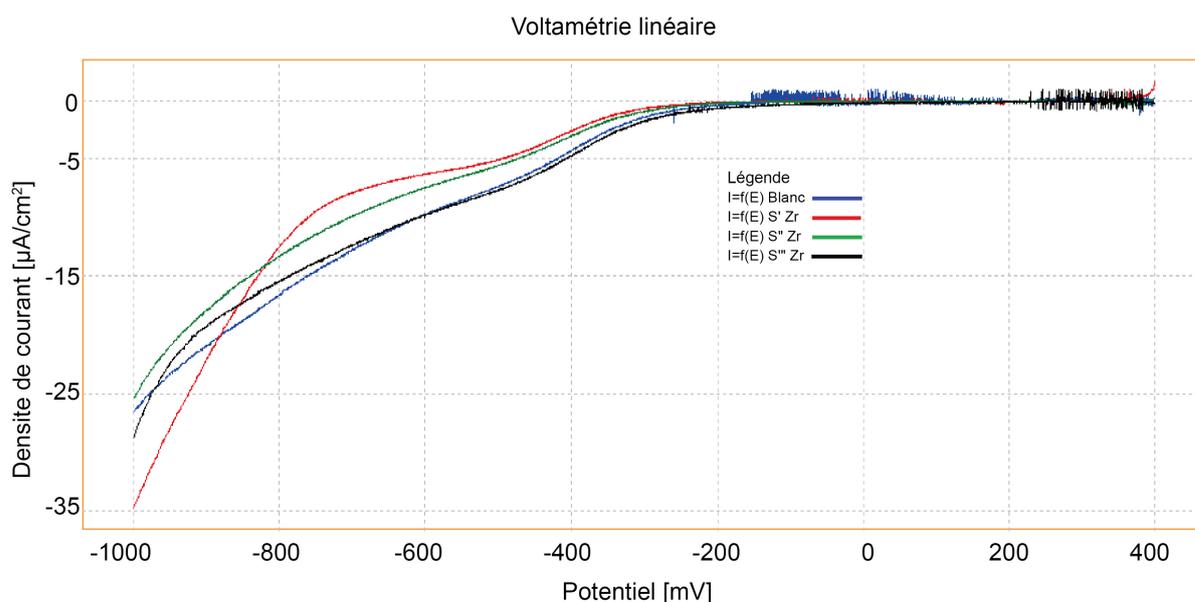


Figure 4. Curves $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in the blanc, then in 3 Zr solutions $S' = 0.001$ M, $S'' = 0.003$ M, $S''' = 0.005$ M; Bubbling N_2 ; 30 min; $\omega = 1000$ rpm, $r = 20$ mV/s, E. Aux: Pt, E. Ref: ECS.

which was not removed by the nitrogen bubbling. The potential of the couple O_2/H_2O being equal to 1.475 V/CSE at 298.15 K [26], it is deduced that the potentials of all the elements of the system are lowered. It is deduced from this that zirconium ions form with fluoride and chloride ions complexes which have a lowering potential effect.

We also observe the phenomenon of passivation through the formation of a layer of zirconium dioxide on the surface of the electrode thus preventing the reduction of the species present in solution. The tendency of zirconium to oxidize spontaneously in an acid media and to form a film of zirconia which protects it has been confirmed by E. GOBERT *et al.* in one of their studies which focused on the electrochemical behavior of zirconium in an acid media [12].

b) Reduction of zirconium: effect of Argon bubbling

In the continuation of our studies relating to the analysis of zirconium in an acid environment, a sample of zirconium coming from the mine, dissolved under the same operating conditions as before, was analyzed in reduction on a rotating glassy carbon disk. The bubbling gas used in this time was argon (Ar).

The concentration of zirconium in the solution was first determined by ICP analysis in order to confirm the presence of zirconium in the solution.

The result of the ICP analysis revealed this following mass concentration:

$C_{mZirconium} = 0.5 \text{ g/dm}^3$. **Figure 5** below, shows the profile of the potential intensity curves obtained in reduction on a rotating glassy carbon disk.

Argon bubbling, completely removes dissolved oxygen in the solution. Moreover, the two voltammograms show the same shape, which means that the zirconium has not been reduced. The wave which appears towards -1 V corresponds

