Electrical Conductivity Modeling of SiO_2/CuBr Composite Sensitive Layer for Ammonia Gas Sensor Application

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***Abstract*—Skin-perspired ammonia (NH_3) could be used for non-invasive medical monitoring of patients suffering from chronic kidney disease. Copper-bromide (CuBr) based sensors are known to be very selective to ammonia at room-temperature, making them specially adapted for such applications. However, their sensitivity remains insufficient and requires further improvement, as around 100 ppb of NH_3 must be detected. In a previous work, this limitation is addressed by employing a sensing layer based on a mesoporous SiO_2 matrix impregnated with a CuBr solution. To better understand the mechanisms involved in electrical conductivity of this layer, a numerical model is introduced here. Based on random unit conductivity lattice, the model considers both porosity and disorder. Total conductivity is deduced from the calculation of electrical potential at each node of the conductivity lattice. Numerical results show that 18% of impregnated CuBr is required to observe an increase in total conductivity. This concentration is consistent with the value of 13% experimentally observed, and for which the sensor performance is optimal.**

Keywords-Sensors; Simulation; Modeling.

I. Introduction

Non-invasive devices that enable continuous medical monitoring offer numerous benefits to patients, such as a reduced risk of infection, data storage, and ability to perform examinations at home. As an alternative to urine and blood tests, detection of skin-emitted ammonia on patients suffering from chronic kidney disease is chosen. Indeed, previous studies showed that ammonia rate in blood is linked with transdermal ammonia concentration [1][2].

Most NH_3 microsensors are based on metal oxides such as SnO_2 or WO_3. While these materials are widely used, metal-oxide-based sensors generally require high operating temperatures in the range of $200 - 450°C$ and exhibit poor selectivity due to their sensitivity to a broad variety of interfering gases. An alternative strategy for improving microsensor selectivity relies on molecular recognition, which is based on specific interactions between the target gas and highly mobile species in solids, especially mobile ions in ionic or mixed conductors. In this sense, previous studies showed that CuBr is a promising candidate. Indeed, upon exposure to ammonia, Cu^+ ions migrate toward the surface, where they form $[Cu(NH_3)_2]^+$ complexes. This ionic redistribution induces an accumulation of copper vacancies at the surface and a depletion of interstitial Cu^+ ions, resulting in a widening of the depletion layer and a decrease in the overall electrical conductivity [3][4]. In addition to this high selectivity, CuBr-based sensors exhibit high sensitivity toward ammonia and operate at room temperature, which is crucial for sensors intended for skin contact. Then, in this work, CuBr is chosen for NH_3 detection, as transdermal ammonia concentrations are estimated around 100 ppb [5]. The sensitive layer of the sensors developed in a previous work [6] is made of small CuBr nanocrystals, obtained by impregnating the ionic conductor within a mesoporous silica matrix synthesized by a sol–gel process. The regular repartition of CuBr within the pores and the large specific surface area of the mesoporous network promotes high sensitivity as well as fast response and recovery kinetics. Gas sensing measurements in the presence of very low concentrations of NH_3 $(100 - 500$ ppb) demonstrated that the sensor combines high sensitivity with strong selectivity, thereby supporting the validity of the approach.

For better understanding, effect of the porosity on total conductivity is studied in this work by introducing a numerical model, which considers both the morphology of the layer (size of CuBr particles and pores, composition) and the different constitutive conductivities, as silica is an insulator and CuBr a mixed conductor.

The organization of the paper is the following. The numerical model is introduced in Section II. Then, results are presented and discussed in Section III. Finally, the paper concludes with Section IV.

II. Numerical Model and Methods

A two-step approach is used in this study. First, the sensitive layer is modeled by considering its structural properties (porosity, composition, grain size). Secondly, a conductance lattice whose total conductivity is calculated by classical method is build.

A. Mesoporous Layer Modeling

Sensor realization, along with the morphological and electrical characterization of the sensitive layer, has been detailed in our previous work [6]. Structural analysis revealed that the mesoporous SiO_2 layer exhibits a disordered, worm-like porous network with a porosity of 56% (Figure 1). Impregnation of the mesopores by CuBr is clearly visible (CuBr appears light grey).

