Sensors and Actuators B 215 (2015) 1–8

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Hydrogen microsensors with hydrogen sulfide traps

Michael Nielsen[a,b,1], Lars Hauer Larsen[b], Lars Ditlev Mørck Ottosen[c,d,2], Niels Peter Revsbech[a,*]

[a] Department of Bioscience, Aarhus University, Ny Munkegade 114, 8000 Aarhus C, Denmark
[b] Unisense A/S, Tueager 1, 8200 Aarhus N, Denmark
[c] DTI Life Science, Kongsvang Alle 29, 8000 Århus C, Denmark
[d] Department of Engineering, Aarhus University, Hangøvej 2, 8200 Århus N, Denmark

ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form 5 March 2015
Accepted 16 March 2015
Available online 27 March 2015

Keywords:
Hydrogen
Interference
Sensor
Hydrogen sulfide
Oxygen
Guard

ABSTRACT

Hydrogen is often formed in sulfidic environments where interference from hydrogen sulfide has prevented its analysis by amperometric hydrogen microsensors. Hydrogen microsensors were made insensitive to hydrogen sulfide by placing a sulfide trap (guard) containing solutions of heavy metal ions, sulfide-oxidizing ferricyanide, or alkaline chemicals at the sensor tip. The overall most efficient sulfide guard consisted of a solution of $ZnCl_2$ in propylene carbonate which resulted in absence of interference from 5 mmol L^{-1} hydrogen sulfide and also alleviated any interference from oxygen. The hydrogen sensors with $ZnCl_2$-propylene carbonate traps could be used at temperatures up to 60 °C without exhibiting excessive baseline currents. The ability of a guarded sensor to resolve the hydrogen distribution in a sulfidic microbial mat with up to 2.4 μmol L^{-1} H_2 was demonstrated.

1. Introduction

Interferences are limiting the fields of application by just about any type of electrochemical sensor. Electrochemical detection of oxygen is one of the most frequently performed sensor analyses, and for O_2 most problems with interferences were solved when Clark [1] invented the membrane-covered sensor, where the whole electrochemical circuit with cathode and anode is shielded from interferences by ionic and high-molecular weight substances by a sheet of O_2 permeable polymers like polyethylene and polypropylene. It is possible to make micro-scale Clark-type oxygen sensors with tips down to 2 μm [2] and such sensors can be used for analysis of stratified microbial communities [3], plant tissue [4], animal tissue [5], etc. Basically the same micro-scale sensor design has subsequently been used for analysis of other gases such as N_2O [6], NO [7], H_2S [8] and H_2 [9,10].

Hydrogen is a key intermediate in anaerobic microbial communities, and the transformations of hydrogen by microorganisms have been extensively studied. During recent years hydrogen has been in focus due to a possible future "hydrogen economy", where fossil fuels would be replaced by fuel cells with hydrogen as reductant. The production of hydrogen for such purposes by anaerobic fermentations [11], genetically modified photosynthetic microorganisms [12] and "artificial photosynthesis" [13] has attracted a lot of interest and extensive funding. Hydrogen might also become important in the biological production of methane [14]. Electricity from for example windmills is often in excess, and could be used for production of hydrogen by electrolysis of water. Feeding this hydrogen into biogas reactors could be an attractive way of upgrading the methane concentration, as the prokaryotes in the slurry combine excess CO_2 in the biogas with H_2 to form CH_4. Studies of microbial H_2 transformations in such microbial communities have been performed using for example gas chromatography [14], but studies of the microdistribution of H_2 producing and H_2 consuming processes by use of microsensors is often prevented by the occurrence of interfering hydrogen sulfide in anoxic environments.

We here describe the design, functioning, and environmental use of a H_2 microsensor that was shielded with different types of aqueous H_2S removing solutions, and one non-aqueous solution

* Corresponding author. Tel.: +45 23382187.
E-mail address: Revsbech@bios.au.dk (N.P. Revsbech).
[1] Present address: Unisense A/S, Tueager 1, 8200 Aarhus N, Denmark.
[2] Present address: Department of Engineering, Aarhus University, Hangøvej 2, 8200 Århus N, Denmark.

http://dx.doi.org/10.1016/j.snb.2015.03.035
0925-4005/

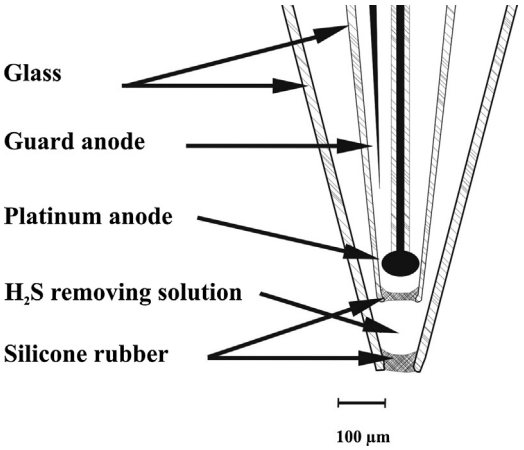

Fig. 1. Tip of a H_2 microsensor equipped with a guard containing a H_2S removing solution. The guard anode shown inside the microsensor reduces the supply of interfering oxidizable impurities in the electrolyte to the sensing anode and thereby lowers the baseline current.

that simultaneously minimizes the entry of H_2S and H_2O to the sensing anode.