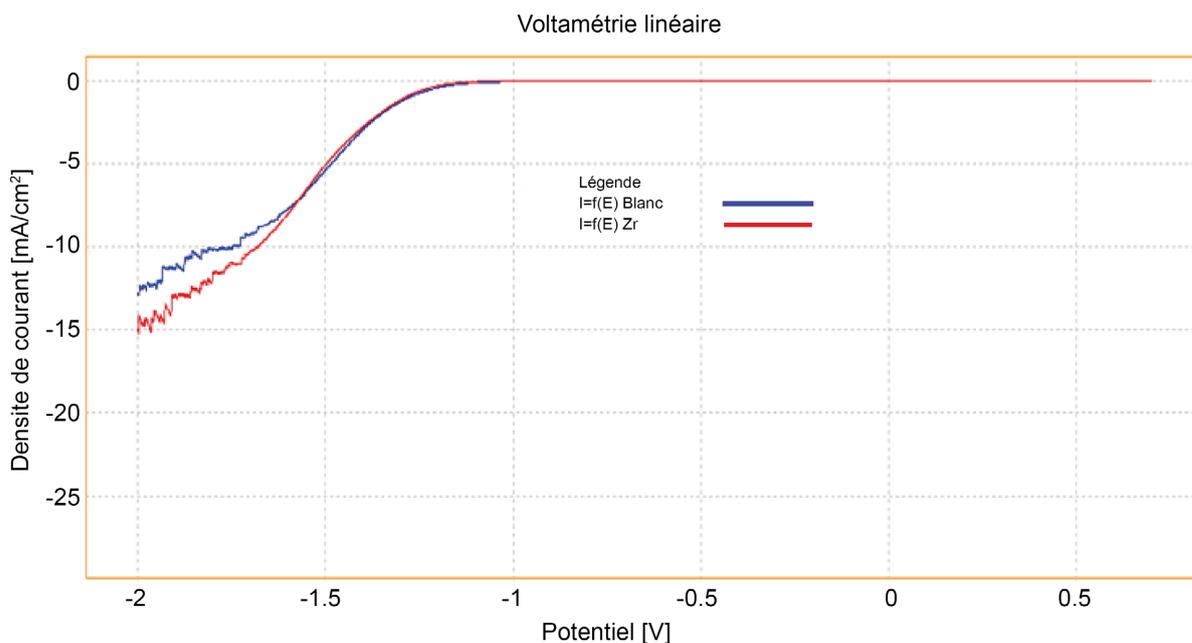


Figure 5. Curve $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3 \text{ mm}$, immersed in the blanc and in a second solution of Zr 0.001 M; Bubbling Ar: 30 min; $\omega = 1000 \text{ rpm}$, $r = 20 \text{ mV/s}$, E. Aux: Pt, E. Ref: ECS.

to the reduction of the “free” protons because the medium is strongly acidic ($\text{pH} \leq 1$). The free proton concentration being high in the solution, beyond the potential of 1.6 V, the wall of the solvent appears, thus preventing the electrochemical reduction of any other species present in solution.

3.1.2. Electrochemical Studies of Zirconium in Organic Medium

Since previous electrochemical studies had revealed difficulties related to the study of zirconium in aqueous media, in particular acidic ones, in order to promote its study we made the medium basic, which created even more opportunities thanks to the deficit of free protons.

In effect, the latter had a relatively low reduction potential on DHW, consequently leading to the formation of a solvent wall which prevented the reduction of the dissolved zirconium in solution.

a) Effect of alkalization of the solution with NaOH

Here we have demonstrated the action of NaOH by gradually adding to the zirconium solution dissolved with the aqua regia, a saturated sodium hydroxide solution, making the mixture basic with a final pH of between 12 and 13. The results are presented in **Figure 6** below.

Alkalinization caused a wave to appear from -1.5 V/DHW, corresponding to the reduction of Zirconium (IV) to Zr(0), the current density amounting to about 7 mA/cm^2 .

In reality, according to the pourbaix diagram, in a basic medium zirconium is in the form of HZrO_3^- it is reduced in Zr(0) towards the potential of -1.5 V. The reaction is as follows:

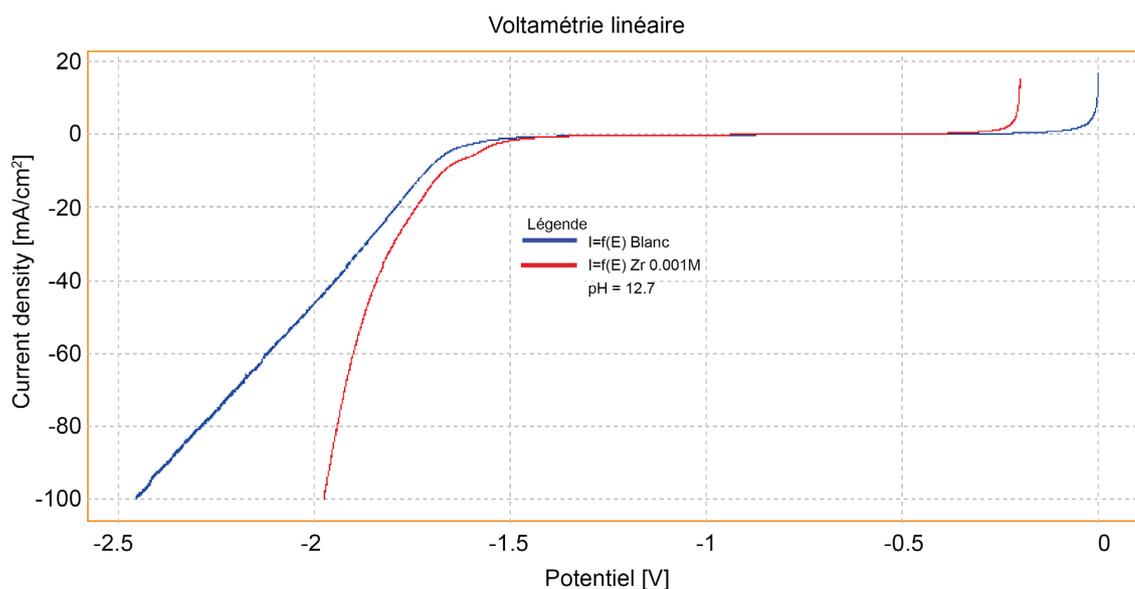
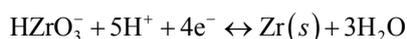


Figure 6. Curve $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in a solution without Zr and in a second solution of $\text{Zr}^{(\text{IV})}$ 0.001M, alkalinized to pH between 12 and 13 with saturated NaOH; Bubbling Ar: 30 min; $\omega = 1000$ rpm, $r = 20$ mV/s, E. Aux: Pt, E. Ref: ECS.

