

**Robson Fernandes de Farias**

Departamento de Química - Universidade Federal de Roraima - UFRR - 69310-270 - Boa Vista - RO

Recebido em 9/3/99; aceito em 21/10/99

**Iron and arsenic oxide grains are coated with the conducting organic polymer polyaniline. The obtained samples were characterized by infrared spectroscopy, SEM, conducting measurements and thermogravimetry. The thermal stability of both oxides are increased. For As<sub>2</sub>O<sub>3</sub> the sublimation temperature is increased from 165°C in the pure oxide to 206°C in the polymer modified sample. The pure Fe<sub>3</sub>O<sub>4</sub> sample exhibits sublimation at 780°C whereas the polyaniline coated oxide is stable until at least 1000°C.**

**Keywords:** polyaniline; thermal degradation; oxide.

## INTRODUCTION

Polyaniline (PANI) is one of the most studied conducting polymers, not only due the facility in preparation procedures, but also related to high stability to the environmental exposition. The normal polymerization to prepare polyaniline has an enthalpy value of 439 kJ mol<sup>-1</sup> for the emeraldine form<sup>1</sup>, and its protonation (doping)<sup>2</sup> and many other physical-chemical properties are connected to the presence of the -NH- group<sup>3</sup>.

A great number of polymers, such as those derivative of polyaniline or other having some electroactive properties can be inserted into inorganic 2D, 3D or porous host solids<sup>4-6</sup> as phosphonates<sup>7-8</sup>, phosphates<sup>9-11</sup>, sulfides<sup>12</sup> and oxides<sup>13-15</sup>, displaying the so called nanocomposites<sup>16-21</sup>, which have enhanced their uncommon electrical properties.

Since polyaniline has characteristic photocatalytical properties<sup>22</sup>, having a conducting band in the visible region which is activated by solar radiation<sup>23</sup>, some kind of synergic relationship could arise when PANI is used as part of a organic/inorganic mixed material. In this direction, inorganic matrices such many metal oxides, which exhibit a very wide range of electrical resistivity<sup>24</sup> with catalytical<sup>25</sup> or photocatalytical properties<sup>26,27</sup> have been explored. For this purpose, deposition of a layer, or layers of polyaniline on the oxide surface, which polymer is used as a contact interface between oxide and another chemical species and/or electrode surfaces, could exert interesting and important effects on the oxidation-reduction properties of the substrate.

Recently, polyaniline adsorbed on MoO<sub>3</sub> was used to electrocatalyse the oxidation of molybdate ion, enhancing several times the electrode response, and so, can be used as a selective electrode for molybdenum<sup>28</sup>. The effects of polyaniline on redox process on As<sub>2</sub>O<sub>3</sub> were also studied<sup>29</sup>.

The aim of this work is to study the effects of adsorbed polyaniline on the thermal degradation process for iron and arsenic oxides in an attempting to establish a experimental procedure that allows use this oxides at higher temperatures than the usual ones.

## EXPERIMENTAL

Polyaniline was chemically obtained<sup>30</sup>, by using a 0.50 mol dm<sup>-3</sup> solution of bidistilled aniline (Aldrich) in 1.0 mol dm<sup>-3</sup>

HCl (Aldrich) as starting materials. To this solution maintained at 278 K was added, dropwise for 2h, 100 cm<sup>3</sup> of a 0.80 mol dm<sup>3</sup> of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution. After the complete addition of the oxidant solution, the mixture was stirred for 10 h, until finished the polymerization. The final polymer, was washed several times with distilled water and acetonitrile, to remove oligomers as well another possible impurities. The obtained polyaniline was then treated with a 1.0 mol dm<sup>3</sup> of NH<sub>4</sub>OH solution to promote deprotonation.

In the next stage, 0.40 g of the prepared polyaniline was dissolved in 45.0 cm<sup>3</sup> of N,N' dimethylformamide (Merck). This solution was added to 2.0 g of As<sub>2</sub>O<sub>3</sub> (99,9%, Carlo Erba) and 0.50 cm<sup>3</sup> of H<sub>3</sub>PO<sub>4</sub> to promote the doping<sup>2</sup>. The mixture was aged for 48 h at room temperature, before withdrawing the excess of solution and dried at 363 K overnight. The green powder product containing polyaniline adsorbed on oxide As<sub>2</sub>O<sub>3</sub> is named from here as As<sub>2</sub>O<sub>3</sub>.pani. A similar procedure was used to prepare a polyaniline coated Fe<sub>3</sub>O<sub>4</sub> sample, producing Fe<sub>3</sub>O<sub>4</sub>.pani.

