Reference Electrode for Monitoring Cathodic Protection Potential

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Reference electrodes are generally implemented for the purpose of monitoring the cathodic protection potentials of buried or immersed metallic structures. In the market, many types of reference electrodes are available for this purpose, such as saturated calomel, silver/silver chloride and copper/copper sulfate. These electrodes contain a porous ceramic junction plate situated in the cylindrical body bottom to permit ionic flux between the internal electrolyte (of the reference electrode) and the external electrolyte. In this work, the copper/copper sulfate reference electrode was modified by replacing the porous ceramic junction plate for a metallic platinum wire. The main purpose of this modification was to avoid the ion copper transport from coming from the inner reference electrode solution into the surrounding electrolyte, and to mitigate the copper plating on the coupon surfaces. Lab tests were performed in order to compare the performance of the two mentioned reference electrodes. We verified that the experimental errors associated with the measurements conducted with developed reference electrode would be negligible, as the platinum surface area exposed to the surrounding electrolyte and/or to the reference electrolyte are maintained as small as possible.

Keywords: reference electrode, cathodic protection, corrosion

1. Introduction

Reference electrodes are used for monitoring cathodic protection potentials of buried or immersed metallic structures [1-6]. In the market, many types of reference electrodes are available for this purpose, such as saturated calomel, silver/silver chloride and copper/copper sulfate. The latter is the most used for buried pipelines and consists of a copper rod immersed in a saturated copper sulfate aqueous solution both involved by a polymeric cylindrical body. These electrodes contain a porous ceramic junction plate located at the cylindrical body bottom to permit ionic flux between the internal electrolyte of the reference electrode(copper sulfate) and the external electrolyte (generally soil). In this paper, this type of electrode was named Cu/CuSO$_4$-ceramic.

According to Greff *et al.* (1985), the junction potential of reference electrodes, including the Cu/CuSO$_4$-ceramic, is negligible [7]. However, the Cu/CuSO$_4$-ceramic electrode presents a practical problem for the cathodic protection sector, contamination of the external electrolyte with copper ions. This contamination causes important measurement errors especially for cathodic protection of buried pipelines where corrosion probes are used. These probes are constituted of a copper/copper sulfate reference electrode and corrosion coupons with the same material as the pipelines. The reference electrode is used for monitoring the buried pipeline potential and the corrosion coupons are used to determine the pipeline external corrosion rate [1-6]. Measurement errors are caused due to surrounded soil contamination by copper ions. These ions diffuse toward the coupons and are plated on the carbon steel surfaces causing the mentioned errors.

To solve this problem, the copper/copper sulfate reference electrode was modified by replacing the porous ceramic junction plate by a metallic platinum wire. The main purpose of this modification was to avoid the ion copper transport from the inner reference electrode solution to the surrounded soil and to mitigate the copper plating on the coupon surfaces. The modified reference electrode was named Cu/CuSO$_4$-Pt. Fig. 1 shows the Cu/CuSO$_4$-Pt.

For the validation of this modified electrode, some electrochemical tests were performed and a theoretical justification was presented. We concluded that the modified reference electrode can be used safely for monitoring buried pipeline cathodic protection potentials.

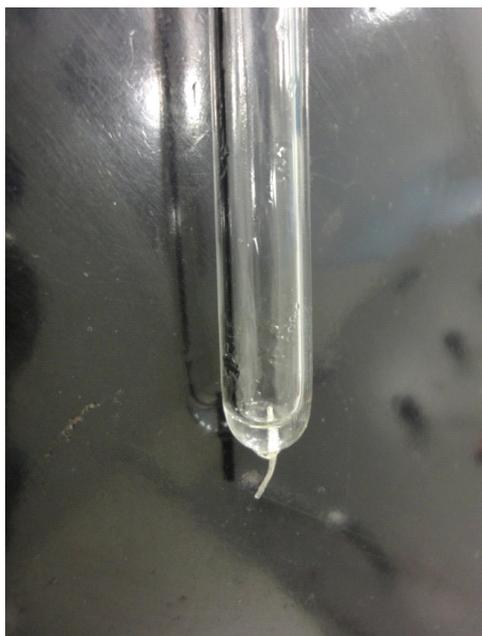† Corresponding author: zepanossian@gmail.com

Fig. 1 Bottom of the reference electrode consisted by a platinum wire.

