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Combined Amperometric/Field-Effect Sensor for the Detection of Dissolved Hydrogen in Biogas Reactors

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Abstract:
A one-chip integrated combined amperometric/field-effect sensor for monitoring the dissolved hydrogen (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 proposed approach has been demonstrated by simultaneous amperometric/field-effect measurements of dissolved H_2 concentration in electrolyte solutions. Both, the amperometric and the field-effect transducer show a linear response 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.

Key words: dissolved hydrogen, amperometric gas sensor, field-effect sensor, biogas

Introduction

The use of biogas as energy source is currently establishing in the group of alternative energies. Accompanied by the growing number of biogas plants, the demand for online monitoring and control of biogas production is increasing [1]. An implementation of chip-based multi-parameter monitoring and control systems could improve the biogas process stability and prevent digester breakdowns. Moreover, process performance for better economy of the biogas plants could be enhanced.

The concentration of dissolved hydrogen (H_2) represents one of the most important parameters for biogas process control and early warning of process disturbances [2, 3]. Accumulated hydrogen strongly inhibits the degradation of volatile fatty acids, such as propionate and butyrate, resulting in a consequent deterioration of the normal operation [4, 5]. 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 H_2 is a key factor in the intricate balance between microbial species involved in the multi-step degradation during anaerobic digestion, making it as useful parameter for process monitoring [6].

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 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 sensor device has been tested in electrolyte solutions with different concentration of dissolved H_2.

Structure and functioning principle of the combined H_2 sensor

The schematic layer structure of the combined hydrogen sensor and measurement setup for simultaneous amperometric and field-effect detection of dissolved H_2 in electrolyte solutions is shown in Fig. 1. The developed sensor combines a pH-sensitive capacitive electrolyte-insulator-semiconductor (EIS) sensor consisting of an Al-p-Si-SiO_2-Ta_2O_5 structure and a thin-film Pt electrode for field-effect and amperometric measurements, respectively. Since the part of the gate region of the field-effect sensor is covered with the Pt-metal electrode, it represents a parallel connection of a pH-sensitive capacitive EIS sensor and the well-known Pt-gate MIS (metal-insulator-semiconductor) structure. The latter one is widely used for H_2 detection in gaseous atmospheres (see e.g., [7, 8]). As a result, the field-effect part of the combined sensor is able to detect dissolved H_2 *via* two mechanisms: a) detection of the product of H_2 oxidation with the pH-sensitive sensor, i.e. H^+ ions generated at the polarized working electrode of the amperometric part of the combined sensor, and b) flat-band-voltage variations caused from the formation of hydrogen dipoles at the metal-gate/insulator interface of the MIS structure.

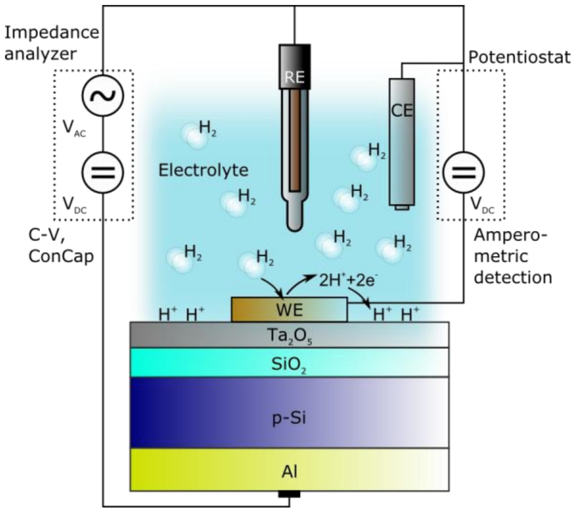

Fig. 1. Schematic layer structure of the combined hydrogen sensor and measurement setup for the simultaneous amperometric/field-effect detection of dissolved hydrogen in electrolyte solutions. WE: Pt working electrode; CE: counter electrode; RE: reference electrode.

