LEAD-FREE GALVANIC OXYGEN SENSORS-
A CONCEPTUAL APPROACH

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Abstract–*Within this paper we present a thermodynamic methodology for the selection of non-toxic metals which could be used as lead-free consumable anodes in electrochemical galvanic oxygen sensors. Starting from thermodynamic nobility theory, metals like copper, bismuth or antimony are proposed to replace lead in future galvanic* O_2 *sensors. The thermodynamic theory provides voltage windows which increase from copper (0.7 V), to bismuth (0.857 V) and antimony (1.076 V). The experimental voltage windows are smaller than the theoretical ones, but these experimental values increase in the same order from Cu, to Bi and Sb, as predicted by our methodology.*

Keywords: *lead-free* O_2 *galvanic sensors, noble metal anodes, antimony, bismuth, copper*

1. INTRODUCTION

The electrochemical, galvanic sensors based on consumable lead anodes have been extensively used for ambient oxygen detection in low cost, portable instruments for industrial safety applications. These sensors have excellent functional performances in terms of sensitivity, lifetime, response time, and zero-power consumption, the last one being possible due to its battery like operation principle [1]. However, detailed toxicity studies have shown deleterious impact of small concentrations of lead on people health and environment. For this reason, lead will be eliminated from detection instruments from 2024, as per the EU Parliament final decision [2] on the application of the well known "Restriction of Hazardous Substances (ROHS) EU-Directive.

Under these circumstances, in the last decade, there has been a large effort by OEM manufacturers on lead anode replacement in O_2 galvanic sensors. Thus, new materials like zinc, aluminum [3] or tin [4; 5] have been proposed to replace lead anodes, but these concepts for lead-free galvanic O_2 sensors are not yet widely accepted in the market.

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It is the purpose of this paper to give a theoretical and experimental support for using noble metal candidates, like antimony, bismuth or copper as anode electrodes in future lead-free galvanic oxygen sensors [6]. We have selected this family of noble metals by investigating the thermodynamic theory of the electrochemical equilibria of reactions between metals and different aqueous electrolytes, as well as the thermodynamic nobility scale of metals [7], in the whole pH range, as described by reference [8].

2. STATE OF THE ART

The principle of a two-electrode galvanic O_2 sensor is presented in Fig.1, where the sensing electrode (cathode) is made of a polytetrafluoroethylene (PTFE) membrane impregnated with high surface area platinum catalyst embedded in a carbon matrix, and the anode is made of lead wool with large surface area [1]. The two electrodes are immersed in an alkaline electrolyte, which creates an aqueous ion conducting region between the two electrodes. The battery-like (galvanic) sensor operation simply means that the electrochemical potentials from anode and cathode are able to support the redox electrode reactions without the need of an external power supply. Therefore, the electrons generated by metal anode oxidation will flow through the external load resistor to the cathode, where a Pt-catalyzed oxygen reduction reaction takes place (Fig.1). These flowing electrons will become the sensor current, which should be proportional to the external O_2 concentration, for a good device operation. For this reason, the sensor should operate in the diffusion-controlled regime, where the rate of oxygen diffusion through the capillary (Fig.1) should be always lower than the rate of above redox reactions, and thus the O_2 concentration at the sensing electrode should be equal to zero.

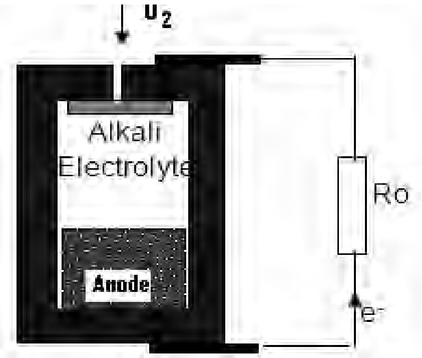

Fig. 1. Schematic view of an O_2 galvanic sensor.

The load resistor has an electrical resistance of maximum 100 Ω and this value will assure the sensor operation almost in the short-circuit regime [1], i.e., with a mV-level potential difference between the two electrodes, when the sensor current is about 100 μA. This low value of resistance is necessary for obtaining a short response time and a low cathode biasing due to this 100 μA current flowing through it, and thus to prevent the decrease of rate of O_2 reduction reaction due to its self-biasing.