2. Materials and methods

2.1. Sensor design and construction

The developed composite H_2 microsensor consists of two main elements; (1) an electrochemical Clark-type H_2 microsensor, sensitive to both H_2 and H_2S, and (2) an outer glass capillary with a gas permeable silicone membrane at the tip, surrounding the tip of the Clark-type H_2 sensor and containing a guard solution designed to remove H_2S (Figs. 1 and 2). The physical design of the new H_2 sensor is identical to that of the guarded O_2 insensitive N_2O microsensor [6], where an about 50–100 μm thick layer of alkaline ascorbate prevents the entry of O_2 into the Clark-type N_2O sensor where it would otherwise interfere. Clark type H_2 microsensors with tip diameters between 30 and 70 μm were acquired from Unisense A/S. The Unisense sensors are physically similar to the H_2 sensor developed by Witty [9] but contain a non-aqueous electrolyte that results in a much more stable H_2 sensitivity. The protocols that were used for the construction of the outer glass capillary and subsequent attachment of the capillary to the "naked" H_2 microsensor were similar to those described for a NO_x^- biosensor by Larsen et al. [15]. In order to evaluate and optimize sensor performance, a large number of guarded H_2 microsensors was constructed with variations in both tip dimensions and geometry. The outer tip diameter was thus varied between 35 and 80 μm, the distance between the two membranes ranged between 75 and 150 μm, and the tip of the outer glass capillary was shaped more or less conical.

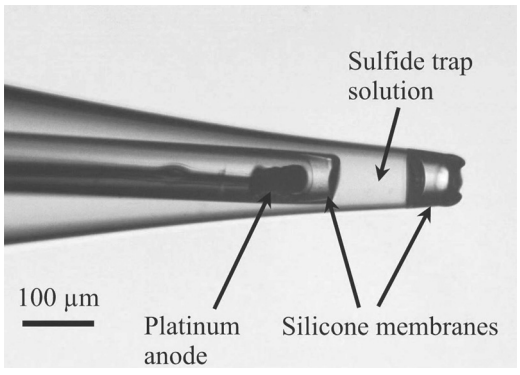

Fig. 2. Photo of guarded H_2 microsensor. The guard anode shown in Fig. 1 is not visible on the photograph.

2.2. Guard solutions

A number of different solutions were assessed for their potential use as functional H_2S guard in the guarded H_2 microsensor. The applied guards were based on three different principles for chemical removal of free H_2S: Oxidation, precipitation, and conversion of H_2S to HS^- by high pH. The tested solutions included (no solvent mentioned means aquatic solution): (1) 0.3 mol L^{-1} K_3FeCN_6 in 0.1 mol L^{-1} K_2CO_3 buffer (pH 10.2), (2) alkaline 0.7 mol L^{-1} sodium ascorbate (pH 12.8), (3) 100 g L^{-1} $ZnCl_2$ in anhydrous propylene carbonate, (4) 100 g L^{-1} $AgNO_3$, and (5) 0.1 mol L^{-1} NaOH. From its use in H_2S sensors ferricyanide is known as a very efficient H_2S oxidizer [16]. Heavy metal ions like Ag^+ and Zn^{2+} form insoluble sulfides with H_2S. Alkaline solutions like 0.7 mol L^{-1} ascorbate at pH 12.8 and 0.1 mol L^{-1} NaOH with a pH of 13 convert H_2S to HS^- that cannot penetrate the silicone membrane in front of the platinum anode. Best sensor performances were achieved for solutions 1–3, and the results for sensors applying these guards are thus presented in this paper.

2.3. Sensor characterization

The H_2S interference test was performed in a buffer solution consisting of 1.56 g L^{-1} Na-citrate x$2H_2O$ and 0.76 g L^{-1} citric acid. The buffer was sparged with N_2 gas for several minutes to create anoxic test conditions, and hydrogen sulfide was added from a 50 mmol L^{-1} Na_2S stock solution. The low pH of the buffer of about 3.8 ensured that all added sulfide was found as H_2S. The sensor signals of the guarded H_2 sensors were evaluated at progressively higher H_2S concentrations up to about 5 mmol L^{-1}. The effect of long-term exposure to 5 mmol L^{-1} H_2S for 6 h was also tested for the different H_2S guarded sensor versions.

In addition to the testing of sulfide interference, a range of other important characteristics were described, including interference from O_2 and H_2 response and baseline current as a function of polarization voltage (0.5–0.8 V) and temperature in the range 20–60 °C. For comparison, general sensing characteristics of several unguarded H_2 sensors were also characterized.

2.4. Micro-profiling of a microbial mat system

Sediment cores having a well-developed cyanobacterial mat community on top were collected at a brackish site at Løgstør Bredning in the Danish Limfjord near the city of Aggersund (57°00′02.15N, 9°17′12.89E). The collection area is influenced by wind-induced changes in water level with periods (hours to weeks) of either inundation or air exposure. The surface microbial community on the sampled location is dominated by cyanobacteria with the filamentous, bundle-forming *Microcoleus chthonoplastes* being the most abundant. The sediment mat environment was characterized by strong process zonation and steep chemical gradients, and during nighttime sulfide penetrates to the very surface of the mat as evidenced by black color and presence of a white surface cover of sulfide oxidizing bacteria.

The microbial mat was analyzed at room temperature (22 °C) while incubated in an aquarium with seawater from the sampling location. It was profiled with a guarded 70-μm tip H_2 microsensor in combination with microsensors for O_2, H_2S and pH (Unisense A/S). The tip diameters of the O_2, H_2S and pH microsensors used for profiling were 25 μm, 50 μm and 50 μm, respectively. The vertical position of the microsensor tips relative to the mat surface was determined using a dissection microscope.