Moreover, it should be noted that the appearance of the zirconium reduction wave is favoured by the medium which is highly basic and consequently poor in H^+ ion.

The reduction of the zirconium was followed by the reduction of the solvent from -1.7 V/DHW, which caused the solvent wall to appear.

b) Dosed addition

In order to confirm the reduction of zirconium in alkaline medium, we have prepared 3 solutions of Zirconium. First 0.03 g of ZrO_2 powder was dissolved with aqua regia; the first solution obtained was S_0 . The concentration of Zr in S_0 was determined by ICP, $S_0 = 0.001$ M.

From S_0 we have prepared two solutions S_1 , and S_2 . We took from S_0 two volumes equivalent to 25 ml each then we introduced them into a 50 ml beaker. We added then to beakers 1 and 2 respectively the following volumes $V_1 = 8$ cm³ and $V_2 = 20$ cm³ volumes of commercial zirconium solution 0.01 M. The two solutions obtained S_1 and S_2 were analyzed by ICP in order to determine their molar zirconium concentration.

The results showed respectively these concentrations [$S_1 = 0.003$ M] and [$S_2 = 0.005$ M].

All the solutions are alkalized to a pH of 13 with saturated NaOH. The intensity-potential curves were then plotted in reduction on a rotating glassy carbon disk. The results are presented in **Figure 7** below.

The addition of 8 cm³ of commercial Zirconium with a molar concentration of 0.01 M has increased the amplitude of the reduction current density, which

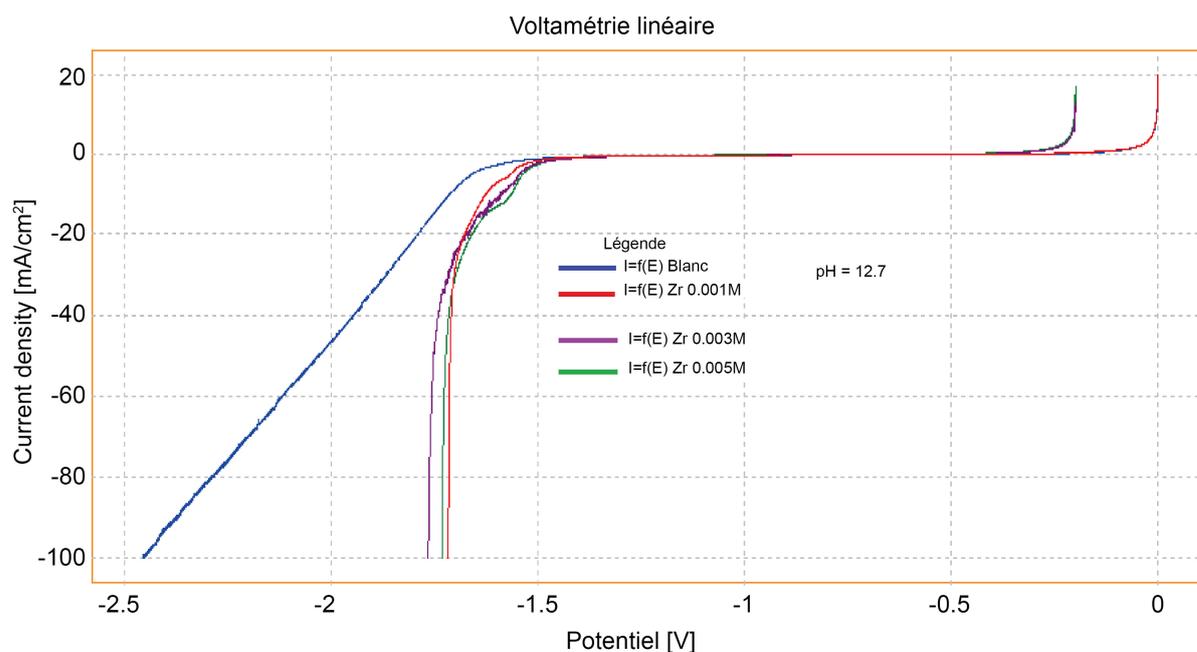


Figure 7. Curves $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in the blanc, then in 3 Zr solutions $S_0 = 0.001$ M, $S_1 = 0.003$ M, $S_2 = 0.005$ M, alkalized to $pH = 12.7$; Bubbling Ar: 30 min; $\omega = 1000$ rpm, $r = 20$ mv/s, E. Aux: Pt, E. Ref: ECS.

increased from 07 mA to about 12 mA on DHW. This is what was observed with the purple curve. This is explained in fact by the increase in the concentration of zirconium in solution, due to the supply of zirconium, relatively considerable, forming with OH^- ions, the HZrO_3^- which is then reduced to $\text{Zr}(0)$. The green curve further confirms the reduction of zirconium.

This is observed through the increase in the amplitude of the reduction current density which passes from 12 mA to 18 mA.

Exploitation of the curves obtained in **Figure 7** allowed us to highlight the effect of the concentration of zirconium on the amplitude of zirconium reduction current density.

