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LIFETIME CONSIDERATIONS FOR LEAD-FREE OXYGEN GALVANIC SENSORS

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Abstract. *In this paper we perform an electrochemical characterization of noble metals like copper, bismuth and antimony which were selected from thermodynamic considerations to replace the lead anode in future lead-free galvanic oxygen sensors. The aim of this study was to estimate by Coulombic calculations the amount of metal and optimum metal-electrolyte system, which may assure a five-year lifetime of the sensor, in the ideal case, when the anode consumption is the only failure mode limiting the sensor life. This study has shown that under ideal conditions, when no other failure modes are present, antimony has very attractive electrochemical properties, which may assure a minimum anode mass of about* 6.5 *grams for a five-year lifetime of the galvanic sensor. Failure modes, like anode passivation and self-corrosion, which are also predictable from the thermodynamics of the reactions between metals and aqueous solution, are briefly described here. Thus, a more realistic picture of the complex electrochemical processes to be considered for the design of the lead-free oxygen galvanic sensors is shown here.*

Keywords: oxygen, galvanic sensors, passivation, self-corrosion, lead-free, noble metal, antimony, copper, bismuth

1. Introduction

Electrochemical sensors for toxic gas and oxygen detection are extensively used by industry for process control, personal safety and ambient monitoring [1]. Due to their powerless, low cost and reliable operation, the lead-based electrochemical galvanic sensors for environmental oxygen measurement at room temperature represent the most important technical solution in fixed and portable instruments. However, considering the lead carcinogenic character and toxic effects on the environment, the European Directive on “Restrictions of Hazardous Substances” (EU-ROSH) followed by the 2011/65/EU Directive of EU Parliament Directive have requested that lead be eliminated from the design of gas monitoring instruments by 2024 [2].

Today, the manufacturers of oxygen galvanic sensors are making huge efforts to replace the lead anode, which is consumed by electrochemical oxidation during

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sensor operation by another metal, which should meet the toxicology and technical requirements [3-5]. Starting from theory of chemical reactions of metals with aqueous solutions, under equilibrium conditions [6], recently, we have described our methodology for lead replacement in O_2 electrochemical galvanic sensors by non-toxic, relatively noble metals, like copper, bismuth and antimony [7, 8]. Briefly, our approach for lead anode replacement consisted of using the theoretical Pourbaix equilibrium diagrams of those three noble elements in aqueous solutions as a function of the pH and electrochemical potential conditions and trying to correlate them with the sensor functional requirement, as much as possible. From these diagrams, we have identified the immunity, corrosion or passivation regions as a function of the pH-potential conditions at equilibrium, for each metal. The thermodynamic approach has started from the existence of a varying overlap between the stability regions of the more noble metals and the stability regions of water, under certain pH-potential conditions, which is increasing for more noble metals. This approach is similar to that used in building a thermodynamic nobility scale, where a metal with a higher area of the overlapping region is ranked higher on this scale [9]. According to this scale, all our three metals selected are noble under certain pH-potential conditions, while this nobility decreases from copper, to bismuth then antimony. It is worth mentioning that according to this nobility criterion, the lead, forming the anode of the present state of the art O_2 galvanic sensors, is also a noble metal under operating alkaline pH conditions. Considering the fact that lead-based O_2 galvanic sensors are the best on the market, this could be a guarantee that our methodology is on the right path.

It is the purpose of this paper to present early-stage theoretical considerations of device lifetime for the O_2 galvanic sensors containing the anode made of either copper, or bismuth or antimony, in order to perform the final metal selection. In the next section, we shall briefly describe the operational principles of electrochemical galvanic sensors [10], which will allow us to define the terms which will be used in this paper. Then, a theoretical prediction of the lifetime of different, lead-free oxygen galvanic sensors, under ideal operation conditions in either acidic or basic electrolytes will be shown. The electrochemical processes which are decreasing the lifetime of the sensor in the field will be also presented, so that a good leverage between the ideal, theoretical lifetime and realistic lifetime of the lead-free O_2 galvanic to be envisioned.