2. Materials and Methods

Three series of tests were conducted for experimental validation of the Cu/CuSO$_4$-Pt.

2.1 Open circuit potential measurements

The first series of tests was conducted with three different reference electrodes: Cu/CuSO$_4$-ceramic, Cu/CuSO$_4$-Pt and saturated calomel. The tests consisted of open circuit potential measurements for 760 h of the two copper/copper sulfate reference electrode regarding a saturated calomel reference electrode. Three different electrolytes were used:

- saturated CuSO$_4$ aqueous solution, pH = 0 (acidification made with H$_2$SO$_4$ 50 % w/w);
- Na$_2$SO$_4$ aqueous solution 0.5 % (w/w), pH = 0 (acidification made with H$_2$SO$_4$ 50 % w/w);
- NaCl aqueous solution 0.5 % (w/w) pH = 0 (acidification made with HCl 50 % w/w).

The pH = 0 was adopted because this is the pH value of the copper sulfate solution of Cu/CuSO$_4$ electrodes. Fig. 2 shows the experimental arrangement of the first series of tests.

2.2 Polarization curves

In the second series of tests, anodic and cathodic polarization curves were obtained using a 2-cm^2 carbon steel plate as a working electrode and a 35-cm^2 platinum basket as a counter electrode. Two types of reference electrodes were used: Cu/CuSO$_4$-ceramic and Cu/CuSO$_4$-Pt. The objective of these tests was to verify whether the performance of the modified electrode is influenced by carbon-steel cathodic or anodic polarization.

Polarization curves were obtained using zero-pH Na$_2$SO$_4$ 0.5 % (w/w) aqueous solution. A Potentiostat/Galvanostat *Princeton Applied Research* model 2273 was used.

Three anodic polarization curves and three cathodic polarization curves for each reference electrodes were obtained. All curves were started after the open circuit potential stabilization.

2.3 Influence of the platinum wire area immersed in the electrolytes

The objective of the third series of tests was to verify the influence of the platinum wire area immersed both in the internal Cu/CuSO$_4$-Pt electrolyte and in different
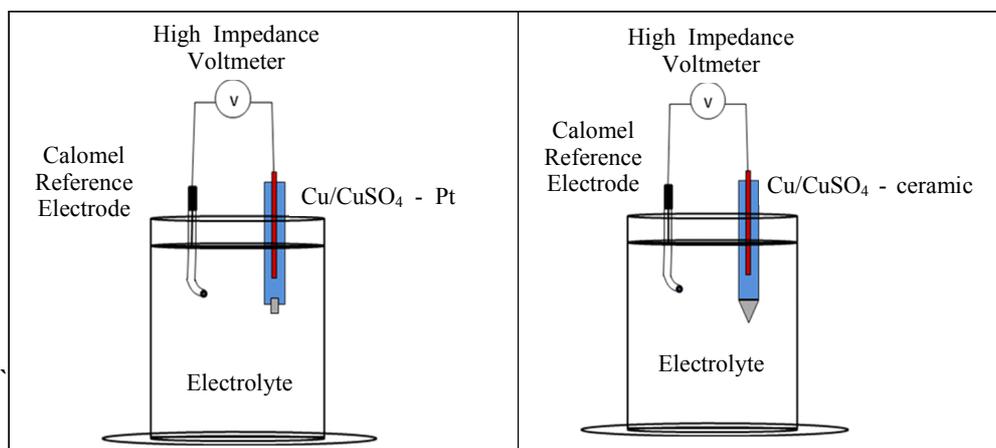