We have thus plotted the curve $[\text{Zr}] = f(I)$ (**Figure 8** below), which allowed to deduce the concentration of zirconium in the solution when the amplitude of the current density is known (see **Table 2**).

c) Comparative studies

In this section we conducted a comparative study working with commercial zirconium solutions with known zirconium concentrations. In order to validate the electrochemical method and confirm the reproducibility of the system, we have performed the analysis of two commercial zirconium solutions with the same concentrations as the industrial samples which were dissolved. The concentration of the commercial zirconium solutions are $C_{1\text{comZr}}$ and $C_{2\text{comZr}}$ respectively equal to 0.001 mol/dm^3 and 0.005 mol/dm^3 . The two commercial solutions were subsequently analyzed through electrochemistry. The diagrams are presented in **Figure 9** below.

Table 2. Equivalence between Zr concentration and Zr amplitude reduction current density.

[Zr]	0.001	0.003	0.005
I	7	12	18

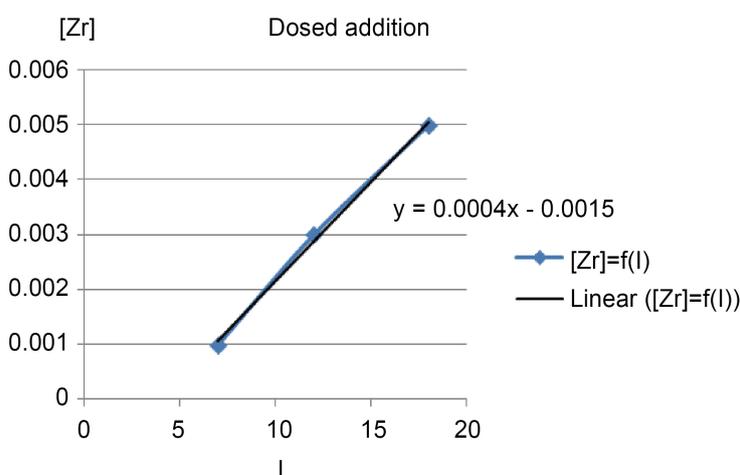


Figure 8. Curve $[\text{Zr}] = f(I)$.

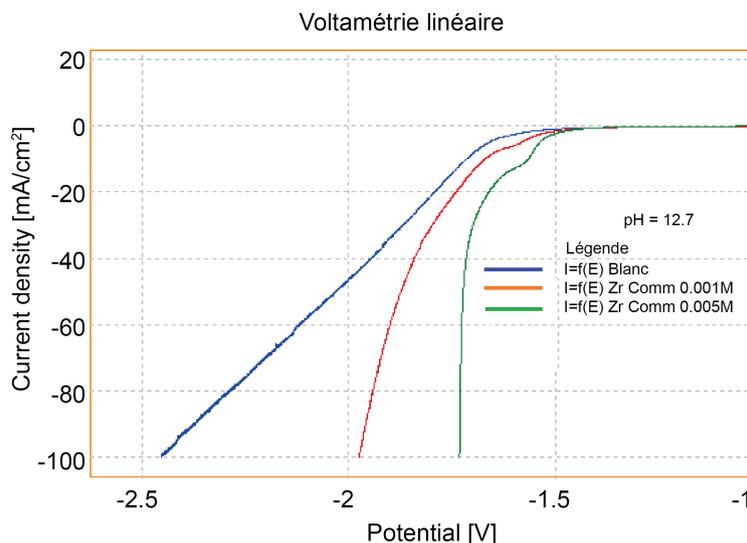


Figure 9. Curve $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in a NaOH solution at pH 12.7 containing commercial Zr 0.001M, then in a second NaOH solution at pH 12.7 containing commercial Zr 0.005 M; Argon bubbling (30 min); $\omega = 1000$ rpm, with $r = 20$ mV/s, E. Aux: Pt, E, Ref: ECS.

The operating protocol used remained unchanged. The two solutions were alkalinized to a pH of 12.7. Intensity-potential curves were plotted in reduction on a rotating glassy carbon disk.

The curves $I = f(E)$ show reduction waves which start from -1.5 V/DHW.

This potential value corresponds in the literature to the reduction potential of zirconium, thus confirming the reduction of zirconium in an alkaline medium. This reduction has moreover been observed at almost the same potential, with the various dissolved zirconium solutions analyzed previously. In addition, the shape of the $I = f(E)$ curves obtained with commercial zirconium solutions, demonstrates that the system is reproducible.

The amplitude of zirconium reduction current density increases proportionally with the increase in the concentration of zirconium in solution; it went from 7 mA/cm² to 18 mA/cm².

This is the consequence of a high presence of zirconium on the surface of the electrode, generated by an increase in the molar concentration of the latter in solution. By considering in **Figure 8**, the equation of the straight line determined from the curve $[Zr] = f(I)$, we deduce the following concentration values $C_{1\text{comZr}} = 0.001$ mol/dm³ and $C_{2\text{comZr}} = 0.005$ mol/dm³, which thus confirms the results obtained previously but also the method of analysis.

3.2. Electrochemical Study of Zirconium in an Organic Medium

In this last part, we studied the effects of the dehydration of the solution, the addition of a commercial zirconium solution, dilution and scanning speed. All the results are presented below.

3.2.1. Study of the Effect of the CaCl₂ Dehydrating Agent

To study the effect of dehydration, the intensity-potential curves were plotted in linear voltammetry (Figure 10). The concentration of zirconium in solution was of the order 10⁻³ M.

*Indications: The blue curve, the curve of the white, is the one drawn with the solution without zirconium and the red curve with zirconium.

