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Development and characterization of a miniaturized hydrogen gas sensor system for safety monitoring

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Summary:
This work reports on recent advances in the development and characterization of a miniaturized hydrogen sensor system based on the combination of an yttria-stabilized zirconia (YSZ) solid electrolyte coulometric (SEC) detector and a gas chromatographic (GC) separation process. A commercial oxygen-pumping cell was characterized for its sensitivity, long-term stability and accuracy under different operational conditions. The resulting insights were used to define appropriate boundary conditions and construction guidelines for miniaturizing different components such as the sample injection system, the GC column heating/cooling module and the SEC detector.

Keywords: Yttria-stabilized zirconia (YSZ), coulometry, gas chromatography, trace gas analysis

Background, Motivation and Objective

Scientific studies indicate that the ever-increasing energy demand and concern over greenhouse gas emissions has to be resolved using an environment friendly mixed energy infrastructure [1]. For hydrogen (H_2) to be widely accepted as a potential alternative energy carrier in the diverse and distributed energy infrastructure of the future, more sensitive, selective, long-term stable and standalone H_2 sensors are needed covering the whole supply chain. The ability to reliably detect trace concentrations < 10 Vol.-ppm in oxygen containing gaseous mixtures is essential in safety monitoring and quality management [2].

In the presented work, a Pt/YSZ/Pt-based SEC gas sensor is used as a GC detector. The system enables selective and calibration-free detection of oxidizable (H_2, CH_4) and/or reducible gas components in the vol.-ppb range [3]. This contribution is directed towards the miniaturization of such a sensor system and its characterization under varying GC and detector parameters, and thus, enabling a systematic and insight-driven miniaturization process.

Description of the New Method or System

For the characterization of sensor properties, a commercial oxygen-pumping cell was coupled with a table top GC [3]. The results were used to optimize operational parameters for reaching both the required lower limit of detection (LLOD) with minimum error and widest possible concentration measurement range. Fig 1 shows the some of the measured H_2 –peaks.

Miniaturization was carried out for the three main components of the sensor system, i.e. the sample injection unit, the GC column oven and the SEC detector. A miniaturized sample injection unit was realized using miniaturized solenoid valves mounted upon a hydraulic manifold. In comparison to the currently used 10-port rotational valve, it offers an increased control autonomy for establishing tailored injection procedures, higher long-term stability and a compact, rugged design without redundant tubing. The manifold was first constructed using stainless steel 3D printing, and further, was optimized using precision drilling of a stainless steel block. The new design exhibits reduced inter-canal leakage, no need of post processing for gas tightness, and minimized dead volumes [4]. In [4], also the basic concept for a miniaturized GC column oven was introduced using resistive heating of a cylindrical aluminum fixture. An optimized construction consists of packed GC columns coiled over a 3D-printed aluminum structure with embedded cooling fins as shown in Fig. 2A. In comparison to the conventional air bath oven, the miniaturized element enables rapid heating/cooling rates with reduced power consumption and increased compactness. Fig. 3 shows the optimized laboratory prototype of a miniaturized SEC detector using an YSZ (3 mol-% Y_2O_3 stabilized ZrO_2) tube with sintered Pt electrodes on the outer and inner side, and mantled in a heated quartz glass tube. The new detector has a reduced size and a working electrode, which is sintered on the outer side of the YSZ tube, thus increasing the total surface

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area of the available triple phase boundary (TPB) sites. This enhances the intensity of electrochemical titration of incoming hydrogen in the sample, further decreasing LLOD.

Results

The analysis of hydrogen peaks in Fig. 1 showed that reducing the column length by half, resulted in hydrogen peak areas according with the amount calculated by Faraday's law with an error < 5 %, down to the trace concentration range (~0.2 vol.-ppm) at 600 °C.

