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OXYGEN SENSING: A REVIEW
PART 1: MATERIALS AND METHODS FOR OPTICAL AND GALVANIC LEAD-FREE OXYGEN DETECTION

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Abstract. *This paper reviews two of the most important optical and electrochemical principles for oxygen detection. In the first part it outlines materials and methods for the fluorescence quenching – based oxygen detection (types of fluorophores, strategies for covalent or noncovalent immobilization of fluorophores into the polymeric matrix), while the second part deals with galvanic oxygen sensor and alternatives to replace lead, which is the most used metal as anode in this type of sensors.*

Keywords: Oxygen sensing, Fluorescence Quenching, Polymer Matrix, Galvanic Sensor, Lead-free

1. Introduction

Oxygen is the most abundant element in the Earth's crust and represents one-fifth of the Earth‘s atmosphere. Measuring the oxygen concentration is important in various fields, such as: industrial processes monitoring, automotive, medicine (i.e., anesthesia monitors), food packaging, environmental and marine monitoring [1]. Among the traditional oxygen sensing principles, one can enumerate: electrochemical, chemical (Winkler titration), optical, metal oxide semiconductor sensors, etc. [2, 3].

A lot of working principles - such as reflectometry, fluorescence quenching, infrared and Raman spectroscopy, interferometry, luminescence - have been used in manufacturing oxygen sensors. However, the majority of the optical sensors developed for the oxygen detection in the last years are based on the fluorescence quenching of organic or inorganic fluorophores induced by molecular oxygen.

Among the electrochemical devices for oxygen sensing, galvanic sensors are widely used due to reliability, stability and ease of manufacture. This paper presents a brief review of the materials and methods used in detection of oxygen using fluorescence quenching and lead-free galvanic sensors.

2. Fluorescence–quenching based oxygen sensing

When exposed to light at an appropriate wavelength, the fluorophores (F) absorb energy and are promoted from their ground state energy level (S_0) into an excited state energy level (S_1).

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Fluorescent based oxygen sensing devices work on the principle that relaxation of the S_1 state can also occur through interaction with another molecule, which is determining the fluorescence quenching. Oxygen molecules are an efficient quencher of fluorescence due to its atypical triplet ground state:

Fluorescence: $F^* \rightarrow F + h\upsilon$ (fluorophore emits radiation at longer wavelengths).

Fluorescence quenching: $F^* + O_2 \rightarrow F + O_2^*$ (degree of quenching is proportional with oxygen concentration), where "*" denotes an excited state of the fluorophores.

Recently, a lot of organic and inorganic fluorescent molecules were synthesized and used as key components for the manufacturing of fluorescence quenching-based oxygen sensors [1, 2]. The best choices are fluorophores with strong fluorescence, high quantum yield and long life time.

The most used fluorophores for O_2 sensing are: pyrene and its derivatives (1-pyrene-acetic acid, 1- pyrene-butyric acid, 1- pyrene decanoic acid, 1-pyrene- dodecanoic acid, 1-pyrenil methanol, 1–pyrenil butanol, silicon-based pyrene derivatives [4-6], decacyclene and its derivatives (mono-terbutyl decacyclene, penta-tertbutyl-decacyclene, hexa-terbutyl-decacyclene) [7] quinoline, phenantrene, erythrosine B, fluoranthrene, aluminum 2, 9, 16, 23, tetraphenoxy-29H, 31H phthalocyanine-hydroxide, metal complex organic dyes [dichloro (tris-1,10–phenantroline, platinum octaethylporphyrin, tris (2,2'-bipyridine) ruthenium (II), palladium octaethyl-porphyrin, tris (4, 7- diphenyl-1, 10 phenanthroline) ruthenium II [8 - 12].

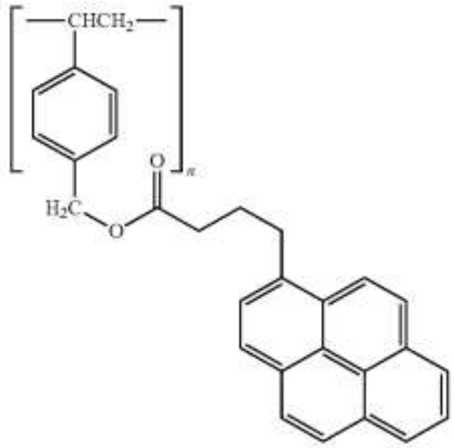


Fig. 1. Immobilization of 1-pyrene butyric acid through covalent bonding into on functionalized polystyrene backbone.

