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Electrochemical Sensors - at the Heart of Dräger Gas Detection Systems

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Abstract:

Dräger offers a wide variety of gas detection systems for medical applications, potentially explosive gases in hazardous atmospheres, breath alcohol and toxic gases in breathing air. Among our detector portfolio electrochemical sensors belong to our key technology, which we try to improve continuously in terms of sensitivity, selectivity and stability.

Ionic Liquids electrolytes display a huge electrochemical “open window” with negligible background currents. They can be designed task specific for the application they are used in and besides outstanding chemical inertness they offer the intrinsic advantage of being nonvolatile, which makes it possible to construct sensors that even can be used under extreme climatic conditions which e.g. can be found for H_2S monitoring under dry atmospheric conditions e.g. in oil fields in deserts.

In our lab electrochemical H_2S detectors using an ionic liquid as electrolyte have been realized with excellent response characteristics for concentrations ranging from ppb-level up to high ppm-levels. The sensor shows a linear signal and fast response and recovery times together with excellent selectivity.

Key words: gas detection, H_2S, ionic liquid electrolyte

Introduction

Proper choice of the electrolyte plays a major role in electrochemical gas sensor design. The electrode/electrolyte/gas three phase boundary together with the applied potential determines the sensors properties as e.g. stability, sensitivity and selectivity. Moreover the overall size of the sensor, and thus of the resulting instrument, is a consequence of electrode size and electrolyte choice. Aqueous electrolytes tend to dry out upon exposure to warm, dry atmospheres and therefore relatively large electrolyte reservoirs are needed for such a sensor in order to reach an appropriate lifetime even under dry climatic conditions.

We screened among combinations of different Ionic Liquid (IL’s) and electrode materials and finally choose 1-Ethyl-3-methylimidazolium acetate (EMIMace) as electrolyte and CNT (Carbon Nano Tube) casted on a porous Teflon membrane as sensing electrode for H_2S as analyte.

Experimental

The experiments reported here have been performed using Drägers XS-sensor housing, which has cylindrical 2x3cm (outer diameter and overall length) design. The major electrochemical cell setup like sizes of the electrodes and distances between electrodes together with a three electrode cell setup follow Drägers conventional fabrication techniques. Sensors have been biased to constant working potential using conventional potentiostats. A pseudo reference electrode consisting of platinum/platinum oxide in contact to electrolyte, saturated with oxygen from ambient atmosphere and a screen printed platinum electrode as counter electrode have been used. The CNT-film sensing electrode was homemade from pretreated purified multi walled CNT´s which were casted on a porous polymer membrane which allows gas entry.

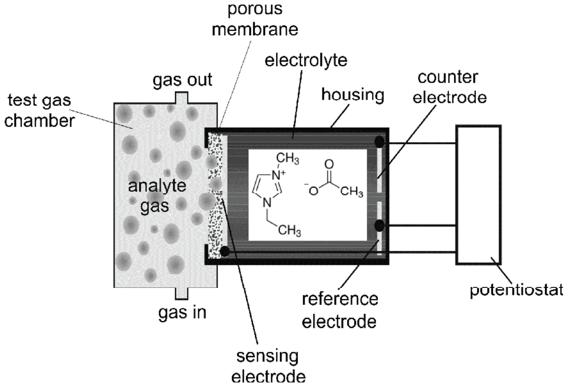


Figure 1. Schematic representation of sensor setup used for amperometric measurement of H_2S

Prior to use EMIMace, purchased from Sigma Aldrich in 97% purity, had to be purified according to a procedure consisting of a first dilution of EMIMace in acetonitrile (ACS reagent from Sigma Aldrich) followed by extensive stirring of the mixture with charcoal followed by chromatography of the black suspension over a solid Al_2O_3 phase. Afterwards acetonitrile was evaporated at elevated temperatures.

As model analyte for this first preliminary study H_2S has been chosen because sensing of hydrogen sulfide is well established in many products and well understood (1) and its importance in field monitoring devices is continuously growing.

The test gas was supplied using a conventional heated permeation chamber (Model 150 Dynacalibrator® from VICI Metronics) for concentrations below 1,5ppm H_2S and certified test gas cylinders for the higher concentrations. Mass flow controllers have been used to ensure reproducible mixing of gases and fast exchange of the test gas in front of the sensor. Humidity, temperature and pressure has been monitored in order to ensure correct gas handling and experimental conditions. The sensor was mounted to a specially designed adapter which ensured free diffusional analyte supply conditions and fast gas exchange rates. The humidity and temperature of the test gas and sensor environment was measured and could be varied widely. Measurements reported here were taken at room temperature and under laboratory atmosphere conditions.