*For the blue curve, from 1 V to -3 V, there is no reduction step except that of the solvent reduction starting from -1.8 V. The amplitude of the current density gradually increases as the potentials become lower. A wall of the solvent is thus formed, beyond the potential of -3 V, consequently preventing the reduction of all other variants present in the solution. This is justified by the large volume of solvent (15 cm³ of DMF) used during electrochemical analysis.

*The red curve indicates two waves of reductions: the first corresponds to the reduction of Zr^(IV) to Zr(0) and the second relates to the reduction of Ca²⁺ ions present in the solution.

It should be noted that neither a signal nor any wave of zirconium reduction was detected when intensity-potential curves were plotted without the presence of CaCl₂. The presence of the latter made it possible to bring about a considerable reduction in the water present in the solution, which facilitated observing the reduction of the zirconium present in the solution. This reduction is observed from -1.6 V/DHW and continues up to -2.3 V.

A new wave of reduction then appears from -2.5 V, corresponding to the reduction of the Ca²⁺ ions resulting from the dissolution of the CaCl₂ present in excess in solution.

3.2.2. Effect of Dosing with a Commercial Zirconium Solution

In order to confirm the reduction of zirconium observed in the previous paragraph

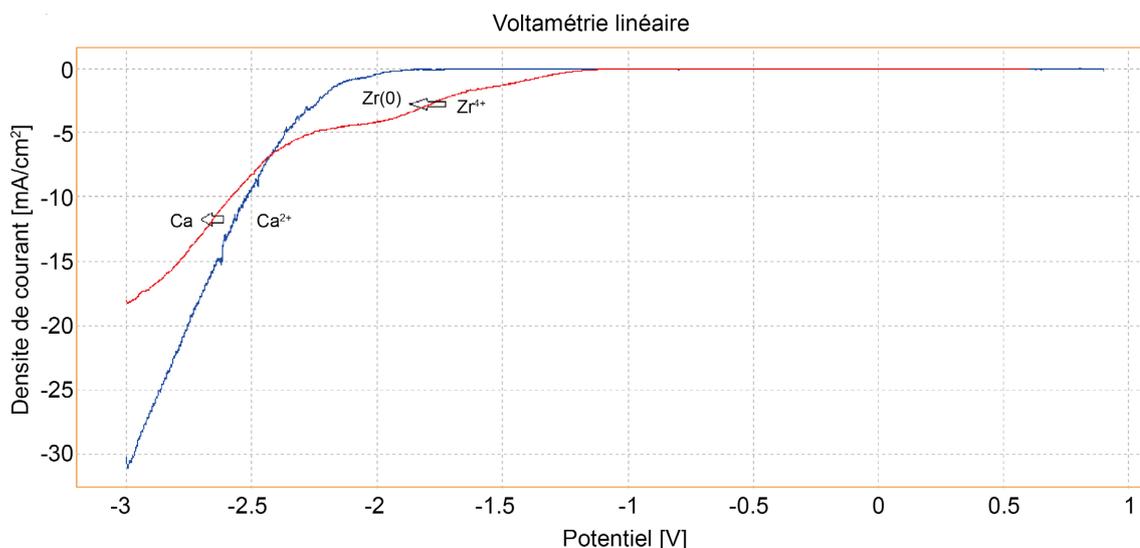


Figure 10. Curves $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in a solution containing DMF, HCl and CaCl₂ (White), then in a solution containing Zr (0.001 M), DMF, HCl and CaCl₂, in the presence of Ar; $\omega = 1000$ rpm, with $r = 10$ mv/s, E. Aux: Pt, E, Ref: ECS.

(3.1.2), we proceeded to test the previous solution by adding a commercial zirconium solution 10^{-1} M.

The concentration of zirconium in the final solution is then equal to 10^{-2} M; this value has been determined by ICP.

Several intensity-potential curves were plotted under the same operating conditions as the previous ones.

The diagrams below (Figure 11), show the intensity-potential curves obtained by reduction on a vitreous carbon disk rotating at a speed of 1000 revolutions/min, the electrochemical window ranging from 1 V to -3 V and the scanning speed amounting to 10 mV/s.

The plotting of the intensity-potential curves allowed us to confirm the reduction of zirconium dissolved in solution.

*The curve in red (curve representative of white) shows no signal from zirconium. Its profile is linear up to the potential of -1.8 V, corresponding to the reduction of the solvent.

*The curve in blue, on the other hand, shows a reduction wave from -1.5 V/DHW.

The amplitude of the density of the reduction current gradually increases and reaches a maximum value of 15 mA/cm², a value literally greater than three times the value of the reduction current density obtained during the analysis of zirconium dissolved in solution ($J = 4$ mA/cm²) whose molar concentration previously determined by ICP is equal to 10^{-3} M. This increase in the amplitude of the reduction current is in fact the consequence of the increase in the concentration of the zirconium dissolved in soil generated by the addition of the commercial zirconium solution with a molar concentration equal to 10^{-1} M.

