

## CO<sub>2</sub> Sensing Layers for SAW/BAW Devices

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**Abstract.** The CO<sub>2</sub> sensing performance of several coating layers deposited on piezoelectric devices (Surface and Bulk Acoustic wave – SAW/BAW) are discussed and compared. The layers are amino groups-based polymers and their selection was based on two principles: Hard Soft Acid Bases (HSAB) and Bronsted-Lowry. Experimentally measured CO<sub>2</sub> frequency shifts and sensitivities of emeraldine, 4-sulfocalix[4]arene-doped polyaniline, matrix based emeraldine and carbonic anhydrase (PACA) are compared to previously reported results obtained for coatings such as: polyallylamine (PAA), polyethyleneimine (PEI), nanocomposite matrix based on PAA-aminocarbon nanotubes and PEI-aminocarbon nanotubes.

### 1. Introduction

The sensing of carbon dioxide (CO<sub>2</sub>) is of crucial importance in a broad variety of applications: hospitals (for capnography), building ventilation and control systems, green chemistry, CO<sub>2</sub> capture and sequestration, chemical industry, agriculture. For these applications, nondispersive infrared sensors, despite of their increased selectivity and sensitivity, are limited by their large power consumption and significant size. Since they employ smaller and cheaper devices, surface and bulk acoustic wave (SAW/BAW) sensors represent a viable alternative for CO<sub>2</sub> detection.

Various CO<sub>2</sub> sensitive coatings have been developed for use in these types of sensors. Organic polymers that contain amino groups were often tested in CO<sub>2</sub> sensors. Examples include polyethylenimine, polyvinylamine, Versamide 900, poly (3-amino-propyl-trimethoxysilane propyltrimethoxysilane copolymer – PAPPs), poly (amido-amines) [1–5], polyallylamine (PAA), nanocomposite matrix based on PAA and amino-carbon nanotubes, polyethyleneimine (PEI) and aminocarbon nanotubes emeraldine [6–10], doped polyanilines with 4-sulfocalix[4]arenes, matrix nanocomposite based on emeraldine-carbonic anhydrase [11–14]. Small organic molecules with amino-groups have also been tested in CO<sub>2</sub> SAW detection. Among these, one can mention dipropylamine, tri-n-octylamine, 7, 10 dioxo-3,4 diaza-1,5,12, 16 hexadecatetrol, benzylamine, tri-n-octylamine, N,N, diethyl-p-phenylendiamine, diethanolamine (DEA). However, all these compounds exhibit small frequency shifts: between 10 and 210 Hz. Poor stability and reproducibility are other drawbacks of these types of coatings [13].

The selection CO<sub>2</sub> sensing materials based on the Hard Soft Acids Bases (HSAB) theory was previously demonstrated [9]. A plethora of the reported CO<sub>2</sub> sensitive layers can be understood in the view of this theory. These materials were further used in SAW-based CO<sub>2</sub> sensing devices.

The present paper is focused on a comparison between a sensing mechanism based on the HSAB theory and another sensing mechanism, based on the Bronsted–Lowry theory. Following this second mechanism, emeraldine, 4-sulfocalix[4]arene-doped polyaniline, matrix based emeraldine and carbonic anhydrase (PACA) are identified as suitable coating layers and original experimental results, demonstrating their performance as CO<sub>2</sub> sensing materials in SAW/BAW devices, are presented. The two sensing mechanisms are compared against reported experimental results.

## 2. Sensing mechanisms based on interaction between coating layer and target molecule

### 2.1. Lewis interaction

The HSAB theory explains the interaction between CO<sub>2</sub> molecules and amino-group based polymers or small molecules. According to this theory, hard Lewis acids prefer to bond to hard Lewis bases, and soft Lewis acids prefer to bond to soft Lewis bases, while a borderline Lewis acid prefers to bond with a borderline Lewis base. CO<sub>2</sub> is an example of hard acid, thus it can interact with primary and secondary amines, which are hard bases [15–16]. The interaction between CO<sub>2</sub> and polymers having primary and secondary aliphatic amino groups is ionic, reversible, yielding to carbamates. A common example is the reaction of CO<sub>2</sub> with polyallylamine (PAA), as presented in Fig. 1.