The polymer matrices for supporting fluorescent molecules should have high oxygen permeability, high compatibility with fluorophore, good adhesion to glass or plastic fiber, simple and cheap synthesis, etc.

The most used polymers are: polystyrene and its derivatives, cellulose acetate butyrate, poly(methylmetacrylate), dimethylsiloxane, diphenylsiloxane, dimethyl-diphenylsiloxane copolymer, polyethyleneglycol hydrogel, polyvinyl chloride, etc. [10].

The major drawback in achieving the dispersion of the fluorophore in the polymer matrix is the crystallization - as a direct consequence of its poor solubility. In order to overcome aggregation and crystallization, the fluorescent molecule can be immobilized in the polymeric backbone through covalent bonding (**Fig. 1-6**).

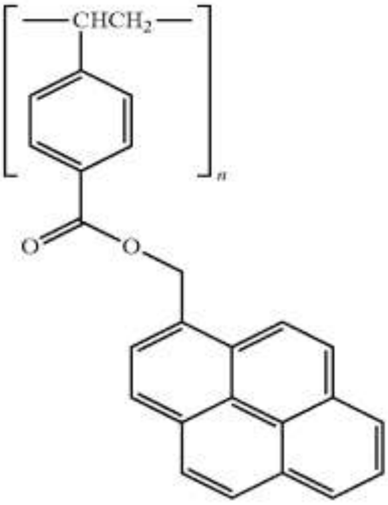


Fig. 2. Immobilization of 1-pyrenyl methanol through covalent bonding into on functionalized polystyrene backbone.

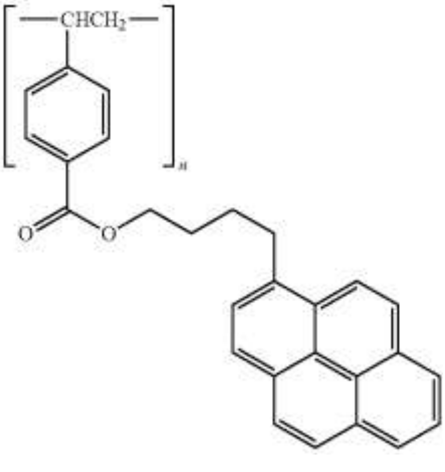


Fig. 3. Immobilization of 1-pyrenyl butanol through covalent bonding into on functionalized polystyrene backbone.

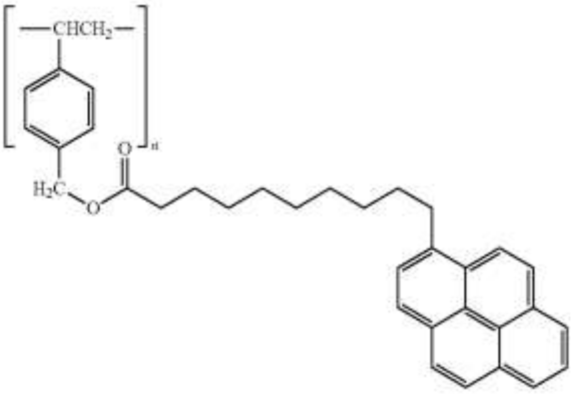


Fig. 4. Immobilization of 1-pyrene decanoic acid through covalent bonding on functionalized polystyrene backbone.

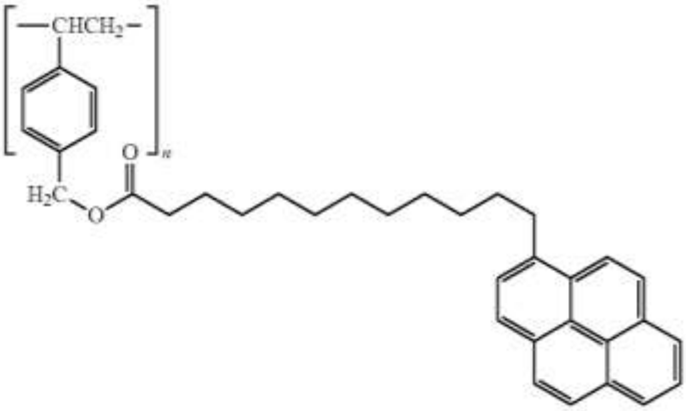


Fig. 5. Immobilization of 1-pyrene dodecanoic acid through covalent bonding on functionalized polystyrene backbone.