Fig. 2 Experimental arrangement used in the first series of tests.
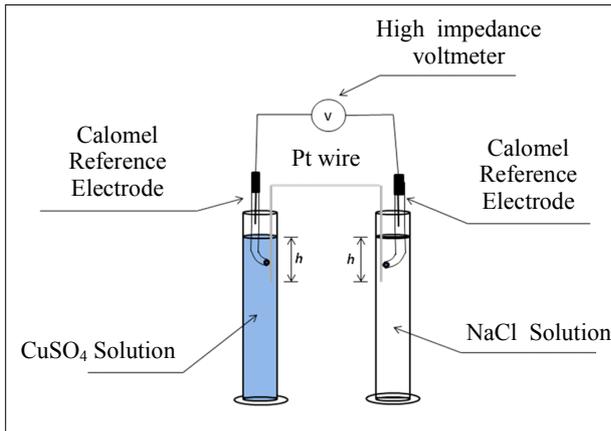
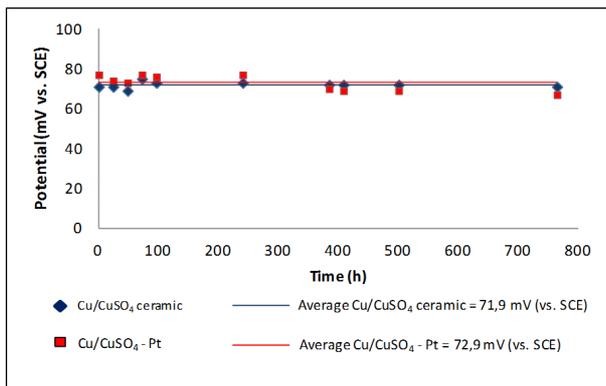**Fig. 3 Experimental arrangement used in the third series of tests.**

Fig. 4 Cu/CuSO₄-ceramic and Cu/CuSO₄ – Pt open circuit potencial measurements versus saturated calomel reference electrode. Electrodes immersed in zero-pH CuSO₄ aqueous solution.

Fig. 5 Cu/CuSO₄-ceramic and Cu/CuSO₄ – Pt open circuit potential measurement versus saturated calomel reference electrode. Electrodes immersed in zero-pH Na₂SO₄ aqueous solution.

Fig. 6 Cu/CuSO₄-ceramic and Cu/CuSO₄ – Pt open circuit potential measurement versus saturated calomel reference electrode. Electrodes immersed in zero-pH NaCl aqueous solution.
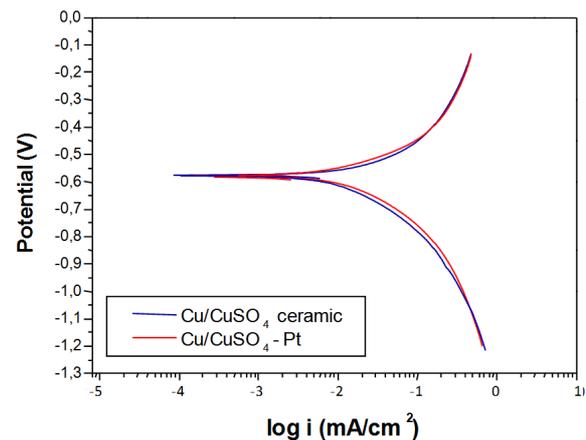
Fig. 7 Carbon steel polarization curves obtained in 4-pH Na₂SO₄ aqueous solution. Electrodes potential values measured regarding Cu/CuSO₄-ceramic and Cu/CuSO₄ – Pt reference electrodes.

external electrolytes. These tests were conducted because it is known that the junction potential between references electrodes and working electrolytes depends on the conductivity and geometry of the junction itself [8]. The commercial reference electrodes are designed aiming at minimizing the junction potential and the majority of the electrochemical experiments are conducted using high conductivity electrolytes.

Two graduated cylinders were used for these tests. The first one was filled with a zero-pH saturated CuSO₄ solution and the second cylinder was filled with NaCl 0.5 % (w/w) solution with different pH values: 1.5; 3.2; 6.6; 9.4 and 12.5. The pH was modified by using an HCl solution or a NaOH solution.

