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Quantitative fluctuation-enhanced sensing in amperometric NO_2 sensors

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ABSTRACT

Nitrogen dioxide represents threat to human health even at low concentrations. A new amperometric sensor with three-electrode topology (platinum/solid polymer electrolytes/carbon) was developed to overcome limitations of standard solid NO_2 sensors based on inorganic materials. The paper aims to the study of fluctuation phenomena in amperometric sensor and presents preparation technology. The sensor has been exposed to NO_2 concentration from 0 to 3 ppm. Experimental results show that thermal noise is only apparent for zero concentration. For higher NO_2 concentrations, adsorption–desorption (A–D) noise and diffusion noise become main components of current fluctuations, and the noise spectra exhibit Lorentzian-like shape. The spectral density of current noise at frequency 0.2 Hz depends linearly on NO_2 concentration. This linear behavior can be described by adsorption–desorption model for the interaction for two reservoirs. Thus, considering adsorption–desorption noise as a dominant noise source, the noise model is introduced based on Langmuir theory.

1. Introduction

Many fields of life require fast, cheap and reliable gas sensors. The development of these sensors still belongs among actual problems. There are currently several different kinds of sensor device, each employing different operational features. For the detection of NO_2 we may mention, e.g., chemiresistive [1], potentiometric [2], amperometric [3], gravimetric [4], electrical and optical [5] sensors. The promising nowadays seemed to be chemiresistive type of sensors. They are exceptionally simple in preparation and usage. However, they suffered lack of selectivity, which was usually overcome using arrays of different sensing elements [6–9]. The second problem represents long term stability. Solid NO_2 sensors based on inorganic materials very often operate at high temperature [10,11], which limits their applications. Therefore, great attention was paid to reducing the operating temperature [12]. Sensors based on organic sensing layers partly overcome this problem. However, NO_2 is strong acceptor and, therefore, sensitive layers can be non-reversibly destroyed [13,14] which influences sorption/desorption process and its kinetics and stability of baseline. A typical example are sensors based on phthalocyanine films [15], even that these molecules are generally very stable.

The problem of stability can be partly solved using electrochemical sensors, both potentiometric and amperometric ones, see e.g. [16–21] and references therein. Critical factor of these sensors is quality and stability of electrodes, especially potential stability of the reference electrode. Recently, there has appeared an interest in substituting a standard reference electrode by a pseudoreference or quasi-reference electrode in amperometric sensors [22]. Langmaier et al. [23], e.g., designed a solid-state NO_2 sensor with a Pt/air pseudoreference electrode and a gold mesh working electrode. Many other examples can be mentioned. Michalska et al. showed that amperometric sensors do not require high stability of the reference electrode, unlike potentiometric sensors [24]. It was also the reason why we used for our study amperometric type of sensors. In the last time an attention was paid to solid polymer electrolytes [25,26] and to use of ionic liquids in solid electrolytes [27,28]. Kubersky et al. published recently sensor with solid electrolyte based on ionic liquid 1-ethyl-3-methylimidazolium

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bis(trifluoro-methylsulfonyl) imide immobilized in poly(vinylidene fluoride) [29].

The important parameter of sensors with electrical detection which influences accuracy is signal to noise ratio. Electronic noise seems to be unwanted and distracting component, however, it contains also information about significant processes taking place in electronic devices due to stochastic nature of matter. For example, the kinetics of many physicochemical, electrochemical, and bioelectrochemical processes is known to be accompanied by noise generation, which virtually represents the dynamic fluctuations of electrical potential or current [30]. Generally, noise measurements mainly define the detection limits of sensing devices in the first step. In the second step, noise measurements give us integral information about a whole state of the device and may inform about issues in a design of device, a quality of electrical contacts and vias, applied manufacturing processes, long-term stability, etc. Increased level of noise or unusual shape of noise spectra usually indicates failure mechanisms in particular devices [30–35].

Concerning the chemical sensors, noise derives from external environmental interfaces (interactions on interface sensitive layer/ambient environment) and inherent noise sources [36–39]. Several authors showed [40–46] that fluctuation analyses represent the approach of extracting more selective response from the chemical sensors, beside quality indication and determination of sensitivity limit. Several sources of electronic noise exist in amperometric sensors with solid electrolyte, namely, generation–recombination noise of charge carriers in solid electrolyte, noise in electrolyte–electrode interface, thermal equilibrium fluctuations, and, during the gas exposure, noise of sorption–desorption process.

This paper deals with the study of fluctuation phenomena in amperometric NO_2 sensor Pt/solid electrolyte/carbon and also presents the preparation technology of the sensor.

