

Alternative solvents containing phenyls and isoprenic units to fabricate polyaniline-based layers sensitive to ammonia

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Summary:

Sensors based on conductive polymers constitute promising technologies to monitor ammonia. Polyaniline (PAni), doped with an acid, is commonly used for these applications. However, PAni is poorly soluble in most of organic solvents. When m-cresol is identified as a good solvent to stabilize PAni, it can't be used in industrial fabrication processes due to its toxicity. The objective is to study alternative solvents having similar structures than m-cresol to disperse PAni and provide sensing performances to ammonia from obtained active surface layers.

Keywords: Chemiresistive Sensor, Ammonia detection, Conductive Polymer, doped Polyaniline, Polyaniline dispersion.

Background and Motivation

Gaseous species from polluted air may be toxic and drive to health problems after inhalation. For instance, ammonia gas mostly produced by agriculture and industrial facilities (microelectronic, fertilizer, refrigerants fields) may lead to chronic lung diseases and respiratory inflammations [1]. To guarantee workers' health, efficient sensors are needed. Among ammonia sensors, usual metal oxides ones suffer from high operation temperature and lack of flexibility [2]. Conversely, sensors based on conductive polymers work at room temperature. Their structural and mechanical properties are easily tuneable making them a promising alternative [3].

Polyaniline (PAni) constitutes a common conductive polymer used for sensing applications. The choice of a solvent to make the device by depositing the conductive ink on the electrodes remains challenging. Doped polyaniline is soluble in few organic solvents. Among efficient solvents, m-cresol was identified as one of the best, displaying high solubility of PAni protonated by Camphor-10-sulfonic acid (CSA), due to favourable hydrogen bond interactions and to van der Waals forces between phenyl groups of molecules [4]. However, m-cresol is a Carcinogenic, Mutagen and Reprotoxic solvent which can't be used anymore in industries with hygiene and safety standards. Therefore, the objective of this study is to find other alternative solvents to disperse doped PAni without decreasing its sensing performances to ammonia.

Knowing that organic solvents with similar structures to m-cresol could have favourable interactions with PAni:CSA [4], solvents having π -bonds with phenyls or isoprenic units were selected. The ability of these solvents to fabricate PAni layers sensitive to ammonia was investigated.

Experimental part

Polyaniline-emeraldine ($M_w = 65000 \text{ g mol}^{-1}$) and (+)-Camphor-10-sulfonic acid (CSA), chosen as the doping agent were provided by Sigma Aldrich. They were mixed together to obtain a doping rate of 50%. The solid content was fixed to 15 g/L. The powder mix was then incorporated in four solvents: Toluene (T), Benzyl alcohol (BA), Alpha Pinene (AP) and DL Limonene (DLL). Solutions stayed under stirring at 700 rpm for 5 days and were sonicated for 1 hour. Then, 1.5 μL of each solution was drop-casted onto gold interdigitated electrodes deposited on polyimide (200 μm gaps and fingers). Three sensors were obtained per solution. The sensors were finally dried on a hot-plate at 100°C for one night, and during 7 days at 100°C in an oven under vacuum. Then, the surface microstructure of PAni:CSA layers was characterized using Scanning Electron Microscopy at 10 kV and a magnification size of 2000. Sensing performances of the PAni:CSA layers were tested at various ammonia concentrations (from 50 to 2000 ppb). The temperature and the relative humidity were respectively fixed to 20°C and 45%. Relative responses of all sensors were calculated as a function of the resistance

under clean air (R_0) and real-time resistance (R) as followed:

$$\text{Relative Response} = \frac{R - R_0}{R_0} \times 100$$

Results

Except for the uniform Benzyl alcohol (BA) solution, most of solutions present two phases (Fig.1). The dispersion of PANi:CSA in solvent is unstable and the difference of solubility directly impacts the polymer microstructure after solvent evaporation. Indeed, only PANi:CSA:BA sample presents a continuous morphology with some holes at the surface. The good stability of PANi in BA can be explained by hydrogen bonds formed between the dopant and the hydroxyl group (OH) of the solvent. Other samples made from apolar solvents (T, AP, DLL) display more aggregated and porous active surface layers. Some sticks and needles even appear on the active surfaces from samples made in DLL limonene and Toluene, respectively. The morphology of T, AP and DLL seem to present a higher specific surface area which may facilitate gas-solid interactions.

