Chemosensitive properties of electrically conductive Cu(I) compounds at room temperature

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ARTICLE INFO

ABSTRACT

Changes of the electrical conductance of a number of inorganic copper(I) conductive compounds including $Cu_{12}Sb_4S_{13}$, Cu_2O, CuI, CuBr and CuCl were tested on exposure to different gases and vapors, including ammonia, nitrogen monoxide, octanethiol, hydrogen chloride, acetic acid, formic acid, ethanol, humidity and piperidine. The sensitivity of the resistivity to ammonia was estimated as 2.7%/ppm for CuBr, 1.4%/ppm for Cu_2O, 1.2%/ppm for CuCl, 0.013%/ppm for CuI, but only 0.0028%/ppm for $Cu_{12}Sb_4S_{13}$. The highest selectivity for ammonia was observed for $Cu_{12}Sb_4S_{13}$. The sensitivity patterns of these materials to the tested gases and vapors are very different which makes them applicable for sensor arrays for identification and quantification of these species.

1. Introduction

Accurate and reliable sensors for gaseous and volatile compounds are important for industrial, scientific, environmental and medical applications, for monitoring of security regions and chemical processes, to control combustion engines and waste incineration facilities and for other applications. They are often expected to work under harsh conditions, for example in chemically aggressive media, at high pressure or temperature. Solid-state inorganic materials are the most promising candidates for these applications due to their high stability under such conditions.

Gas sensors are usually based on metal oxide semiconductors (i.e. tin oxide, zinc oxide or titanium dioxide). Electrical properties of semiconductor compounds depend on the composition of the surrounding gas atmosphere. Based on these effects, the development of conductometric gas sensors using thin films or porous ceramics of n-type semiconductor oxides, such as ZnO and SnO_2, started in 1962 [1]. These sensors work at high temperature, typically 350 °C for SnO_2-based systems. In this case, the surface conductivity of the sample is modified by adsorption of gases and related electrostatic effects. Their electrical behavior is governed by the formation of double Schottky potential barriers at the interface of adjacent grains, caused by charge trapping at the interface. In an oxidizing atmosphere, the oxide surface is covered by negatively charged oxygen adsorbates and the adjacent space charge region is electron-depleted. Hence, a metal oxide layer displays a high resistance. Under reducing conditions, the oxygen adsorbates are removed by reaction with the reducing gas species and the resistance of the oxide layer decreases. This unspecific reaction is used for the detection of reducing gases. The main drawback of this sensing principle is its resistive response to almost any reducing gas.

Another way for developing conductometric gas sensors is based on the transfer of approaches of wet chemistry to solid and gaseous phases. For example, the development of ammonia sensors requires an exploiting of receptor molecules which react selectively with this analyte. The affinity of NH_3 to Ag^+ is well known in aqueous chemistry, similar effects are observed for gaseous ammonia [2]. Consequently, ammonia is adsorbed on the surface of a solid Ag^+ ion conductor, attracting mobile Ag^+ ions and creating a negatively charged region with increased concentration of silver vacancies. This leads to a modification of the resistance of ammonia sensors based on silver halides in the presence of the analyte.

The well known strong affinity of Cu^+ towards NH_3 is the main idea to use copper(I) as a selective receptor for ammonia. This approach was realized by Lauque and co-workers [3–5] suggesting to use copper(I) bromide. The interactions between copper ions and NH_3 leads to the formation of an interfacial layer at the contact
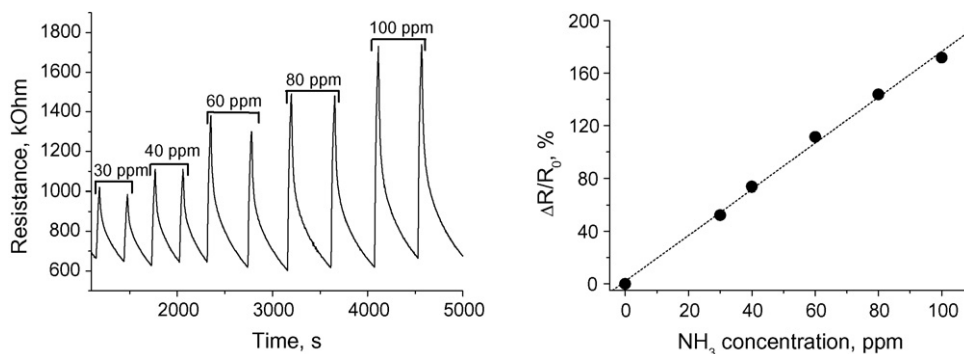