In each cylinder, a saturated calomel reference electrode was immersed and a platinum wire was used for the electric connection of the two solutions. Fig. 3 shows ex-
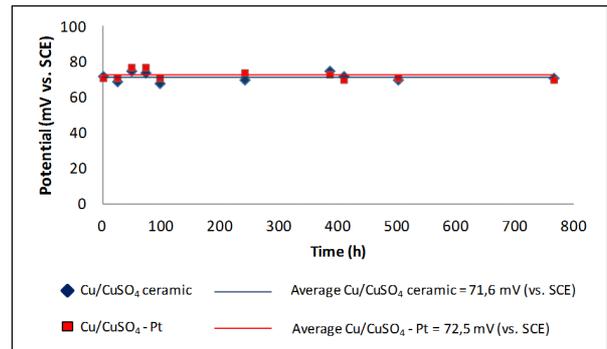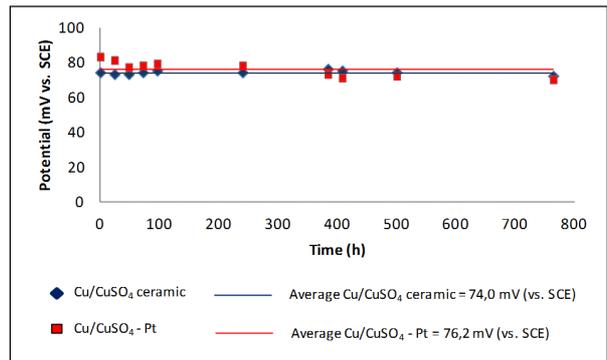
Table 1 Potential values difference between two saturated calomel reference electrodes immersed in 1.5-pH NaCl aqueous solution

pH solution	Height h of the platinum wire immersed in CuSO$_4$ solution (mm)	Platinum surface area immersed in CuSO$_4$ solution (mm^2)	Height h of the platinum wire immersed in NaCl solution (mm)	Platinum surface area immersed in NaCl solution (mm^2)	ΔE (mV)
1.5	1	3	1	3	1
	2	10	2	10	4
	10	35	10	35	6
	20	70	20	70	7
	1	3	1	3	2
			2	10	4
			20	70	4
			40	130	4
			60	200	5
			80	260	5
	1	3	1	3	2
	2	10			2
	20	70			3
	40	130			3
	60	200			4
	80	260			3

Table 2 Potential values difference between two saturated calomel reference electrodes in 3.2-pH NaCl aqueous solution

pH solution	Height h of the platinum wire immersed in CuSO$_4$ solution (mm)	Platinum surface area immersed in CuSO$_4$ solution (mm^2)	Height h of the platinum wire immersed in NaCl solution (mm)	Platinum surface area immersed in NaCl solution (mm^2)	ΔE (mV)
3.2	1	3	1	3	2
	2	10	2	10	6
	10	35	10	35	8
	20	70	20	70	5
	1	3	1	3	3
			2	10	2
			20	70	6
			40	130	6
			60	200	2
			80	260	2
	1	3	1	3	3
	2	10			3
	20	70			5
	40	130			4
	60	200			2
	80	260			2

perimental arrangement used in these tests.

The potential difference between the two calomel references electrodes (*ΔE*) was measured varying the height (h) of the platinum immersed in each solution. A 10-MΩ internal impedance voltmeter was used for the measurements.

3. Results and Discussion

The results and discussion of each series of tests are presented individually.

3.1 Open circuit potential measurements

Fig.s 4 to 6 show the results of Cu/CuSO$_4$-ceramic and Cu/CuSO$_4$-Pt open circuit potential measurements versus a saturated calomel reference electrode for 760-h tests. From these figures, it can be observed that the open circuit potential values of Cu/CuSO$_4$-ceramic and Cu/CuSO$_4$-Pt regarding saturated calomel reference electrode are almost the same and they do not vary with time.

3.2 Polarization curves

Fig. 7 shows the polarization curves obtained for Cu/CuSO$_4$-ceramic and Cu/CuSO$_4$-Pt regarding saturated calomel reference electrode. From this Fig. 7, an overlap of the curves was observed showing that the obtained val-

Table 3 Potential values difference between two saturated calomel reference electrodes in 6.6-pH NaCl aqueous solution

pH solution	Height h of the platinum wire immersed in $CuSO_4$ solution (mm)	Platinum surface area immersed in $CuSO_4$ solution (mm²)	Height h of the platinum wire immersed in NaCl solution (mm)	Platinum surface area immersed in NaCl solution (mm²)	ΔE (mV)
6.6	1	3	1	3	1
	2	10	2	10	3
	10	35	10	35	6
	20	70	20	70	16
	1	3	1	3	2
			2	10	4
			20	70	5
			40	130	5
			60	200	6
			80	260	4
	1	3	1	3	1
	2	10			5
	20	70			2
	40	130			5
	60	200			4
	80	260			4