The pure and polymer coated samples were characterized by FR-IR in a Bomem apparatus, with pressed KBr pellets and 25 scans, TG in a Shimadzu TGA-50 under argon atmosphere with heating rate of 8.3 x 10<sup>-2</sup> Ks<sup>-1</sup>. The SEM images were obtained in a Jeol, JSM T-300 apparatus, using an accelerating voltage of 15 kV. Conductance measurements were taken in a four probe apparatus, using pressed sample discs. No success was achieved in the attempting to obtain <sup>13</sup>C CP-MAS spectra for oxide-polyaniline samples.

## RESULTS AND DISCUSSION

In comparing the infrared spectra of PANI in Figure 1 with that for As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>.pani as shown in Figures 3 (a) and (b), the spectra of As<sub>2</sub>O<sub>3</sub>.pani shows three bands, which could be assigned as derived from pani bands: at 579 cm<sup>-1</sup>, 1146 cm<sup>-1</sup> and 1255 cm<sup>-1</sup>. In an attempting to assign the last two bands can be associated to those located in free pani at 1140 cm<sup>-1</sup> and 1301 cm<sup>-1</sup>, respectively, which are usually attributed to the doping process<sup>1</sup>. However, the band at 579 cm<sup>-1</sup> has not a clear attribution. For Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>.pani samples (Figure 2), a broad peak at 1088 cm<sup>-1</sup> which could be associated with the free band at 1140 cm<sup>-1</sup> in free polyaniline is observed. Emeraldine has two types of basic sites capable of coordinating Lewis acids: amine and imine nitrogens. In the polymer chain they are present in equal numbers. As observed for Lewis acid doped polyaniline<sup>31</sup>, both types of sites could be involved in the interaction (coordination) process.

e-mail: defarias@uol.com.br

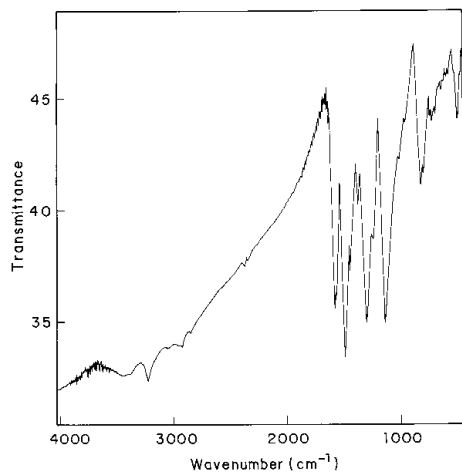


Figure 1. Infrared spectra of polyaniline.

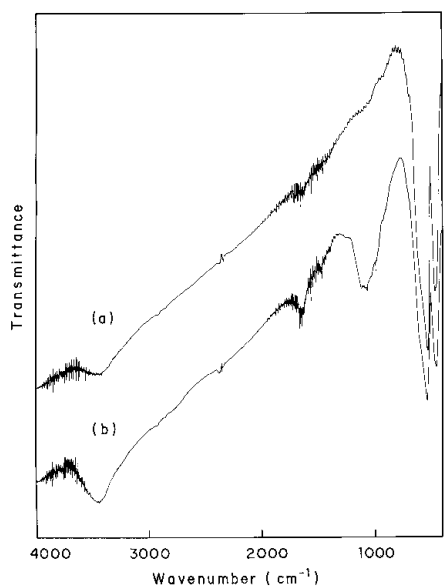


Figure 2. Infrared spectra of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4.pani$ .

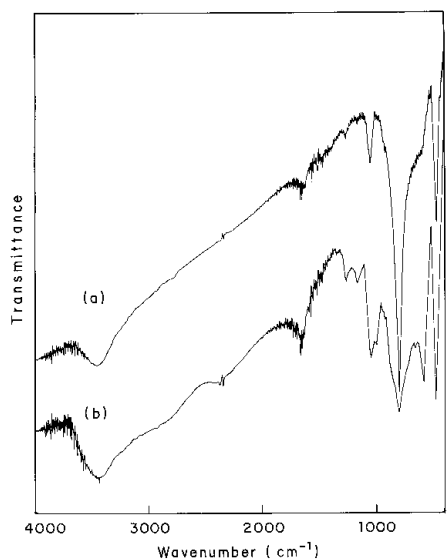


Figure 3. Infrared spectra of (a)  $As_2O_3$  and (b)  $As_2O_3.pani$ .

