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Aquivion® ionomer based electrochemical sensor for ammonia detection

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***Abstract* – Electrochemical and capacitive sensors based on Aquivion® D83-06A as sensing element are designed and tested. Electrodes are produced by modifying the sensing element with KOH and/or MWCNTs addition, and casting it on the surface of stainless steel plates. A sandwich sensor is obtained by coupling two steel plates with the thickened Aquivion® D83-06A layer. Devices are tested for ammonia sensing in the range 10-100 ppm in liquid, obtaining an electrochemical and capacitive response in presence of the analyte.**

I. INTRODUCTION.

Ammonia is one of the most used and synthesized compound in process manufacturing. In fact, in the European economic area, the amount of produced and imported ammonia ranges from 10 000 000 to 100 000 000 tons every year [1]. For ammonia in water, Italian law establishes that water intended for the human use must not have ammonia concentration higher than 0.5 mg/l [2], however experiments have shown that the lethal concentration for some fishes ranges from 0.02 to 0.2 mg/l. Essentially, there are four kind of ammonia sensors: semiconductor, catalytic, polymeric and optical sensors [3]. The first type of sensor is based on the capability of semiconducting materials to change their resistance in the presence of reducing gases, such as ammonia. Usually the materials used for this type of sensors are metal oxides, such as WO_3 [3] and SnO_2 [4]; the sensitivity of the latter can be increased by adding some additives, such as Pt, Bi and $AlSiO_3$ [5] or Pt and SiO_2 [6]. Semiconductor sensors based on the heterojunction between hexadecafluorinated nickel phthalocyanine and nickel phthalocyanine have also been reported [7]. Semiconductor sensors usually show limits of detection (LOD) ranging from 1 to 1000 ppm. An experimental sensor based on single-walled carbon nanotubes functionalized with indium tin oxide, having a sensitivity of 13 ppb has also been reported [8]. Catalytic sensors use a catalytic metal, usually platinum, in order to oxidize gaseous ammonia; this reaction produces a temperature rise with a consistent change in the metal resistance. The use of catalytic sensors is hindered by their need of high operating temperature (400-600 °C) and by the fact that the catalytic metal could be poisoned by other volatile chemical compounds. Amperometric sensor has been created using a polypyrrole (PPY) film [9], but it had a too high operating range (100-1000 ppm), and suffered from interferences by ascorbic acid and uric acid. In order to solve this problems, other experiments have been made adding Nafion® or polyphenol [10] to the polypyrrole film: both proved to be effective in solving the interferences. Polyaniline (PANI) is another polymer used as sensitive component in sensors, but it needs to be protonoted by an acid before being used. Resistive PANI-based sensors have shown a sensitivity range from 1 to 10000 ppm [11-12]. In order to improve the reversibility, good results have been obtained doping the polyaniline with acrylic acid [13]. Zhang and collaborators have obtained excellent results using PANI-functionalized carbon nanotubes, in this way they are able to reach a sensibility of 50 ppb [14]. Commercial capacitive polymeric sensors, produced by the Finnish company Vaisala, have a sensibility range from 1 to 1000 ppm [15]. Optical sensors can be divided into two categories: the ones operating on a colorimetric principle and the ones based on optical absorption spectroscopy [3]. The former employ a dye, like bromophenol blue, that changes its color when absorbing ammonia. These sensors are very selective and they have a sensitivity range from 200 ppb to 20 ppm [16]. The second kind of optical sensors is based on the spectroscopy measurement of refractive interferences produced by ammonia absorption into the sensitive element. Pisco and collaborators have produced an experimental device using optical fibers coated with SnO_2, obtaining a lower LOD of 2 ppm [17]. The most sophisticated commercial sensors based on optical analysis employ a laser and a spectrograph, and they can detect up to 1 ppb of ammonia,

however they are very expensive and bulky [18]. The aim of this work is to show the results of a preliminary study on electrochemical and capacitive ammonia sensor based on Aquivion® ionomer as the sensitive component. The effect on the sensitivity of the pH of the ionomer solution and the addition of multiwalled carbon nanotubes (MWCNTs) is also evaluated.

II. EXPERIMENTAL.

A. *Preparation of Aquivion® solutions.*

Aquivion® is a short side chain (ssc) copolymer obtained by Tetrafluoroethylene and a Sulfonyl Fluoride Vinyl Ether copolymerization produced by the Solvay company [19]. Aquivion® D83-06A was used in this work. The ionomer content in the solution is 6%$_{wt}$ in a solvent system composed of 20% water, 40% 1-propanol and 40% 2-propanol. In order to improve the ionomer porperties some changes have been made during the experimental activity, such as the solution pH alteration or the adding of MWCNTs. The former, obtained by adding KOH to the solution, had the purpose of increasing the pores size of the ionomeric matrix, facilitating the diffusion of the analyte [20]. The latter, which aims to increase the sensitive surface, was obtained by adding MWCNTs. The amount of the MWCNTs added to the solution is the 20%$_{wt}$ of the ionomer. The resulting black suspension was put under magnetic stirring for 1 hour and ultrasonication for 3 hours. Six different solutions have been prepared:

- Aquivion® D83-06A,
- pH 4 Aquivion® D83-06A,
- pH 7 Aquivion® D83-06A,
- Aquivion® D83-06A with MWCNTs,
- pH 4 Aquivion® D83-06A with MWCNTs
- pH 7 Aquivion® D83-06A with MWCNTs.