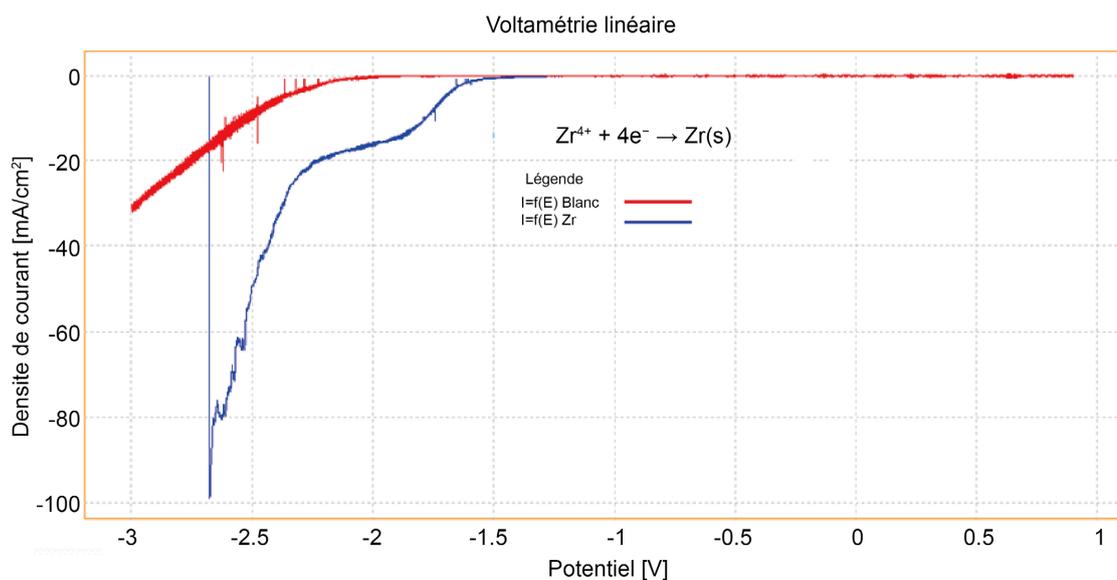


Figure 11. Curves $I = f(E)$ in reduction on a rotating glassy carbon disk, $d = 3$ mm, immersed in a solution containing DMF, HCl and CaCl (White), then in a commercial solution containing Zr (0.01 M), DMF, HCl and CaCl₂, in the presence of Ar; $\omega = 1000$ rpm, with $r = 10$ mv/s, E. Aux: Pt, E, Ref: ECS.

Zirconium metal was gradually formed and deposited on the surface of the electrode, thus catalyzing the reduction of the solvent. This phenomenon thus amplified the density of the current (100 mA/cm^2).

3.2.3. Effect of the Scanning Speed

To study the impact of the scanning speed, we plotted intensity-potential curves in cyclic voltammetry between potentials between -3 V and 1.5 V . A first experiment was carried out in order to determine the different values of the potential peaks in forward and return scanning. The voltammograms below (Figure 12), show the oxidation and reduction peaks of several species in solution in round trip scanning.

*The peak obtained at -2.4 V/DHW corresponds to the reduction of Zr(IV) to Zr(0) , which starts from -1.6 V/DHW [27].

*The second corresponds to the reduction of Ca(II) to Ca(0) at -2.8 V/DHW , which was then reoxidized at the same potential in return scanning.

However, no oxidation peak of the Zr(0) was observed in return scanning; this is due to the formation of a passive film on the surface of the electrode, thus preventing the oxidation of the Zr metal. This passivation phenomenon was mentioned by C. E. Coleman *et al.* [28] in the course of a study on the metallurgy of zirconium, where they demonstrated the high affinity of zirconium with oxygen, thus leading to the formation of a passive film of zirconium oxide on the surface of the electrode, which consequently ensured the stability of the latter and prevented any electrochemical reaction on the surface of the electrode.

During the electrochemical reaction, the amplitude of the density of the diffusion current gradually decreased as a function of time, thus showing the decrease