Fig. 1. Response kinetics (left) and concentration dependence (right) of resistance changes of CuBr to different ammonia concentrations. Ammonia was diluted with artificial air.

between the gas phase and the Cu^+ ion-conductor with modified concentrations of mobile copper atoms and copper vacancies. Recently some other copper(I)-ion-conductors were suggested for gas sensing, in particular cuprous oxide for the detection of nitrogen dioxide [6], ethanol [7] and hydrogen sulfide [8] and cuprous chloride for carbon monoxide [9]. The aim of the present work is to investigate the sensing properties of different ionic and mixed conducting copper(I) compounds for gases and vapors, in particular for ammonia.

2. Materials and methods

Cuprous bromide was obtained from Riedel (www.sigmaaldrich.com) and cuprous chloride from Alfa Aesar (www.alfa-chemcat.com). $Cu_{12}Sb_4S_{13}$ was synthesized according to Ref. [10]. The gases NH_3, NO and synthetic air were purchased from Linde (www.linde-gas.de). All other chemicals were from Aldrich (www.sigmaaldrich.com). The electrodes for the conductivity measurements were prepared by photolithographic lift-off technique on oxidized silicon substrates. The thickness of the evaporated gold layer was 250 nm, and a 5 nm chromium sub-layer was used for better adhesion of gold to oxidized silicon. The electrodes had a shape of interdigitized structure with gaps of 5 μm and widths of the contact strips of 10 μm. The electrodes were cleaned before the experiments with a hot "piranha" mixture consisting of 30% hydrogen peroxide and 96% sulfuric acid (1:3, v:v). *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.*

A home-made automated system based on a source-meter (Keithley, www.keithley.com, model K2400) and a high-impedance voltmeter (Keithley, model K617) was used for conductivity measurements [11,12]. The measurements were performed in the quasi-AC pulse mode with two subsequent 1 s long voltage pulses of +50 and −50 mV, respectively; the resistance was measured from the difference of currents to such pulses. The gas mixing system included computer controlled mass flow valves (MKS Instruments,

www.mksinst.com, model 1179) [13,14]. Gases were delivered to the glass flow-throw cell via steel and Teflon tubes. This automated gas-mixing system was used for quantitative determination of the sensitivity of copper(I) materials to ammonia. Other compounds were injected into the cell using a syringe. The vapors were collected from closed volumes above corresponding liquids (1 M aqueous solution was used for gaseous HCl) after at least 30 min equilibration at 25 °C and diluted by air. Mass fractions of the vapors in the measurement cell were estimated as about 0.3% for acetic acid, 1% for ethanol and piperidine, 0.3% for water and 0.02% for octanethiol. NO in nitrogen (320 ppm) was injected into the measurement cell without further dilution. The cell volume was 4.6 mL, and the flow rate was 1.7 mL/s.

Sensing materials were deposited on interdigitated gold electrodes from suspensions of the corresponding copper compounds in acetonitrile (0.12%, w/w) by dropping of 0.5 μL and drying at 70 °C. Then the sensors were heated at 150 °C for 1 h to remove the residual organic solvent and to partially sinter the material. The thickness of sensitive layers estimated by shift of the focus plane of optical microscope was below 2 μm.

