

# Towards Drift Modeling of Graphene-Based Gas Sensors Using Stochastic Simulation Techniques

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**Abstract**—Due to environmental conditions as well as internal processes, the lack of long-term stability of electrochemical gas sensors poses a severe problem with respect to their applications, e.g. in tracking air quality on a large scale. Thus far, the development of suitable algorithms to face these problems relies on long-term datasets obtained from sufficiently good reference devices. Since such measurements on actual sensor systems are not always available, especially in the development phase of them, simulated approaches would be a great benefit for algorithm development and the further analysis of the sensors. Those simulators, however, require proper models to capture the general principles of the functionalized materials in such sensor arrays. In this work, we propose a stochastic model that can be used for this purpose, i.e. that allows for simulating the behavior of graphene-based electrochemical gas sensors in particular. The proposed approach allows to properly map different material-related microscopic effects on the sensor surface to a signal output. Evaluations show that the proposed model is able to capture the drift dynamics of such sensors in particular when comparing the results to real measurement data.

**Index Terms**—stochastic modeling; electrochemical sensors; gas sensors; e-nose; adsorption processes; sensor simulation

## I. INTRODUCTION

Electrochemical gas sensors exploit the adsorption behavior of gases on metal-oxide or other surfaces for determining the type or concentration of certain target gases in the air. This is accomplished by measuring the change of the surface conductivity or resistance of the surface caused by the corresponding chemical reactions. Moreover, differently functionalized materials can be arranged in arrays in order to differentiate between different gases by assessing their adsorption behavior which is considered an *e-nose* in literature [1].

One drawback of the method above, however, is its instability in longer time-scales, which constitutes a so-called drift behavior and leads to a baseline change of the measurements over time (see Fig. 1). This behavior is caused by various intrinsic and extrinsic factors affecting the sensor behavior [2] depending on the sensing material in use, e.g. graphene.

In order to study these effects in different scenarios of long-term exposure to a set of gases, a suitable model is needed to cut down for time- and cost-extensive experiments.

So far, there have been different approaches to model electrochemical sensors, for instance, by using simulation tools based on PSpice to get the conductance of a MOX-sensor [3], [4]. Moreover, the behavior of the adsorption-desorption noise in

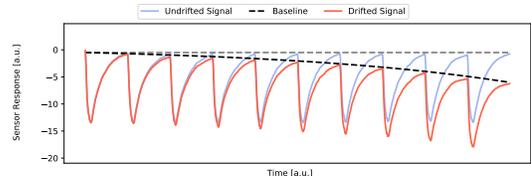


Fig. 1. Illustration of baseline drift. The blue curve shows the undrifted signal, the red curve shows the drifting signal with its changing baseline.

such gas sensors has been studied extensively by Gomri et al. [5], [6]. A more recent approach was developed by Monroy et al. [7] with a focus on the recovery of MOX sensors. These methods mainly rely on analytical descriptions of the adsorption and desorption behavior, such as the Langmuir theory of chemisorption, and focus on modeling the behavior of the sensor at single concentration pulses primarily for gas classification. In [8], [9], Skafidas et al. introduced a Monte-Carlo technique in order to model different effects on thick Tin-Oxide sensors. Their method shows to be insightful for analyzing certain chemical effects on the surface, but lacks expandability to long-term simulations of different concentration and sensor settings in order to address drift modeling. Inspired by this approach, however, we want to present and analyze a system-level model for simulating the long-term sensing and drift behavior of a thin graphene-based gas sensor.

## II. STOCHASTIC SENSOR MODEL

The proposed model operates on two different levels: At the *microscopic level*, we create a flexible structure to implement microscale effects that affect our sensor behavior – building the basis of a bottom-up approach. At the *macroscopic model*, we map the microscopic sensor behavior to a relative resistivity.