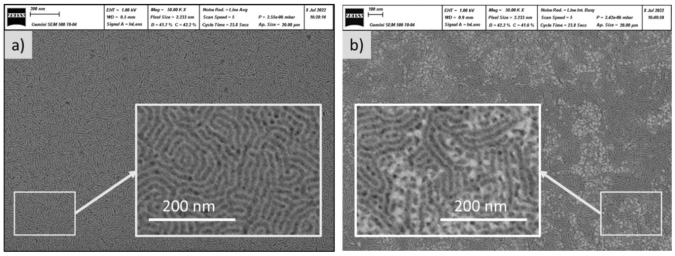

Figure 1. SEM images of the mesoporous SiO_2 film: before (a) and after (b) impregnation with CuBr, from [6].

Moreover, the mapping obtained by Energy-Dispersive X-ray (EDX) spectroscopy shows a homogeneous dispersion of CuBr throughout the thickness of the layer (Figure 2).

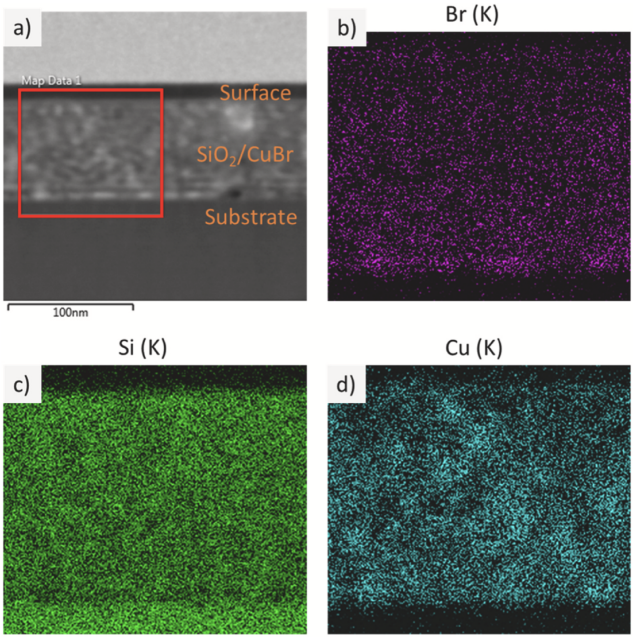

Figure 2. EDX mapping of the CuBr-impregnated SiO_2 mesoporous layer: distribution of the K line, for Br (b), Si (c) and Cu (d) atoms, in the area outlined in red on the image obtained by STEM (a), from [6].

Based on these observations, the sensitive layer is modeled by a simple cubic lattice. Each lattice site is the center of a unit cube corresponding either to CuBr crystal or to SiO_2 crystal. Then, sites are randomly occupied by CuBr (with a probability p) or by SiO_2 (with a probability $q = 1 - p$) (Figure 3-a). This lattice is converted to a cubic array of conductance by adopting the following rules: if two nearby sites are occupied by CuBr, the bond that connects them has a conductance g_{CuBr}; if they are occupied by SiO_2, the corresponding bond takes the value g_{SiO_2}; finally, if the two sites are occupied one by CuBr and the other by SiO_2, the conductance of the bond is an interface conductance noted g_{int} (Figure 3-b).

Porosity is introduced by removing 60% of the lattice sites consisting solely of SiO_2. Then, the unoccupied sites are randomly filled by CuBr in the concentration range of 0 to 100%. Thus, the CuBr filling in the overall volume, i.e., SiO_2 plus pores, varies from 0 to 60%. When at least one site is unoccupied, the corresponding bond is set to g_{por}. Figure 3 illustrates this approach for a two-dimensional lattice without porosity, which is easier to represent. However, its generalization to three dimensions is very simple.