The plastic sensor package is provided with a laser-drilled capillary, whose micrometric-size diameter and millimeter-length dimensions are essential for determining the sensor operation in the diffusion-controlled regime, as explained above. For a sensor operating in this regime, there is a cell voltage domain, called experimental voltage window (EVW), for which the sensor current remains constant at constant O_2 concentration, even if, during sensor life the anode electrochemical potential will vary due to passivation products deposited or released from its surface, or due to excessive decrease of anode mass [9]. This voltage window is also known as limiting current region. The excellent stability performance of lead-based O_2 sensors comes from the existence of a large EVW value of about 0.8 V able to cope with electrochemical potential variation during sensor life.

The first tentative steps toward lead-free O_2 galvanic sensors were done by using zinc, aluminum or tin as anode electrode [3-5], but it appears that self-corrosion and passivation of the anode surface may limit the sensor life, and probably these phenomena prevented the penetration of these concepts of lead- free O_2 galvanic sensors on the market.

By analyzing the electrochemical equilibrium reactions of the above metals with the aqueous solutions [7], one can notice that Zn, Al and Sn are all base metals, which do not have a thermodynamic stability region in common with the stability region of aqueous solutions as a function of electrolyte pH and electrochemical potential of that electrode in the chosen electrolyte. Therefore, the thermodynamics predicts that it is impossible to avoid the metal anode self-corrosion with hydrogen evolution, either at anode or at cathode. On the other hand, the Pourbaix diagram of lead for neutral and alkali electrolytes shows a good overlap region between Pb stability domain and water stability domain, which proves the noble metal behavior of lead in that pH range. This is a reason for which we have proposed to study the behavior of noble metals like copper, bismuth and antimony as lead-free alternative anodes for the O_2 sensor.

3. NOBLE METALS: THEORETICAL AND EXPERIMENTAL RESULTS

In order to have a comprehensive view of metals which have a common electrochemical stability region with water and select these potential noble candidates, we have evaluated the thermodynamic nobility scale of metals as defined in [8] and voltage window demands of O_2 sensor. The criterion for nobility ranking is the amount of area overlap between the metal thermodynamic stability region and water stability region, with gold on the top position in nobility. After eliminating the toxic (like cadmium, also already restricted material, as per EU-ROHS Directive) or radioactive metals (like polonium, technetium) from the candidates, we have further narrowed its number by defining and calculating a thermodynamic voltage window (TVW), which was then correlated with the experimental voltage window (EVW), described in the previous section. The TVW value of a candidate metal for O_2 detection is calculated as a potential difference between the oxygen (evolution) electrochemical potential and the electrochemical potential of the metal at its upper border line of immunity region, in the same aqueous electrolyte. For this study we have considered alkaline electrolyte. These TVW theoretical results for Pb, Sb, Bi and Sb are presented in Table I from below.

Table 1. Thermodynamic voltage window calculated for O_2 sensor with anodes made of Cu, Bi, Sb and Pb.

Metal	Cu	Bi	Sb	Pb
TVW (V)	0.7	0.857	1.076	0.98

From Table 1 one can notice that antimony has the highest TVW of 1.076 V, which is close to the TVW value of lead of 0.98V. In order to determine the experimental voltage window value, we have applied an external voltage supply to the fresh galvanic sensors built with different anode candidates and measured the experimental sensor current response at constant O_2 concentration. The response time (T_{90}) as a function of applied bias, was obtained with the gas being switched from air to 100% N_2. Such experiments will mimic the long-term operation of sensor, by identifying the maximum acceptable variation of anode electrode potential, which can be tolerated by the sensor before sensor current starts to go out of its constant value specific to limiting current region, or response time will be longer than the specified value, whichever is the first. Our experience has shown that the response time has been in general the first parameter to fail. Thus, in Figs. 2-4, we present the experimental results of sensor current and T_{90} as a function of applied voltage for O_2 sensor made with Cu, Bi, and Sb anode, respectively, while the aqueous KOH electrolyte was used in all candidate sensors.

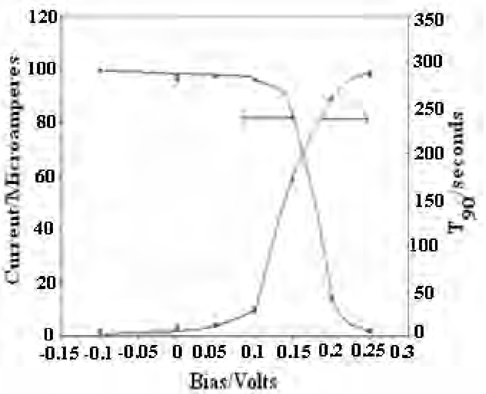

Fig. 2. Experimental dependence of sensor current and response time (T90) for an O_2 sensor with Cu anode and aqueous KOH electrolyte, as a function of externally applied voltage bias.