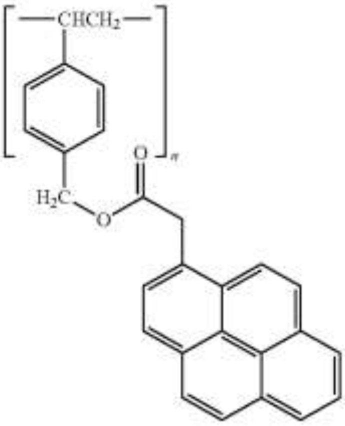
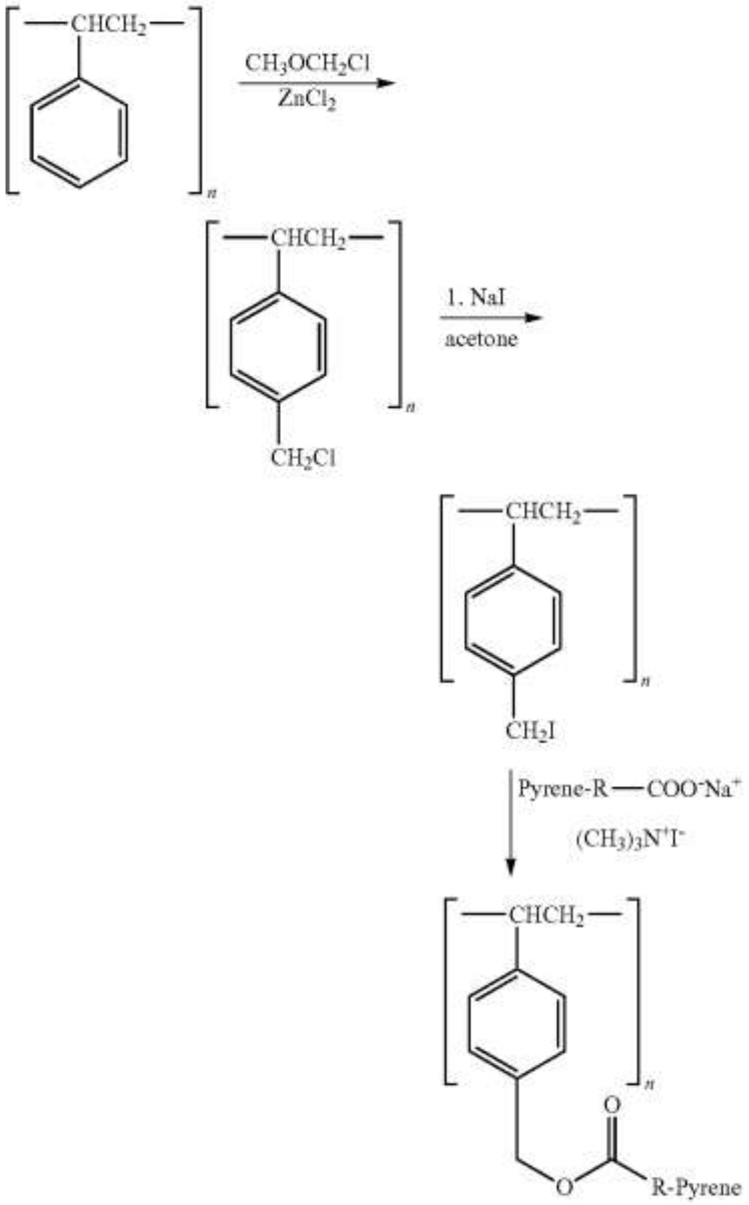


Fig. 6. Immobilization of 1-pyrene decanoic acid through covalent bonding on functionalized polystyrene backbone.

From this perspective, polystyrene is a good candidate (permeable to oxygen, inexpensive and easy to be functionalized) [13]. A possible route of synthesis for compounds 1, 4, 5 and 6 is depicted as follows:

Scheme (I)-Preparation of Polystyrene-

CH_2—O—(C=O)—R-Pyrene-



However, the covalent bonding may suppress the fluorescent properties of the molecules. In order to retain the chemical properties of the fluorophore (especially the fluorescence properties), Serban *et al* [14, 15] have immobilized the 1-pyrene butyric acid through doping of polyanilines–free base (**Figs. 7 - 8**):

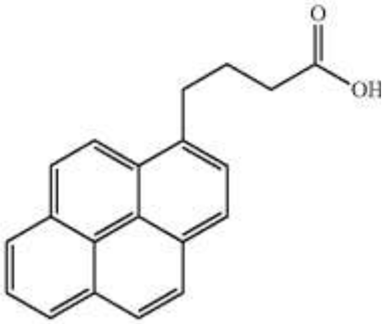


Fig. 7. The structure of 1-pyrene butyric acid.

