

Enhanced studies on the mechanism of gas selectivity and electronic interactions of SnO₂/Na⁺-ionic conductors

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Abstract

The selectivity of metal oxide gas sensors (MOG) can be improved significantly by forming composites with solid ionic conductor additives. First investigations were done using model composites of SnO₂/Natrium Super Ionic Conductor (NASICON) with the result of a huge sensitivity enhancement to substances ending with R–OH, R–HO or R–COOH groups and a reduction of sensitivity to other gas components. This selectivity of the new composite to those functional groups could be confirmed by catalytic conversion measurements with FTIR-spectroscopy at three gas components, respectively. The specific conductivity of the NASICON containing composites is significantly lower than that of pure SnO₂. Advanced studies show that the activation energy of the bulk-conductivity increases by approximately 30% in the presence of NASICON. In spite of high volume parts of NASICON (20%), no polarization effects were found (a complete Ohmic current–voltage behavior) and mainly the resistive part of the electrical impedance is influenced.

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1. Introduction

Metal oxide gas sensors (MOG) based on tin oxide are attractive devices for the detection of numerous gas components like volatile organic compounds (VOC), CO, NH₃, H₂, etc. [1]. They own high but different sensitivities to specific gas components depending on the gas type and concentration. The mechanism is determined by molecular specific surface reactions with chemisorbed oxygen in surface states [2]. Correspondingly, the main drawback of the MOG is their low selectivity and therefore poor ability of molecular identification. Therefore, in the last years many efforts were devoted to improve the performance of this type of sensor. In special applications the adjustment of the operation temperature, optimized on the kind of gas, may be sufficient to get enough selectivity. As shown in recent years higher quality results in gas analysis could be obtained with this type of sensor by numeric analysis of so called conductance-over-time profiles, which are

sampled during periodic variation of the working temperature [3]. However, independent of the kind of sensor operation, the addition of classical materials like noble metals (Pt, PdO [4,5], etc.) or several metal oxides finely dispersed at the surface of the SnO₂ grains [6–8] or doping of metals [9] is still important to cultivate the sensitivity performance for special applications.

Rather new categories of additives for MOG are solid electrolyte powders [10]. The investigation of composites with these families of additives is still at the beginning. Not only the volume part of the ionic conductor additives in the layer can be varied, but also the type of mobile ions (sodium, lithium, silver, protons and oxygen), their concentration and the ionic conductivity σ . If at all, and how significant these parameters influence the gas sensitivity and the electronic behavior of the composite layer is of great interest and the underlying mechanisms are still a matter of research.

In a first step different SnO₂/Natrium Super Ionic Conductor (NASICON) composites were investigated with respect to their dc-conductivity and their sensitivity to various gas components [11]. For these investigations NASICON (Na_{1+x}Zr₂Si_xP_{3-x}O₁₂, $0 \leq x \leq 3$) was chosen, because the Na⁺-ion content and the ionic

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conductivity can be varied without great effect on the framework structure [12]. Furthermore, the structure is stable in humid air and at high temperatures (>900 °C).

The sensitivity S was defined as the relative conductivity change (Eq. (1))

$$S = \frac{G_i - G_0}{G_0} \quad (1)$$

and was shown to be significantly higher for the composites with high Na⁺-ion content (e.g. NASICON, $x=3$) in comparison to pure SnO₂ when exposed to molecules with R–OH, R–CHO or R–COOH functional groups [11]. In contrast, no sensitivity enhancement is observed in the presence of 2-propanol, propanone and ethylacetate and many other organic and inorganic gas components like H₂, NH₃, methane, propene, etc. The reason for this surprising behavior is still under investigation, but it is a matter of fact that it is possible to improve the selectivity of MOG to some substances with special functional groups by adding NASICON-additives with high Na⁺-content.

Simultaneously the specific electronic conductivity σ of the composite layers drops with increasing Na⁺-concentration in the admixed NASICON. The conductance of the layers of SnO₂/NASICON, $x=3$ composite is even significantly lower as compared to an isolator containing composite (SnO₂/Al₂O₃) with identical volume ratio of 80%/20%. This drop in conductivity was interpreted to be due to e⁻/Na⁺ interactions across the SnO₂/NASICON-interfaces [11].

