

Ammonia Sensors based on Conducting Polymers

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Ammonia dosage was always a subject of great interest for being a very important task for the diagnosis of some diseases, such as renal and hepatic inadequacy and diabetes. Ammonia is excreted during amino acids metabolism and, due to its high toxicity; any accumulation at higher levels of its critical values must be avoided. At the liver, ammonia is reduced to urea with the consequent elimination by the urine and it is converted to NH_4^+ at the kidney. Another important factor that motivates to improve ammonia sensing is that, its presence in drinking water or food, is an indication of organic matter decomposition that could be harmful to the human health. On the other hand, the determination of the ammonia concentration in soils, where ammonia is used in fertilizers, is also important due to the fact that ammonia excess alters the acidity of the soil, breaking the nutrition cycle and the ecological balance. Based on needs as those mentioned above, researchers have been providing efforts in the study of new sensors for ammonia. One of the first practical applications of conducting polymers was in sensors[i], but, sensibility was very low and the response was completely irreversible. One of the pioneer paper using polypyrrole modified electrode showing its potentiality for ammonia detection was presented by Kanazawa et. al. [ii] whose results revealed that ammonia detection could be associated to a decrease of polypyrrole conductivity by a factor of 10. Even so, these authors stated that ammonia reacts weakly with PPy and it can be removed easily recovering the polymer conductivity to its original value. The motivation of this article is the improvement of amperometric analysis of ammonia, using a polypyrrole film doped with DBSA anions. This large amphiphilic dopant promotes changes on the polymeric film conferring a more accentuated response and also enlarges the linear range of concentration, when compare with films doped with small inorganic anions, in this case chloride. The response of the sensor was followed by EQCM and Raman Spectroscopy experiments. UV-Visible absorption spectroscopy and DEMS analysis of the solution during ammonia detection experiments, will be use as tools for determining the products form during ammonia detection. Raman spectra were obtained in a Renishaw Raman Imaging Microscope System 3000, containing an Olympus microscope and a CCD detecto: (Wright 600x400 pixels) refrigerated by Peltier. A He-Ne laser ($\lambda_0 = 632.8 \text{ nm}$, Spectra Physics Mod. 127) was used as the exciting radiation.

Polypyrrole films were electrochemically formed onto the surface of gold evaporated 6 MHz AT-cut quartz crystals (25 mm diameter, piezoelectric active area = 0.20 cm^2). The resonance frequency shift was measured with a HP 5370B Universal Time Counter and electrochemical measurements were performed by a FAC 2001 potentiostat/galvanostat. Polypyrrole films were prepared potentiostatically from a 0.1 mol L^{-1} pyrrole + 0.1 mol L^{-1} KCl solution, by holding the potential at 0.70 V vs. Ag/AgCl for different times in order to obtain different amounts of charge density (20 to $90 \mu\text{C cm}^{-2}$). Polypyrrole films doped with the surfactant DBSA were prepared in the same conditions, with a 0.05 mol L^{-1} pyrrole + 0.025 mol L^{-1} DBSA solution. The analysis of the sensor was skilled in 5 mL buffer borate 0.1 mol L^{-1} pH = 10, degassed for 5 minutes and continually stirred. The response of electric current density was measured at + 0.35 V. The reference electrode was a Ag/AgCl/Cl⁻ (3 M) and the auxiliary electrode a Pt foil. Experiments for the spectroscopic determination of nitrate and nitrite ions were performed in a HP8453 Diode Array Spectrophotometer. DEMS is a technique that consists in determining simultaneously the electrochemical current and the mass signals of reaction products in a mass spectrometer. The connection of the electrochemical cell with the high vacuum chamber is made through a highly hydrophobic PTFE membrane, where the electrode is deposited for maximum pumping efficiency. The technique has been reviewed in detail by different authors [iii].

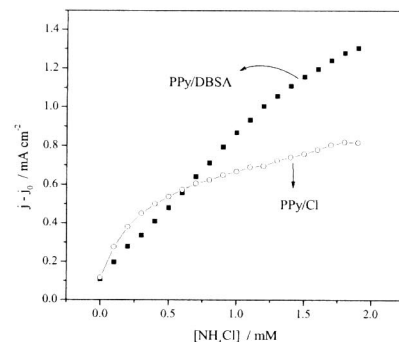
DBSA doped films presents a slightly lower sensibility in relation to chloride doped films, both sensibilities ($S_{\text{PPy/Cl}^-}$) and ($S_{\text{PPy/DBSA}}$) were calculated being equal to 2.2 and $1.5 \text{ AM}^{-1}\text{cm}^{-2}$, respectively. In this way, $S_{\text{PPy/Cl}^-} / S_{\text{PPy/DBSA}} = 1.5$. Thus, the main difference between both polymeric films regarding ammonia determination

resides in the fact that DBSA doped polymer presents a wider concentration range (from 0 to 1 mmol L^{-1}) of linearity when compared with PPy doped with chloride ions. The charge

compensation in the polymeric film during the ammonia detection is affected by the dopant anion: small changes are observed by films doped with large anions, as it was followed by EQCM experiments. Raman spectroscopy revealed that no drastic changes occur in the polymeric chain during the detection, except the diminution of the band at 1250 cm^{-1} .

The use of UV spectroscopy and "on line" mass spectrometry allow to determine the sensing ammonia mechanism onto polypyrrole films. Only NO was detected as the oxidation product independently on the chemical nature of polypyrrole dopants (Cl⁻ or DBSA) and electrode substrate (Pt or Au). By this way, it is possible to infer that it is actually the polymeric film the ammonia oxidation mediator and results show that a redox reaction between the film and the analyte, takes place. Besides, experiments performed with poly(N-methyl pyrrole) films showed that, even at higher potentials used for ammonia determination, the oxidation product obtained by mass spectrometry was always NO and no N₂ or N₂O traces were detected.

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