### A. Microscopic Model

The microscopic model treats the chemical reactions on the sensor surface as a time- and spatially discrete Markov process with the adsorption and desorption process modeled by binomial statistics.

$$\mathbf{X}_t = \mathbf{X}_{t-1} + \mathbf{A}_t - \mathbf{D}_t \quad (1)$$

$\mathbf{X}_t \in \{0, 1\}^{N \times N \times M}$  describes a N-squared plane with M channels modeling the binding sites on the sensor surface at time t. The different channels represent the different molecules that can bind onto the surface and get adsorbed according to  $\mathbf{A}_t \in \{0, 1\}^{N \times N \times M}$  and desorbed by  $\mathbf{D}_t \in \{0, 1\}^{N \times N \times M}$ .

For each time step, these matrices get sampled binomially by the pixel-wise *hit probabilities*

$$p_a[gas] = k_a \cdot c[gas], \quad (2)$$

$$p_d = k_d \cdot e^{-\frac{E}{k \cdot T}}, \quad (3)$$

for adsorption and desorption, respectively. Here,  $c[gas]$  describes the concentration of the particular gas and  $k_a$  as well as  $k_d$  are constants describing the interaction rates.  $E$  is a term for the adsorption energy of a gas molecule on the adsorption site and  $T$  denotes the temperature on the sensor surface.

The output of the microscopic model is the adsorption fraction  $f_a$ , which describes the ratio of the adsorbed sensor sites (irregardless of the molecule type) compared to the total number of binding sites and is defined by

$$f_a = \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N \sum_{m=1}^M X_{ijm}. \quad (4)$$

An advantage of this way of defining an adsorption model is the rather easy implementation of additional effects that can be seen in experiments using such types of sensors, in this case graphene-based sensors. In the outline of this implementation, three major effects causing baseline drift have been implemented and studied:

**Slow Recovery (SR)** describes the effect of different time-scales of adsorption and desorption on the sensor surface resulting in an accumulation of yet-to-desorb molecules on the sensor leading to an overall downwards drift. This effect is even increased by high-energy state sites occurring especially on the boundaries of the graphene flakes and epoxide molecules on the surface due to chemisorption processes [10]. Slow Recovery is implemented by using two different energy bands for low- and high-energy sites on the simulation grid and with rates  $k_{a,s}$  and  $k_{d,s}$  for Equations 2 and 3, where  $s$  denotes the energy state.

A second reason for a downwards drift is the adsorption of molecules on deeper layers of the sensor material, here denoted as **Secondary Layers Adsorption (SLA)**, which occurs due to overlapping graphene flakes on the sensor electrode. The implication of this phenomenon on the sensor resistivity is modeled by an additional adsorption layer with slower adsorption and desorption probabilities leading to a second adsorption fraction  $f_s$  defined in analogy to Equation 4.

**Ozone Oxidation** describes the process of chemisorption of an  $O_3$  molecule adsorbed on the graphene surface by physisorption on a low-energy binding site. In consequence, epoxide groups can be formed on the sensor surface [11] onto which new molecules can adsorb. Furthermore, the oxidation leads to a resistance shift of the material resulting in an upwards drift of the sensor response and can even alter the reaction rates [12]. This effect is simulated by an additional stochastic process describing the chemisorption process and its reverse process by the following equations:

$$p_{ox} = k_{ox} \cdot e^{-\frac{E_{ox}}{k \cdot T}}, \quad p_{de-ox} = k_{de-ox} \cdot e^{-\frac{E_{de-ox}}{k \cdot T}}. \quad (5)$$

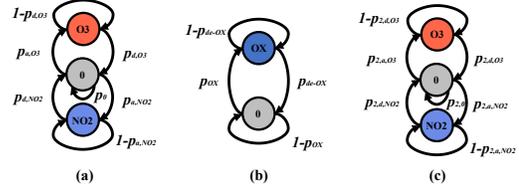


Fig. 2. Markov Chain Graphs describing the adsorption and desorption dynamics of (a) the sensor surface, (b) the chemisorption process ( $O_3$  oxidation) and (c) the secondary layers for SLA drift modeling.