2. Operational principles of O_2 galvanic sensors

The O_2 galvanic sensor is a passive amperometric sensor, where the electric current flowing through a load resistor is proportional to the oxygen partial pressure from the ambient to be monitored. As these sensors do not need a power supply for their operation, but, instead convert the chemical energy into electrical energy, they operate on the fuel cell (or metal/air battery) principle.

A simplified schematic of a galvanic sensor is presented in Fig. 1. This shows the core components namely, capillary through which oxygen diffuses to the cathode electrode, where oxygen reduction reaction (ORR) takes place, the anode electrode, where metal oxidation occurs, an electrolyte through which ions can travel in order to generate an ionic current which is equal to the electronic current flowing through the load resistor. In order to obtain a good sensor, which is able to indicate accurately and as fast as possible, the O_2 partial pressure from outside ambient, the reaction rate of the two interconnected redox reactions from above should be much faster than the diffusion rate of oxygen from air through the capillary.

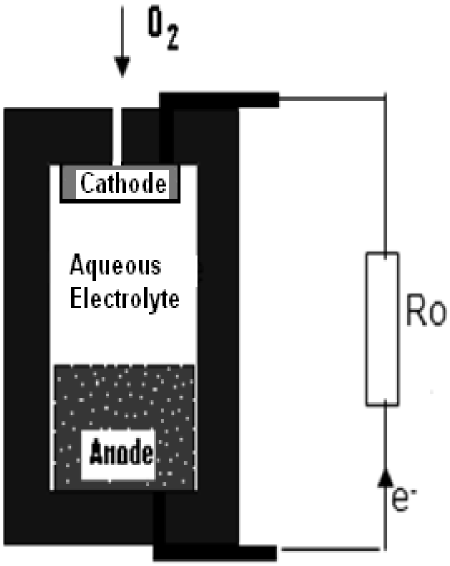

Fig. 1. Schematic picture of a two-electrode galvanic sensor.

Thus, a diffusion limited regime should be obtained for an O_2 sensor, over a large temperature range. The set of redox reactions for the lead based O_2 galvanic sensor are presented below:

Cathode: Oxygen reduction reaction: E^o_c =0.401 V vs SHE

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

Anode: Lead oxidation reaction: E^o_a = – 0.580 V vs HSE

$$2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^- \quad (2)$$

Overall cell reaction:

$$2Pb + O_2 \rightarrow 2PbO \quad (3)$$

The above equations show that by consumption of two lead atoms during anode oxidation, one gets a redox system generating four electrons at the anode electrode, which then travel through the external load resistance to the cathode electrode where they are consumed with the generation of four hydroxyl ions, forming the ionic current through the electrolyte.

From the equilibrium half-cell voltages of the cathode (E^o_c = 0.401 V) and anode electrodes (E^o_a = – 0.580 V vs SHE) with respect to standard hydrogen electrode (SHE), in the same electrolyte, one can get the equilibrium cell voltage (E^o_{oc}), as shown below:

$$E^{o}_{oc} = E^{o}_{c} - E^{o}_{a} = 0.981 \text{ V} > 0. \tag{4}$$

This positive value determines a negative value for free-Gibbs energy of the redox cell, as follows:

$$\Delta G = -n {*} F {*} E^{o}_{oc} < 0, \tag{5}$$

where n is the number of electrons resulting from the electrode redox processes, F is the Faraday constant (96485 Coulombs per mole of electrons). This is a very simple theoretical demonstration, that the electrochemical cell with consumable lead anode has a metal/air battery-like, galvanic operation. Closing the electrochemical circuit between anode and cathode electrodes by means of a load resistor, which is about 50-100 **Ω**, and exposing the sensor to the air, an electronic current flows through the load resistor, which can be measured by the voltage developed across it. The expression of the electronic current under these limiting conditions is given below [10]:

$$i_{\mathrm{lim}} = 2.05 {*} 105 {*} D_{\mathrm{O2}} {*} T^{½} {*} n {*} d^{2} {*} p_{\mathrm{O2}}/\mathrm{L} \tag{6}$$

Where D_{O2} is the diffusion coefficient of oxygen, T is the absolute temperature, p_{O2} is the ambient oxygen partial pressure and d and L are the diameter and the length of the capillary, respectively. This current can be rather easily calculated if one considers the sensor operation in the diffusion-limited regime, which means that the oxygen concentration at the cathode electrode tends to zero (i.e. the oxygen reduction reaction rate is much faster than the oxygen diffusion rate through the capillary). To reach such a limiting regime, and to create a high redox reactivity reserve, even at low negative temperatures, the dimensions of the capillary are designed accordingly, i.e., smaller diameters and longer lengths.