Experimental work – using PAA as coating sensing layer – showed a frequency shift of nearly 2.5 kHz for 2500 ppm CO<sub>2</sub> concentration [7, 9]. Although they are also hard bases, according to the HSAB theory, tertiary aliphatic amines react with CO<sub>2</sub> and water following a different scheme than the one corresponding to primary and secondary aliphatic groups :

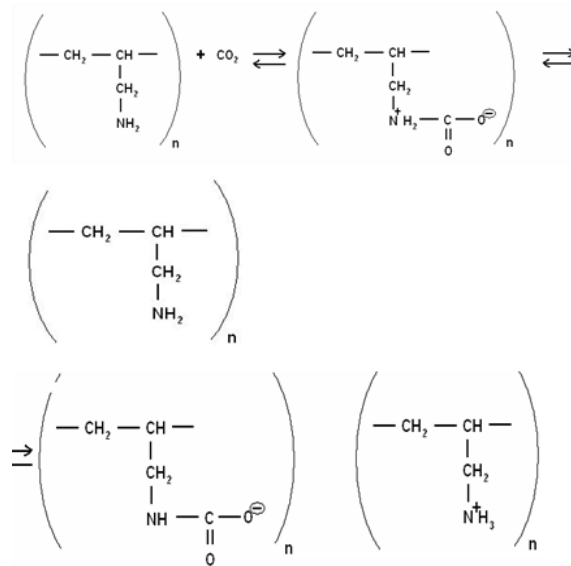
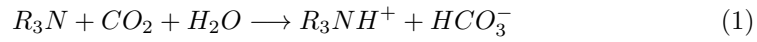


Fig. 1. Reaction of PAA with  $CO_2$ .

For this reason, polyethyleneimine (PEI) (which has tertiary amino groups in the backbone) interacts both with  $CO_2$  and water. A major drawback of using these polymers as  $CO_2$  sensitive coatings is their cross-sensitivity to other acidic gases, like  $SO_2$ ,  $NO_2$ , mainly due to the high humidity levels in open air.

The addition of amino carbon nanotubes (Fig. 2) into the mass of the polymers exhibits some advantages: carbon nanotubes (CNTs) are antioxidant and increase the lifetime of the coating, improve mechanical properties of the polymeric film, increase hydrophobicity.

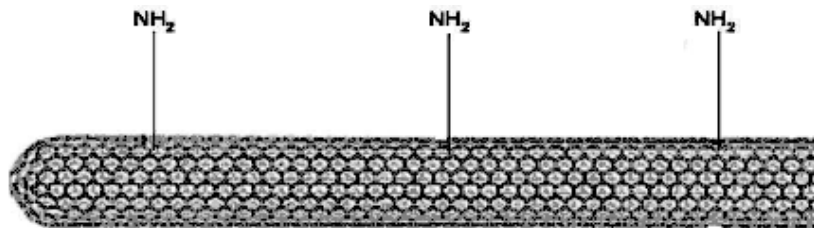


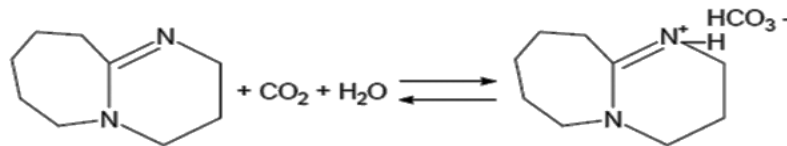
Fig. 2. The structure of amino-carbon nanotubes.

However, the sensitivity of the sensing layer, tested in the same conditions, decreases. A reasonable explanation relates to the type of amino groups which are present at the surface of the carbon nanotubes. These amino groups are borderline bases, and their preference for  $CO_2$  molecules is lower in comparison with that exhibited by the aliphatic amino groups which exist in PEI and PAA [6–9]. For this

reason, both PEI–aminocarbon nanotubes (aCNT-EI) and PAA-aminocarbon nanotubes (aCNT-PAA) matrix nanocomposites exhibit lower sensitivity than simple polymers. For 2500 ppm CO<sub>2</sub> concentration, frequency shifts of 1.1 kHz and 0.7 kHz were obtained for aCNT-PAA and aCNT-PEI, respectively [7, 9].