3. Results and discussion

The effect of ammonia on the resistance of different copper materials was characterized quantitatively. Ammonia interaction leads to an increase of the electrical resistance (Fig. 1, left). Typical response times are in the range of a few tens of seconds. In the studied range of ammonia concentrations (between 2 and 100 ppm) the resistance changes of all materials were almost linearly dependent on the gas concentration (Fig. 1, right). The recovery kinetics after replacement of the test gas by artificial air was in the range of hundreds of seconds.

The analytical sensitivity of the tested copper compounds to ammonia is demonstrated in Table 1. The highest sensitivity was observed for CuBr, the lowest one for $Cu_{12}Sb_4S_{13}$. These values depend on the transducing factors (the ratio between conductivity

Table 1
Chemosensitive properties of copper(I) compounds towards ammonia

Material	Sensitivity (%/ppm(NH_3))	Kinetic constant of adsorption ((s ppm)$^{-1}$)	Kinetic constant of desorption (s^{-1})		Binding constant (ppm^{-1})	
			Fast	Slow	From fast desorption	From slow desorption
CuBr	2.7	0.0011	0.071	0.0037	0.015	0.30
Cu_2O	1.4	2.30×10^{-4}	0.05	–[a]	0.0046	–[a]
CuCl	1.2	7.70×10^{-4}	0.043	0.0077	0.018	0.1
CuI	0.013	5.90×10^{-5}	0.1	0.025	5.9×10^{-4}	0.024
$Cu_{12}Sb_4S_{13}$	0.0028	–[a]	[a]	[a]	[a]	[a]

[a] The value was not measured/calculated because of too high measurement or fitting error.

changes and amount of the bond ammonia) and on binding constants. The transducing factors depend on the chemical mechanism of ammonia binding and the conductivity characteristics which is different at least for $Cu_{12}Sb_4S_{13}$ which is a metallic conductor instead of a mixed conductor. Assuming that the resistivity changes are proportional to the amount of adsorbed analyte, one can apply a usual approach developed for data analysis in affinity sensors and recently tested also for gas sensor [15]. The approach is based on the Langmuir adsorption model. In this case, the adsorption kinetics can be described as

$$\frac{d\theta}{dt} = k_{ads}(1 - \theta)c_A - k_{des}\theta \qquad (1)$$

or

$$\frac{d\theta}{dt} = -\theta k_s + k_{ads}c_A \qquad (2)$$

where k_s is the apparent binding kinetics ($k_s = k_{ads}c_A + k_{des}$), θ is the coverage of the sensor surface, c_A is the analyte concentration, k_{ads} and k_{des} are the kinetic adsorption and desorption constants, respectively. The solution of Eq. (2) with postulated proportionality between θ and material resistivity gives for the adsorption:

$$R(t) = \alpha \frac{c_A K}{1 + c_A K}[1 - \exp(-k_s t)] \qquad (3)$$

and for the desorption:

$$R(t) = \alpha \frac{c_A K}{1 + c_A K} \exp(-k_{des}t) \qquad (4)$$

where K is the binding constant ($K = k_{ads}/k_{des}$), and α is the proportionality coefficient between surface coverage and measured resistance $R(t)$.

The apparent kinetics of the resistance changes k_s calculated from the initial slope was proportional to the analyte concentration (Fig. 2). Taking into account that $k_s = k_{ads}c_A + k_{des}$, one can calculate the kinetic adsorption constants from the slope and the kinetic desorption constants from extrapolation to zero concentration. The values of k_{ads} are presented in Table 1 (column 3). The highest value of the kinetic adsorption constant was obtained for CuBr. No value was obtained for $Cu_{12}Sb_4S_{13}$ because of a too low signal/noise ratio. It is not surprising that the kinetic adsorption constant correlates well with the analytical sensitivity of the corresponding substance (Table 1, column 2).

