Noise in Amperometric NO2 Sensor

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***Abstract*— Nitrogen dioxide (NO2) is a highly toxic gas harmful to the environment, which can be threat to human health even at low concentrations. To overcome limitations of standard solid NO2 sensors based on inorganic materials, a new sensor with solid polymer electrolytes (SPE) was developed. Our study deals with investigation of fluctuation phenomena in the electrochemical NO2 sensor, which is based on three-electrode topology and solid polymer electrolyte. Experimental result shows that generation-recombination (G-R) noise seems to be main components of current fluctuations in this sensor. The concentration of detected matter affects noise spectral density of sensor. As the concentration increases, G-R noise rises and is supposed to be connected with chemical processes on active layer of sensor. The shift of G-R component is supposed to be caused by increased flux density between active layer and environment.**

Keywords—amperometric gas sensor;generation-recombination noise; nitrogen dioxide; solid polymer electrolyte.

I. INTRODUCTION

Due to stochastic nature of the matter, physical processes in materials are considered to be stochastic, and they reveal as fluctuation of measurable quantities macroscopically. Not only in sensorics, these fluctuations are usually called noise, since they are assumed to be unwanted and distracting components, which do not carry any information. Generally, users are trying to minimize the impact of fluctuation mechanisms on the measurement to achieve maximum signal-to-noise ratio. However, these fluctuation mechanisms may also contain useful information concerning the physical or chemical processes occurring in the sensor. Noise measurements might give us additional information about issues in suitable sensor design, used contact, applied manufacturing process etc [1-3], but also analyses of noise measurements represent the approach of extracting more selective response from the chemical sensors, such as conductometric sensors [4-7], surface acoustic wave sensors [8] and resonant sensors [9].

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In the paper, experimental results are discussed in situation when a new amperometric sensor NO_2 [10] is exposed to neutral environment and NO_2 environment. Generation-recombination (G-R) noise seems to be main components of current fluctuations in this type of sensor. The concentration of detected matter affects noise spectral density of sensor. As the concentration increases, G-R noise rises and is supposed to be connected with chemical processes on active layer of sensor.

II. AMPEROMETRIC NO2 SENSOR

The amperometric gas sensor belongs to a group of electrochemical gas sensors, which play an important role in environmental monitoring, medical and health applications, industrial safety, security, surveillance, and the automotive industry [10, 11]. Sensors based on organic sensing layers gain importance as a new materials are developed [12].

A. Principle of Operation

This type of electro-chemical sensor consists of several electrodes (three in our case) and an electrolyte, which is ionically conducting medium. The role of electrolyte is to transport charge within the sensor, contact all electrodes, etc [11]. An electrode is the combination of an ionic (non-metallic) conductor and an electrical conductor where reactions with the environment such as oxidation and reduction take place [13]. The working electrode (WE) reacts with the gas to be measured and generates a current function as a function of its

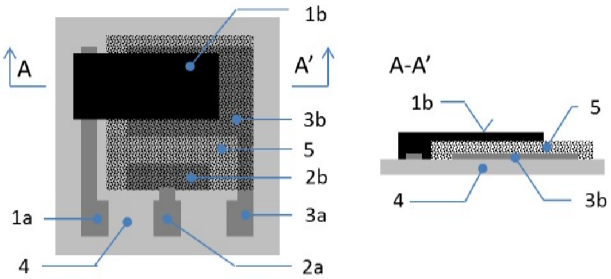

Fig. 1. Topology of the sensor: (1a) working electrode contact, (1b) carbon working electrode, (2a) pseudoreference electrode contact, (2b) platinum pseudoreference electrode, (3a) counter electrode contact, (3b) platinum counter electrode, (4) basic ceramic substrate, (5) solid polymer electrolyte (SPE) [10].

concentration. The counter electrode (CE) acts in the opposite way to balance the charges added or removed from the electrolyte by the reactions at the WE site [14]. In order to maintain a linear response of the sensor, the reference electrode (RE) is added to have the potential between both ends at a specific potential. Because no reaction occurs at the RE, no current flows through it and its potential remain constant. The WE is then held at a fixed potential relative to the RE. With such an architecture, the CE is still free to polarize without affecting the WE [13,14]. The electrode reaction, i.e., electron-transfer reaction at the WE, involves several steps, including adsorption of the analyte onto the surface, electroreaction, and desorption of products from the electrode surface [11].