3. Theoretical prediction of lifetime of different lead-free oxygen galvanic sensors

In practice, the lifetime of oxygen galvanic sensors is determined by a large variety of failure modes, which will not be extensively treated here. At this stage, we assume an ideal behavior of the galvanic sensor, which means that the sensor lifetime is determined only by the total coulombic consumption of anode material and type of electrolyte used. In other words, the maximum lifetime of galvanic sensors can be calculated from the maximum electrical charge flowing through the load resistor, at a certain limiting value of the electric current, in our case let us say 100 µA. In the galvanic sensor design, it is important to theoretically predict how much mass of consumable anode is necessary for getting a desired lifetime, during which a constant electric current will flow through the load resistor. Such coulombic calculations, based on Faraday's Laws of Electrolysis, will be shown below, and they can be used for the evaluation of the charge capacity of different noble metals, as well as the theoretical prediction of the anode mass necessary to assure the operation of the sensor for a number of years, at a constant current value of 100 μA. Finally, such calculations may help to select the best noble metal candidate material to replace lead in the next generation of oxygen galvanic sensors. Below, we show the formulae for electrochemical characterization of the noble metal candidates in terms of charge capacity (equation (7)) and the anode mass to be fully consumed for reaching a certain target lifetime (equation (8)), as follows:

$$\textit{Capacity}\ \text{(Ampere}*\text{hour/gram)} = n*F/(A_w*3600) \qquad (7)$$

$$\textit{Anode mass}\ \text{(gram)} = (31.536*A_w*i*t)/(n*F) \qquad (8)$$

where "*i*" is the sensor current in microamperes (100 μA), "*t*" is the time in years, "*n*" is the number of electrons released per atom of metal in the redox process of a given metal-electrolyte system, "A_w" is the molar mass of the metal (grams/mole), *F* is the Faraday constant. The constant from formula (8) of 31.536 comes from expressing the time in years, and current in microamperes. For the determination of "*n*", both the reduction reaction at the cathode and oxidation reaction at the anode should be known, as well as the overall cell reaction corresponding to the summation of the reactions at the two electrodes, all of them taking place in the same electrolyte. The value of 'n' equates to the valency (or oxidation state) change of the metal in undergoing the oxidative change to the final product in the discharged anode. In the case of the three candidate metals Cu, Bi and Sb, the electrochemical reactions at each electrode are as follows:

Electrochemical reactions for copper;

a) Alkaline electrolyte

Cathode reaction (reduction): $O_2 + 2H_2O + 4e^- = 4OH^-$ (9)

Anode reaction (oxidation): $4Cu + 2H_2O = 2Cu_2O + 4H^+ + 4e$ (10)

(*Electrolyte reaction:* $4OH^- + 4H^- = 2H_2O$) (11)

Overall cell reaction: $4Cu + O_2 = 2Cu_2O$ (12)

b) Acid electrolyte

Cathode: $O_2 + 4H^+ + 4e^- = 2H_2O$ (13)

Anode: $2Cu = 2Cu^{++} + 4e^-$ (14)

Cell reaction: $2Cu + O_2 + 4H^+ = 2Cu^{++} + 2H_2O$ (15)