## 2.2. Bronsted-Lowry Interaction

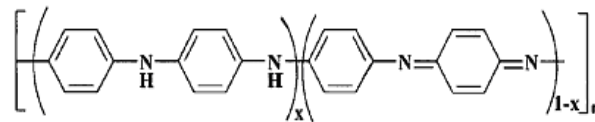
According to Bronsted–Lowry theory, a base is defined as proton acceptor, and an acid as proton donor. Simply speaking, an acid–base reaction consists in transfer of a proton from an acid to a base. In the literature, several organic compounds, classified as bases according to Bronsted–Lowry theory, were used for CO<sub>2</sub> sensing: 1,8-diazabicyclo[5,4,0] undec-7-ene (DBU) (Fig. 3) or 1,5-diaza [3,4,0]-non-5-ene (DBN), polyguanidines, polyamidines, DBU-methyl phenylsilica, polyether DBU, etc. [17–21].



**Fig. 3.** The reaction of DBU with CO<sub>2</sub> and water at room temperature.

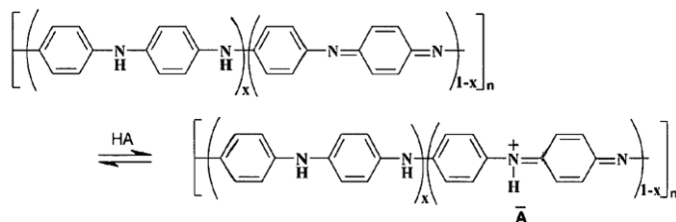
At the same time, polyanilines (as emeraldines or in protonated form) were proposed and tested as sensitive layer for CO<sub>2</sub> detection with SAW/BAW devices [11–14, 22]. At first glance, a Lewis interaction is less susceptible in the case of polyanilines, because aminic nitrogen (the backbone of the polyanilines) can be classified as borderline base. According to Ogura [23], polyaniline (in the dielectric emeraldine form) can sense CO<sub>2</sub> only if water molecules are present in the system. This is because CO<sub>2</sub> reacts with water and the liberated proton reacts with emeraldine. During the protonation of the nitrogen atoms, the conductivity of the coating increases. A change in the polymer conductivity changes the electric field created by the wave and thus influences its propagation velocity. However, this mechanism is still under debate. MacDiarmid et al. claimed the impossibility of emeraldine protonation [24].

We conceived two experiments which support Ogura’s mechanism. One experiment compares the sensitivity of dielectric emeraldine (Fig. 4) with that of 4-sulfocalix [4]arene-doped polyaniline.

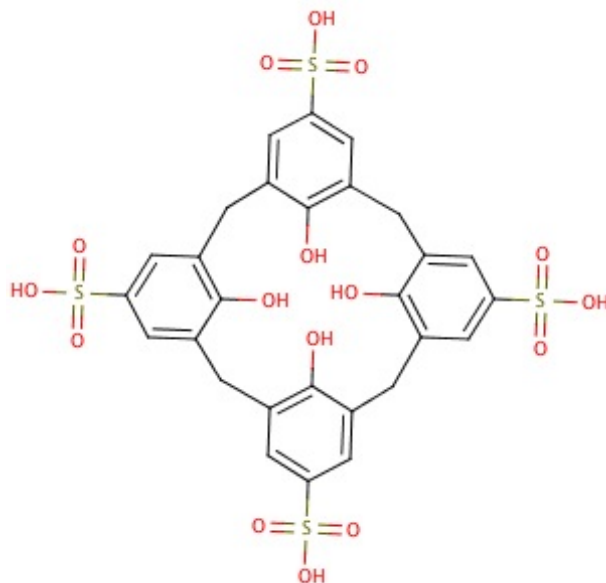


**Fig. 4.** The structure of dielectric emeraldine.

The doping of emeraldine (Fig. 5 and Fig. 6) was performed as described in [12].