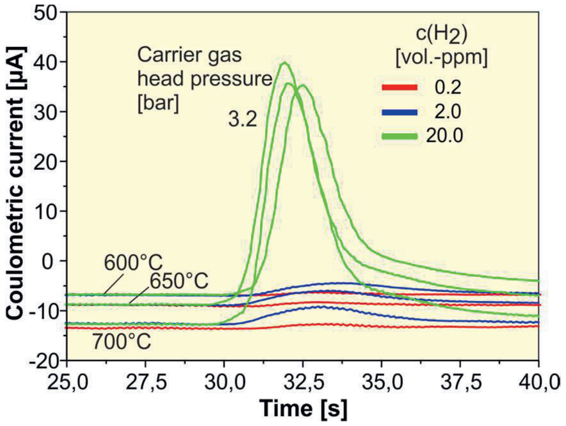

Fig. 1 H_2-Peaks for 1 m mol. sieve 13X + 1 m silica gel-Gel packed GC columns, carrier gas flowrate: 31,5 mL/min, detector temperature: 600-700 °C, injected H_2 concentration: 0.2-20 vol.-ppm.

The first prototype of the miniaturized column oven already meets the required heating (10 K/min) and cooling (30 K/min) rates but with an undesired large power consumption > 100 W [4]. Fig. 2B shows that the improved prototype offers clear advantages in terms of decreased heating power consumption (< 80 W), much faster heating rates (~ 15 K/min) due to the reduced thermal mass and rapid cooling rates (~80 K/min) due to the efficient heat dissipation from the rough surface of the 3D-printed structure. More linear temperature ramps and higher end- point temperatures were observed for stepwise increase in heating power (~ 5 W/min) in comparison to constant heating**.** The miniaturized SEC detector is being tested for gas tightness and initial potentiometric characterization in laboratory.

References

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Illustrations, Graphs, and Photographs

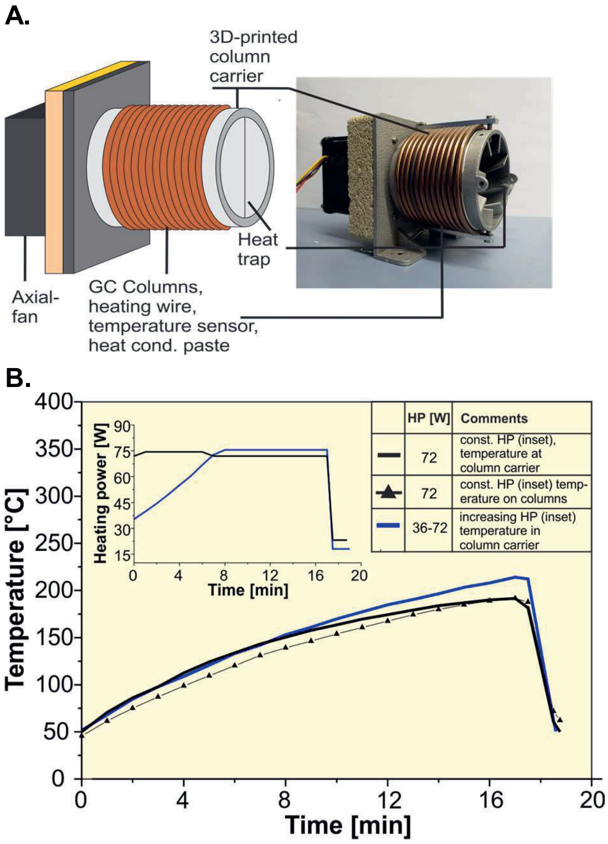
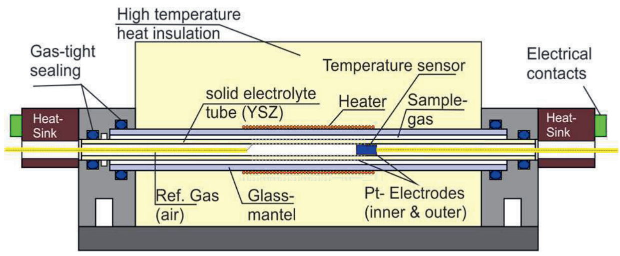


Fig. 2. **A.** Improved prototype of a miniaturized GC column oven. **B.** Heating/cooling ramps for the improved prototype. Heating power (HP) and resp. experimental conditions are listed in the inset table.



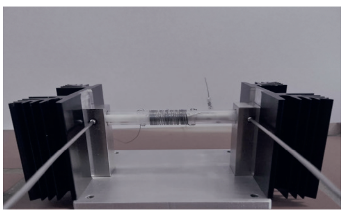


Fig. 3.

Schematic (above) and picture (below) of miniaturized SEC detector laboratory prototype