Results and Discussion

Upon switching the sensors gas environment from clean air to a H_2S/air mixtures an oxidation current can be observed at the sensing electrode. In these experiments the gas exchange rate in the test gas chamber in front of the sensor has been very fast in order to have a complete change in atmosphere within several hundred milliseconds. Figure 2 shows the sensors response to changing H_2S concentrations from 0ppm to ~200ppm and back. In order to evaluate the quality of the sensor signal the background current I(Zero) was determined as average of the current measured during the last 60s before gas exchange. The signal current I(Gas) as average of the last 60s of analyte exposure and I(End) as average of the last 60s of the experiment (= 6min after analyte exposure ends). The corresponding sensor output is marked with a grey box. Forward signal and backward signal are the corresponding values as difference between I(Gas) and I(Zero) respectively I(Gas) and I(End). The rising time t(0-90) has been determined as time between the begin of analyte detection and reach of 90% current. t(100-10) is defined between end of H_2S exposure to reach of 10% backward current. Sensitivity was defined as quotient of signal fwd. in µA and analyte concentration in ppm.

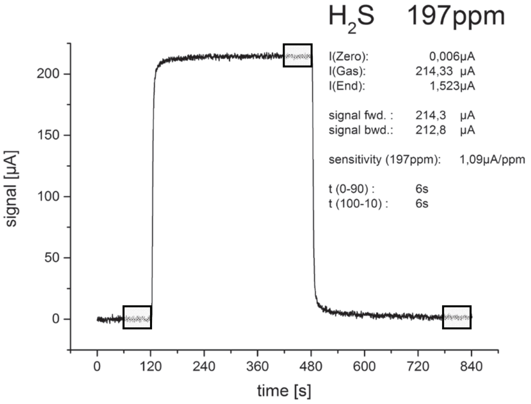


Figure 2. Sensor response upon ~200ppm H_2S; 0-120s:dry air, 120-480s:H_2S/dry air, 480-840s:dry air

The curve shows a stable response of the sensor with almost now drift in the H_2S signal part. Comparison of signal fwd. and signal bwd. prooves that the sensors response is highly reversible and the response times for rise and decay of the signal are the same within the accuracy of the experiment.

The corresponding results for ~270ppb as the lowest concentration used in this study is displayed in figure 3.

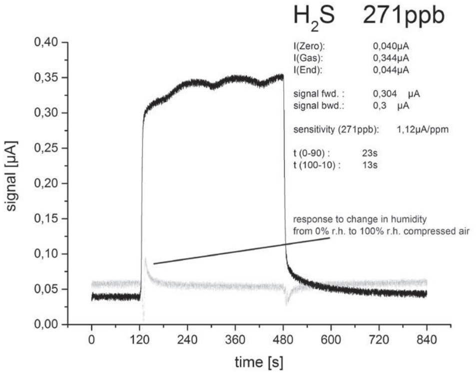


Figure 3. Sensor response upon ~270ppb H_2S and response to a sudden change in ambient humidity; black line-0-120s: dry air, black line-120-480s: dry air + H_2S, black line-480-840s: dry air; grey line-0-120s: dry air, grey line-120-480s: 100% r.h. humidified air, grey line-480-840s: dry air

The oxidation current for H_2S detection is displayed as black line and still clearly exceeds the signal depicted in gray that has been obtained in a similar experiment where air, fully saturated with water, was used as test gas. Sudden changes in humidity that often occur in real life use of the sensor cause these transient current signals probably due to water interactions at the electrode/electrolyte double layer.

As mentioned before, for these small concentrations highly diluted test gas from a heated permeation chamber was used. The corresponding sensor signals shows a sinusoidal disturbance due to on-off switches of the permeation oven. Beside this, adsorbance effects of the test gas e.g. to the walls of the gas line tubing and test gas chamber becomes increasingly dominant at low concentrations as can be seen from the increase in rising time and decay time.

Even for 1000 fold higher concentrations a reproducible linear response is given. High concentrations do not affect the integrity of the sensor.

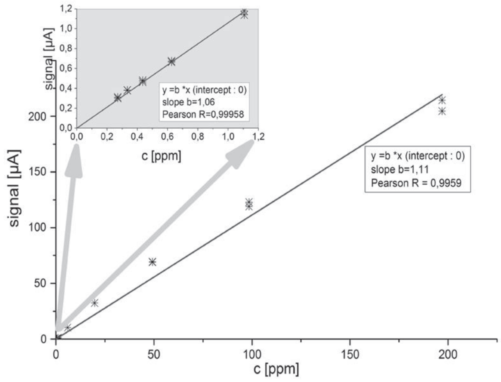


Figure 5. Linear Regressions of sensor data, signal vs. concentration of H_2S

Since February 2010, the American Conference of Governmental Industrial Hygienists (ACGIH®) adopted the threshold limit value (TLV®) recommendation for H2S 8-hour TWA to 1.0 ppm, and the STEL to 5.0 ppm. Both concentrations could easily be monitored with this sensor.