**Fig. 5.** The doping of emeraldine with 4-sulfocalix[4]arene.



**Fig. 6.** The structure of 4-sulfocalix[4]arene.

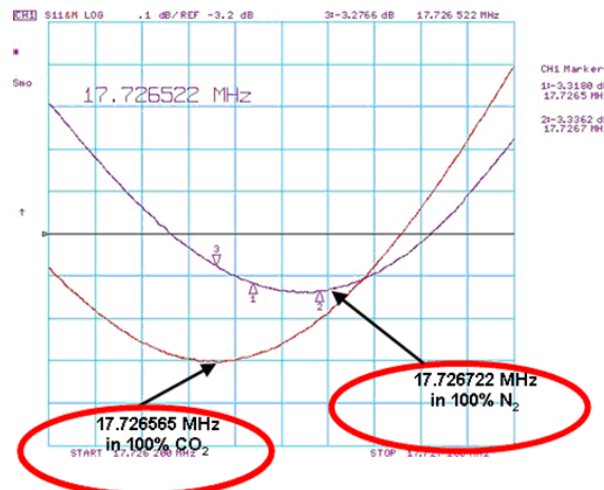
Both polyanilines (doped and undoped) were tested in a BAW device. The device was coated with different sensing layers and the shift of resonance frequency versus  $\text{CO}_2$  concentration was measured. The measurement results are presented in Fig. 7 and Fig. 8.

Both sensing layers have extremely weak  $\text{CO}_2$  sensing response:

- frequency shift of 157 Hz and sensitivity (normalized frequency shift =  $\Delta f/f_0$  = frequency shift / resonant frequency in the absence of  $\text{CO}_2$ ) of  $8.86 \times 10^{-6}$  Hz/Hz for 100%  $\text{CO}_2$  concentration variation in the case of doped emeraldine;
- frequency shift of 176 Hz and sensitivity of  $9.92 \times 10^{-6}$  Hz/Hz for 100%  $\text{CO}_2$  concentration variation in the case of undoped emeraldine.

Doped polyaniline has a smaller number of sites susceptible for protonation in comparison with undoped polyanilines (which is already doped in some extent), thus the frequency shift is lower. Overall, these results are in agreement with Ogura's mechanism.

The second experiment employs a SAW delay-line and matrix based emeraldine and carbonic anhydrase (PACA) as coating layer. Carbonic anhydrase is a metallo-enzyme and plays a crucial role as an efficient catalyst for the conversion of CO<sub>2</sub> to bicarbonate and water. Low protonation occurs in the absence of this enzyme. In terms of frequency shift, the sensor response (Fig. 9) is still weak, but more than twice better (361 Hz) compared to those exhibited when using undoped emeraldine as coating layer. With respect to the sensitivity, the PACA SAW solution exhibits an inferior value:  $5.77 \times 10^{-6}$  Hz/Hz. However, this value is obtained for a significantly lower CO<sub>2</sub> concentration variation: from 390 ppm (equivalent to dry air) to 2500 ppm. This variation of around 2100 ppm (0.21%) of CO<sub>2</sub> is approximately 475 times lower than the one which led to the experimental results in Fig. 5 and Fig. 6. Even though, usually, SAW devices (used, in this paper, for PACA experiments) are more sensitive than BAW devices (used, in this paper, for doped and un-doped emeraldine experiments), one can clearly conclude that, if exposed to a 100% CO<sub>2</sub> concentration variation, PACA leads to CO<sub>2</sub> sensitivity at least one order of magnitude higher than emeraldine. This conclusion confirms the protonation of dielectric polyaniline as the driving force in CO<sub>2</sub> sensing with using polyanilines as sensing layer.



**Fig. 7.** Frequency shift for 4-sulfocalix[4]arene doped emeraldine ( $\Delta f = 157$  Hz).

When comparing the two sensing mechanisms described in this paper, the one based on the HSAB theory proves superior, both in terms of frequency shift and sensitivity (Fig. 10 and Fig. 11). For the Bronsted-Lowry selection, the sensing is based on the reaction between the coating layer and the protons generated in the CO<sub>2</sub>-H<sub>2</sub>O reaction. When using the HSAB principle as selection tool, the sensing is based on direct reaction between the coating layer and CO<sub>2</sub>. Since the amount of protons generated in the first case is limited, while in the second case the vast majority of the coating layer sites are potentially active, the HSAB principle-based selection leads to coating layers with increased sensitivity for CO<sub>2</sub> detection.