Analysis of the desorption demonstrated that the simple mono-exponential model (4) does not provide an adequate fitting of the experimental data: the desorption kinetics was bi-exponential and
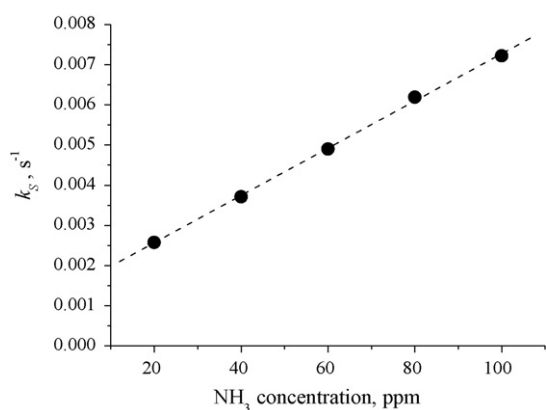
was much better described by the equation:

$$R(t) = \frac{c_A K}{1 + c_A K}[\alpha_1 \exp(-k_{des1}t) + \alpha_2 \exp(-k_{des2}t)] \qquad (5)$$

where $\alpha_1 + \alpha_2 = \alpha$. Interestingly, the characteristic times of these exponents were constant while the contribution of the fast exponent increased with an increase in analyte concentration. The values of these time constants for different materials are shown in Table 1, columns 4 and 5. This behavior does not correspond to the simple Langmuir adsorption model and indicates an additional process influencing the observed desorption kinetics or a heterogeneity of binding sites. Bi-exponential kinetics was also observed for conductometric NO sensors based on nickel phtalocyanine [15].

The almost linear concentration dependencies of the sensing materials indicate that the binding constant should be lower than the reciprocal value of the highest concentrations used for the test, i.e. $K \leq 1/(100 \, ppm)$. Estimation from the kinetic measurements gives approximately such values when the fast desorption kinetic constants are used for calculation (Table 1, column 6). The use of the slow desorption kinetics results in very high-binding constants (Table 1, column 7), which are not compatible with the observed linear concentration dependencies. We therefore assume that the slow component of the desorption kinetics corresponds to another process as, for example, the diffusion of an analyte into the bulk phase of the material.

The compounds selected for the interference test included nitrogen monoxide, octanethiol, hydrogen chloride, acetic acid, formic acid, ethanol, humidity and piperidine. Nitrogen monoxide was selected as another reducing compound, piperidine as another basic compound, octanethiol because of its strong affinity to copper, and water vapor as a typical compound accompanying each analyte in real samples. The results are shown in Fig. 3. CuCl was not included into this test because of experimental difficulties caused by poor chemical stability of this compound. It was demonstrated that $Cu_{12}Sb_4S_{13}$ as a sensing material for ammonia exhibits the highest selectivity: no effect on addition of any interferent was detected.

The sensitivity patterns of Cu_2O, CuI and CuBr and (Fig. 4) to the tested gases and vapors are very different and almost orthogonal for some of the analytes (acetic acid, nitrogen monoxide). Therefore, these materials can be considered as candidates for the development of highly selective resistive sensor arrays for gas and vapor analysis.
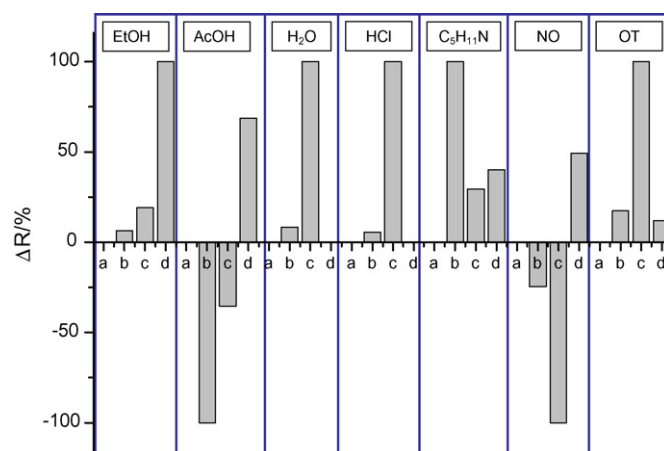

Fig. 2. Dependence of the apparent binding kinetics on the analyte (NH$_3$) concentration. Sensing material: CuI.