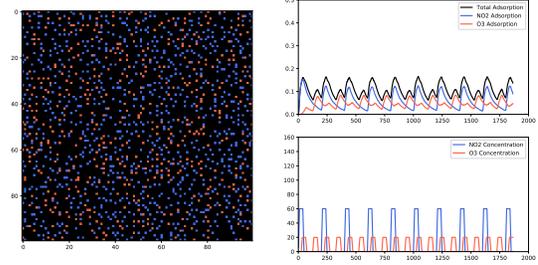


Fig. 3. Simulation Visualization of the Microscopic Model. The left image shows the adsorption distribution of different gas components on the sensor surface simulated on the sample grid. The blue and red dots represent  $NO_2$  and  $O_3$  molecules, respectively. The two plots to the right show the adsorption fraction of the different adsorbants and their input concentrations.

The different stochastic processes are summarized in Fig. 2.

### B. Macroscopic Model

The macroscopic model takes the outputs of the microscopic model and maps them to a relative resistance describing the signal output of electrochemical sensors. It can also be extended with macroscopic environmental conditions such as temperature and relative humidity. The basic formula is derived from the resistivity relation to the charge carrier densities  $n_e, n_h$  and their mobilities  $\mu_e, \mu_h$  for electrons and holes in the material, respectively.

$$\rho^{-1} = e \cdot (n_e \mu_e + n_h \mu_h). \quad (6)$$

Oxidizing gases increase the number of holes in the material in the adsorption process. Therefore, it can be seen as an additional term to the hole density. By simplifying the equation and setting the resistivity inverse at clean air exposure to 1, the relative resistivity is defined by

$$\rho_{rel} = \frac{1}{1 + \alpha_a \cdot f_a + \alpha_s \cdot f_s} - 1 + \alpha_{ox} \cdot f_{ox}, \quad (7)$$

where  $\alpha_a, \alpha_s$  and  $\alpha_{ox}$  describe scaling factors, whereas  $f_a, f_s$  and  $f_{ox}$  describe the adsorption fractions and the oxidation fraction determined in the microscopic model.

In combination, the two models describe a method to simulate the sensor signal created by the adsorption processes of several gases under various environmental conditions. The advantage of this split into two models is that the first model ensures the flexibility towards effects on the chemical level whereas the second model can transfer this information to interpretable output signals in a rigorous way. Moreover, since the dynamics on the sensor panel are simulated at each time step, the sensor behavior can be visualized thoroughly as shown in Fig. 3.

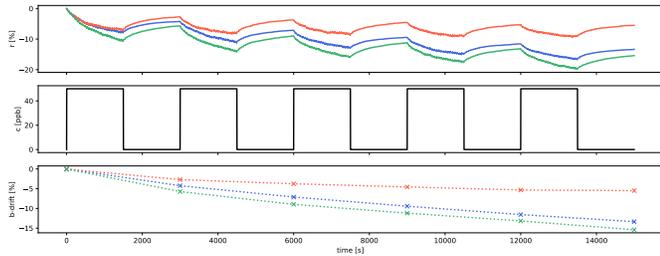


Fig. 4. Five  $O_3$  pulse sensor response with different drift sources: solely SR (blue), SR +  $O_3$  Oxidation (red) and SR + SLA (green). The first row shows the relative resistivity, the second one the concentration profile and the third row shows the baseline drift.

### III. RESULTS AND DISCUSSION

In this section we summarize the results obtained with the proposed model. The first part of the discussion focuses on the analysis of the impact of different drift effects implemented in the model and their alignment with the expected physical behavior. In the second part we want to show how well the model can reproduce an experimentally measured response for a given concentration profile.