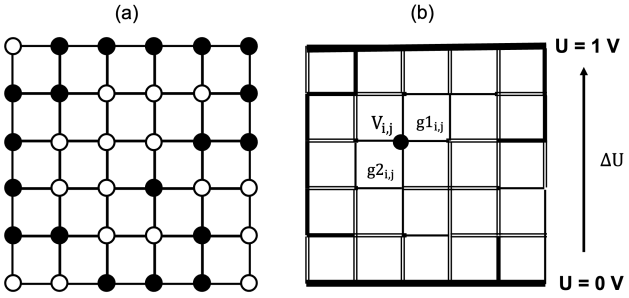

Figure 3. Two-dimensional representation of the conductance array (b) derived from the site lattice (a): the thick lines connect two sites occupied by SiO_2 (black sites); the thin lines connect two sites occupied by CuBr (white sites) ; finally, the double lines connect sites occupied by both. $V_{i,j}$ is the potential at the node (i, j) from which the two conductances, $g1_{i,j}$ and $g2_{i,j}$, are defined.

The choice of conductivity values is based on our knowledge of the various components of the sensitive layer. Copper bromide (CuBr) is a mixed conductor whose conductivity is highly dependent on the processing conditions and the temperature at which the measurement is carried out. Indeed, β-CuBr phase has an ionic conductivity greater than 1 S/cm, whereas the γ-CuBr phase presents a smaller value of ionic conductivity, the transition temperature being around 380 °C [7]. Then, the conductivity of CuBr layers deposited by radio frequency magnetron sputtering from compacted powder target is $\sigma \approx 5.10^{-7}$ S/cm at T = 25°C [8]. At the same temperature, grain conductivity measured by impedance spectroscopy on poly-crystallin CuBr is $\sigma \approx 3.10^{-5}$ S/cm [7]. On the other hand, SiO_2 is an insulator whose conductivity is between 10^{-16} and 10^{-12} S/cm (crystal) and less than 10^{-18} S/cm (amorphous).

Thus, the ratio of conductances being between 10^{-5} and 10^{-13}, simulations are carried out with $g_{CuBr} = 1$ and $g_{SiO_2} = 10^{-9}$.

It is more difficult to determine the interface conductivity, g_{int}, which is unknown and not estimated by experiments. However, previous work on CuBr/TiO_2 composite showed that conductivity is increased at the CuBr-TiO_2 interfaces [9]. By considering that CuBr-TiO_2 composites are like CuBr-SiO_2 ones, the arbitrary value $g_{int} = 10$ is used. Finally, the porosity bond is set to $g_{por} = 10^{-12}$, corresponding to an insulator.

Moreover, to minimize size effects, periodic boundary conditions are applied: the bonds of the two terminal planes are copied, such as the plane at abscissa 0 is equal to the plane at abscissa L, and that for the two directions perpendicular to the electrode planes.

B. Total Conductivity Calculation

Kirchoff's law says that the sum of currents is null at each node. The total dissipated power is given by:

$$P_T = \sum_{i,j} g1_{i,j}(V_{i,j} - V_{i+1,j})^2 + g2_{i,j}(V_{i,j} - V_{i,j+1})^2, \quad (1)$$

where $V_{i,j}$ is the potential at the node (i,j) and $g1_{i,j}, g2_{i,j}$ are conductances between (i,j) and $(i+1,j)$ sites, and between (i,j) and $(i,j+1)$ sites, respectively (Fig. 3-b). Otherwise, the dissipated power is:

$$P_T = G_T \Delta U, \quad (2)$$

where ΔU is the electrical potential difference applied to the conductance lattice (Fig. 3-b). If $\Delta U = 1$V, the total conductance is numerically equal to total power.

Therefore, the problem can be reduced to the calculation of the potentials $V_{i,j}$ at each site, using an exact or an approximated method. Because of the disorder and the relatively large size of the considered systems, the choice of approximated method is done here.

By applying Kirchhoff's law, the potential at each node is expressed as a function of the conductance of the links connecting it to neighboring nodes as follows:

$$V_{i,j} = \frac{g1_{i,j}V_{i+1,j} + g1_{i-1,j}V_{i-1,j} + g2_{i,j}V_{i,j+1} + g2_{i,j-1}V_{i,j-1}}{g1_{i,j} + g2_{i,j} + g1_{i-1,j} + g2_{i,j-1}} \quad (3)$$