The above electrochemical reduction reactions are specific to the pH of electrolyte used, and they are generally accepted by the scientific community. The above electrochemical oxidation reaction of copper in alkaline electrolyte is thermodynamically favorable in both weak acid, neutral and alkaline electrolyte (up to pH of about 14), according to the Pourbaix equilibrium diagram for this metal [11]. However, in order to minimize the passivation risk of copper oxidation in acid electrolytes, we have considered very strong acid electrolytes, (pH<2.5), where the above oxidation reaction is thermodynamically favourable, according to the same Cu Pourbaix diagram [11]. After doing the coulombic calculations for copper anodes in both acid and alkali electrolytes, one option may be to consider the copper-acid system, as the amount of copper in acid electrolyte would be reduced by half with respect to amount of copper to be used in alkali electrolytes. Also, according to thermodynamic theory, the risk of passivation of copper in strong acid electrolyte would be much reduced. However, as shown below, there are some drawbacks for the copper-acid system. The Cu cell reactions from above teach us that in the alkaline electrolyte there is no water consumption or generation due to the overall cell redox process, while, in the case of acid electrolyte, there is water generation, and, even more importantly, a depletion of protons (ion of hydrogen atom, H+), as two protons are irreversibly consumed from the electrolyte for the oxidation of each copper atom. Such a proton depletion will gradually increase the pH of the electrolyte. Based on this observation one can calculate the amount of protons to be consumed for the oxidation of the entire copper anode, and this is given below:

$$\text{H-ion } \textit{weight} \text{ (gram)} = 1 * 31.536 * i * t / F \qquad (16)$$

Considering the dissociation capability of the acid electrolyte to be used, one can calculate the amount of electrolyte needed to generate this amount of protons. Actually, as we need to assure that the pH of the acid electrolyte will not increase too much due to proton depletion, the total volume of acid electrolyte should be even higher so as to compensate for this effect. Such calculations have shown that one cannot obtain a stable sensor without significantly increasing the electrolyte volume, which is not a good option for gas sensors incorporated in portable gas detectors. For copper, in alkaline electrolyte, only the $1e^-$ anode process is considered with Cu/Cu^+ electrode potential of 0.47 V versus NHE, because the Cu^+/Cu^{++} electrode potential (about 0.67 V with respect to NHE, in the same electrolyte) may be too anodic to support a well-defined cathode limiting current. As shown in Table 1, the amount of copper fully consumed for a five-year operation in aqueous solution of KOH is equal to 10.5 grams.

Electrochemical reactions for bismuth;

a) Alkaline electrolyte

Cathode: $3O_2 + 6H_2O + 12e^- = 12OH^-$ (17)

Anode: $4Bi + 6\,H_2O = 2Bi_2O_3 + 12H^+ + 12e^-$ (18)

Cell reaction: $4Bi + 3O_2 = 2Bi_2O_3$ (19)

b) Acid electrolyte

Cathode: $3O_2 + 12H^+ + 12e^- = 6H_2O$ (20)

Anode: $4Bi = 4\ Bi^{+++} + 12e^-$ (21)

Cell reaction: $4Bi + 3O_2 + 12H^+ = 4Bi^{+++} + 6H_2O$ (22)

The case of Bismuth is similar to that of copper. This can be understood by analyzing the Pourbaix equilibrium diagrams of bismuth in aqueous solutions, and the equilibrium reactions considered by Pourbaix for his Bi equilibrium diagrams [12].

In this case, we reach similar conclusions on the invariance of the electrolyte with respect to redox reactions at the two electrodes in alkaline electrolyte, while the hydrogen ion depletion and water generation are noted again in acid electrolytes.

The amount of bismuth for five-year operation sensor in KOH electrolyte is 11.45 grams, similar to the amount of Bi in acid electrolyte, and close to those for Cu in either acid or alkaline electrolyte.

Electrochemical reactions for antimony;

a) Alkaline electrolyte

Cathode: $6O_2 + 6H_2O + 12e^- = 12OH^-$ (23)

Anode: $4Sb + 6\ H_2O = 2\ Sb_2O_3 + 12\ H^+ + 12e^-$ (24)

Cell reaction: $4Sb + 6O_2 = 2Sb_2O_3$ (25)

b) Acid electrolyte :

Cathode: $3O_2 + 12\ H^+ + 12e^- = 6H_2O$ (26)

Anode*:* $4Sb + 6H_2O = 2Sb_2O_3 + 12H^+ + 12e^-$ (27)

Cell Reaction: $4Sb + 3O_2 = 2Sb_2O_3$ (28)

The reduction reactions from above are similar to those described for copper and bismuth, but in this case, in a very large pH domain from pH > 0 and pH < 14, the most favorable reaction from thermodynamic point of view is the one written above, as suggested by Pourbaix equilibrium diagrams of antimony [13]. This is a big difference with respect to the case of copper and bismuth based electrochemical cells.