B. *Preparation of the electrodes.*

Selected metal for the electrodes was 316 stainless steel, due to its resistance to acids and low cost. On the metal substrate, a surface of a known area has been selected using Kapton® tape, in order to prevent electrical interferences made by the uncoated electrode surface. Thereafter a thin film of solution has been casted using a wire bar coater. Electrodes obtained with this method are suitable for voltammetrical and potentiostatic studies. However for the creation of a capacitive sensor, a thicker layer is needed, since a single layer of ionomer is too thin to create a sandwich of two electrodes, which is a rudimentary capacitive ammonia sensor (Fig. 1).

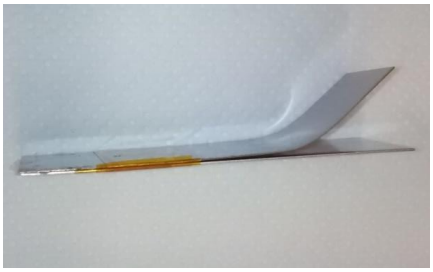

Fig. 1 Sandwich sensor.

Two approaches have been studied in order to increase the thickness of the sensitive element: the first one consisted of multiple ionomer depositions using a brush, while the second option was achieved by soaking a piece of blotting paper in the Aquivion® solution. Both approaches need a specific heat treatment in order to guarantee the contact between the two electrodes and the ionomer. Multilayer electrodes have been exposed to a thermal ramp of 3°C/min from room temperature to 75°C, followed by an hour at the curing temperature of 75°C. Blotting paper-based electrodes underwent milder curing condition: the thermal ramp was equal to the previous, but the final temperature was 55°C, along with a vacuum treatment to ensure the elimination of the solvent system. This techniques allowed to create sandwich electrodes (Fig. 1), nevertheless they introduced a lot of practical manufacturing problems and only few samples could be used for the capacitive tests. Morphological analysis have been carried out using a Zeiss Evo 50 EP scanning electron microscope (SEM). Cyclic voltammetries have been performed in deionized water using a common three electrodes cell, equipped with the sample as working electrode, a platinum wire as counter-electrode and saturated calomel as reference electrode. Cyclic voltammetries have been registered for each monolayer sample and the studied range is from 0 to 100 ppm of ammonia, divided into 10 aliquots of 10 ppm each. The potential is varied from -1.2 V to 0.8 V (vs SCE) and backwards, applying a 20 mV/s scan rate. Capacitive tests have been realized using a multimeter, having an operating range from 1 nF to 9999 µF. Instrument was connected to the sandwich sensor (Fig. 1) submerged into deionized water, thereafter 10 additions of 10 ppm of NH3 have been done. The capacity values were manually registered after each addition every 5 seconds, in order to follow the evolution of the capacity of the system through the time.

III. RESULTS AND DISCUSSION.

Morphology of composite electrodes with MWCNTs was firstly investigated. As shown in fig. 2, the MWCNTs dispersion is fairly homogenous and areas without carbon

nanotubes were not observed. According to fig. 2b, dispersion of MWCNTs was better achieved when the pH was increased. Figure 3 reports voltammetries registered with increasing concentration of ammonia in water. As shown, samples can sense the ammonia presence at 10 ppm and this is also true by all the other Aquivion® solutions. Nevertheless, clear peaks are usually detected at higher concentrations (20-30 ppm). In fig. 4 the comparison between the cyclic voltammograms obtained with the six different single layer electrodes is shown. The registered current densities were similar in all the samples, while both reduction and oxidation peaks were found at different potentials in the different samples. The most evident peak is the reduction peak obtained with the pH 4 Aquivion® D83-06A. Amperometric studies were carried out with the same cell employed in cyclic voltammetry. This kind of tests are usually made with magnetic stirring, however in this specific case it is preferred to avoid it, due to the turbulence produced by the stirring interfering with the current recording. Voltage was selected from the peaks registered in cyclic voltammetry. In order to evaluate the effect of ammonia concentration on the electrical current, 10 additions of 10 ppm have been made. Each addition was done after the stabilization of the current after the previous addition. Amperometric diagrams were obtained for all the single layer samples. Electrode made of Aquivion® D83-06A prepared at pH 7 with MWCNTs showed the best results results (Fig. 5). The aforementioned manufacturing technical problems encountered during the sandwich sensor realization allowed to obtain only the samples based on multilayer Aquivion® D83-06A film, multilayer pH 4 Aquivion® D83-06A with MWCNTs film and blotting paper soaked in Aquivion® D83-06A. As shown in fig. 6, sandwich sensors were characterized by a capacitance variation with increasing ammonia concentration. This trend, even though there was no direct linearity between ammonia concentration and capacitance increase, was found in all sandwich sensors tested. The other samples showed a current variation after each ammonia addition, even though a non linear response to NH_3 additions was obtained.