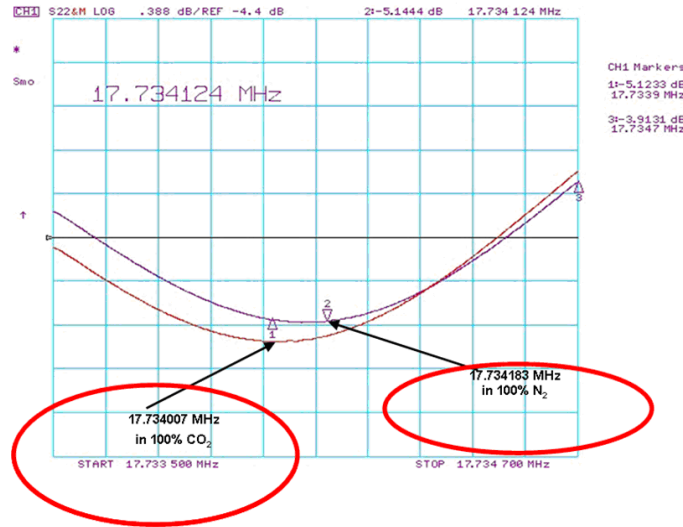


Fig. 8. Frequency shift for emeraldine ( $\Delta f = 176$  Hz).

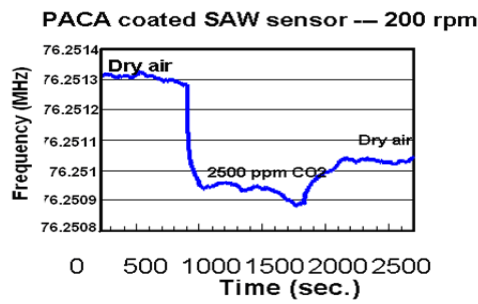


Fig. 9. Test results on PACA using 2500 ppm CO<sub>2</sub> and dry air as baseline ( $\Delta f = 361$  Hz).

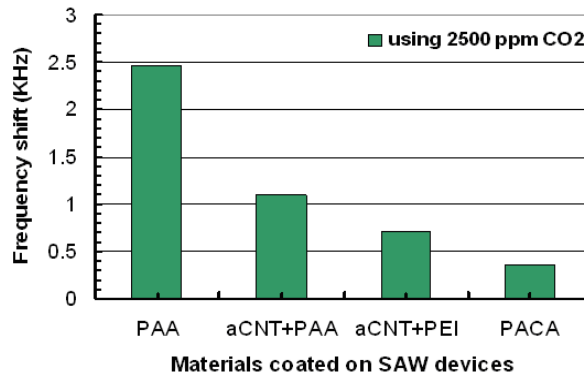


Fig. 10. Frequency shifts at 2500 ppm CO<sub>2</sub> concentration for different sensing layers used to coat SAW devices.

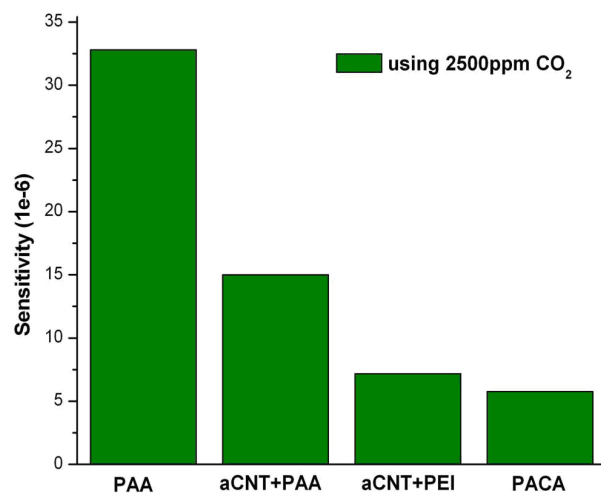


Fig. 11. Sensitivities (normalized frequency shifts) at 2500 ppm CO<sub>2</sub> concentration for different sensing layers used to coat SAW devices.

### 3. Conclusions

Two CO<sub>2</sub> sensing mechanisms, based on the HSAB and Bronsted–Lowry theories, were discussed. They were evaluated by selecting amino groups–based coating layers, which were deposited on SAW devices for CO<sub>2</sub> detection. Experimentally measured sensitivities exhibited by coating layers such as PAA, PEI, nanocomposite matrix based on PAA–aminocarbon nanotubes and PEI–aminocarbon nanotubes, emeraldine, 4-sulfocalix[4]arene–doped polyaniline, and matrix based emeraldine and carbonic anhydrase (PACA) were presented and assessed according to their corresponding sensing mechanism. Experimental data show that the HSAB principle is better than the Bronsted–Lowry theory as selection tool for choosing CO<sub>2</sub> sensitive coating layers in SAW devices.

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