Fabrication of the combined sensor structure

For the fabrication of the combined sensor, capacitive Al-Si-SiO_2-Ta_2O_5 (p-Si, ρ = 1-10 Ωcm; 30 nm thermally grown SiO_2) structures with Ta_2O_5 as pH-sensitive gate insulator have been fabricated. Ta_2O_5 is widely used for field-effect pH sensing, due to its high pH-sensitivity [9] as well as high corrosion-resistance properties in a wide pH range [10]. The Ta_2O_5 films were prepared by means of thermal oxidation of an electron-beam deposited 30 nm Ta layer in a dry oxygen atmosphere at 517 °C for about 0.5 h, yielding a ~60 nm thick Ta_2O_5 layer. A 300 nm Al film was deposited as rear-side contact for the field-effect sensor. For the realization of the amperometric transducer, a 200 nm thick platinum electrode was prepared onto a 20 nm thick titanium adhesion layer by means of electron-beam evaporation and patterned by photolithography and lift-off technique, respectively. Finally, the structures were cut into chips with a size of 10 mm x 14 mm and assembled onto a printed circuit board (PCB). For electrical connection of the EIS structure, the Al rear-side contact was glued with electrically conductive adhesive onto the PCB substrate. The front-side contacts to the thin-film Pt electrodes were provided by means of an ultrasonic wedge bonder.

Gas-sensing setup and testing methodology

For experiments, the PCB substrate with the combined sensor structure was mounted into a home-made measuring cell and tested in electrolyte solutions with different concentrations of dissolved H_2 from 0.05 to 3%v/v. The sidewalls and rear-side contact of the combined sensor chip were protected from the electrolyte solution by means of an O-ring, thereby circumventing the need for a complicated encapsulation process. The contact area of the EIS sensor with the solution was about 0.5 cm².

Hydrogen gas was dissolved in the electrolyte through a perforated tube by mixing with nitrogen in various ratios using commercial mass-flow controllers (Bronkhorst High-Tech). As electrolyte a 0.25 mM polymix multi-component buffer solution (pH 7) containing 100 mM NaCl as an ionic-strength adjuster was used [11, 12]. The pH of the polymix buffer was adjusted by titration either with NaOH or HCl.

The combined sensor structure has been characterized by means of amperometric method using a voltage source (Keithley 2400) and constant-capacitance (ConCap) method using an impedance analyzer (Zahner Elektrik) as presented in Fig. 1. For the amperometric detection of dissolved H_2 a standard three-electrode configuration under potential control was used. The potential of the working electrode was set at +0.55 V *versus* the Ag/AgCl reference electrode (conventional liquid-junction Ag/AgCl electrode, Metrohm) and the hydrogen concentration-dependent current was detected between the working and the counter electrode (Metrohm). The ConCap mode allows dynamic characterization of the EIS structure. In this mode, the capacitance of the EIS sensor is kept constant (usually within the depletion region of the capacitance-voltage curve at ~60% of the maximum capacitance) using a feedback-control circuit, and potential changes at the transducer/electrolyte interface have been directly monitored. For operation, a DC polarization voltage is applied *via* the reference electrode to set the working point of the EIS sensor, and a small AC voltage (20 mV) is applied to the system in order to measure the capacitance of the sensor. All measurements were carried out at a frequency of 120 Hz in a dark Faraday cage at room temperature.

Results and discussion

Before H_2 experiments were performed, the pH sensitivity of the capacitive field-effect Al-p-Si-SiO_2-Ta_2O_5 structure had been investigated in Titrisol buffers.