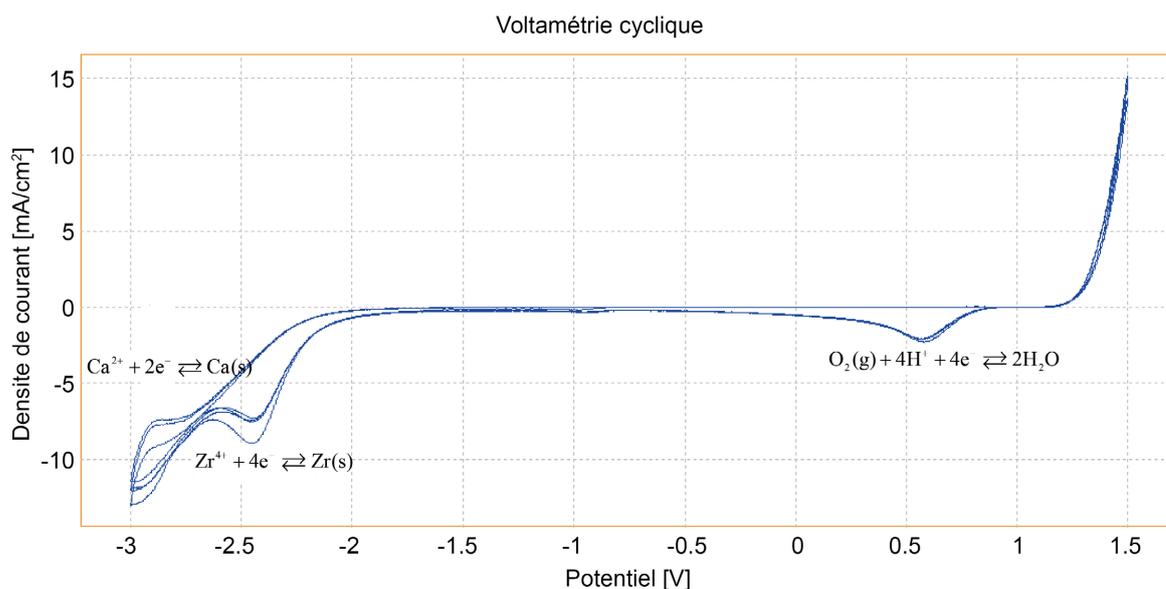


Figure 12. Curves $I = f(E)$ in cyclic voltammetry on a rotating glassy carbon disk, $d = 3 \text{ mm}$, immersed in a solution containing Zr (0.001 M) DMF, HCl and CaCl_2 , presence Ar ; $\omega = 0 \text{ rpm}$, with $r = 200 \text{ mV/s}$, E. Aux: Pt, E, Ref: ECS.

in the concentration of the electroactive species near the surface of the electrode, which reveals a relatively slow diffusion. The third peak (at 0.6 V/DHW) was that of the reduction of oxygen from the oxidation of water.

In order to study the effect of the scanning speed, we performed a second experiment typically based on the variation of the latter.

Thus, several intensity-potential curves were plotted, with scanning speeds ranging from 10 mV/s to 200 mV/s.

The voltammograms below (**Figure 13**), were plotted under the same operating conditions as previously, with different scanning speeds.

The careful study of these various curves shows that the amplitude of the density of the current in forward scanning (reduction) increased gradually parallel to the increase in the scanning speed. The curve in blue had the highest scanning speed (200 mV/s) and the curve in pink the lowest (10 mV/s).

Through the data obtained with the plots of the various voltammograms, we also studied the reversibility of the system by plotting the curve $i_p = f(\sqrt{v})$.

The results are presented in the diagram below (**Figure 14**).

Curve $i_p = f(\sqrt{v})$ is quasi-linear, which allows us to conclude that the system is reversible and that the mass transfer is controlled by the diffusion phenomenon.

3.2.4. Effect of Dilution

In this part we studied the effect of the gradual addition of water in order to show the impact of dilution on the amplitude of the density of the reduction current, but above all to confirm the zirconium signal previously obtained. Thus, several intensity-potential curves were plotted by adding different volumes of distilled water to the initial solution; the operating conditions remained unchanged.

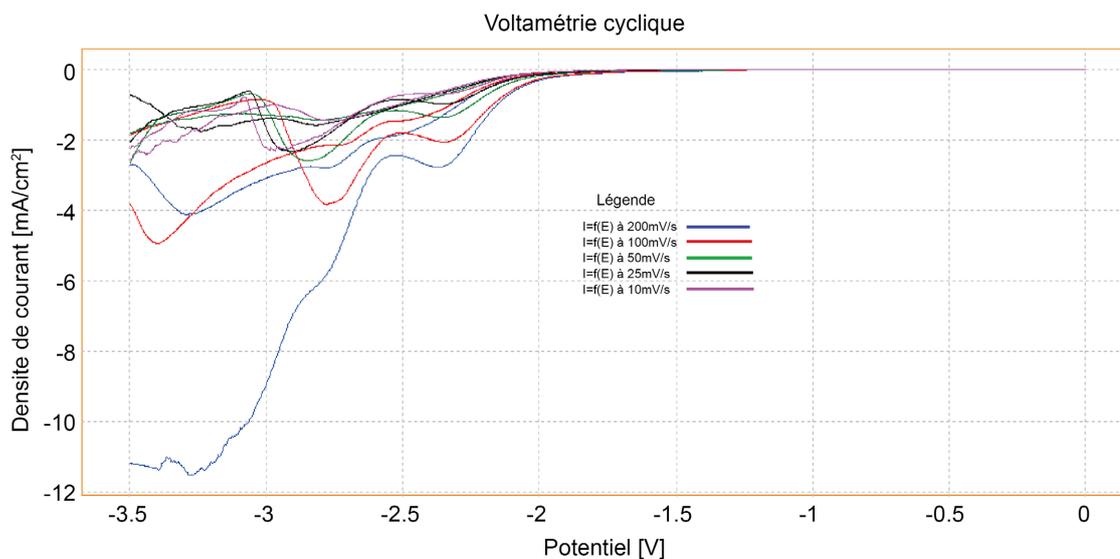


Figure 13. Curves $I = f(E)$ in cyclic voltammetry on a rotating glassy carbon disk, $d = 3$ mm, immersed in a solution containing Zr (0.001 M), DMF, HCl and CaCl_2 , presence Ar; $\omega = 0$ rpm, with $r = 200$ mv/s, E. Aux: Pt, E, Ref: ECS.

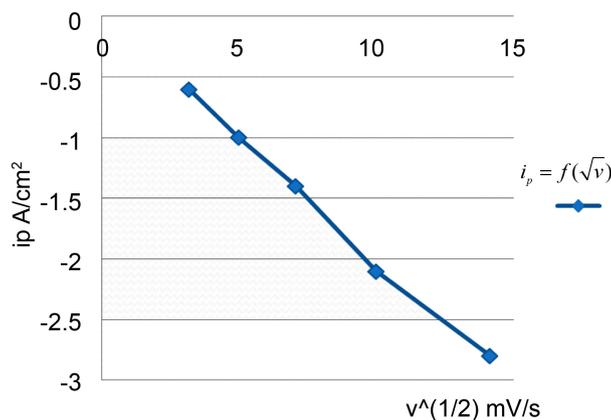


Figure 14. Curve $i_p = f(\sqrt{v})$.