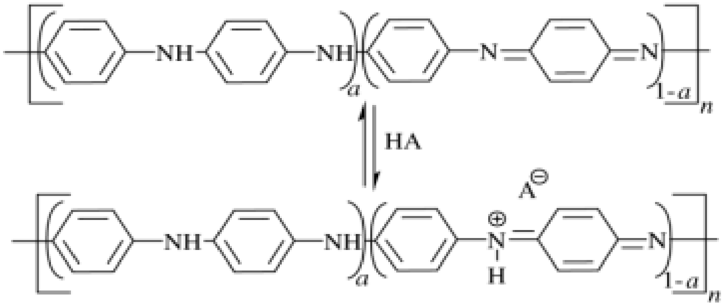


Fig. 8. Synthesis of doped PANI, where the doping agent (HA) is 1-pyrene butyric acid.

This type of noncovalent immobilization has the advantage that it maintains the fluorescence of the 1-pyrene butyric acid due to the minimum change in molecular structure. Additionally, polyaniline is a polymer with a good permeability for oxygen, good environmental stability, inexpensive and its synthesis is very versatile. Other types of fluorophores have been proposed for immobilization through doping of polyanilines are: 1- pyrene decanoic acid, pyrene-1-acetic acid, 1- pyrene- dodecanoic acid (**Figs. 9 - 11**):

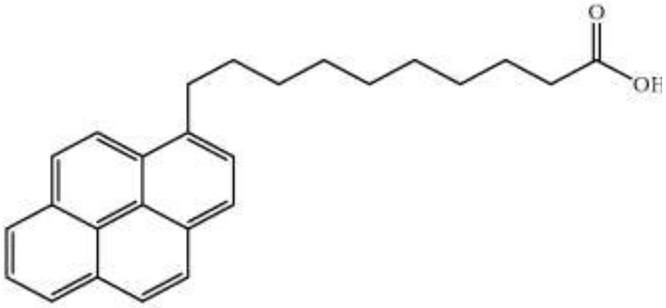


Fig. 9. The structure of 1-pyrene decanoic acid.

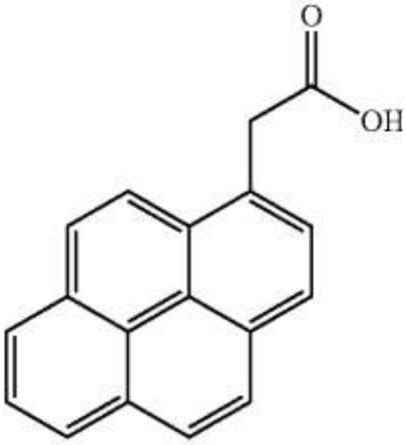


Fig. 10. The structure of 1- pyrene acetic.

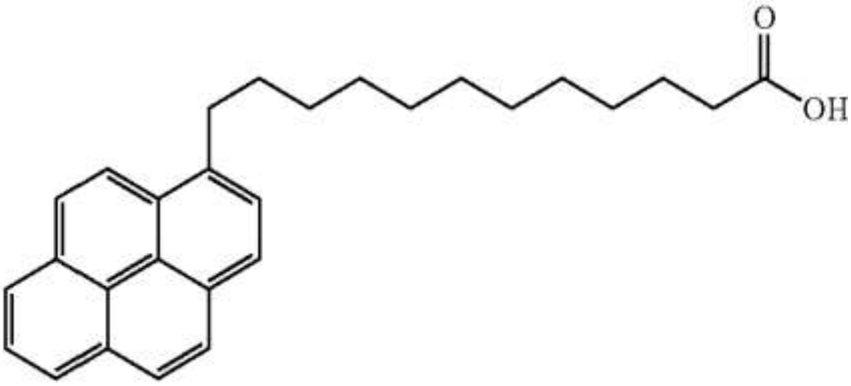


Fig. 11. The structure of 1-pyrene dodecanoic acid.

In the last decades, inorganic filler such as alumina, zirconia, Fe_2O_3, Cu_2O, highly dispersed onto the surface of cellulose and its derivatives, were used in manufacturing of fluorescence quenching – based sensor for oxygen detection.

