Sensors and Actuators B 187 (2013) 168–173

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Combined amperometric/field-effect sensor for the detection of dissolved hydrogen

C. Huck[a,b], A. Poghossian[a,b], P. Wagner[c], M.J. Schöning[a,b,*]

[a] Institute of Nano- and Biotechnologies (INB), Aachen University of Applied Sciences, Campus Jülich, 52428 Jülich, Germany
[b] Peter Grünberg Institute (PGI-8), Forschungszentrum Jülich GmbH, 52525 Jülich, Germany
[c] Institute for Materials Research (IMO), Hasselt University, 3590 Diepenbeek, Belgium

ARTICLE INFO

Article history:
Available online 17 October 2012

Keywords:
Dissolved hydrogen
Amperometric gas sensor
Field-effect sensor
Biogas

ABSTRACT

Real-time and reliable monitoring of the biogas process is crucial for a stable and efficient operation of biogas production in order to avoid digester breakdowns. The concentration of dissolved hydrogen (H_2) represents one of the key parameters for biogas process control. In this work, a one-chip integrated combined amperometric/field-effect sensor for monitoring the dissolved H_2 concentration has been developed for biogas applications. The combination of two different transducer principles might allow a more accurate and reliable measurement of dissolved H_2 as an early warning indicator of digester failures. The feasibility of the approach has been demonstrated by simultaneous amperometric/field-effect measurements of dissolved H_2 concentrations in electrolyte solutions. Both, the amperometric and the field-effect transducer show a linear response behaviour in the H_2 concentration range from 0.1 to 3% (v/v) with a slope of 198.4 ± 13.7 nA/% (v/v) and 14.9 ± 0.5 mV/% (v/v), respectively.

1. Introduction

A stable and efficient operation of the biogas production has the potential to replace some of the limited fossil fuels [1]. The use of biogas as energy source is currently establishing in the group of alternative energies. In general, the natural process of anaerobic digestion is a relative stable system that occurs in nature without the need for precise process control. However, under high loading conditions, process failures such as disadvantageous biogas yield or stoppage of the biogas production due to acidification of the medium are known to occur [2–4]. Therefore, real-time and reliable controlling and monitoring of the biogas process is crucial for a stable and efficient operation of biogas production in order to avoid digester breakdowns.

The concentration of dissolved hydrogen (H_2) represents one of the most important parameters for biogas process control in anaerobic digesters [5,6]. Accumulated H_2 strongly inhibits the degradation of volatile fatty acids, such as propionate and butyrate, resulting in a consequent deterioration of normal operation [7]. A build-up of hydrogen above a critical concentration of higher than 0.04 μM has been reported as initial stage of digester overloading [7,8]. If hydrogen production exceeds the maximum ability of the methanogenic biomass to degrade hydrogen, there will be a rapid and large increase in the hydrogen concentration prior to digester failures. Thus, dissolved hydrogen is a key factor in the intricate balance between microbial species involved in the multi-step degradation during anaerobic digestion, making it a useful parameter for biogas process monitoring and early warning of process disturbances [2,3,9–12].

Most of hydrogen sensors, used for monitoring the anaerobic biogas production, are based on the detection of H_2 in the gas phase of the digester [5,13–15]. Dissolved H_2 in the liquid medium is thus calculated from the gas fraction, assuming that the hydrogen-transfer rate between the gas and the liquid phase is not limited. However, H_2 mass-transfer coefficients in anaerobic digesters are much smaller than those typically found in aerobic fermentation digesters [16]. That is because the culture broth of anaerobic digestion consists of a complex physico-chemical composition with respect to the H_2 solubility [17,18]. This limits the rapidity with which an increase in H_2 concentration in the biomass can be detected in the gas phase of the digester. As a consequence, serious overloading of the digester may occur before the raised H_2 concentration in the gas phase is detected. Therefore, having a practical, reliable and low-cost instrumentation that provides a continuous and in situ measurement of dissolved hydrogen in anaerobic digesters would be highly advantageous.