The over-relaxation method is used to determine these potentials when the system is at equilibrium. This method consists of iteratively calculating the potentials until constant values are obtained. At first iteration, $V^0_{i,j}$ potentials are set to 0, then at the $n+1$ iteration, the potential at node (i,j) is:

$$V^{n+1}_{i,j} = \omega \tilde{V}_{i,j} + (1-\omega) V^n_{i,j}, \quad (4)$$

where the potential $\tilde{V}_{i,j}$ is obtained by substituting the potential $V^n_{i,j}$ in (3). The value of the relaxation parameter ω plays a major role in the convergence speed of the algorithm [10]. Among its properties, it is worth noting that it must be between 1 and 2 and that there is an optimal value for which the number of iterations is minimal:

$$\omega_{opt} = \frac{2}{1 + \sqrt{1 - \rho^2_{Jacobi}}} \quad (5)$$

In these simulations, Jacobi's spectral radius, ρ_{Jacobi}, is equal to $cos(\pi/L)$, where L is the size of the lattice.

III. Results and discussion

To determine the optimal lattice size, in terms of balance between accuracy and computing time, the total conductivity is calculated as a function of volume fraction of CuBr without considering porosity. The results obtained for $L = 10, 15, 20$ and 25 are plotted in Figure 4. Only one configuration is considered for each volume fraction of CuBr. Beyond $L = 20$, the curves converge and present a bell-shape with a maximum around 0.6 volume fraction of CuBr, which agrees with previous works on composite systems like Au-YBCO [11] or CuBr-TiO_2 [9]. From these results, $L = 25$ is kept in the following calculations.

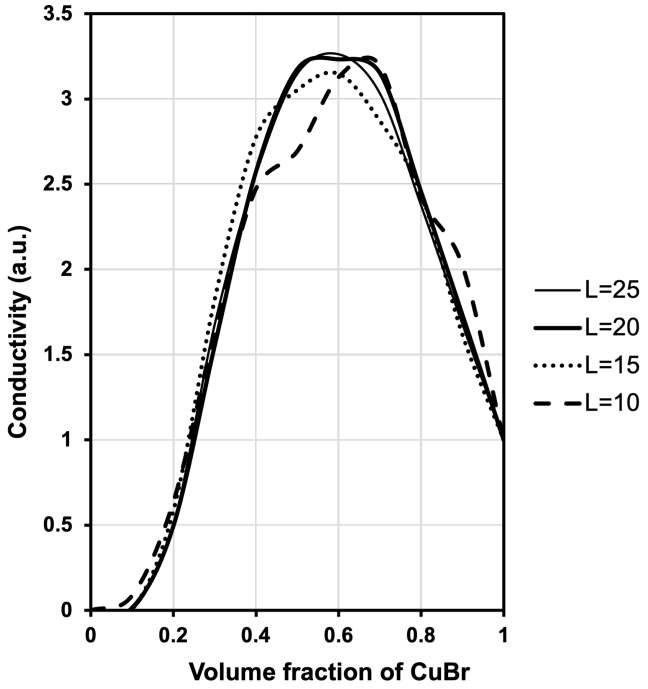

Figure 4. Variation of the total conductivity as a function of the volume fraction of CuBr. Results obtained for $L = 10$ (dashed line), $L = 15$ (small dots), $L = 20$ (thick line) and $L = 25$ (thin line). Interface conductance is $g_{int} = 10$.

When 60% of porosity is introduced, and gradually filled by CuBr, the total conductivity begins to increase around 0.18 volume fraction of CuBr (Figure 5). This value corresponds to the percolation threshold, p_c, which is the volume fraction

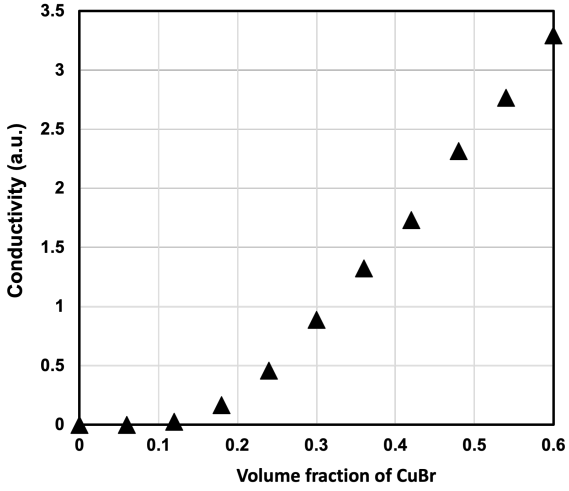

Figure 5. Variation of the total conductivity as a function of the volume fraction of CuBr into a sample made of SiO_2 with a random porosity of 60%.

