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(54) LEAD-FREE GALVANIC OXYGEN SENSOR

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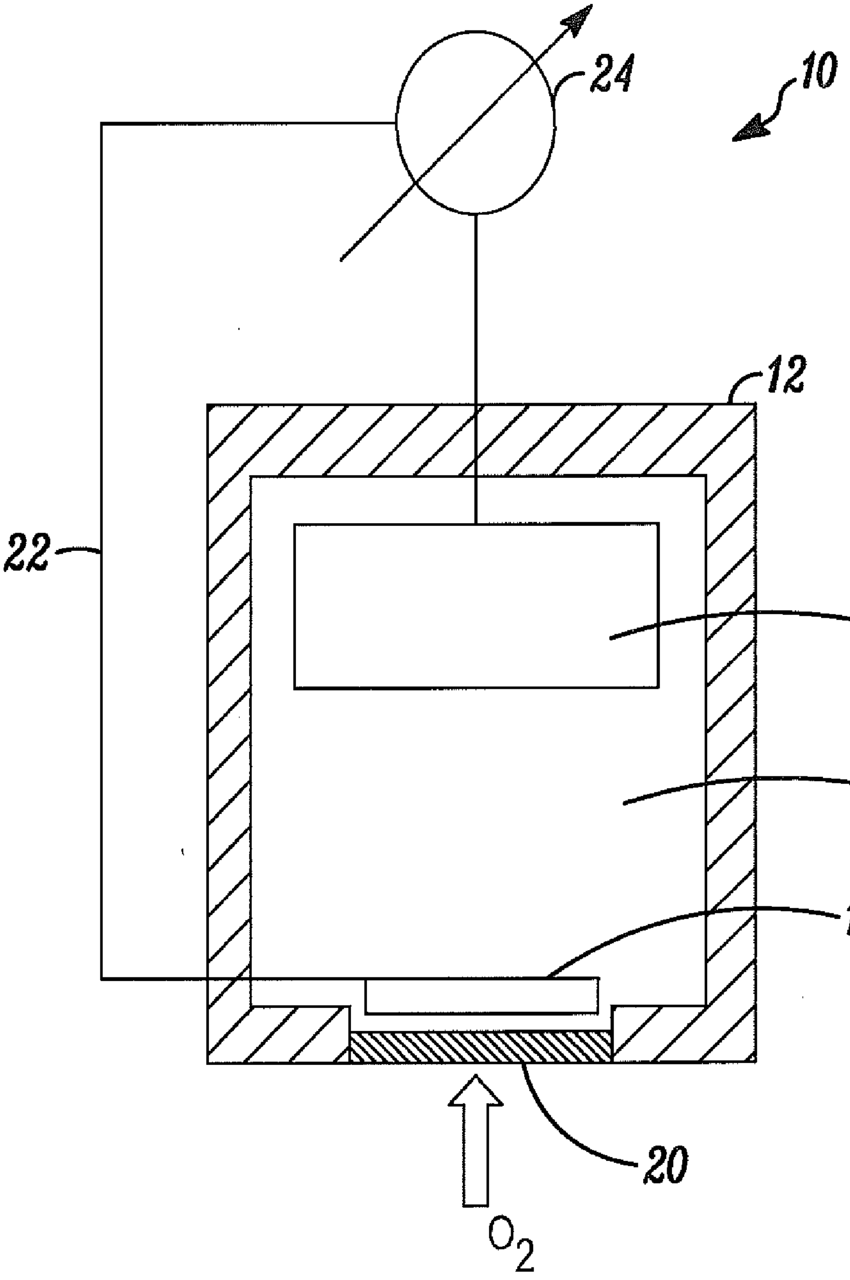
(57) ABSTRACT

A lead-free galvanic oxygen sensor having an aqueous electrolyte and a bismuth anode is disclosed. The electrolyte contains a polyol in addition to water and a salt. Surprisingly, a sensor with such an electrolyte has an increased resistance to passivation.



