



## Development of gas sensors coatings by polyaniline using pressurized fluid

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### ABSTRACT

The objective of this work was to develop gas sensors using three different techniques for the deposition of polyaniline film: (a) precipitation of polyaniline particles doped with dodecylbenzenesulfonic acid (DBSA) using supercritical carbon dioxide (SC-CO<sub>2</sub>), (b) rapid expansion with SC-CO<sub>2</sub> (modified RESS) of polyaniline doped with DBSA, and (c) in situ polymerization polyaniline doped with chloridric acid. The sensors responses were evaluated at moisture and volatile organic compounds (VOCs). All of the sensors presented a satisfactory sensitivity and reversibility when exposed to VOCs. The films morphology was characterized by scanning electronic microscopy for field emission (FE-SEM). Results showed a difference regarding phase formation and behavior for the sensors obtained using SC-CO<sub>2</sub> coatings with polyaniline and by in situ polymerization, indicating that techniques the use of supercritical fluid techniques are promising in manufacturing such electronic devices.

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### 1. Introduction

Electronic noses consists usually by a set of sensors that uses conducting polymers as transducers [1–3], whose electrical conductivity modifies when exposed to volatile chemicals. Conducting polymers have a high potential for application in these devices, since they can experience various physical and structural changes in the presence of certain chemicals, due to change in its oxidation state. Therefore, application of conducting polymers as active materials and transducers for chemical and biological systems has resulted in an increased sensitivity and selectivity of the sensors manufactured. Associated with the facilities of the synthesis, low cost is often mentioned as another reason that these polymers are used in electronic noses [1,4–6].

Among the conducting polymers, polyaniline has received great attention in recent years due to its chemical stability in ambient conditions, good processability, low cost, easy polymerization and doping, allowing multiple technological applications [7,8]. As many other polymers, the electrical conductivity of polyaniline depends on the oxidation state, the number of electrons added or removed from the polymer structure.

Current techniques generally used in the preparation of these sensors with conducting polymers result in uneven polymeric films with respect to the morphology and size distribution of the particles. These peculiarities imply in some changes in the sensor performance, decreasing its stability, sensitivity and reproducibility. Thus, the development of sensors with techniques that allows obtaining a uniform polymeric film will result in an increase of the features cited above, which are desirable in the performance of any sensor [9,10].

Film deposition techniques most commonly used are *spin-coating*, *casting*, self-assembled and *spray* [11] that allow a limited control over the properties of the surface, creating films with deformities randomly distributed, often due to the residual solvent. Such deformities degrade the performance, reversibility and stability of the sensor. Therefore, new methods for the formation of the film are required to produce more uniform polymeric surfaces.

A possible alternative to this problem is the use of supercritical or pressurized fluids as solvents and antisolvents. Several researches have shown that this technology is useful in modifying the properties of materials such as particle size, size distribution and morphology of the particles produced [9,10]. Another feature of this technique is the efficient separation of the solvent and particles after precipitation, avoiding waste solvents in the product and providing a beneficial reuse of them [12,13]. These processes offer many advantages due to the sudden change in solubility by the expansion of the supercritical solution which leads to a uniform

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film formation of small particles and/or fibers and particles with a narrow size distribution [10,14–16].

In this context, the objective of this work was to develop gas sensors using three different techniques for the deposition of polyaniline film in the emeraldine oxidation state as active layer: (a) precipitation of polyaniline particles doped with dodecylbenzenesulfonic acid (DBSA) using supercritical carbon dioxide (SC-CO<sub>2</sub>), (b) modified RESS with SC-CO<sub>2</sub> (RESS – rapid expansion of supercritical solutions) of polyaniline doped with DBSA, and (c) in situ polymerization polyaniline doped with chloridric acid (HCl). The performance of the sensors was evaluated in electronic nose in the presence of moisture and volatile organic compounds.

## 2. Experimental

### 2.1. Materials

Aniline (Aldrich) was purified by distillation. Ammonium persulfate (APS), chloroform, toluene, dimethyl formamide, acetone, ethanol, hexane, ethyl acetate, HCl (Merck) and DBSA (TCI) were used without any previous treatment. Nitrogen and carbon dioxide (99.9%) were purchased from White Martins S.A. Commercial aqueous graphite paste Aquadag E (Acheson Co.) was used. Vellum paper (grammage 63 g/cm<sup>2</sup>) was purchased in local market.

### 2.2. Development of sensors and polyaniline synthesis: doped with DBSA (Pani-DBSA) and in situ polymerization doped with HCl (Pani-HCl)

The interdigitated electrodes of graphite were obtained using the line patterning technique and the polymers synthesis of polyaniline as described previously by Steffens et al. [15,16].