The cross sensitivity of the sensor to a variety of other gases (NO, O_3, B_2H_6, Ethanol, CO, H_2, NH_3, SO_2, AsH_3, H_2O_2, …) has been determined. Only for SO_2 the sensor shows a significant response with sensitivities that are 10 times smaller compared to H_2S.

The zero current of the detector seems to depend slightly on the water content of the electrolyte. I(Zero) shifted towards higher values when the sensor was exposed to very dry atmospheres for a long period of time and the electrolyte was dried out. This effect could be due to instabilities of the pseudo reference used in this study. Water loss of the electrolyte could be monitored indirectly using the sensor weight. Figure 5 shows a series of experiments in which the sensor was repeatedly exposed to 0.6ppm H_2S. In between the exposures the sensor was purged with dry synthetic air for 1h in order to remove water from the electrolyte. The effect on I(zero) can be clearly observed and disappeared on exposure to humid ambient atmospheres.

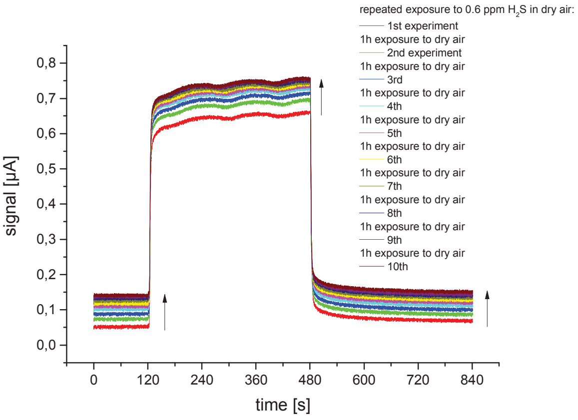
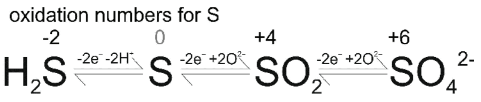


Figure 4. Repeated experiments with 0.6ppm H_2S/air. Sensor was purged with dry air between measurements for 1h

Under all experimental condition the sensor didn´t show any malfunction or loss of electrolytic contact between electrodes even under extreme dry conditions.

Oxidative sensing of H_2S in aqueous electrolytes e.g. sulfuric acid [2] is already known for a long time [3] and numerous products based on these sensors are already out on the market, fulfilling most of the needs of customers satisfactory. Nevertheless, for applications under high temperature stress and low humidity these sensors suffer from disadvantageous loss of water through evaporation from the corresponding electrolytes which in the end cause a sensor malfunction. In this case Ionic Liquid electrolytes

The reaction pathway for the oxidation of H_2S in aqueous media has widely been investigated [4, 5] and can be summarized as depicted in scheme 1.



Scheme 1: reaction pathway for oxidation of H_2S in aqueous media

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The oxidation involves a multistep mechanism with increasing number of O^{2-} bound to sulfur in the respective products. Under very dry, non-aqueous conditions this mechanism becomes unclear.

In our test configuration, using a sensor with a working electrode of same size and the same test gas equipment, a sensitivity of 2µA/ppm had been found for sensors containing sulfuric acid as electrolyte. For the IL electrolyte together with the CNT electrode we measured a sensitivity of ~1µA/ppm.

Assuming that the 8 electron pathway depicted in scheme 1 is valid for aqueous electrolyte this finding suggests a 4 electron mechanism which can't be explained by scheme 1 because sulfur in oxidation state +2 does not appear as any product.

Another possible explanation would be that the overall amount of oxidized gas varies between the two configurations and or the formation of a mixture of different products occurs. Our ongoing research comprises electroanalysis of the oxidation reaction under controlled atmospheres at different temperatures and long term stability tests followed by thorough analysis of the electrolyte and electrode in order to examine the product formed in the oxidation steps.

References

[1] Sudhir Kumar Pandey, Ki-Hyun Kim, Kea-Tiong Tang, *Trends in Analytical Chemistry*, **Vol 32**, p.87-99, (2012)

[2] Silvester, D. S. and Compton, R. G., *Z Phys. Chem*., 220, p.1247-1274, (2006)

[3] John M. Sedlak, Keith F. Blurton, *Talanta*, **Vol 23 (6)**, p.445-448, (1976)

[4] Najdeker, E. and Bishop, E., *J. Electroanal. Chem.*, **41** , p.79-87, (1973)

[5] Ramasubramanian, N., *J. Electroanal. Chem.*, **64**, p.21 -37, (1975)