In this work, a Si-based combined chemosensor capable for the simultaneous amperometric/field-effect detection of the concentration of dissolved H_2 has been developed for biogas applications. Such a combination of two different transducer principles for

* Corresponding author at: Institute of Nano- and Biotechnologies (INB), Aachen University of Applied Sciences, Campus Jülich, 52428 Jülich, Germany.
Tel.: +49 241 6009 53215; fax: +49 241 6009 53235.
E-mail address: schoening@fh-aachen.de (M.J. Schöning).

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http://dx.doi.org/10.1016/j.snb.2012.10.050

the detection of the same parameter might allow a more accurate, selective and reliable measurement of dissolved H_2 as an early warning indicator of digester failures. The functioning of the developed one-chip integrated dual amperometric/field-effect chemosensor has been tested in electrolyte solutions with different concentrations of dissolved H_2.

2. Experimental

2.1. Structure and functioning principle of the combined H_2 sensor

The schematic layer structure of the combined dissolved H_2 sensor and the measurement set-up for the simultaneous amperometric/field-effect detection of dissolved H_2 in electrolyte solutions is shown in Fig. 1. The developed sensor combines a pH-sensitive capacitive EIS (electrolyte-insulator-semiconductor) sensor consisting of an Al–p-Si–SiO_2–Ta_2O_5 structure and two circular-type thin-film Pt electrodes. The specific feature of the combined H_2-sensor chip is the implementation of the field-effect pH sensor in addition to well-known amperometric measurements. The field-effect pH sensor is a basic structural element of current chemical sensors and biosensors [19–25] and is used in this approach for an indirect detection of the dissolved H_2 gas. This new approach has been introduced by the authors for the first time in [26]. Thus, two transduction principles are closely combined at the microscale, enabling new electrochemical detection opportunities.

The operation principle of the combined sensor structure is assumed to be as follows. Dissolved H_2 diffuses to the polarized Pt working electrode and is electrochemically oxidized according to the following reaction [27,28]:

$$H_2 \rightarrow 2e^- + 2H^+ \quad (1)$$

This causes a current depending on the dissolved hydrogen concentration. If the potential of the working electrode is adjusted (usually +0.55 V vs. Ag/AgCl reference electrode) that any hydrogen molecule reaching the electrode surface is immediately oxidized, then the current will be controlled solely by the diffusion rate of hydrogen to the electrode surface. The most important difference of our H_2-sensor chip and other macro- or miniaturized amperometric H_2 sensors reported in literature [15,27,29,30], is the existence of the one-chip integrated field-effect sensor, capable for an indirect detection of dissolved H_2. The product of H_2 oxidation, i.e., H^+ ions generated at the working electrode (see Eq. (1)), will diffuse to the pH-sensitive gate-insulator surface (in this study, Ta_2O_5) and will be detected there. A resulting local pH decrease near the surface of the pH-sensitive layer leads to a change in the surface charge and thus, modulates the space-charge capacitance in the Si and consequently, the flatband voltage and capacitance of the EIS structure. In previous experiments, field-effect devices have been successfully used for the detection of H^+ ions that have been electrochemically generated via electrolysis of water [31,32]. The output signal of the combined sensor is considered as "H_2 signal" only, if the signal changes of both the amperometric and the field-effect sensor are nearly simultaneous (with a small delay time necessary for the diffusion of H^+ ions generated at the amperometric electrode to the gate region of the field-effect sensor) and if the signal of the field-effect sensor is shifted towards more negative potentials that corresponds to an increase of the H^+ concentration. In this way, the selectivity of the combined sensor to H_2 detection can be achieved.