The SEM micrographs for the pure and polymer oxide samples are shown in figures 4 and 5. As can be noted, mainly to arsenic oxide, the polymer are adsorbed on the grains surface.

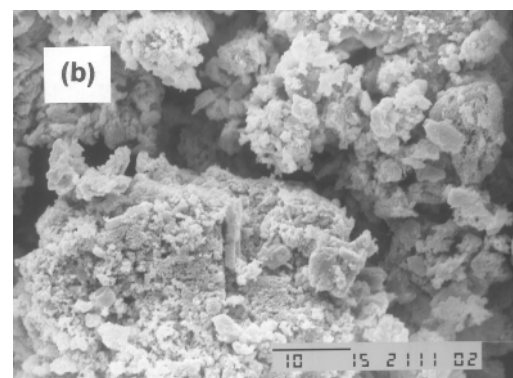
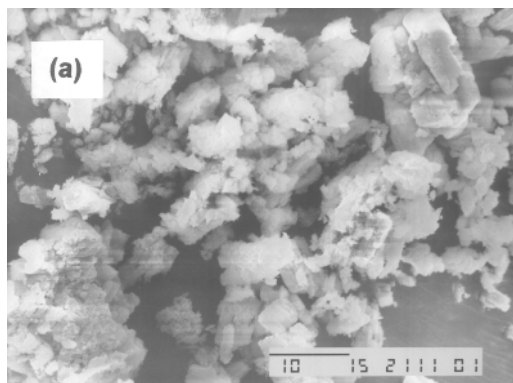


Figure 4. SEM micrographs of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4.pani$ .

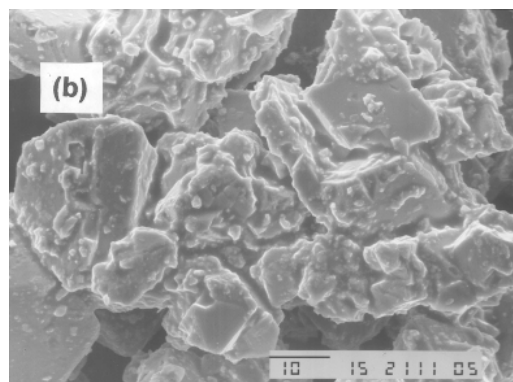
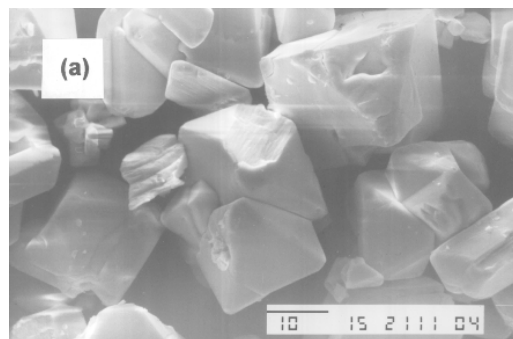


Figure 5. SEM micrographs of (a)  $As_2O_3$  and (b)  $As_2O_3.pani$ .

The conductivity of pellets obtained by pressing powders are  $3.4 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$  and  $34.2 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ , for  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ :pani, respectively. These values indicated that the material with polyaniline has a conductivity, which is about ten times larger than that of the pure oxide. This result corroborated that the polymer deposition occurred on the substrate surface.

The thermogravimetric curve of  $\text{As}_2\text{O}_3$  presents a total mass lost due to the sublimation of the oxide, whereas the TG curve of  $\text{As}_2\text{O}_3$ :pani shows a first mass loss step of 87% due to oxide sublimation and a second one of 13%, due to the thermal degradation of the organic moiety. The second mass loss step exhibits a profile consistent with the thermal degradation of emeraldine<sup>32-33</sup>. Thermogravimetric technique can be considered as a reliable tool to characterize solid surfaces<sup>34,35</sup>, and then, the fraction of 13% can be assumed as been the total amount of deposition of polyaniline on  $\text{As}_2\text{O}_3$  surface.

For  $\text{Fe}_3\text{O}_4$ :pani a mass loss of 11% can be observed due to the release of polyaniline molecules. So, for both oxides the total amount of adsorbed polyaniline is almost the same.

For both oxides an increase in the thermal stability was observed since the sublimation temperature of arsenic oxide is about 165°C for the pure oxide and 206°C for the polymer modified one. The pure iron oxide sample used sublimates at 780°C whereas the polyaniline modified sample do not sublimate until the maximum temperature used, 1000°C.