In this paper results of advanced studies are presented concerning the electronic and the catalytic properties of different SnO₂/NASICON composites in order to elucidate the mechanism of gas interaction on such sensitive layers.

2. Experimental

2.1. Preparation

The SnO₂- and the NASICON-powders were prepared separately by sol–gel methods, which are described in ref. [10], ground and sintered. They were characterized with XRD, BET, SEM and particle size distribution analysis and the results were published in ref. [11]. The obtained powders of SnO₂ and NASICON were now blended in volume ratio of 80%/20%. This mixture was used with an organic carrier for screen-printing, for preparation of discs or directly as a powder mixture and sintered at $T=750$ °C for 20 min, respectively, to get the final composite.

Different samples were prepared, i.e. (i) a screen printed four-fold sensor-chip (Fig. 1a), connected with gold wires for dc-conductivity and impedance measurements, (ii) sintered powder-blocks (10 mm × 3 mm × 1 mm) with four embedded platinum electrodes to study the dc bulk conductivity and (iii) poured powder samples in a quartz-boat and several stacked discs of the sintered composite were prepared in a cylindrical quartz reactor, for catalytic conversion experiments (Fig. 1b).

2.2. Gas sensitivity experiments

Each sensitive layer (Fig. 1a) was printed on microstructured, thin-film inter-digital gold electrodes and was contacted by two bonded wires. Before starting the measurements, the sensitive layers were conditioned for several hours at constant temperature $T=250$ °C in the actual gas composition (flow $Q = \Delta V/\Delta t = 100$ ml min⁻¹) adjusted with the gas mixing setup shown in Fig. 1c. Sensitivity tests were performed by measurement of the dc-conductivity G_0 in synthetic air ($p_{\text{H}_2\text{O}} = 13,000$ ppm) and G_i with an additional concentration of the desired gas component ($c=400$ ppm). The relative response S (Eq. (1)) at this well defined concentration step was calculated for a huge number of gas components and published elsewhere [11].

Impedance measurements were performed on the identical samples. Each sensitive layer in the quartz glass reactor was connected with two gold wires, which were separated into a four-wire connection outside. The frequency of the applied voltage was varied in a range of 100 mHz < f < 1 MHz at $U_{\text{ac}} = 10$ mV ($U_{\text{dc}} = 0$ V).

2.3. Gas reaction studies on poured powders and pressed discs

Some investigations of the catalytic behavior were done on poured powder in a streaming propene containing gas mixture (0.5% C₆H₆, 2% O₂ in N₂, $Q = 10$ ml min⁻¹) [13]. The concentrations of the provided gas components and the products of conversion (CO, CO₂ and H₂O) were determined by FTIR analysis downstream at the gas outlet of the reactor. To measure the samples under nearly equal conditions, the BET-values of the different powders were determined firstly and the amount of powder in the quartz boat was related to equal surface areas. These measurements were done on powders of pure SnO₂ and SnO₂/NASICON, $x=2.2$ (60/40 vol.%) composites.

In another test, two different gas mixtures (1 vol.% of 1-propanol and 2-propanol, in dry synthetic air, respectively, $Q = 100$ ml min⁻¹) were converted on the surfaces of a stack of six sintered discs (Fig. 1b). The selected SnO₂/NASICON, $x=0$ and SnO₂/NASICON, $x=3$ (80/20 vol.%) composites show similar BET-surface areas; therefore, the same numbers of discs were inserted directly in the quartz reactor without using a boat.

For determination of the conversion rate and the conversion onset-temperature, the gas mixtures were dosed and the temperature was stepwise increased starting at 100 °C. The integral of absorbency measured in a defined wavelength range was used as a concentration proportional value $c(T)$ of the corresponding gas component. Details of measurement are summarized in Table 1. To provide a comparable value of conversion for all different test gas components, the actual conversion kinetics can be interpreted by the conversion function which is the quotient of the measured concentration $c(T)$ divided by the maximum measured concentration c_{max} . The constant c_{max} is the concentration of the reacting educts at room temperature ($T \ll T_{\text{onset}}$) and of the product component (value at T_{max}), respectively.

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