#### A. Experiments on Different Drift Effects

In order to study the impact of various additional effects on the sensor surface, a test concentration profile containing 5 gas pulses at 50ppb lasting 1500 seconds each followed by another 1500 seconds of clean air (no gas concentration) has been implemented. The simulation setup included regular temperature pulses which were applied for several seconds at  $300^\circ\text{C}$  in between the sense phases. Fig. 4 shows the modeled sensor response as well as the baseline and sensitivity drift for 3 different drift sources: (i) solely slow recovery (ii) slow recovery paired with Ozone oxidation (iii) slow recovery paired with secondary layer adsorption.

It can be seen that the response follows the typical dynamics of electrochemical sensors when exposed to a concentration pulse which involves a high decrease of resistivity in the beginning and a slower decrease at a different slope until saturation in the second part of adsorption. The desorption phase shows a typical concave shape. In comparison, the drift with additional SLA in case (iii) exceeds the slow recovery drift seen in scenario (i). Moreover, scenario (ii) shows only a slight downwards drift. This is due to Ozone oxidation drift moving the baseline upwards which almost cancels out the downwards drift caused by slow recovery. Overall, the simulated response follows the drift behavior described by the physical effects.

#### B. Comparison to Real Sensor Data

The model was also applied on a concentration profile measured with an array of 3 state-of-the-art graphene sensors with different functionalizations in order to study the similarity in terms of sensor dynamics. The measurements were taken with regular short heat pulses at an increased temperature  $T_H$  followed long sense phases at ambient temperature and changing  $NO_2$  and  $O_3$  concentrations.

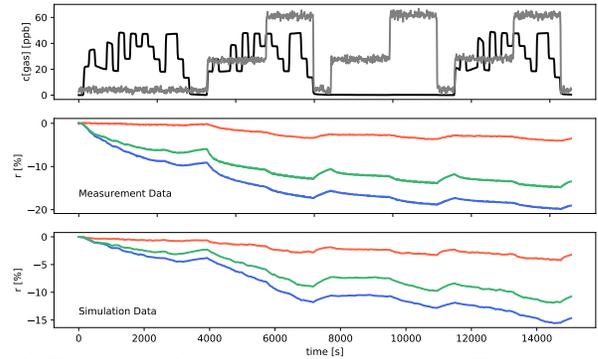


Fig. 5. Experimental data compared to simulation data. The first row shows the  $O_3$  (grey) and  $NO_2$  (black) concentration profile of the experiment. The experimental response for three different material functionalizations is shown in the second row, whereas the third row shows simulated responses with different energy parameters.

The model parameters were chosen partially by suggestions in literature [11] and partially fitted heuristically to the response of another measurement profile in order to test, if the model can generalize the sensor behavior. As a drift source, only slow recovery was used for the simulation, since the heat pulse temperature was well beneath the critical threshold for oxidation and the time span was comparably short for secondary adsorption to have a strong effect on the baseline drift. It can be seen in Fig. 5 that the sensor in general replicates the dynamics of the real measurements properly. The sensitivity to  $NO_2$  is slightly underestimated in the simulation which might be improved by determining the binding energy experimentally. The baseline drift due to slow sensor recovery also occurs throughout the simulation.

### IV. CONCLUSION

The presented stochastic model can be used to properly simulate the dynamical behavior of a graphene-based gas sensor signal. Especially for mixtures containing  $O_3$ , the responses obtained by the model are in-line with general responses measured by real sensors. Due to the flexibility of the bottom-up approach, additional microscopic effects affecting the baseline drift can be implemented easily, their responses are seen to be in-line with their physical effects and their impact can be studied and visualized in a straight-forward manner. Furthermore, this easy adaptability of the microscopic model is a big advantage compared to analytical methods found in literature. By conducting additional experiments on the material properties of sensors to be modeled, the accuracy could be increased by choosing the model parameters analytically and the results could be refined in future investigations. Further drift effects that shall be researched in depth in future work are the degradation of the electric contacts [2] and defects on the graphene surface [13].

### V. ACKNOWLEDGMENT

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