Table 4 Potential values difference between two saturated calomel reference electrodes in 9.4-pH NaCl aqueous solution

pH solution	Height h of the platinum wire immersed in $CuSO_4$ solution (mm)	Platinum surface area immersed in $CuSO_4$ solution (mm²)	Height h of the platinum wire immersed in NaCl solution (mm)	Platinum surface area immersed in NaCl solution (mm²)	ΔE (mV)
9.4	1	3	1	3	3
	2	10	2	10	8
	10	35	10	35	28
	20	70	20	70	30
	1	3	1	3	2
			2	10	7
			20	70	6
			40	130	7
			60	200	9
			80	260	7
	1	3	1	3	3
	2	10			7
	20	70			7
	40	130			5
	60	200			4
	80	260			4

ues are not influenced by the modification of the Cu/CuSO₄-ceramic reference electrode.

3.3 Influence of the platinum wire area immersed in the electrolytes

Tables 1 to 5 show the results of the third series of tests. The platinum surface area immersed in each electrolyte and the potential difference values between the two reference electrodes are included in these tables.

In Table 1 (NaCl pH = 1.5 aqueous solution), it can be observed that smaller potential difference (ΔE) values were obtained when a small portion of platinum wire was immersed in both of the electrolytes or in only one of them. Higher ΔE values were obtained when the platinum wire area was higher in both of the electrolytes. This fact can be explained by the platinum-wire impedance, the higher platinum-wire impedance the higher is ΔE values. For the 3.2-pH NaCl solution (Table 2) and for the 6.6-pH NaCl solution (Table 3), the obtained results were very similar to the ones obtained for the 1.5-pH NaCl solution. For the 9.4-pH NaCl solution (Table 4) and for the 12.5-pH NaCl solution (Table 5), the ΔE values were more significative. However, when the platinum area was mini-

Table 5 Potential values difference between two saturated calomel reference electrodes in 12.5-pH NaCl aqueous solution

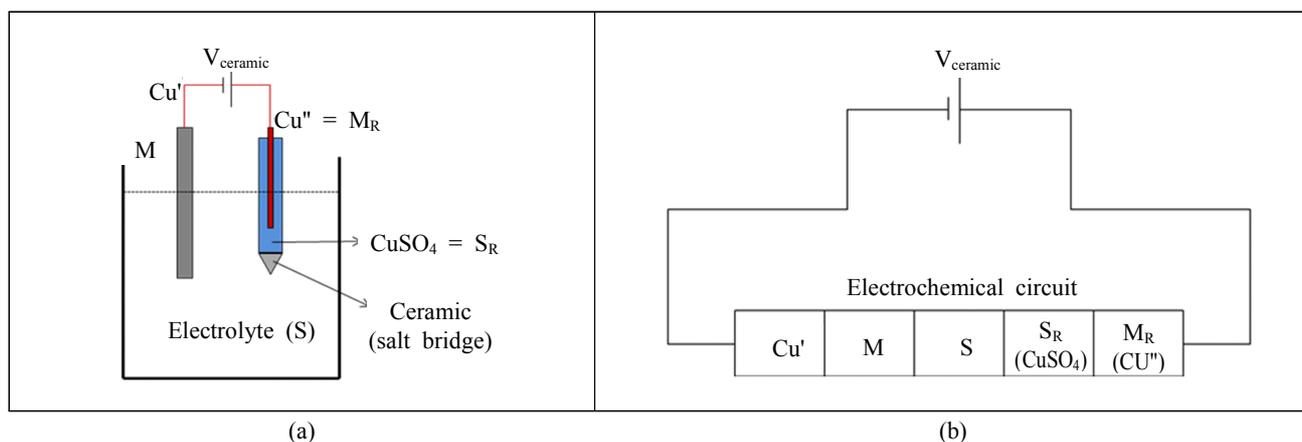| pH solution	Height h of the platinum wire immersed in CuSO$_4$ solution (mm)	Platinum surface area immersed in CuSO$_4$ solution (mm^2)	Height h of the platinum wire immersed in NaCl solution (mm)	Platinum surface area immersed in NaCl solution (mm^2)	ΔE (mV)
12.5	1	3	1	3	9
	2	10	2	10	50
	10	35	10	35	121
	20	70	20	70	181
	1	3	1	3	7
			2	10	9
			20	70	8
			40	130	10
			60	200	9
			80	260	8
	1	3	1	3	7
	2	10			8
	20	70			7
	40	130			9
	60	200			9
	80	260			8