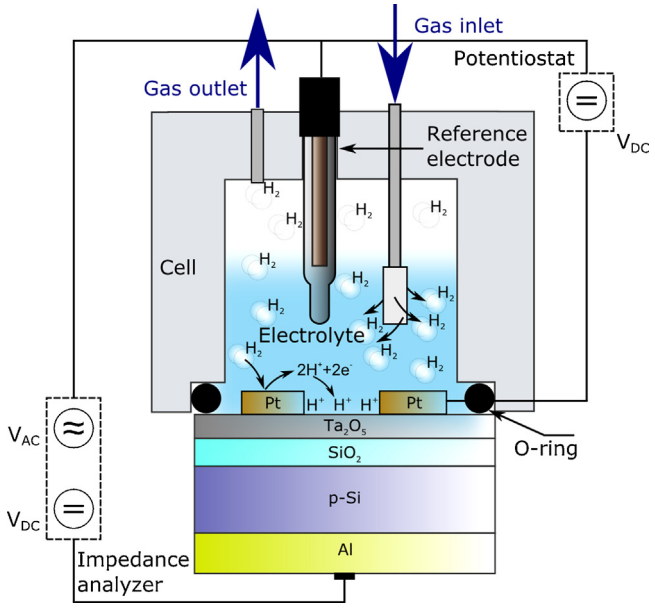

Fig. 1. Schematic structure and measurement set-up of the combined amperometric/field-effect dissolved H_2 sensor.

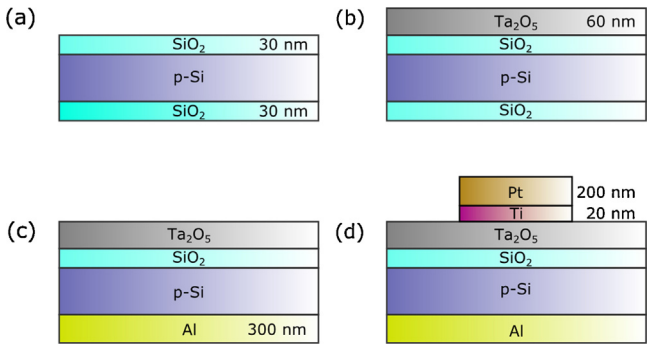

Fig. 2. Flowchart for the fabrication of the combined dissolved H_2 sensor: (a) p-Si wafer with thermally grown SiO_2; (b) deposition of tantalum and thermal oxidation to Ta_2O_5; (c) etching of SiO_2 on the rear side and deposition of the Al back-side contact; (d) deposition and patterning of the circular Pt thin-film electrodes.

2.2. Fabrication of the combined sensor structure

The flowchart for the fabrication of the combined amperometric/field-effect H_2 sensor is shown in Fig. 2. For the realization of the field-effect sensor, capacitive Al–Si–SiO_2–Ta_2O_5 (p-Si, ρ = 1–10 Ωcm; 30 nm thermally grown SiO_2 (Fig. 2a)) structures with a Ta_2O_5 layer as pH-sensitive gate insulator material have been fabricated. Ta_2O_5 is widely used for field-effect pH sensing, due to its high pH sensitivity [33] as well as high corrosion-resistance properties in a wide pH range [34]. The Ta_2O_5 films were prepared by means of thermal oxidation of an electron-beam deposited, 30 nm thick tantalum layer in dry oxygen atmosphere at 517 °C for about 30 min, yielding a ~60 nm thick Ta_2O_5 layer (Fig. 2b). After etching the SiO_2 from the rear side of the wafer, a 300 nm Al film was deposited as a contact layer for the field-effect sensor (Fig. 2c).

For the preparation of the amperometric transducer, a Pt layer with a thickness of 200 nm was deposited together with an adhesion layer of 20 nm Ti by means of electron-beam evaporation and patterned as circular electrodes via photolithography and lift-off technique, respectively (see Fig. 2d). Platinum has an excellent electro-catalytic activity for hydrogen oxidation as compared to other metals [35,36]. In a following step, the wafer was separated into single sensor chips with a size of 10 mm × 14 mm and assembled onto a printed circuit board (PCB). For electrical connection of the field-effect sensor, the Al rear-side contact of the EIS structure was glued with electrically conductive adhesive onto the PCB