In order to ensure a strong interface between fluorofor and inorganic filler, Serban *et al* have proposed to use the Pearson's Hard-Soft Acid-Base (HSAB) rule/principle as a new approach in selecting the appropriate filler – fluorofor combination [16]. HSAB principle establishes the reactivity rules between molecules: *hard acids prefer to react with hard bases and soft acids prefer to react with soft bases* (soft likes soft, hard likes hard), while borderline acids prefer to react with borderline base [17, 18].

Organic fluorophores can be functionalized with appropriate moieties which can act as hard, soft or bordeline base.

For instance, pyrene 1-decanoic acid in the basic medium (as carboxylate salt) can act as hard base. Pyrene alkane thiols (**Figs. 12 - 14**) which are depicted below, can act through the thiols groups as soft bases [19]:

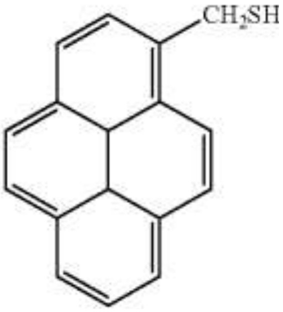


Fig. 12. The structure of 1-pyrene-1yl-methanethiol.

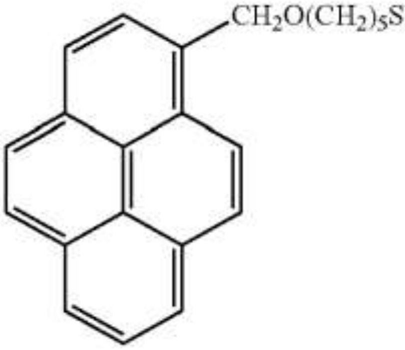


Fig. 13. The structure of 5- (pyrene 1-yl methoxy pentane 1-thiol).

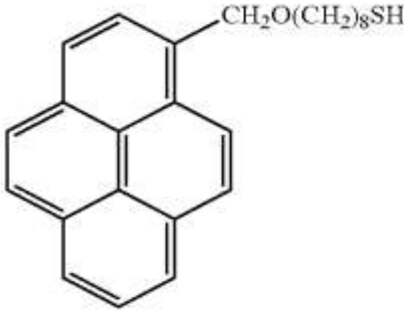


Fig. 14. The structure of 8-(pyrene 1-yl methoxy pentane 1-thiol).

The Lewis acid (hard, soft, or borderline) are, in fact, the cations of the metal oxides or bulk metal (e. g., Au, Ti^{4+}, Cu^+, etc). Using this approach, ionic interaction (i. e., tandem hard acid-hard base) or covalent interaction (i. e., tandem soft acid- soft base) can be tailored at both interfaces.

For instance, if Ti^{4+} (hard acid) is a major species at the surface of the metal oxides (in the case of Al_2O_3 used as filler), pyrene carboxylic acid is converted in the carboxilate form (hard base). The interface is ensured by ionic interaction between anion and cation. If Cu_2O is used as inorganic filler (Cu^+ acts as a soft acid), pyrene thiols and appropriate mercaptides (soft bases) can be used for generation of a covalent bond.

3. Galvanic oxygen sensors

The galvanic oxygen sensor is actually an electrochemical transducer which comprises a cell part (positive electrode, negative electrode) and an oxygen permeable membrane. The output of this device is a current signal which is proportional and linear with the partial pressure of oxygen sample gas monitored [20]. Such galvanic sensors are usually manufactured with a lead anode due to its stability and reliability. Despite of these advantages, lead is a well- known toxic metal that should be avoided from commercial applications [21].

In the last decades many efforts have been spent to replace lead anode from the oxygen galvanic sensors with other metal anodes, less harmful to people and environment. For instance, tin was proposed as useful material for the anode manufacturing in galvanic oxygen sensor [22, 23]. The electrolyte solution has pH larger than 12 and contains a chelating agent such as hydroxyethyl ethylene diamine triacetic acid (HEDTA), 1,3–diamino-2 hydroxipropane tetraacetic acid (DPTA-OH), diethylene triamine pentaacetic acid (DTPA), 1, 3 propane diamine Tetraacetic acid (PDTA), triethylene tetraamine hexaacetic acid (TTHA), dihydroxiethyl glycine (DHEG), dicarboxymethyl glutamic acid (GLDA). The role of the chelating agent is to catch an intermediate of the reaction.