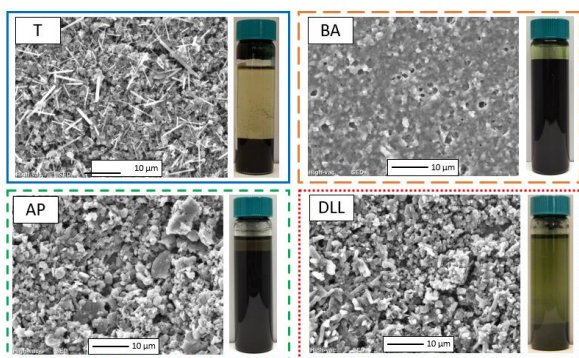


Fig. 1. SEM images of PANi:CSA surfaces from different solutions observed after 24 hours of rest.

The resistivity of the device measured before ammonia injection indicates that AP layer has the highest resistivity ($3.0 \cdot 10^5 \Omega$), followed by T and DLL samples with similar resistivities ($4.0 \cdot 10^4 \Omega$) and finally by the BA sample ($8.8 \cdot 10^2 \Omega$).

Fig.2 presents the evolution of the relative responses toward different concentrations of ammonia. Independently of the solvent, sensors present the same behaviour characterized by an increasing relative response with ammonia concentration. Calibration curves have shown that samples made in toluene have the highest sensitivity of $393 \pm 18 \text{ \%/ppm}$, followed by DLL Limonene sensors ($306 \pm 46 \text{ \%/ppm}$) and AP sensors ($223 \pm 13 \text{ \%/ppm}$). Sensors elaborated in BA display the lowest sensitivity of $51 \pm 6 \text{ \%/ppm}$. Then, limits of detections (LOD) are calculated according to IUPAC recommendation. Samples from Toluene, Alpha Pinene and DLL Limonene display a similar and very low LOD around 2 ppb when the LOD of samples

from Benzyl alcohol is slightly higher around 4 ppb. Sensors elaborated in the three apolar solvents (Toluene, Alpha Pinene, DLL Limonene) are very interesting and promising given their high sensitivity values and low limits of detection. That can be due to the higher specific surface area of the samples [5], allowing the gas to deeper penetrate into the active surface layer and to better interact with the active sites of PANi.

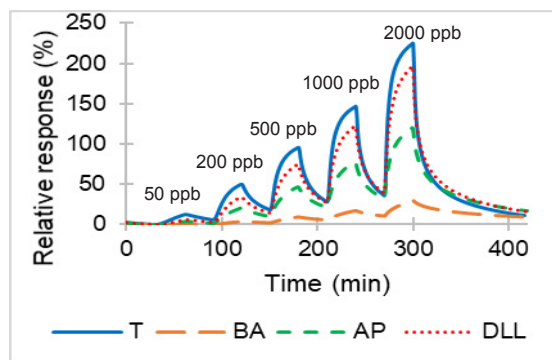


Fig. 2. Responses toward ammonia concentration from 0 to 2000 ppb of PANi:CSA sensors from solutions T, BA, AP, DLL (45% RH and 20.4 °C).

Conclusion

The objective of the study was to investigate alternative solvents having similar structures than m-cresol to prepare organic ammonia sensors. Even if PANi is poorly soluble in apolar solvents, those solvents lead to morphologies with high specific surface area and very good sensing performances. Hence, the next step will be to find additives able to stabilize the polymer in solution, to enhance the reproducibility of the devices made by ink printing processes.

References

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