B. Sensor Construction

The object of our study is amperometric gas sensor, which is a planar three-electrode configuration. The sensor was prepared on an alumina ceramic substrate (9 mm × 7 mm × 1 mm). Platinum electrodes (the pseudo-reference (2b) and the counter (3b) electrode, see Fig. 1) with a modified topology were prepared by "lift-off" technology. A solid polymer electrolyte (SPE) was applied by a glass rod onto the surface of the alumina substrate and spread out over both platinum electrodes. The solid polymer electrolyte consists of ionic liquid [C2mim][NTf2], poly(vinylidene fluoride) matrix (PVDF) and 1-methyl-2-pyrrolidone (1:1:3 weight). Thereafter, the carbon working electrode was prepared by "drop-casting" a mixture consisting of spherical glassy carbon powder and chloroform (see Fig. 1) [10]. The experiments were carried out on four sensors of different area of working electrode (S1-8.5mm^2, S2-15.0mm^2, S3-35.0mm^2, S4-24.0mm^2). Sensors S1 and S4 were involved in measurements in neutral environment for study of intrinsic noise in amperometric sensors, while other two were involved in noise measurements in artificial environment for study of noise due to chemical environment.

III. Intrinsic Noise in Amperometric Sensor

The fluctuation phenomena in chemical sensors might be divided into two groups [5, 7, 9]; the first one is directly related to sensor, and the second one is related to the chemical processes in/on a sensing layer.

Essential generation of intrinsic noise in amperometric sensor is associated with thermal agitation, diffusion and electrochemical reactions of mobile ions in an electrolyte and at contacts [15, 16]. Thermal noise is only anticipated, when there is no net current flowing through the interface between electrode (electrical conductor) and electrolyte (ionic conductor), which corresponds to no charge transfer process present at the interface. Thus, current noise spectral density is determined by temperature and real part of electrical impedance of the sensor [17]. In the case in which charge transfer occurs at the interface, a current-dependent fluctuation becomes apparent (i.e.shot noise), in addition to incessant thermal noise, originating from all dissipative components. The 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. Hassibi et al [16] showed that the noise spectra

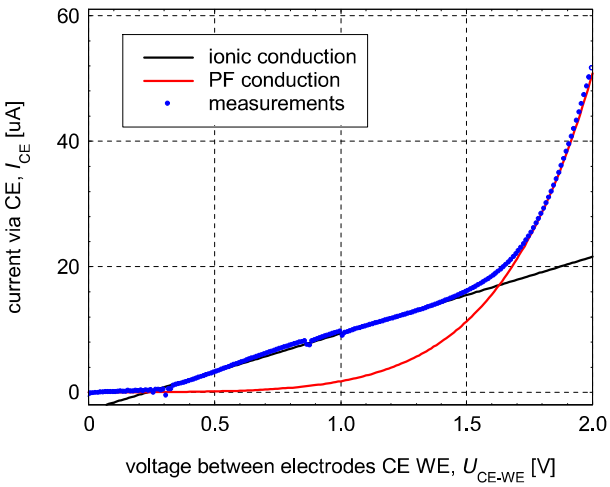

Fig. 2. Sensor S4: I-V characteristic at temperature 24°C for the voltage on reference electrode U_{RE} = 0.1 V with fitted conductive processes, ionic conduction mechanism and Poole-Frenkel conduction mechanism.

possess f^{-2} dependency of the mass transfer process is dominated by electric field effects, while in diffusion-dominant electrodes, ionic relocation can potentially bring about excess noise obeying an inverse frequency power law, i.e. 1/*f* noise.

A. I-V Measurements in Neutral Environment

Experimentally observed electrical noise reflects ion transport dynamics in the bulk material. Conductivity in polymer electrolytes is believed to arise from the ion migration between coordination sites repeatedly generated by the local motion of polymer chain segments [18]. Thus, the measurements of IV characteristics were provided on sensors S1 and S4 to estimate conduction mechanisms in neutral environment. Both sample were investigated by using Keithley system (4200-SCS) with voltage on reference electrode URE = 0.1, 0.3, 0.5 V for voltage between counter electrode and working electrode form 0.0V up to 2.0V. Curve fitting analysis of all acquired curves showed that ionic conduction and Poole-Frenkel process [19] are main mechanisms of charge transport in our sensors, which are not exposed to detected matter. Fig. 2 presents fit of conduction mechanisms on experimental data.