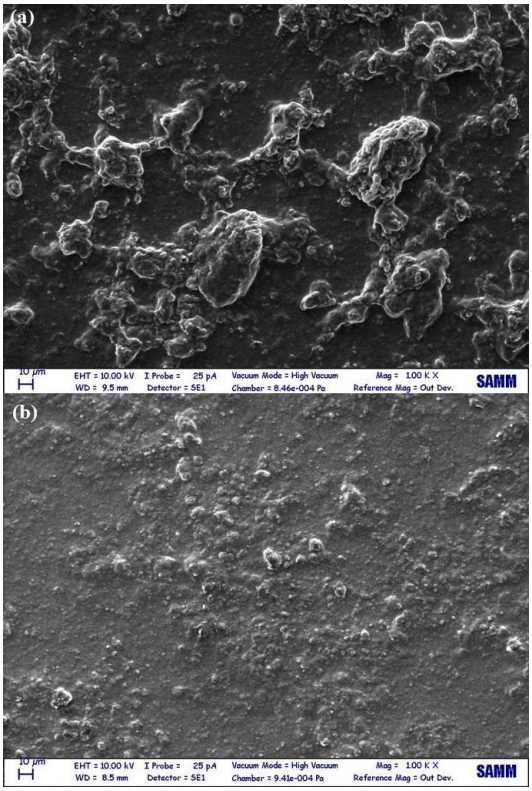

Fig. 2. SEM image of Aquivion® single layer surface with MWCNTs (a) and SEM image of pH 4 Aquivion® single layer surface with MWCNTs (b).

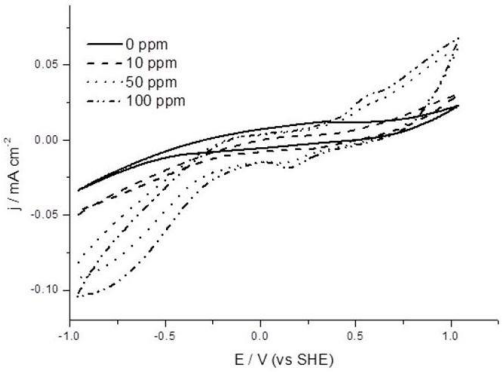

Fig.3. Cyclic voltammograms of Aquivion® D83-06A at four different ammonia concentration (0, 10, 50, 100 ppm).

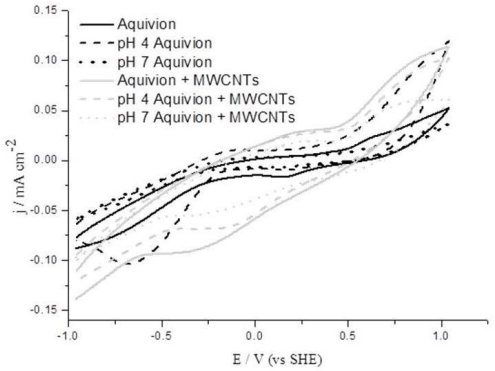

Fig. 4. Cyclic voltammograms of six different Aquivion® electrodes at ammonia concentration of 30 ppm.

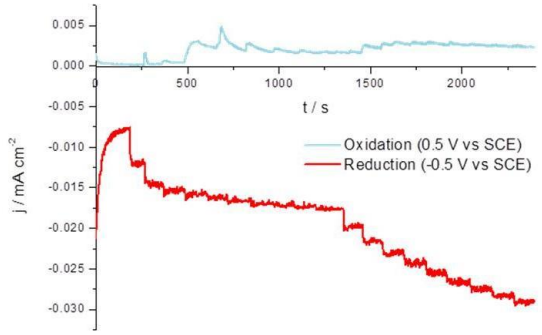

Fig.5. Amperometric *diagrams of the pH 7 Aquivion® D83-06A with MWCNTs sample at two potentials.*

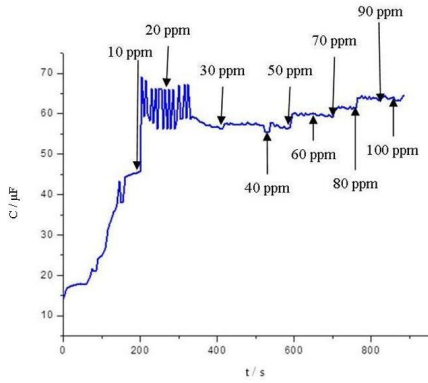

Fig. 6. Capacitance trend of the Aquivion® D83-06A sandwich sensor.

IV. CONCLUSIONS.

Different setups of electrochemical sensors for ammonia detection were tested in this work. Sensors were based on Aquivion® D83-06A as sensing element, and its modification with KOH and/or MWCNTs addition was studied. A capacitive sensor was obtained by coupling two stainless steel plates with the sensing element, although manufacturing problems hindered the obtaining of robust electrodes. Sensors demonstrated the possibility to obtain a good response in ammonia detection, and a capacitive response was registered in the range of 10-100 ppm. Considering the results obtained with ammonia, some preliminary studies were performed on formaldehyde with promising results.

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