The results are presented in the diagram below (**Figure 15**).

*The curve in blue, drawn without the presence of water, shows a clear signal of reduction of the zirconium in forward scanning.

*The red curve, on the other hand, shows a zirconium reduction signal with a reduction in the amplitude of the current density.

*The green curve presents a signal which corresponds to the reduction of the water present in solution, due in fact to its strong presence in the medium; reduction starts from -1.2 V/DHW in an organic medium (DMF).

The Zirconium signal thus ended up disappearing with the gradual addition of water.

This is explained by the phenomenon of passivation of zirconium, favoured by the presence of oxygen generated by the reduction of water, the latter forming zirconium dioxide (ZrO_2) through the zirconium in solution. This zirconium dioxide was deposited on the surface of the electrode and thus prevented any electrochemical reaction on the surface.

4. Conclusions

Analysis of zircon ore was carried out using electrochemistry. The main objective of this study is to define the electrolytic environments favorable to the electrochemical analysis of zirconium and determine the parameters and operating conditions allowing a qualitative and quantitative analysis of zirconium in these environments.

In view of the insufficiency of studies of zirconium in aqueous and organic media, our work focused particularly on those environments. In an aqueous medium aqua regia was used as the support electrolyte, while in an organic medium, Dimethylformamide (DMF) was used. The ore was dissolved according to an operating protocol typically based on alkaline melting with NaOH as the melt.

The main results and conclusions of this work are presented in the paragraph below.

First, this study has revealed that the acidic environment is not favorable for

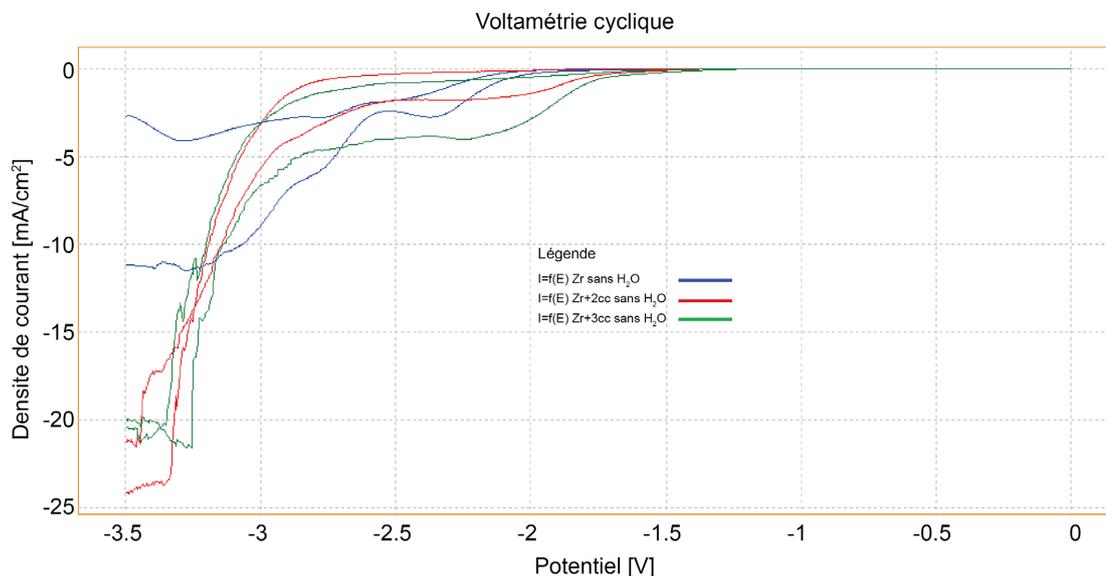


Figure 15. Curves $I = f(E)$ in cyclic voltammetry on a rotating glassy carbon disk, $d = 3$ mm, immersed in a solution containing Zr, DMF, HCl and H_2O , presence Ar; $\omega = 0$ rpm, with $r = 200$ mv/s, E. Aux: Pt, E, Ref: ECS.

the detection of zirconium. In fact, the electrochemical window of the acid electrolyte is considerably reduced thanks to the high concentration of H^+ ions in solution, which makes difficult the zirconium reduction; the reduction potential of the latter being equal to -1.539 V/DHW [27].

With regard to the alkaline media, the intensity-potential curves obtained in linear voltammetry in reduction in a rotating glassy carbon disk, show easily that the alkaline medium is favorable for the electrochemical detection of zirconium. In this medium, the zirconium acquired the form $HZrO_3^-$, which was easier to reduce.

The reduction of zirconium in an alkaline medium was found to be enabled by the low concentration of the medium in H^+ ion, which led to an increase in the solvent window.

Finally the different results of the electrochemical analyzes, carried out on zirconium in an organic media show sufficiently that this medium is also favorable to the electrochemical study of zirconium. This is due to the solvent window offered by Dimethylformamide, which ranges from 1 V to -3 V. The zirconium was reduced to the potential of -1.5 V/DHW. The amplitude of the current density of zirconium in an organic medium was found to be proportional to its concentration in solution. This was confirmed through ICP analyses carried out on two commercial zirconium samples.

The choice of the method is related to its simplicity, the cost of its implementation, and its accuracy; a reflection of its detection limit is of the order of 10^{-6} .

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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