Fig. 3. Relative sensitivity of copper(I) compounds to different gaseous and vapors. The data were normalized to maximal response of each analyte. Sensing materials: (a) $Cu_{12}Sb_4S_{13}$, (b) CuI, (c) CuBr, and (d) Cu_2O. *Abbreviations of analytes*: EtOH, ethanol vapor; AcOH, acetic acid vapor; $C_5H_{11}N$, piperidine vapor; OT, octanethiol.
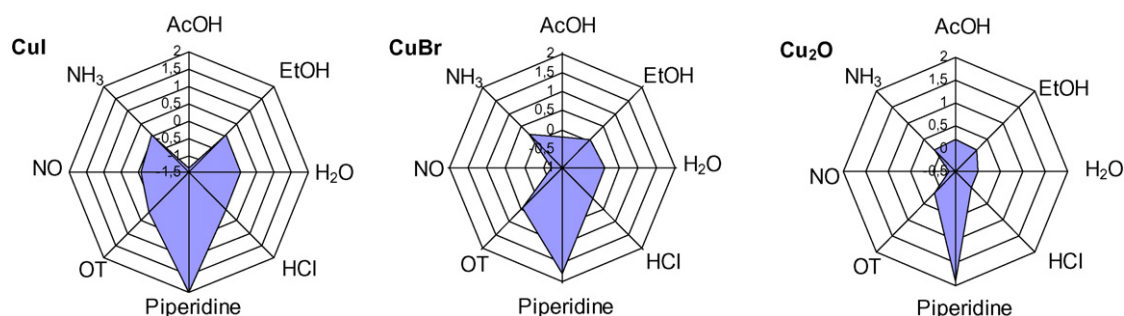
Fig. 4. Resistive sensitivity patterns of the Cu(I) compounds. The resistivity changes are presented in logarithmic scale and normalized to the maximal value.

4. Conclusion

Investigation of resistivity changes of a number of copper(I) compounds under exposure to ammonia revealed high selectivity of $Cu_{12}Sb_4S_{13}$ and high sensitivity of CuBr, CuCl and Cu_2O. Different chemosensitive properties of copper(I) compounds demonstrated clearly the role of the second (non-copper) component of these compounds on analytical sensitivity and selectivity pattern: the effect of this component is so strong that one can suggest a sensor array with very high selectivity based only on different copper(I) compounds. One can expect further improvement of chemosensitive properties by introduction of additives, by variation of the grain size and by improvement of the electrode materials. The technology of such screening of chemosensitive properties was described in Refs. [11,14,16,17] and reviewed in Refs. [18–20]. Most probably, not the whole phase but only the surface of grains of the sensing materials contributes to chemosensitive resistance measurements. This question can be analyzed by comparison of such materials with different grain size. If this suggestion is correct, a decrease of the grain size down to nanometer scale is also a way to improve the sensor performance.

Acknowledgements

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Biographies

Benjamin Wolpert received his diploma in Chemistry in 2007 at the University of Regensburg. He was involved into research and development of gas sensitive materials in the group of V.M. Mirsky at the Institute of Analytical Chemistry, Chemo- and Biosensors of the University of Regensburg and participated in industrial projects on the development of gas sensors for automotive industry.

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Arno Pfitzner obtained his doctoral degree in Chemistry from the University of Siegen (Germany) in 1991. Since 2000 he is full professor for Inorganic Chemistry at the University of Regensburg (Germany). His fields of interest include inorganic and solid-state materials, ionic conductors and adduct compounds.

Vladimir M. Mirsky graduated Moscow Medical University with diploma in Biophysics, then he studied Physical Chemistry and Electrochemistry and in 1986 obtained PhD from the Frumkin Institute of Electrochemistry. In 1991 he was awarded by the Alexander-von-Humboldt Research Fellowship. Since 1995 he is working in the Institute of Analytical Chemistry, Chemo- and Biosensors of the University of Regensburg (Germany), currently as professor in Analytical Chemistry. His research interests comprise development of new chemical and biological sensors, applied biophysics and physical chemistry of interfaces.