Kitazawa *et al.* proposed the use of alternative metals, like aluminum and zinc [24]. When negative electrode contains zinc, the electrolyte is an aqueous solution with pH between 7 and 12, while when negative electrode contains aluminum, the electrolyte is an aqueous solution with pH in the range 3-9.

Cobianu *et al.* proposed antimony for replacement of lead from oxygen sensors [25]. The schematic architecture of sensor is depicted in the **Fig. 15**:

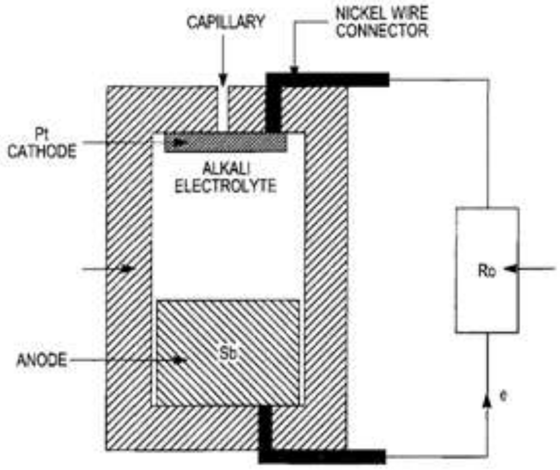


Fig. 15. The schematic architecture of Sb- galvanic oxygen sensor.

The process of oxygen sensing in both alkaline and acidic electrolyte may be summarized as follows:

Cathode (carbon platinized with 5% platinum): $O_2 + 2H_2O + 4e^- = 4HO^-$

Anode: $2Sb + 3H_2O + 4e^- = Sb_2O_3 + 6H^+ + 6e^-$

Cell reaction: $2Sb + 3O_2 = 2Sb_2O_3$

An alkaline electrolyte like CH_3COOK, KOH, or ammonium quaternary hydroxide $R_4N^+OH^-$ (where R is methyl , ethyl, propyl, butyl, or a combination of two or more methyl, ethyl, propyl, and butyl) was proposed and tested for the Sb-based galvanic cell. Theoretical investigations predict a consume about 6,5 grames Sb for a period of five years (sensor operation at 100 µA, no premature failure modes during the sensor life) [25, 26].

Another metal proposed to be used as anode in galvanic oxygen sensor was Bi [27]. The process of oxygen sensing in alkaline electrolyte may be summarized as follows:

Cathode (carbon platinized with 5% platinum): $3O_2 + 6H_2O + 12e^- = 12HO$

Anode: $4Bi + 6H_2O + 4e^- = 2Bi_2O_3 + 12H^+ + 12e^-$

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

An alkaline electrolyte like CH_3COOK, KOH, or ammonium quaternary hydroxide $R_4N^+OH^-$ (where R can be either methyl , ethyl, propyl, butyl, or a combination of two or more methyl, ethyl, propyl, and butyl) was proposed and tested for the Bi^- based galvanic cell.

Theoretical investigations predict a consume of about 11,45 grams of Bi in alkaline electrolyte for a period of five years (sensor operation at 100 µA, no premature failure modes during the sensor life) [27].

Another metal proposed to be used as anode in galvanic oxygen sensor was Cu [27]. The process of oxygen sensing in acidic electrolyte may be summarized as follows:

Cathode (carbon platinized with 5% platinum): $3O_2 + 4H^+ + 4e^- = 2H_2O$

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

Cell reaction: $2Cu + 3O_2 + 4H^+ = 2Cu^{2+} + 2H_2O$

An acid electrolyte like H_3PO_4 or CH_3SO_3H was proposed and tested for the Cu-based galvanic cell.

Theoretical investigations predict a consumption of about 10.5 grams Cu in alkaline electrolyte for a period of five years (sensor operation at 100 µA, no premature failure modes during the sensor life) [28, 29].

4. Conclusions

Two types of the most important optical and electrochemical principles for detection of oxygen are presented.

Fluoresce quenching - based oxygen sensors are reviewed from materials point of view (structures of fluorophores, methods for covalent or noncovalent entrapping of fluorophores into the polymeric matrix, HSAB approach design strong interfaces fluorophor- metal oxides and selection of polymeric matrices for fluorophores encapsulation).

Lead free galvanic oxygen sensor are described as alternatives to replace lead, which is the most used metal as anode in this type of sensors. Antimony stibium, copper, bismuth together with appropriate electrolyte are presented as nontoxic alternatives.

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