Electrical characterization of polypyrrole synthesized by plasma doped with copper oxide particles

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Abstract:
In this paper, the electrical characterization of polypyrrole (PPy) synthesized by plasma doped with copper oxide particles (CuO_x) conditioned by an impregnation process in acidic and basic media of NaOH and NaCl solutions is presented. The electrical conductivity of the PPy increased with the doping of CuO_x in a temperature range from 25 to 100° C. The analysis of the activation energy (Ea) indicated that in acidic NaOH media more than one charge transfer process occurs, compared with the basic ones where only two process occur.

Keywords: impregnation, metal oxides, plasma polymerization, electrical conductivity

1. Introduction

Being inorganic compounds, CuO_x has application in the area of optoelectronics because it absorbs energy in the UV region of the electromagnetic spectrum generating interest in the conversion of solar energy to electricity [1]. Hence the interest in forming hybrid materials of organic and inorganic nature with specific properties for a given application [2]. In this sense, the metallic doping to conjugated polymers induces to changes in the optical and electrical properties acquiring great interest in photovoltaic processes. In particular, polypyrrole (PPy) has a five-membered ring with a nitrogen heteroatom in its chemical structure. It is one of the polymers with applications in electrical and electrochromic devices, and due to the conjugate structure, "*p*" or "*n*" type doping can be carried out with the insertion of other types of particles [3]. According to the above, the objective of the present work was to form PPy/CuO_x compounds through an impregnation process to study the influence of CuO_x particles in an acidic and basic environment on electrical conductivity.

2. Methodology

To obtain the PPy/CuO_x compound, the methodology was carried out in three stages:

1) PPy was synthesized by plasma at $3.4x10^{-1}$ mbar, 100 W supplied by radiofrequency source at 13.56 MHz with resistive coupling for 180 min. The reactor consists of a Pyrex glass tube of 1500 cm^3 held at each end by stainless steel flanges, each with two ports of entry. At one end a Pirani type sensor is connected to measure the pressure and a vacuum pump; at the opposite end the monomers to be polymerized are introduced, as shown in Fig. 1.

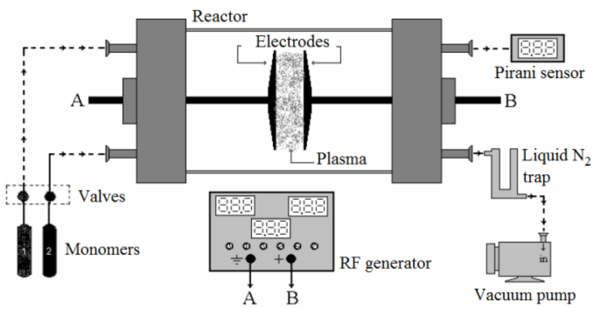

Fig. 1 Polymerization of PPy.

2) CuO_x particles were obtained by electrosynthesis in an acid medium (blue color) and basic (red color) NaCl and NaOH.

3) For the impregnation the PPy was contacted with CuO_x for 24 hours. The solution was then evaporated at 60° C for 12 hours.

For the characterization of the materials, the morphology was analyzed with Scanning Electron Microscopy JEOL JSM-6010LA. The electrical resistance of the PPy / CuOx compounds was measured with a device having two parallel electrodes with the sample in the center. The material was heated in a temperature range from 25 to 100° C and the electrical resistance was measured with a LCR GW Instek LCR-95 meter at 10 KHz.

3. Results and discussion

3.1 Morphology:

In Fig. 2 the morphology of PPy / CuOx impregnated in $NaCl_{(A)}$ and $NaOH_{(A)}$ acids is presented. In general, it is observed that the compound treated with $NaCl_{(A)}$ favors the dispersion of CuO_x particles on the PPy compared with that of $NaOH_{(A)}$ where agglomerated particles of irregular morphology are observed, see Fig. 2(a) and (b), respectively. For PPy/CuO_x with solutions of $NaCl_{(B)}$ there is a morphology in the form of bubbles corresponding to the PPy, on the surface there are deposits of CuO_x filaments of approximately 0.081 µm in length. In the $NaOH_{(B)}$ solution the CuO_x particles are on the surface of PPy, which indicates that the impregnation was not favored, see Fig. 2(c) and (d), respectively. According to the results it was observed that in acid solutions, the impregnation of CuO_x in PPy is optimal, however, there was more dispersion of particles in the solution of $NaCl_{(A)}$ compared with that of $NaOH_{(A)}$ where agglomerates were observed.

