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A solid electrolyte sensor for trace gas analysis

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ABSTRACT

Coulometric solid electrolyte sensors based on yttria-stabilized zirconia were characterized with respect to the electronic conductivity of the solid electrolyte and to their electrochemical activity of oxygen, hydrogen and hydrocarbon conversion. Sensor parameters like the temperature dependency of the electronic conductivity as well as the elevated noise of the coulometric cell at the working temperature determine the limit of detection of coulometric titration. Here we describe investigations on these parameters and approaches to shift the lower detection limit into the ppb-range. Furthermore, it is shown that a coulometric solid electrolyte sensor, positioned behind a gas chromatographic separation unit, allows simultaneous, calibration-free and long-term stable detection of different oxidizable components and oxygen.

1. Introduction

Normally, the measurement of a broad range of very small amounts of volatile substances in gas mixtures with concentrations below 1 vol.-ppm requires the use of expensive, space-occupying and immobile mass spectrometers [1,2]. Although this well accepted and commercially available technology provides very low detection limits, low-cost systems could reach much broader application, for example in clinical routine analysis of human breath gas.

Coulometric solid electrolyte cells are well known devices for measuring oxygen [3], hydrogen [4], hydrocarbons [5] and other oxidizable or reducible components of gaseous mixtures. They are successfully used for a variety of applications [6–8]. In most cases, the key component of such devices is an oxygen-ion-conducting material like yttria-stabilized zirconia (YSZ) with an ionic conductivity many orders of magnitude higher than its electronic conductivity.
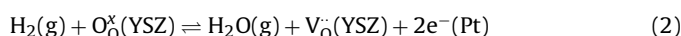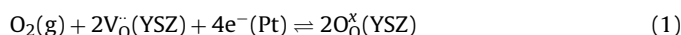
One noticeable advantage of the coulometric sensor principle consists in its strict operation due to Faraday's law, providing high long-term stability without baseline drifting and thus a calibration-free operation. Up to now, the lower limit of detection of coulometric sensors for the relevant gases amounts to 10 vol.-ppm [9,10]. This limit is determined by

- the electronic conductivity of the electrolyte material [11],
- the noise of the current through the electrochemical cell, and

- the design of the circuits providing the constant potential and measuring the cell current.

In this work investigations on parameters influencing the lower limit of detection of coulometrically operated solid electrolyte cells are presented. Possibilities to shift this limit into the ppb-range are shown. Furthermore, a measurement system containing such an optimized coulometrically operated solid electrolyte cell is presented acting as detector for a gas chromatographic separation unit. It is demonstrated that even the very low concentration of atmospheric H_2 can be determined with this kind of coulometric detector.

The principle of the coulometrically operated solid electrolyte sensor, shown in Fig. 1, is based on the complete oxidation or reduction of the gas component to be measured at the working electrode of a solid electrolyte cell resulting in an electronic current. Detectable components are gases existing as ions in the solid electrolyte or are gases which could react with these ions. In case of YSZ as electrolyte material, the reactions of oxygen and hydrogen at the working electrode can be written in the Kröger–Vink notation according to Eq. (1) and (2).

$$O_2(g) + 2V_O^{\cdot\cdot}(YSZ) + 4e^-(Pt) \rightleftharpoons 2O_O^x(YSZ) \tag{1}$$

$$H_2(g) + O_O^x(YSZ) \rightleftharpoons H_2O(g) + V_O^{\cdot\cdot}(YSZ) + 2e^-(Pt) \tag{2}$$

The amount of analyte molecules which is converted at the working electrode results with Faraday's law from the electrolysis current I and the residual current I_R caused by electronic conductivity. Considering also the flow of the measuring gas dV/dt, the

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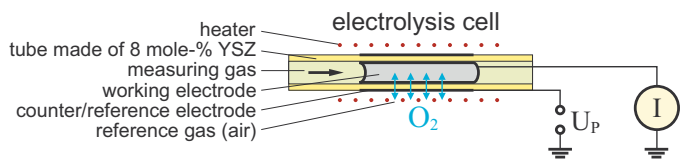guth@ksi-meinsberg.de (U. Guth), michael.mertig@tu-dresden.de (M. Mertig).

Fig. 1. Schematic of a coulometric solid electrolyte sensor.

concentration x of the gas component to be measured is determined according to Eq. (3).

$$x = \frac{I - I_R}{zF} \cdot \frac{V_M}{dV/dt} \tag{3}$$

F is Faraday's constant, z is the number of electrons transferred per molecule and V_M is the molar volume. Therefore, the lower detection limit of such a coulometric detector depends on the absolute value of I_R and its noise, both resulting from the solid electrolyte material properties and the sensor temperature. Due to the fact that YSZ is already widely used as base material for sensors, fuel cells and oxygen generators, the properties of this material are well known [11,12]. The ionic and electronic conductivities of this material in the temperature range between 800 °C and 1200 °C are depicted in Fig. 2 showing the contributions of the electronic conductivity of holes (h) and of electrons (e) [11].