B. Noise Measurements in Neutral Environment

Low-frequency current fluctuations were measured using standard measuring set-up [20] at room temperature with sampling frequency 10 kHz and load resistance R_{L1}=2 kΩ or R_{L4}=10 kΩ, respectively. Particular sensor was powered from batteries during measurements to have constant voltage on reference electrode U_{RE} = 0.5 V and range of voltage across sensor U_{CE}. Fig. 3 shows current noise spectral densities of sensor S1 for U_{CE} = 0.0 V, 1.0 V, 2.0 V. Fig. 4 shows current noise spectral densities of sensor S4 for U_{CE} = 0.3 V, 1.0 V, 2.0 V. Loading resistance was five times higher than in the case of the sensor S1, thus level of current noise is lower. Current nose spectra densities for U_{CE} less than 1.0 V have identical shape of dependency for both sensors, thus noise background of experimental setup is supposed to be higher than current

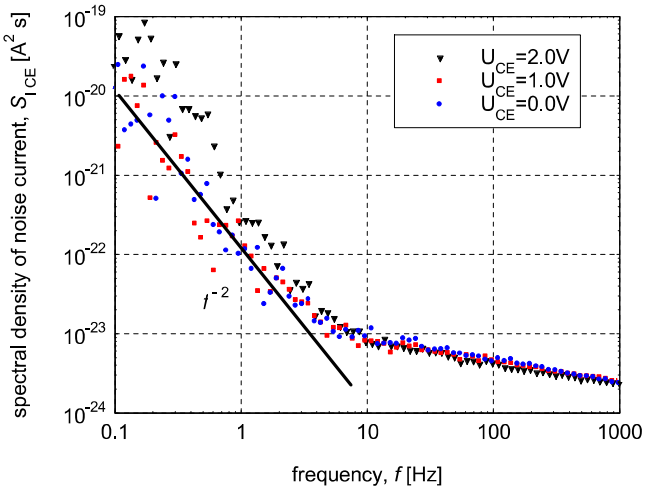

Fig. 3. Current noise spectral density of the sensor S1 at temperature T = 24°C for voltages across sensor U_{CE} = 0.0 V, 1.0 V and 2.0 V with constant voltage on reference electrode U_{RE} = 0.5 V.

noise of both samples. However, current noise spectral densities for $U_{CE} = 2.0$ V show different f^{-2} dependencies which might be explained by drift-constant velocity mass-transfer processes according to Hassibi [16]. Further, the curve for $U_{CE} = 2.0$ V in the case of sensor S4 shows frequency shift in noise spectrum. Such behavior would be obtained after addition of capacity to electrode WE. Thus we assume that this difference is caused by crack on the surface of WE electrode.

IV. Noise due to Chemical Environment

Concerning the electrochemical sensors, the exact origin of the local noise sources, due to chemical environment, is presently unclear [4]. It may be certainly associated with fluctuations of the carrier mobility and density (concentration fluctuation and motion of chemical fragments) originating from the chemical environment. The main noise sources linked to the chemical environment are supposed to be following mechanisms [5, 7]: (i) adsorption-desorption process of gas molecule on the active layer, (ii) diffusion of the adsorbed molecules or molecule fragments on the sensor surface, (iii) current flowing through the potential barriers between nanostructures in the active layer and percolation effects.

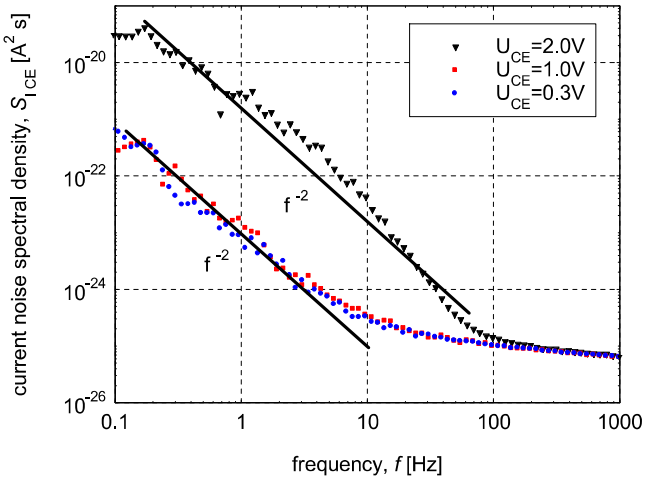

Fig. 4. Current noise spectral density of the sensor S4 at temperature T = 24°C for voltages across sensor U_{CE} = 0.3 V, 1.0 V and 2.0 V with constant voltage on reference electrode U_{RE} = 0.5 V.

Experimental results demonstrated that the noise spectral density of conductometric sensor outputs is modified by the exposure to different gases [5], by the exposure to different gas concentrations [21]. Further, various noise spectral densities were obtained after exposure of one sensor to various gases [7, 22]. The stochastic component of chemical sensor signal contains valuable information that can be visualized not only by spectral analysis but also by the methods of high-order statistics. The high-order statistics enables the extraction of non-conventional features and leads to significant improvements in sensor selectivity and sensitivity [5]. Theoretical description of these experimental results is based on an assumption that the adsorption-desorption process represents the dominant noise source in microsensors [7, 9]. Gomri et al. [6] proposed the model of adsorption-desorption noise in metal oxide gas sensors based on the free electron density fluctuation produced by the gas adsorption considering oxygen chemisorption being involved. In our paper on noise in QCM [9], another model of adsorption-desorption noise was proposed based on Kolmogorov equation for interaction between two reservoirs.