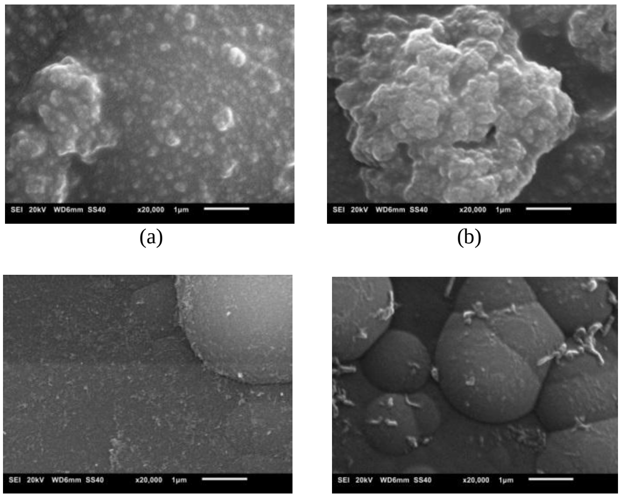

Fig. 2 PPy/CuO_x morphology in acidic and basic medium: (a) $NaCl_{(A)}$, (b) $NaOH_{(A)}$, (c) $NaCl_{(B)}$, (d) $NaOH_{(B)}$, at 20,000x.

3.2 Electrical characterization

3.2.1 Acidic medium:

In Fig. 3 the graph of electrical conductivity as a function of temperature is shown. It is observed that at 25° C the PPy presented a conductivity of $2.15x10^{-8}$ S/m and when increasing to 100° C it was $1.49x10^{-6}$ S/m, which indicates an increase of up to 2 orders of magnitude. For the PPy/CuO_x in NaCl, an almost linear behavior was observed, which seems to indicate that the metal part predominates, however in the NaOH solution from 55° C it had a conductivity of $9.64x10^{-8}$ S/m while at 82° C the maximum was $1.37\ x10^{-5}$ S/m increasing up to 3 orders of magnitude compared to PPy and PPy/CuO_x in NaCl, see Fig. 3.

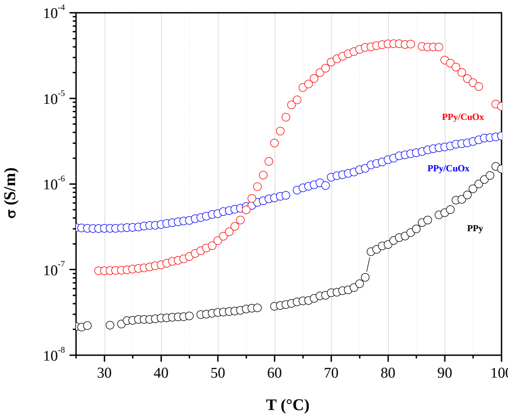

Fig. 3 Electrical conductivity of PPy and PPy/CuO_x in acidic solutions of: NaOH (red) y NaCl (blue).

Subsequently, by means of a linear adjustment and applying the Arrhenius equation, the activation energy (Ea in eV) [4] of PPy and PPy/CuO_x was calculated, as shown in Fig. 4. The Ea for PPy were 0.19 and 1.19 eV, while for PPy/CuO_x in NaCl was 0.40 eV. PPy/CuO_x in NaOH has four inflection points that presented Ea values of 0.23, 2.35, 0.083 and -1.5 eV, respectively.