The electronic current I_R caused by the hole conductivity flowing through a disc of YSZ with an area A and a thickness d is given by Eq. (4).

$$I_R = \frac{ART}{Fd}\left[\sigma_h(p_{O_2}^I)\left\{\left(\frac{p_{O_2}^{II}}{p_{O_2}^{I}}\right)^{1/4} - 1\right\}\right] \tag{4}$$

R is the universal gas constant, $p_{O_2}^I$ is the oxygen partial pressure in reference gas and $p_{O_2}^{II}$ is the oxygen partial pressure in the measuring gas. Following this equation, a usual coulometric electrolysis cell ($A = 1\,cm^2$, $d = 1\,mm$, $p_{O_2}^I = 20.6\,kPa$ and $p_{O_2}^{II} = 2.7 \times 10^{-4}\,Pa$) operated at 800 °C with thermal fluctuations of $\pm 1\,K$ shows residual current deviations of $\pm 37\,nA$. Those deviations cause an error of ± 26 vol.-ppb in hydrogen detection at the gas flow $dV/dt = 10\,ml/min$.

Furthermore, the noise of the electrolysis current is influenced by turbulences of the measuring gas resulting in fluctuations in substance turnover at the working electrode. To get a constant reaction rate, this turbulence has to be avoided or minimized so that the frequencies of the generated noise spectrum are high enough to be
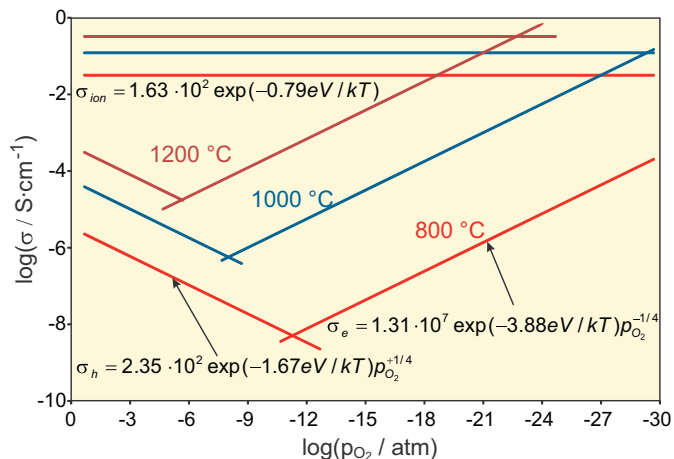

Fig. 2. Ionic and electronic conductivity of 8 mol-% YSZ depending on oxygen partial pressure at different temperatures according to [11].
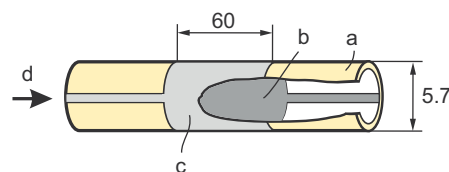

Fig. 3. Schematic drawing of the used coulometric sensor (measures in mm): (a) solid electrolyte tube made of 8 mol-% YSZ, (b) platinum working electrode, (c) platinum reference electrode, (d) measuring gas flow.

filtered out by low-pass filter. This parameter is difficult to predict but can be estimated by utilizing complex simulations taking the electrode morphology into consideration.

Due to the above-mentioned advantages of coulometric sensors, they have been used as detectors in gas chromatographic systems already [13,14], where the gained sensitivities resulted in lower detection limits of >10 vol.-ppm. A chromatogram showing the sensor current I as a function of time t, allows to resolve peaks of different gas components. The peak area equals to the amount of charge Q transferred during the oxidation or reduction process of the analyte molecules. The amount of substance n of the gas component can be determined with Faraday's law according to Eq. (5), where I_B is the baseline current.

$$n = \frac{Q}{zF} = \frac{1}{zF}\int_{t_1}^{t_2}(I - I_B)\,dt \tag{5}$$

2. Experimental notes

The coulometric sensor used in this work is shown in Fig. 3. It consists of a tube made of 8 mol-% YSZ with the outer diameter 5.7 mm and the wall thickness 1 mm.

The tubular platinum electrodes on the inner and the outer surface of this tube are 60 mm in length. Between the working (inner) and the reference (outer) electrode a constant potential of −400 mV is applied by a self-made potentiostat. As shown in Fig. 4, two different designs of electronic circuits of the self-made potentiostat were examined when combining the sensor with a gas chromatograph MG1 (SRI Instruments Europe GmbH, Bad Honnef, Germany).

Fig. 5 shows a scheme of the measuring system, consisting of a sample injection port, one or more gas chromatographic columns and an YSZ cell acting as detector. A gaseous sample, containing volatile trace components, is injected into a carrier gas flow of the gas chromatograph either by using a sampling loop or by injecting with a syringe through a septum. A column packed with molecular sieve provides the separation of hydrogen, methane and other volatile components of the sample gas mixture within 10 min at 50–200 °C column temperature in Ar carrier-gas flow of 20 ml/min.
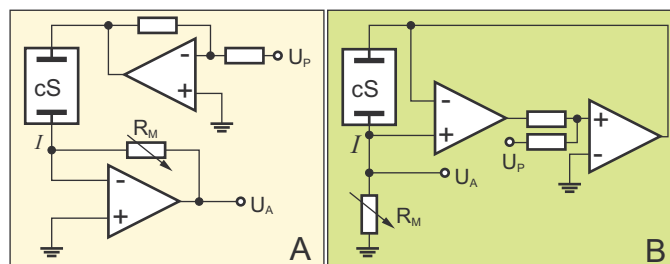

Fig. 4. Different designs of electronic circuits for controlling the coulometric sensor according to Fig. 3: (A) current–voltage-converter ($I = U_A/R_M$), (B) variable current measuring resistor at the working electrode ($I = U_A/R_M$); coulometric sensor (cS), applied polarization voltage (U_P).