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CuO-Loaded Porous SiO_2 Fibers for H_2S Detection

Sebastian Werner[1], Christoph Seitz[1], Bernd M. Smarsly[1]
[1]Justus-Liebig University Giessen, Institute of Physical Chemistry,
Heinrich-Buff-Ring 17, 35392 Giessen, Germany
sebastian.werner@phys.chemie.uni-giessen.de

Abstract:
We present a new functional material as sensing layer for hydrogen sulfide (H_2S) detection. The sensing mechanism is based on percolation effects in the cupric oxide (CuO) – copper(II)sulfide (CuS) system. By rational design of CuO/SiO_2 nano-composite fibers structural stabilization during CuO-CuS phase change can be achieved. This leads to significant improvement in the cycle stability of this new sensor type. A detailed study of the synthesis and the influence of its various parameters on the sensors performance will be shown. This comprises, amongst other methods, nitrogen physisorption, electron microscopy and resistive type sensing measurements under controlled temperature in defined gas atmospheres.

Key words: hydrogen sulfide, cupric oxide, gas detection, percolation effect, biogas

Introduction

Hydrogen sulfide (H_2S) is an unwanted by-product in production of biogas as well as in natural gas sources. High toxicity and corrosive nature lead to harm of man and machine. Therefore H_2S detection and quantification are of great importance to avoid poisoning of workers and to protect metal surfaces and catalysts.[1][2]
Electrochemical sensors (ECs) are frequently used in this field due to relatively low cost, low energy consumption and high selectivity. However the utilization of liquid electrolytes result in a maximum operating temperature. Gas sensitive, semiconducting metal oxides like tin dioxide (SnO_2) present an alternative sensor type. During H_2S exposition a reaction between the gas and the adsorbed oxygen on the semiconductor surface takes place, which results in a change in conductance. Due to the utilization of the solid oxide phase the thermal stability is high compared to electrochemical cells. However, as can be easily guessed, this sensor type does not offer the inherent selectivity to sulfur containing gases as the ECs. By doping of polycrystalline tin oxide (SnO_2) with CuO an increased sensitivity to H_2S by more than three orders of magnitude could be achieved. The phase transition of CuO to CuS at moderate temperatures (ca. 150 °C) leads to a selectivity to H_2S.[3] Moreover, pure CuO has been used for H_2S detection showing highest sensitivity and selectivity. Reason is the before mentioned specific reaction between CuO and H_2S to CuS below 200 °C, which is accompanied by a change in conductance of more than four orders of magnitude. At higher temperatures, the reverse reaction is favored, which enables the subsequent regeneration of the sensor after H_2S detection. However, during the phase transition the specific molar volume changes drastically which causes problems with the (nano)structure and results in poor cycling stability.[4][5]

Stabilization Concept

The here presented approach uses a composite material based on mesoporous silica (SiO_2) fibers (fig. 1, a) infiltrated with CuO nanoparticles.

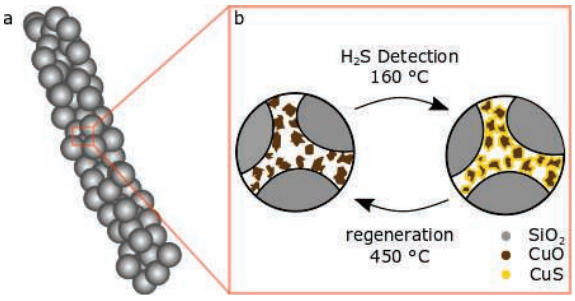

Fig. 1. The schematic shows a microscopic model of the sensing and regeneration (b) of the mesoporous SiO_2/CuO composite fiber (a).

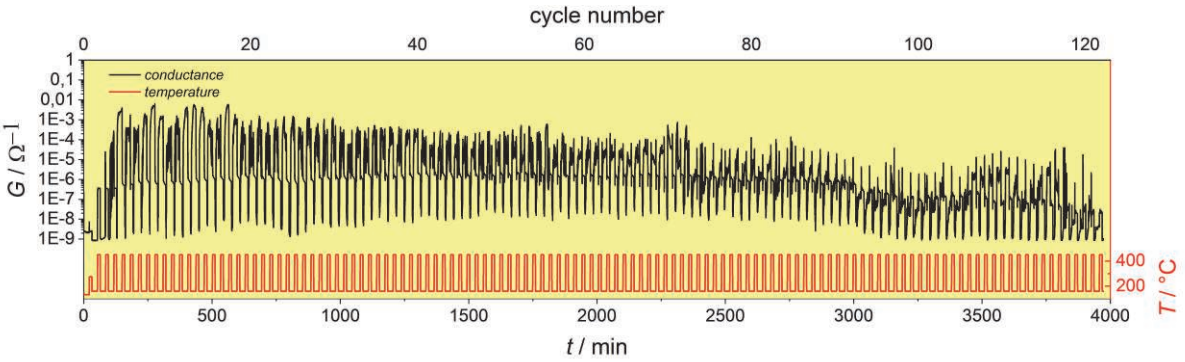

Fig. 2. Longterm conductivity measurement under exposure of 10 ppm H_2S in synthetic air with detection at 160 °C and regeneration at 450 °C.

By partially loading the pores with CuO particles the reduced pore volume and the silica matrix (fig. 1, b) are used to stabilize the cupric oxide during H_2S exposure and compensate the volume expansion caused by the phase transition.

Infiltration and Sensing

Methods for optimization of the CuO pore loading procedure and its influence on the sensor behavior were systematically studied. Sensors were tested in defined gas atmosphere and show percolation induced conductance increases due to H_2S exposure at 160 °C and conductance decreases at 450 °C due to regeneration (fig. 2).

Conclusion

Using mesoporous CuO/SiO_2 composite fibers result in an increase of stability from a few to more than 100 sensing and regeneration cycles.

Acknowledgements

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