(a)   (b)

Fig. 8 (a) Electrochemical cell constituted by a metal M immersed in an electrolyte S and a reference electrode constituted of a metal M$_R$ immersed in an electrolyte S$_R$ (with ceramic junction plate) (b) electrochemical cell representation.

mum in both or in only one of the solutions, the potential difference is negligible.

4. Theoretical Approaches

Several electrochemical tests were performed to validate the developed Cu/CuSO$_4$-Pt reference electrode. We tried to understand the obtained results using a theoretical approach [8].

Based on electrochemical fundamental concepts, the potential difference between a working electrode and a Cu/CuSO$_4$-ceramic reference electrode and the potential difference between a working electrode to Cu/CuSO$_4$-Pt reference electrode were obtained and compared with each other.

Consider **M/S** (metal **M** immersed in electrolyte **S**) electrode and a reference electrode made of a of metal **M$_R$** immersed in an electrolyte **S$_R$** (for example, for Cu/CuSO$_4$ reference electrode, **M$_R$** represents Cu and **S$_R$** represents CuSO$_4$). In the case of Cu/CuSO$_4$-ceramic, there is a ceramic junction plate between **S** and **S$_R$**. Fig. 8a illustrates the described electrochemical cell and Fig. 8b shows the codification. In all the electrochemical cells, the final electrical connection is always done by a copper wire.

Equation 1 shows the potential difference $V_{ceramic}$ measured at the extreme of the electrochemical cell shown in Fig. 8.

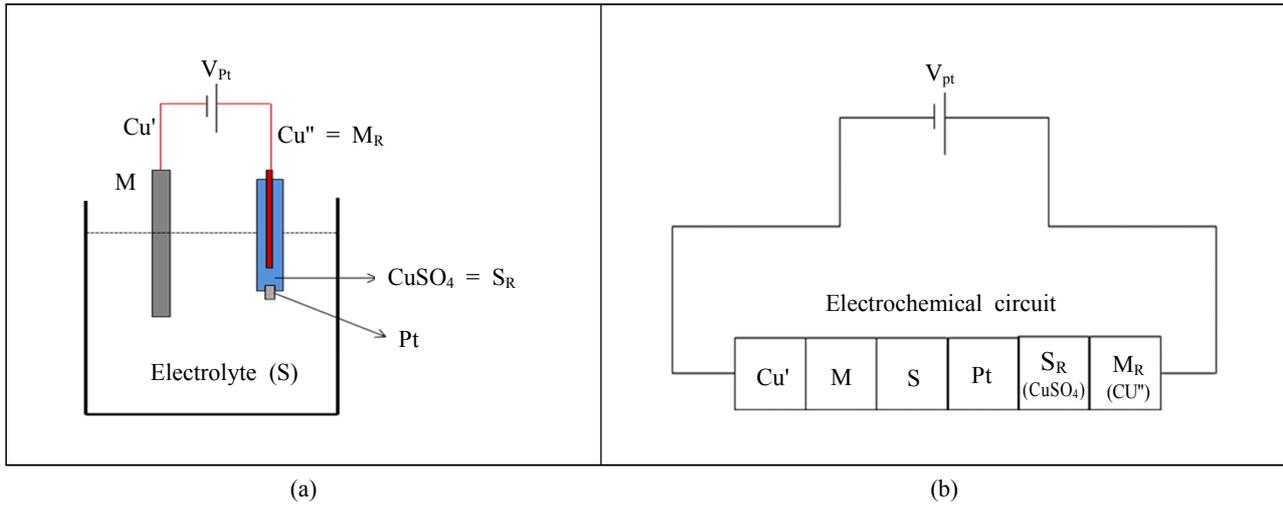(a)   (b)