Advantageously, oxidation of a single Sb atom in both acid and alkaline electrolytes generates 3 electrons. Also, the antimony electrochemical reactions are invariant to either proton or water depletion due to the redox processes in acid and alkaline electrolyte. The amount of antimony required for five-year operation in KOH electrolyte is 6.5 grams, which is about half the mass needed for Cu or Bi.

Table 1. Coulombic calculations of the anode mass for five-year lifetime of O_2 galvanic sensor

Anode type	Sb	Bi	Cu	Pb
Anode *mass* (in grams) needed for five-year operation in alkaline electrolyte	6.5	11.45	10.5	16.9

Therefore, such coulombic calculations further emphasize the importance of the electrolyte selection in meeting the lifetime and a targeted size of the sensor. As mentioned above, these results have finally oriented our research towards relatively noble metals and alkaline electrolytes.

In Table 1, we summarize the coulombic calculations of the anode mass needed for a five-year lifetime, O_2 galvanic sensor, operating in alkali electrolyte, under the ideal condition that the anode material is fully utilized. This Table shows that 16.9 grams of Pb (reference calculation), 11.45 grams of Bi, 10.5 grams of copper, or 6.5 grams of antimony are needed for five-year life at a sensor current of 100 μA.

Such differences in the masses of different consumable anodes for a five-year operation come from the different charge capacity of different metals, whose formula depends on the molar mass of each metal (A_w) and the number of electrons (n) provided by the oxidation of each metal atom in the redox process in either acid or alkali electrolyte. Therefore, on the basis of these idealized assumptions (absence of anode passivation, self-corrosion, water evaporation from the electrolyte, etc.) antimony in alkaline electrolyte seems to be the best coulombic option among the noble metals, with anode immunity line situated above the hydrogen line in the Pourbaix equilibrium diagrams [13].

4. Electrochemical processes decreasing the lifetime of O_2 galvanic sensors during "field" operation

The most important electrochemical processes decreasing the lifetime of the sensor occur at the anode and they consist of anode self-corrosion and passivation, depending on the pH-potential conditions of the electrochemical cell. Both processes can be predicted by the thermodynamic theory after considering the multitude of chemical reactions between metals and aqueous solutions under different potentials and pH conditions.

4.1. Anode self-corrosion

The thermodynamics of the reactions between metals and aqueous solutions provides an indication of metal self-corrosion in the electrolyte, for certain potential-pH conditions. Such an unwanted regime of parasitic self-corrosion of the metals in the aqueous solutions is followed by hydrogen generation and can be explained by the fact that there is no overlap between the stability region of metal and the stability region of the aqueous solution in the pH-potential domain of their Pourbaix diagrams. Self-corrosion of the metal anode in galvanic sensors is a redox process followed by hydrogen generation.

Depending on the region where the hydrogen evolution occurs, there are two cases of anode self-corrosion. In one case, both reduction and oxidation reaction happen on the surface of the anode, where, obviously, hydrogen evolution takes place, too.

In another case, the oxidation takes place at the anode surface, while the reduction reaction of the hydrogen ion (proton) takes place at the cell cathode, and thus hydrogen molecules are generated at the cathode surface. In the first case, both anodic and cathodic sites are located on the surface of the anode. In such a case the electrons will circulate inside the bulk of metal anode, and no current passes in the external circuit.

This type of self-corrosion with local anodic and cathodic sites on the same surface has two deleterious effects: firstly, it generates hydrogen molecules which may increase the internal pressure and contribute to electrolyte leakage; and secondly, reduced lifetime of the sensor due to consumption of the anode results. In the case of a relatively noble metal at the anode, this is a relatively small effect when compared with self-corrosion where hydrogen generation takes place at the cathode (as described below).