A. *Experimental Setup for Artificial Environment*

The particular amperometric sensor was part of potentiostat circuit based on OPA2344 operation amplifiers (Texas Instruments). The signal current response was measured by the source-measure unit (SMU KEITHLEY 2636). To prepare required NO_2 concentrations, experimental apparatus consisted of PC-controlled mass flow controllers, a PTFE testing 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 sensors were covered with a porous cellulose membrane and measured in the testing chamber under laboratory conditions.

B. *Experimental Results and Discussion*

Experimental result shows in Fig. 5 that generation-recombination (G-R) noise seems to be main components of current fluctuations in this type of sensor. Fig. 5 together with Fig. 6 illustrate how concentration of detected matter affects noise spectral density of sensor. As the concentration increases, G-R noise rises and is supposed to be connected with chemical processes on active layer of sensor. The shift of G-R component is probably caused by increased flux density between active layer and the ambient environment, which corresponds to the fact that the area of working electrode significantly changes level of current noise spectra, see Fig. 5. Thus, the level and cutoff frequency of G-R noise depend on an active area of sensor and time constant for adsorption-desorption process of detected matter molecules. This behavior can be described by Gomriho model or by using Kolmogorov equation for interaction between two reservoirs. The probabilities, that surface sites are free or occupied by molecules, are implied by the Kolmogorov equation in the case

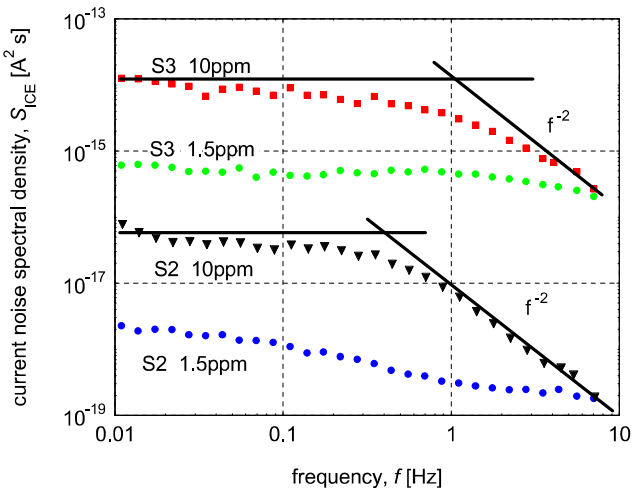

Fig.5. Current noise spectral density of sensors S2(15mm^2) and S3(35mm^2) for contretations 1.5ppm and 10ppm at temperature T= 24°C.

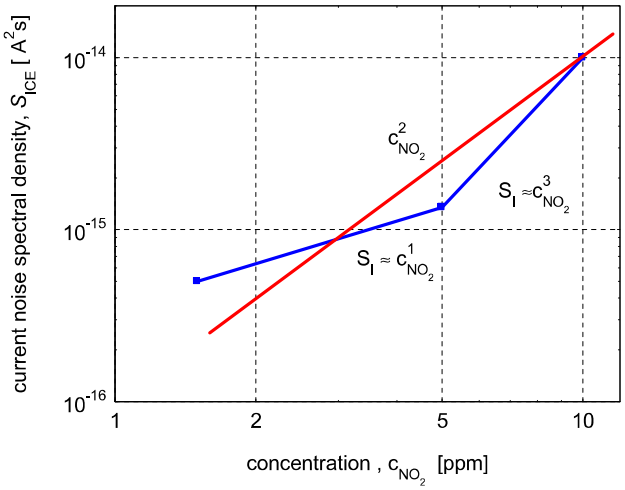

Fig. 6. Current noise spectral density at frequency 10 mHz vs. concentration for sensor S3 (35mm^2) at temperature T = 24°C.

of thermodynamic equilibrium, when the flux of emitted particles is the same as the flux of captured particles on the active layer of the sensor [9].

V. CONCLUCLUSION

Experimental results demonstrated that noise measurements of amperometric NO_2 sensor might give us additional information about quality of sensor structure. Further, these noise measurements might lead to significant improvements in sensor selectivity and sensitivity when model of adsorption desorption models [6,9] are considered. Both these models describe contribution of adsorption-desorption noise to the noise spectra as a Lorentzian component which has a corner frequency and low frequency magnitude which are specifics of the adsorbed gas (mass of adsorbed molecule, adsorption energy, gas partial pressure, time of molecule capture etc).

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