A weak alkaline electrolyte was used for reference lead-based sensors. These figures show that for increased positive applied voltages beyond the EVW, the sensor current starts to decrease and reaches eventually a zero value, where the open circuit voltage cell can be experimentally extracted.

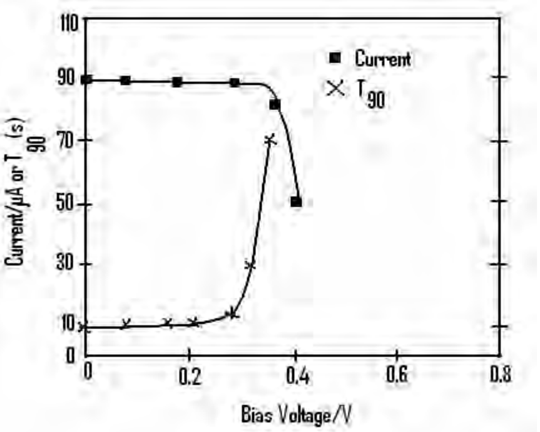

Fig. 3. Experimental dependence of sensor current and response time for an O_2 sensor with Bi anode and aqueous KOH solution, as a function of externally applied voltage bias.

As predicted by thermodynamic theory, at room temperature, the experimental voltage window is increasing from copper (0.15V) to bismuth (0.3V), and then to antimony (0.4V), and, which is lower than the voltage window for lead, which was about 0.8V at room temperature, as can be seen in Fig. 4. These experimental results show that the EVW values are always smaller than the theoretical TVW values. The difference between the theoretical and experimental values could be explained by a number of electrochemical processes like Pt-catalyzed O_2 reduction, anode polarization due to surface passivation, and anode consumption during sensor operation, all these occurring in non-equilibrium conditions, and not considered by the thermodynamic theory. The experimental results from Fig. 4 show that at room temperature, for voltages below a certain small positive value, the sensor current starts to increase, and this is an indication of parasitic anode self-corrosion reaction which is accompanied by hydrogen evolution at cathode, where proton reduction reaction takes place. Further experiments performed at negative temperatures with a Sb-based sensor biased at negative voltages have shown that the EVW shifted to the negative voltage domain, not shown here. Such early stage results indicate that our thermodynamic methodology is a useful tool for selecting the lead-free anodes.

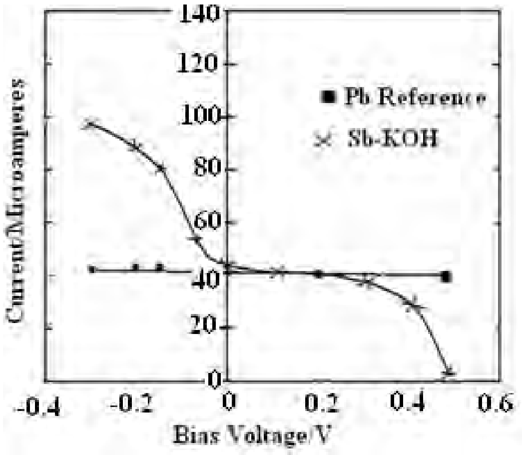

Fig. 4. Experimental dependence of sensor current for Sb-KOH sensor in comparison with Pb reference sensor, as a function of externally applied voltage bias, at room temperature

The above experimental results confirm that among our candidates, in alkali electrolytes, the nobility increases gradually from antimony to bismuth and reaches the highest value for copper anodes. Moreover, as predicted by theory, a weak self-corrosion was experimentally evinced for antimony anodes in highly concentrated KOH aqueous solutions.

4. CONCLUSIONS

This paper has proposed a theoretical methodology based on the study of electrochemical equilibria of the reactions between metal and aqueous solution for the selection of the lead-free metals to be used as consumable anode electrode in fuel cell-like oxygen electrochemical sensors. It is thus proved that noble metals like copper, bismuth and antimony can be strong anode candidates for the next generation of O_2 galvanic sensors. Thermodynamic voltage window concept is introduced for further discrimination between different noble metals in order to find the metal which may mimic the excellent behavior of existing lead anodes, which have also noble character in the pH domain where they are used for O_2 sensor operation, today.

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