of CuBr at which infinite cluster appears. For simple cubic lattice, such as considered in this work, $p_c = 0.247$ in the case of bond percolation, and $p_c = 0.307$ in the case of site percolation, considering geometric arrangement of two types of bonds or sites. The system considered here is different as it involves 3 types of bonds. Notice that the conductivity value for 0.6 volume fraction of CuBr, around 3.25, corresponds to the maximum of the curve obtained without considering porosity.

Good agreement is observed when comparing the variation of sensor resistance (Figure 6) and the calculated resistance in the same range of CuBr filling (Figure 7).

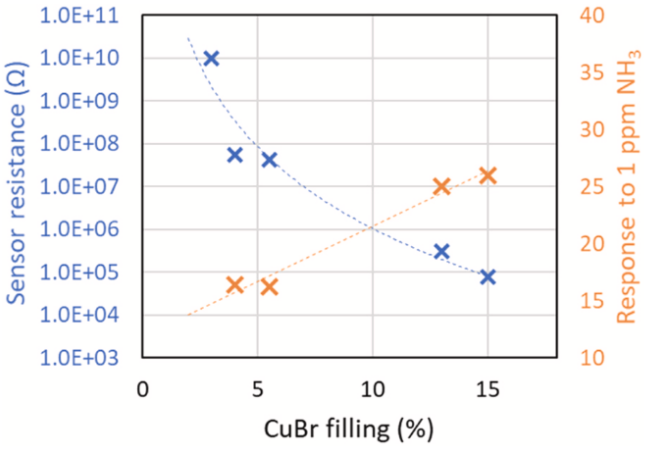

Figure 6. Effect of CuBr filling on the sensor resistance and the sensor response to 1 ppm NH_3, from [6].

Indeed, not only the general trend is recovered, but also the order of magnitude: three decades in resistance sensor as CuBr filling varies from 5% to 15%.

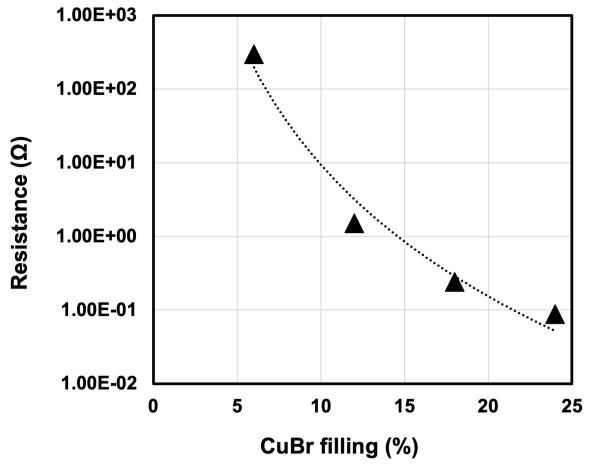

Figure 7. Total calculated resistance in the range 0 to 25% of CuBr filling.

IV. Conclusion and Future Work

In this paper, we developed a numerical model to study the electrical conductivity of SiO_2-sensitive mesoporous layers impregnated with CuBr for ammonia gas sensor applications. The approach consisted of modeling the disordered porous structure by a random conductance network, considering both the porosity and the different conductivities of CuBr, SiO_2 and their interfaces. The total conductivity was then calculated using an over-relaxation method applied to the conductance network. Calculation shows that less than 18% of CuBr in the total volume is enough to obtain a conducting path in the insulator SiO_2 mesoporous matrix. This value agrees with the experiment in which higher sensor performances are reached for a sensitive layer composed of 13% CuBr, 44% SiO_2 and 43% of remaining porosity. The worm-like structure being well modeled by random porosity, it seems unnecessary to build a numerical sample with worm-like porosity. However, additional measurements, such as impedance spectroscopy coupled with calculations for other values of g_{int} would be useful to better characterize the interfaces.

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