### 2.3. Solubility and phase equilibrium

Solubility data of Pani-DBSA in chloroform was measured at 25, 30, 35, 40 and 45 °C. In order to determine phase equilibrium of the conducting polymer with carbon dioxide, measurements of phase transitions were carried out in a variable volume view cell, using a static synthetic method [17].

Phase equilibrium experiments were carried out for the ternary system (Pani-DBSA + chloroform + CO<sub>2</sub>), in which an organic solution (Pani-DBSA dissolved in chloroform) was previously prepared at the concentration of  $1.15 \times 10^{-3}$  g ml<sup>-1</sup>. The solution was ultrasonicated during sixty min. Measurements were performed at 25, 35 and 45 °C with 0.4, 0.6, 0.7, 0.9, 0.95 and 0.97 mass fractions of CO<sub>2</sub>. All pressure transitions were determined in triplicate. The Peng–Robinson equation of state (PR Eos) [18] with the quadratic van der Waals mixing rule was used to represent the phase behavior of systems at high pressures [17].

### 2.4. Film coating of gas sensors

The deposition of Pani-DBSA with precipitation assisted with pressurized fluid was performed in a chamber, where the interdigitated electrode was placed in the bottom of it. The chamber was pressurized to 95 bar. Initially, 10 ml of Pani-DBSA solution was added to the precipitation chamber in a 1 ml/min flow rate at 25 °C, followed by the addition of 200 ml of CO<sub>2</sub> with a flow rate of 20 ml/min. The addition of Pani-DBSA and CO<sub>2</sub> was repeated for three times. Fig. 1 shows a schematic diagram of the experimental apparatus used for preparation of sensors by Pani-DBSA precipitation. A detailed description of the experimental apparatus and procedure for coating the interdigitated electrodes for attainment the gas sensors throughout deposition of polyaniline in situ from

1 mol/l HCl aqueous solution and rapid expansion with supercritical fluid (modified RESS) of Pani-DBSA can be found in the work of Steffens et al. [15,16].

### 2.5. Voltage measurement in electronic nose to the presence of moisture

The gas sensors were connected to an electronic nose system with five channels connected to a computer. The gas sensors were fixed inside a 4.5 l chamber at 25 °C and 50% of moisture. The voltage for all sensors was adjusted to the same baseline at 400 mV and the experiments were carried out in triplicate. The sensors were exposed to laboratory air for 10 min, then for 20 min to dry N<sub>2</sub> inside the chamber for several times. The sensitivity (*S*) and reversibility (*η*) of the gas sensors were calculated from Eqs. (1) and (2) [1]:

$$S = \frac{(V - V_0)}{V_0} 100 \quad (1)$$

$$\eta = \frac{(V - V_f)}{(V - V_0)} 100 \quad (2)$$

where *V*<sub>0</sub> is the initial voltage of the sensor, *V* is the voltage after exposure to a dry N<sub>2</sub> flow and *V*<sub>*f*</sub> is the minimum voltage in the presence of laboratory air after the exposure to dry N<sub>2</sub>.

### 2.6. Sensitivity of the sensors in volatile organic compounds (VOCs)

In order to evaluate the sensitivity of the sensors in the presence of VOCs, the sensors were firstly exposed to ambient conditions (laboratory air), with the data of electrical resistance measured by a (FLUKA771) multimeter every 30 s for 5 min. Later, the sensors were exposed to the vapor VOC (hexane, toluene, ethyl acetate, acetone, ethanol, dimethyl formamide) in a beaker containing 20 ml of each solvent for 5 s, and the data acquisition of resistance was accomplished every second, and finally the sensors were again exposed to ambient conditions (laboratory air) for 5 min. The gas sensors sensitivity to each vapor was calculated by Eq. (1) and the experiments were performed in triplicate.

### 2.7. Morphological characterization by scanning electronic microscopy for field emission (FE-SEM)

Surfaces depositions of polyaniline film in the emeraldine oxidation state, as the active layer in the gas sensors were examined with a Zeiss Supra 35 field emission scanning electron microscope (FE-SEM).

### 2.8. UV-visible spectroscopic characterization

The UV-visible spectroscopic studies were performed with polyaniline solution in the range of 200–1100 nm using the Varian Cary (model 50) spectrophotometer.

## 3. Results and discussion

### 3.1. Solubility and phase equilibrium

The knowledge of phase equilibrium and solubility is a relevant step for process design that makes use of supercritical or pressurized fluids. The lower solubility of polyaniline in organic solvents [19] is due to the difference in chemical nature between the hydrophilic dopant and hydrophobic organic polymer. Table 1 presents the values of Pani-DBSA solubility in chloroform solvent at different temperatures, where it can be observed that the Pani-DBSA solubility increases with temperature. The high value of

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