Fig. 9 (a) electrochemical cell constituted of a metal M immersed in an electrolyte S and a reference electrode constituted of a metal M_R immersed in an electrolyte S_R (with metallic junction) (b) electrochemical cell representation.

$$V_{ceramic} = \Delta_{Cu}^{Cu'}\varnothing = \Delta_{M}^{Cu'}\varnothing + \Delta_{S}^{M}\varnothing + \Delta_{S_R}^{S}\varnothing + \Delta_{Cu''}^{S_R}\varnothing \quad (1)$$

For the $Cu/CuSO_4$-ceramic reference electrode, $\Delta_{S_R}^{S}\varnothing$ is the potential difference between the electrolyte **S** and electrolyte S_R of the reference electrode. The potential drop across S/S_R interface is known as junction potential and is negligible as stated before.

Fig. 9 shows the electrochemical cell and the electrochemical circuit for $Cu/CuSO_4$-Pt immersed in electrolyte **S** and Equation 2 shows potential difference V_{Pt} measured at the extreme of the electrochemical cell:

$$V_{Pt} = \Delta_{Cu}^{Cu'}\varnothing = \Delta_{M}^{Cu'}\varnothing + \Delta_{S}^{M}\varnothing + \Delta_{Pt}^{S}\varnothing + \Delta_{S_R}^{Pt}\varnothing + \Delta_{Cu'}^{S_R}\varnothing \quad (2)$$

The sum $\Delta_{M}^{Cu'}\varnothing + \Delta_{S}^{M}\varnothing + \Delta_{Cu''}^{S_R}\varnothing$ appears in both equation 1 and equation 2 and is named Y. So, equation 1 and equation 2 can be rewritten as a function of Y:

$$V_{ceramic} = Y + \Delta_{S_R}^{S}\varnothing \quad (3)$$

$$V_{Pt} = Y + \Delta_{Pt}^{S}\varnothing + \Delta_{S_R}^{Pt}\varnothing \quad (4)$$

Where:

$$Y = \Delta_{M}^{Cu'}\varnothing + \Delta_{S}^{M}\varnothing + \Delta_{Cu''}^{S_R}\varnothing$$

As stated before, $\Delta_{S_R}^{S}\varnothing$ is negligible [8], thus $V_{ceramic}$ or $\Delta_{Cu}^{Cu'}\varnothing$ is very close to Y.

From the described experimental results, we verified that measurements obtained with $Cu/CuSO_4$-Pt are very similar to those obtained with $Cu/CuSO_4$-ceramic, since a current flow through the platinum wire is maintained negligible. Thus, V_{Pt} or $\Delta_{Cu_R}^{Cu'}\varnothing$ is very close to Y and consequently $V_{ceramic}$ is very close to V_{Pt}.

It is worth mentioning that, for $Cu/CuSO_4$-ceramic, an ionic conduction through the ceramic bridge occurs in order to maintain the electric continuity in the electrochemical cell shown in Fig. 8. For $Cu/CuSO_4$-Pt, the electric continuity is provided both by electronic conduction through the platinum wire and by the charge transfer reactions through S/Pt and Pt/S_R interfaces. The electronic IR-drop through the platinum wire is negligible because of the high conductivity of platinum. The anodic and cathodic overvoltage values of the mentioned interfaces are low because the exchange current density of the reactions $2H^+ + 2e^- \rightarrow H_2$ and $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ are high. Thus, is advisable not to use metal wires made of a metal that presents high exchange anodic and cathodic current densities for the mentioned reactions.

5. Conclusions

A permanent $Cu/CuSO_4$ reference electrode was developed by replacing the ceramic junction plate of a traditional reference electrode for a platinum wire with low dimension. We verified that the experimental errors associated with the measurements conducted with developed

reference electrode are negligible, since the platinum surface area exposed to the working electrolyte and/or to the reference electrolyte are maintained as small as possible.

Acknowledgements

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