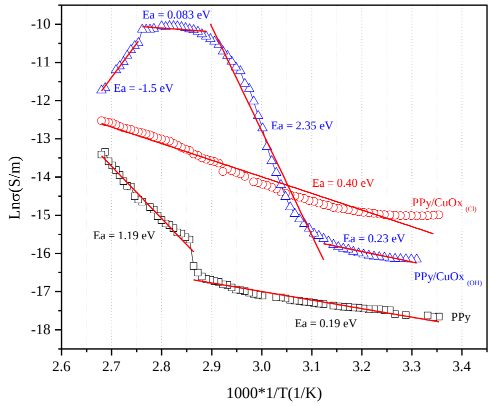

Fig. 4 Activation energy for PPy and PPy/CuO_x in acid solutions of NaOH (blue) and NaCl (red).

3.2.2 Basic medium:

Fig. 5 presents the behavior of the electrical conductivity of PPy/CuO_x in basic solutions. In general, the same behavior is observed for PPy/CuO_x in NaCl and NaOH basic compared with the PPy, however, a slope change at 55° C is observed similar to that of the compounds in an acid medium. For the PPy/CuO_x compound in NaCl, the conductivity value increased from $1.92x10^{-8}$ to $4.75x10^{-6}$ S/m. For the material PPy/CuO_x in NaOH at 25° C it was $2.94x10^{-8}$ S/m and at 100° C it was $8.76x10^{-6}$ S/m, as shown in Fig. 5.

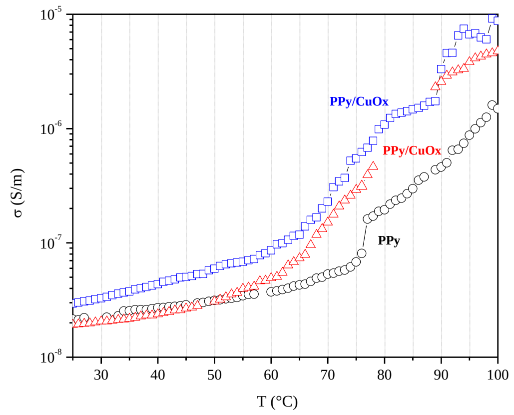

Fig. 5 Electrical conductivity of PPy and PPy/CuO_x in basic solutions of NaOH (blue) and NaCl (red).

The linear adjustment for PPy/CuO_x in basic solutions of NaOH and NaCl is shown in Fig. 6. In comparison with the values of Ea in acid medium, two changes of slope were observed in each of the materials in basic medium. For PPy, the values of Ea were 1.11 and 1.13 eV. For PPy/CuO_x in NaCl were 0.26 and 1.37 eV, while the compound with NaOH had Ea values similar to those of NaCl since they were 0.28 and 1.35 eV.

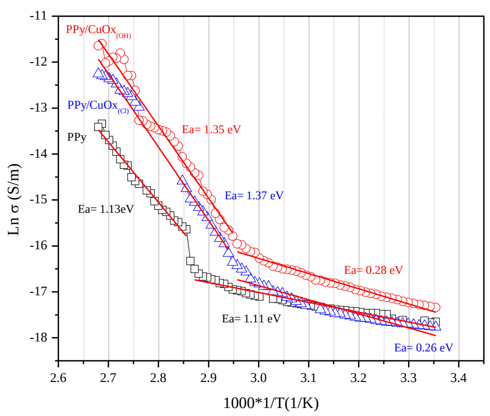

Fig. 6 Activation energy of PPy and PPy/CuO_x in basic solutions of NaOH (red) and NaCl (blue).

With the values of Ea in acidic and basic media, it was observed that the charge transfer mechanism occurs in different conduction processes independent of the medium [5, 6], however, in the PPy/CuO_x compound in a NaOH solution acid up to four mechanisms were observed. This is possibly due to the conjugation of properties that occurs between metal ions with polymer films, causing that the energy necessary for the energy jump is greater in an acidic NaOH medium.

4. Conclusion

The impregnation of CuOx particles in an acid solution of NaCl showed greater dispersion on the surface of PPy, whereas that of NaOH formed agglomerates. The electrical conductivity of the PPy/CuOx compounds in acidic and basic medium of NaCl and NaOH solutions increased up to two orders of magnitude compared to the PPy. Charge transfer occurred in more than one process in acidic NaOH systems because four inflection points were observed corresponding to Ea of 0.23, 2.35, 0.083 and -1.5 eV. For basic systems, the Ea was similar regardless of the solution used.

5. References

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