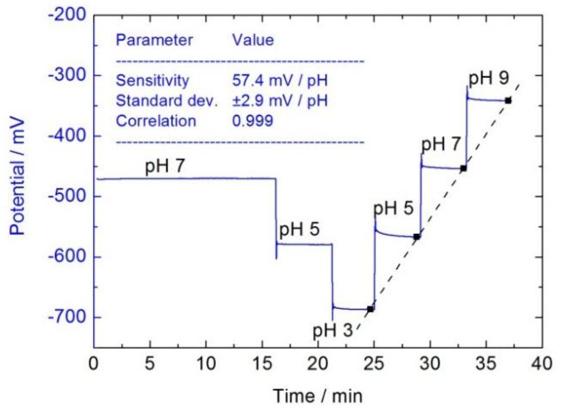

Fig. 2. Typical dynamic ConCap response of the capacitive field-effect Al-p-Si-SiO_2-Ta_2O_5 EIS structure recorded in Titrisol buffer with different pH values from pH 3 to pH 9 and corresponding calibration curve (dashed line).

Figure 2 depicts a typical dynamic ConCap response of the EIS structure recorded in Titrisol buffer solution with different pH values. The bare EIS sensor shows an average pH sensitivity of 57.4 ± 2.9 mV / pH in the range from pH 3 to 9, which is in good agreement with pH-sensitivity values reported in literature for a Ta_2O_5 layer [7, 9].

Figure 3a demonstrates an example of a simultaneous amperometric/field-effect detection of dissolved H_2 in the concentration range from 0.05 to 3%v/v H_2. With ascending and descending H_2 dosages, a good correlation between the ConCap response of the field-effect sensor and the output signal of the amperometric sensor has been observed. The respective calibration curves of the combined sensor evaluated from Figure 3a are presented in Figure 3b. Both, the amperometric and the field-effect transducer show a linear response in the H_2 concentration range from 0.1 to 3%v/v with a H_2 sensitivity of 198 ± 14 nA / %v/v and 15 ± 0.5 mV / %v/v, respectively.

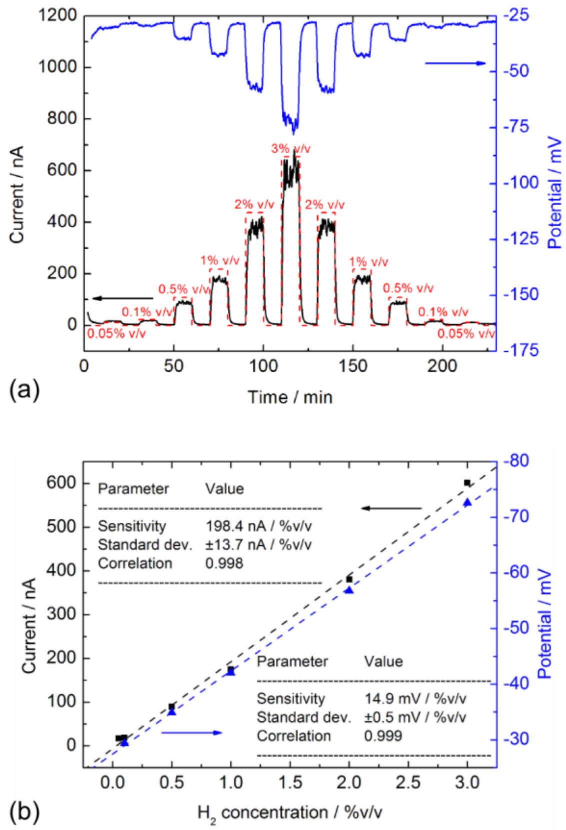

Fig. 3. Simultaneous amperometric/field-effect measurement of dissolved H_2 with the combined sensor chip (a) and calibration curves for the field-effect and amperometric sensor, respectively (b).

Conclusions

The obtained experimental results demonstrate the feasibility of the developed combined sensor chip for the simultaneous amperometric/field-effect detection of dissolved H_2 in electrolyte solutions. Such a combination of two transducer principles, namely, the amperometric and field-effect detection, might allow in future more accurate, selective and reliable measurements of dissolved H_2 in biogas reactors as an early warning indicator of process disturbances or digester failures.

Acknowledgements

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