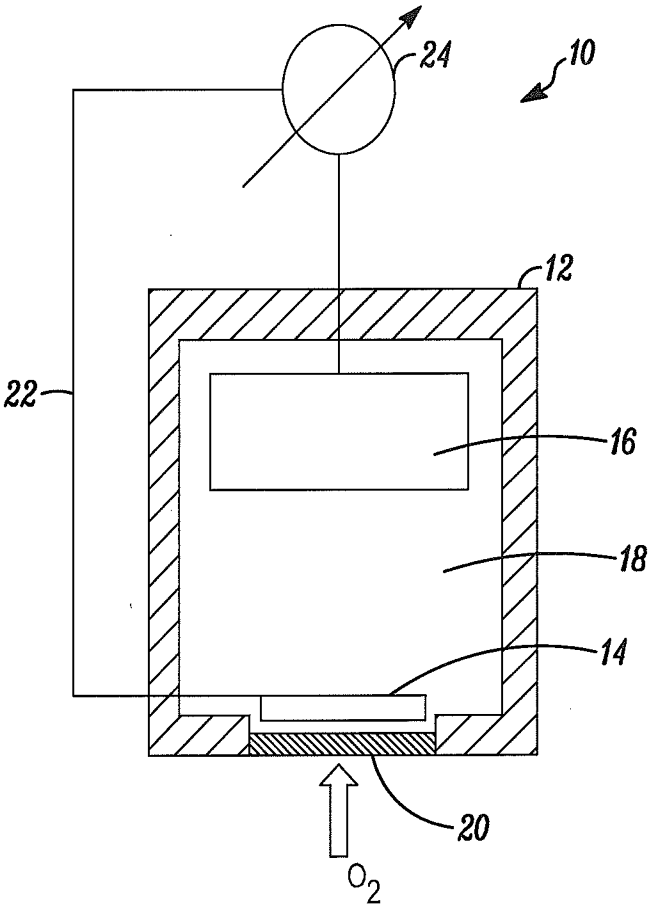


FIG. 1

LEAD-FREE GALVANIC OXYGEN SENSOR

FIELD

[0001] This application pertains to a lead-free galvanic oxygen sensor. More particularly, the application pertains to a lead-free galvanic oxygen sensor having a housing, a cathode, a bismuth-based anode, and an aqueous electrolyte including a salt and a polyol.

[0002] BACKGROUND

[0003] Galvanic oxygen sensors based on consumable lead anodes are well-known. These instruments are generally reliable and have good sensitivity. The presence of lead, however, is undesirable in such an instrument due to environmental and health concerns associated with lead contamination.

[0004] Thus, there is a need for a reliable, sensitive galvanic oxygen sensor, which avoids the use of lead anodes.

[0005] Recently, there have been attempts to replace lead anodes with those made of zinc, aluminum, and tin. It appears that those types of anodes have a very limited lifetime though, due to the self-corrosion and passivation of the anode surface.

[0006] There is thus a continuing need for a lead-free galvanic oxygen sensor. It was surprising and unexpected that the addition of a polyol to an aqueous electrolyte prevents passivation of a bismuth anode in a galvanic oxygen sensor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. **1** is a schematic illustration of a lead-free galvanic oxygen sensor.

DETAILED DESCRIPTION

[0008] While disclosed embodiments can take many different forms, specific embodiments hereof are shown in the drawings and will be described herein in detail with the understanding that the present disclosure is to be considered as an exemplification of the principles hereof, as well as the best mode of practicing same, and is not intended to limit the claims hereof to the specific embodiment illustrated.

[0009] The present invention relates to a lead-free galvanic oxygen sensor. FIG. **1** depicts a lead-free galvanic oxygen sensor **10** shown generally in accordance with one illustrated embodiment. The sensor **10** can be constructed with a plastic or metal housing **12**. Included within the housing **12** are a cathode **14**, a bismuth anode **16**, an aqueous electrolyte including a salt and a polyol **18**, and a barrier **20** (permeable membrane or capillary). The cathode **14** and anode **16** can be coupled to an external load resistor **24** by a set of wire collectors **22**.

[0010] The cathode **14** is an electrically conductive material selected from the group consisting of platinum, gold, silver, palladium, rhodium, iridium and carbon plated with platinum, gold, silver, palladium, rhodium, or iridium or any other suitable material. In one embodiment, the cathode **14** is made of a polytetrafluoroethylene (PTFE) membrane impregnated with a high surface area platinum catalyst embedded in a carbon matrix.

[0011] The anode **16** is made of bismuth, which is thermodynamically stable in water. The standard potential for the following reaction: $Bi_2O_3+3H_2O_{(I)}+6e^-\cdot 2Bi_{(s)}+6OH^-$ is –0.46 volt . There is no self-corrosion due to hydrogen evolution at the anode and no self-corrosion due to hydrogen evolution at the cathode. Importantly, bismuth is commercially available and is not toxic.

[0012] The aqeuous electrolyte in the sensor contains a salt and a polyol. The salt is selected from the group consisting of potassium hydroxide, sodium hydroxide, potassium acetate, and sodium acetate. In yet another embodiment, the salt is potassium hydroxide. The concentration of potassium hydroxide ranges from about 1 M to saturation.

[0013] The salt can also be ammonium quaternary hydroxide, such as $R_4N^+OH^-$wherein R is an alkyl group selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof. The electrolyte is not consumed by the oxygen sensing reaction. Furthermore, water is not involved in the overall electrochemical reaction so that the water level of the sensor will be governed by external factors.

[0014] In other sensors, the electrochemical oxidation of bismuth leads to the formation of a Bi_2O_3 layer on the surface of the electrode in the presence of water in a neutral or an alkaline electrolytic environment. That layer passivates the electrode, which means no current can flow through the surface at moderate voltages.

[0015] Surprisingly, the addition of a polyol to the aqueous electrolyte suppresses passivation of the bismuth anode. The polyol can be glycerol, erythritol, sorbitol, ethylene glycol, and mixtures thereof. In one embodiment, the polyol is glycerol. The glycerol can be present in the range of about 5% to about 70% by volume. In yet another embodiment, the glycerol is present at about 20% to about 30% by volume.

