

## Amperometric Ammonia Sensor Using Polypyrrole and Substituted Polypyrrole with Different Dopants.

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Polypyrrole is the most widely used conducting polymer to the construction of sensors and biosensors, once their conductivity and electroactivity do not strongly depend on pH of the electrolytic. The aim of the present work remains in the improvement of amperometric ammonia analysis, using a polypyrrole film doped with DBSA anions. This large amphiphilic dopant promotes changes on the polymeric film presenting a more accentuated response and extending the linear response over a wide range of concentrations, when compare with films doped with small inorganic anions, such as chloride. The substituted pyrrole monomers, as N-methyl-pyrrole, was also used with the aim of investigating the role played by acid hydrogen present in polypyrrole. The response of the sensor was followed by EQCM and Raman Spectroscopy experiments as tools to propose to elucidate the mechanism of ammonia detection.

Chloride doped polypyrrole films (PPy/Cl) were prepared from a pyrrole 0.1 M and KCl 0.1 M aqueous solution, holding the potential at 0.70 V. The augmentation in charge density (from 20 up to 90  $\mu\text{C cm}^{-2}$ ) of polymer deposited improves the response, but the sensitivity in the concentration linear range (0 up to 0.2 mM) stay unaffected for the different amounts of polymer formed presenting a value around  $2.2 \text{ A M}^{-1} \text{ cm}^{-2}$ . On the other hand, DBSA doped polypyrrole films (PPy/DBSA), growth in the same conditions of PPy/Cl, present a particular behavior, where the sensitivity to the ammonia extends for a range (0 to 1 mM) up to four times bigger than films doped with chloride ions and accentuated current densities response were observed. However, the sensitivity calculated for the linear region was  $1.5 \text{ A M}^{-1} \text{ cm}^{-2}$ . The advantages using the DBSA doped polypyrrole films as electrodes in ammonia sensor resides in the fact of analite concentration range larger than PPy/Cl films, and also accentuated current density response.

With the aim to elucidate ammonia detection mechanism investigation PNMPy films was growth in the same conditions as chloride and DBSA doped PPy. The amperometric detection of ammonia presented a reduced sensitivity, c.a.  $0.85 \text{ A M}^{-1} \text{ cm}^{-2}$ . These results demonstrated the important role played by the acid hydrogen present on polypyrrole on the mechanism of ammonia detection. The low sensibility of the PNMPy/DBSA polymeric films was attributed to the fact that the potentials for ammonia detection, is very close to polymer overoxidation potential, in this state it becomes non electroactive and consequently its response is reduced.

During the amperometric ammonia determination process the polymeric film mass increase, this performance was followed by the electrochemical quartz crystal microbalance. The mass variation is related to the exchange of cations and anions from the buffer solution to the film bulk, once the film has been re-oxidated, and anions should be inserted in the film to compensate the positive charge formed, together with anions also solvent and cation possibly is inserted in to the polymer. The mass change differ for the distinct

dopants, in this case chloride and DBSA. A smaller change is observed for the DBSA, hitherto it is entrapped into the film and the negative charge is used to compensate the charge formed during the oxidation process.

Conductivity loss or structural changes of the polymer can be characterized through changes in the spectra Raman characteristic of a polypyrrole film when exposed to ammonia[1]. The different dopant (DBSA or Cl) in the PPy film, do not show any differences, except by the fact of the band definition due to N-H deformation in the plan observed in  $1250 \text{ cm}^{-1}$ . The bands corresponding to the polymer, are increased by the Raman resonant effect; while dopant, such as chloride and DBSA, are not in resonance condition[1]. This property gives to Raman spectroscopy great advantages over other techniques, like U.V. -visible and Infrared, once dopant and/or electrolyte can hide important results for the numerous amounts of bands presented.

Determination of ammonia by PPy/DBSA films were accompanied during the potential application by Raman spectroscopy, no change can be verified in the spectra, even for long times of exposition and high ammonia concentrations. When, experiments were accomplished using PPy films/DBSA at open circuit, for long times, and high ammonia concentrations, is observed that the band corresponding to N-H plan deformation in  $1250 \text{ cm}^{-1}$  diminishes while the other bands are unaffected. The results for high concentrations of ammonia and in long periods of polymeric film exposition to the analite, have noticed no variations that could be related to structural changes of the polymeric film, only the fact of decreasing of N-H band deformation. From Raman results, it can be inferred that the mechanism of detection is the same as proposed by Gustafsson et. al., for ammonia gas, which states a reversible deprotonation reaction of the polymer provoked by ammonia[2,3].

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