2. Electrical noise in amperometric gas sensor

Due to stochastic nature of matter, physical and chemical processes in electronic devices are also considered to be stochastic, and reveal macroscopically as fluctuation of measurable quantities, such as current or voltage. These fluctuations are inherent for every electronic device, especially sensors. The fluctuation phenomena in chemical sensors might be divided into two groups [37,38]; the first one is directly related to sensor, and the second one is related to the chemical processes in/on a sensing layer.

2.1. Intrinsic noise sources

The intrinsic noise sources in electronic devices are associated with conductive mechanisms [31]. In amperometric sensors, noise sources have similar behavior to those occurred in the devices based on electrode/electrolyte interface, where current and voltage fluctuations originate from either thermal equilibrium noise created by conductors, or nonequilibrium noise mechanisms caused by charge transfer processes produced by intrinsic electrochemical interactions [47,48].

Thermal noise relates to thermal motion of charge carriers in a material as a whole through the dissipative mechanisms. Thus, current noise spectral density is determined by Nyquist relation, i.e. thermodynamic temperature T, Boltzmann constant k and real part of electrical impedance of the sensor Z [47,49]. Although thermal noise represents usual white spectrum, an electrical impedance spectrum of the electrochemical device with electrolyte is usually expressed as a system composed of a number of series-connected resistor–capacitor parallel pairs which represent the impedance contributions of bulk electrolyte, including electrode and electrolyte–electrode interface, respectively [47]. Thermal noise is only anticipated, when there is no net current flowing through the interface between electrode and electrolyte, which corresponds to no charge transfer process present at the interface.

When charge transfer occurs at the interface, a current-dependent fluctuation becomes apparent, in addition to incessant thermal noise, originating from all dissipative components. It is typical for Faradaic electrodes [48]. To quantify the effect of this specific noise source, one should notice that the total observed current in the electrode–electrolyte interface is the sum of all of individual molecular level relocations, where each relocation might be a combination of drift and diffusion processes at the interface. Kuo [47] pointed out that diffusion noise may be a significant fluctuation component in solid electrolytes and electrodes, and is well described by the spectrum fluctuations in the number of diffusion species [47,50]. Electrochemical reaction noise in electrode/electrolyte system can originate from electrolytic reaction or reactions between the solid electrolyte and electrode material or deposition technique [47].

Hassibi et al. [48] published the comprehensive study of noise processes in electrode–electrolyte interfaces, where he demonstrated that excess shot noise is inherently frequency dependent, and its exact spectrum is denoted by the charge transfer and mass transfer processes of the electro-active species, in proximity of the interface. If the mass transfer process is dominated by electric field effects, the noise spectra possess a $1/f^2$ dependency, while in processes with diffusion-dominant electrodes at inhomogeneous current density profiles, ionic relocation can potentially bring about any excess noise exponent obeying an inverse frequency power law (i.e., $1/f$ noise).

2.2. Noise sources due to chemical environment

Focusing on amperometric gas sensor in chemical environment, our results measured on first prototypes of sensors showed that the spectral density of current fluctuations is modified by NO_2 exposure to different gas concentrations [29,33]. The additional noise sources are considered to be associated with fluctuations of charge carrier mobility and density (concentration fluctuation and motion of chemical fragments) originating from chemical environment, and are supposed to have a similar feature as in conductometric sensors published in literature [37,51]: (i) adsorption–desorption process of gas molecule on the active layer, (ii) diffusion of the adsorbed molecules or molecule fragments on the sensor surface. The measured spectral density of current or voltage fluctuations is assumed to result from the superposition of the contributions of these two noise sources as well as inherent noise sources.

3. Experimental setup

In our previous paper [33], two different setups were involved in the measurement of sensor in neutral chemical environment and chemical environment of ppm concentrations of detected matter. Experimental apparatus designed for this study is presented in Fig. 1. To prepare required NO_2 concentrations, experimental apparatus consisted of PC-controlled mass flow controllers, a poly(tetrafluoroethylene) (PTFE) test chamber and two gas tanks: the first one was filled with a reference mixture of gaseous nitrogen dioxide and synthetic air [100 ppm NO_2] while the second one was filled only with synthetic air subsequently humidified to 40% RH. The analyte flow rate was 1 L/min.

The noise measurement setup consisted of a low-noise preamplifier PA15 (3S Sedlak, Ltd), an amplifier with highly selective filters AM22 (3S Sedlak, Ltd) which covered the selected frequency range, 12-bit AD convertor HS3 (TiePie Engineering), and a notebook. To minimize external disturbances, the whole system was