[0016] The permeable barrier **20** is selectively permeable to oxygen. For example, a tetrafluoroethylene resin membrane or a tetrafluoroethylene-hexafluoropropylene copolymer membrane can be used. It is also possible to use a capillary as diffusion barrier.

[0017] As for the wire collectors **22**, these can be made of nickel or platinum.

[0018] It was an unexpected and surprising benefit that the addition of a polyol to the aqueous electrolyte would lead to prevention of passivation of the bismuth anode that leads to decreased sensor life. Such a sensor has an excellent linearity for the oxygen partial pressure. The signal at oxygen is 4.7 times higher than that in air.

[0019] In addition, an accelerated lifetime test of a lead-free oxygen sensor having a bismuth anode was carried out in pure oxygen with an electrolyte containing either 7 M KOH in water or 7 M KOH with a mixture of 30% by volume glycerol in water as solvent. The sensor having the KOH alone stopped working after 7 days due to passivation of the bismuth anode. The expected lifetime in air is one month. Surprisingly, the sensor having the KOH and glycerol mixture worked for 167 days in oxygen. The expected lifetime in air was two years.

[0020] In another test, galvanostatic measurements were done on the different polyols to determine their suitability in the oxygen sensor. Electrolyte solutions were prepared having 3 g of the desired polyol dissolved/mixed in 7 ml of 10 M KOH, with the exception of ethanol in which the solvents did not mix completely. The current on the bismuth electrode was kept constant at 30 mA and the time of a sudden rise in potential was noted.

TABLE 1

	H_2O	ethylene glycol	D-sorbitol	meso-erythritol	glycerol	ethanol
Time to sudden rise in potential (min.)	0.75	8.5	2.5	14.5	36.3	0

TABLE 1-continued

	H_2O	ethylene glycol	D-sorbitol	meso-erythritol	glycerol	ethanol
no. of measurements	2	2	2	2	3	1

[0021] Thus, these experiments demonstrate the suitability of the claimed polyols in the oxygen sensor described herein. Such a bismuth electrode and aqueous electrolyte comprising a polyol and a salt can be useful in other electrochemical sensors and galvanic cells for other purposes, as in batteries.

[0022] From the foregoing, it will be observed that numerous variations and modifications may be effected without departing from the spirit and scope of the invention. It is to be understood that no limitation with respect to the specific apparatus illustrated herein is intended or should be inferred. It is, of course, intended to cover by the appended claims all such modifications as fall within the scope of the claims.

1. An oxygen sensor comprising: a housing, a cathode, a bismuth anode, and an aqueous electrolyte comprising a polyol and a salt wherein the anode is substantially free of lead.

2. The oxygen sensor of claim **1** wherein the cathode comprises an electrically conductive material selected from the group consisting of platinum, gold, silver, palladium, rhodium, iridium and carbon plated with platinum, gold, silver, palladium, rhodium, or iridium.

3. The oxygen sensor of claim **1** wherein the cathode is carbon plated with platinum.

4. The oxygen sensor of claim **1** wherein the salt is an alkaline salt.

5. The oxygen sensor of claim **1** wherein the salt is selected from the group consisting of potassium hydroxide, sodium hydroxide, potassium acetate, and sodium acetate.

6. The oxygen sensor of claim **1** wherein the salt is potassium hydroxide.

7. The oxygen sensor of claim **1** wherein the salt is an ammonium quaternary hydroxide, $R_4N^+OH^-$.

8. The oxygen sensor of claim **7** wherein R is an alkyl group selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof.

9. The oxygen sensor of claim **1** wherein the polyol is selected from the group consisting of glycerol, erythritol, sorbitol, ethylene glycol, and mixtures thereof.

10. The oxygen sensor of claim **1** wherein the polyol is glycerol.

11. The oxygen sensor of claim **1** wherein the polyol comprises about 20% to about 30% by volume.

12. An oxygen sensor comprising: a housing, a cathode, a bismuth anode, and an aqueous electrolyte that includes a salt and a polyol, wherein the anode is substantially free of lead.

13. The oxygen sensor of claim **12** wherein the cathode comprises an electrically conductive material selected from the group consisting of platinum, gold, silver, palladium, rhodium, iridium and carbon plated with platinum, gold, silver, palladium, rhodium, or iridium.

14. The oxygen sensor of claim **12** wherein the salt is selected from the group consisting of potassium hydroxide, sodium hydroxide, potassium acetate, and sodium acetate.

15. The oxygen sensor of claim **12** wherein the salt is potassium hydroxide.

16. The oxygen sensor of claim **12** wherein the salt is an ammonium quaternary hydroxide, $R_4N^+OH^-$.

17. The oxygen sensor of claim **16** wherein R is an alkyl group selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof.

18. The oxygen sensor of claim **12** wherein the polyol is selected from the group consisting of glycerol, erythritol, sorbitol and ethylene glycol.

19. The oxygen sensor of claim **12** wherein the polyol is glycerol.

20. An electrochemical sensor comprising a bismuth anode and aqueous electrolyte comprising a polyol and a salt.

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