As mentioned above, in the second case of self-corrosion with anodic sites at the anode and the cathodic sites located at the cathode the electrons generated by the oxidation reaction are moving through the load resistor, and these “parasitic” electrons will be measured and incorrectly interpreted by the user as a response to ambient oxygen.

For a load resistor of 100 Ω and a sensor current of 100 μA, the voltage drop on the load resistor is about 10 mV, and therefore the sensor is virtually operating in the short circuit condition. Hence, considering the low hydrogen overvoltage of a platinum cathode, such a short-circuited cathode can evolve hydrogen.

In contrast, in a battery, the load resistor is of high value, and the current flowing through that resistor will self-bias the cathode away from the anode potential and therefore this parasitic self-corrosion with hydrogen generation at the cathode can be eliminated.

As mentioned above, this type of self-corrosion can be detected by measuring the baseline current of the sensor, i.e., the sensor current in 100% N_2. Under such conditions there should be no current due to oxygen entering the sensor, and therefore the output current is directly linked to the anode self-corrosion with hydrogen generation at the cathode.

This type of self-corrosion with hydrogen generation at the cathode will have three negative effects on the sensor operation in air; (1) it will create hydrogen at the cathode; (2) it will parasitically consume the anode mass, decreasing its lifetime, and (3) it will reduce the sensor accuracy, supra-estimating the ambient oxygen concentration.

The self-corrosion of the anode accompanied by hydrogen evolution is specific to metals which have no overlap region between the metal stability and water stability domains.

Even more noble metals like antimony can undergo self-corrosion if the cell is operating in domains of high pH, elevated temperature and certain electrochemical potentials, as can be seen in the Pourbaix diagrams from [13]. More details of the electrochemical behavior of antimony in aqueous solutions are given below.

4.2. Anode Passivation

Pourbaix equilibrium diagrams of the three noble candidate materials suggest a high passivation risk (leading to early failure before full anode consumption) for the case of copper and bismuth anodes in alkaline electrolytes, due to the formation of Cu_2O or Bi_2O_3 layers, which can stop further oxidation. Experimental kinetic studies described in the literature for three electrode electrochemical cells have confirmed such behaviour.

For example, it is shown that passivating Cu_2O, $Cu(OH)_2$ and CuO oxide layers can be formed on the surface of copper anodes depending on the concentration of the KOH electrolyte used [14]. In the case of antimony in alkaline electrolyte, passivation is also predicted due to the formation of Sb_2O_3.

This theoretical result was confirmed by XPS spectroscopy of Sb anodes, discharged in 100% O_2 which has revealed the presence of both Sb_2O_3 and Sb_2O_5 oxides in the passivation layers, with a higher fraction of Sb_2O_3.

However, for $pH > 14$, the upper immunity line of antimony is close to the hydrogen line, which means that the stable region of antimony has a small overlap with the stability domain of water.

Actually, the equilibrium diagram of antimony indicates that at $pH = 14$ and higher, soluble SbO_2^- antimonate ions can form. Whilst this may reduce passivation, parasitic corrosion leading to hydrogen evolution might occur.

The above electrochemical phenomena represent a good proof of the complexity of the processes which should be considered when replacing the lead anode with other metals in order to obtain a new generation of lead free oxygen sensors.

5. Conclusions

A thermodynamic methodology was used for the selection of the noble metal to be used as lead free anodes in galvanic sensors for oxygen monitoring by fixed and portable instruments. In a first stage, as a result of this methodology, copper, bismuth and antimony were chosen as potential consumable anode candidates for O2 galvanic sensors.

The electrochemical properties of the three noble metals in both acid and alkaline were evaluated by coulombic calculations, and the amount of consumable metal needed to reach a five-year lifetime was estimated considering an ideal sensor operation, where there is no other failure mode, other than anode consumption, acting during all this time.

Such a comparison has shown that a smaller mass of anode, of about 6.5 grams is required in the case of an antimony anode, with respect to bismuth or copper, but the “field” solution should also consider other electrochemical processes, such as self-corrosion and passivation of anode, which may result in earlier failure than predicted by the purely coulombic calculations.

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