The reasons to the observed phenomena could be attributed to the interaction of nitrogen atoms or  $\pi$  electrons of the aromatic rings of polyaniline with the acidic sites in the oxides surfaces, with polyaniline coating sheets acting as a "thermal barrier", since it absorbs the heat transferred to the polymer coated samples.

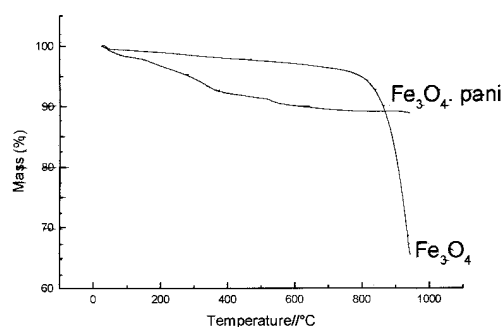


Figure 6. Thermogravimetric curves of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ :pani.

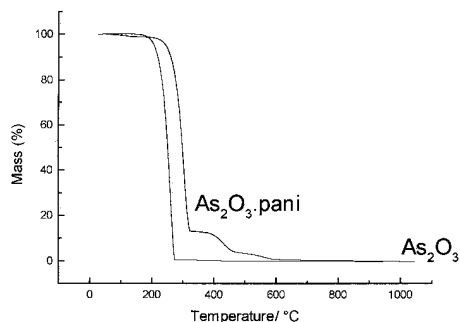


Figure 7. Thermogravimetric curves of  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ :pani.

## CONCLUSION

The obtained experimental results shows that polyaniline can be used to increase the thermal stability of iron and arsenic oxides. Since polyaniline, as well as many metal oxides exhibit

electrical and catalytic properties, an increase in thermal stability could be an desirable improvement in such organic-inorganic materials.

## REFERENCES

1. Fu, Y.; Elsenbaumer, R. L.; *Chem. Mater.* **1994**, *6*, 671.
2. Huang, W. -S.; MacDiarmid, A. G.; Epstein, A. J.; *J. Chem. Soc. Chem. Commun.* **1987**, 1784.
3. Nalwa, H. S. (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, vol.2, John Wiley & Sons, New York, 1997.
4. Ruiz-Hitzky, E.; *Anal. Quím. Int. Ed.* **1997**, *93*, 197.
5. Ruiz-Hitzky, E.; *Adv. Mater.* **1993**, *5*, 334.
6. Ohtsuka, K.; *Chem. Mater.* **1997**, *9*, 2039.
7. Okuno, S.; Matsubayashi, G. -E.; *Inorg. Chim. Acta*, **1995**, *233*, 173.
8. Maia, D. J.; Alves, O. L.; De Paoli, M. -A.; *Synth. Met.* **1997**, *90*, 37.
9. Bonnet, B.; El Mejjad, R.; Herzog, M. -H.; Jones, D. J.; Rozière, J.; *J. Mater. Science Forum* **1992**, *91-93*, 177.
10. Rosenthal, G. L.; Caruzo, J.; Stone, S. G.; *Polyhedron* **1994**, *13*, 1311.
11. Liu, Y. -J.; Kanatzidis, M. G.; *Inorg. Chem.* **1993**, *32*, 2989.
12. Kanatzidis, M. G.; Bissessur, R.; DeGroot, D. C.; Shindler, J. L.; Kannewurf, C. R.; *Chem. Mater.* **1993**, *5*, 595.
13. De Stefanis, A.; Foglia, S.; Tomlinson, A. A. G.; *J. Mater. Chem.* **1995**, *5*, 475.
14. Liu, Y. -J.; Degroot, D. C.; Shindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G.; *J. Chem. Soc. Chem. Commun.* **1993**, 593.
15. Bissessur, R.; DeGroot, D. C.; Shindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G.; *J. Chem. Soc. Chem. Commun.* **1993**, 688.
16. Tudor, J.; Willington, L.; O'Hare, D.; Royan, B.; *J. Chem. Soc. Chem. Commun.* **1996**, 2031.
17. Gulians, V. V.; Benziger, J. B.; Sundaresan, S.; *J. Catalysis* **1995**, *156*, 298.
18. Liu, Y. -J.; DeGroot, D. C.; Shindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G.; *Adv. Mater.* **1993**, *5*, 369.
19. Ouahab, L.; *Chem. Mater.* **1997**, *9*, 1909.
20. Schöllhorn, R.; *Chem. Mater.* **1996**, *8*, 1747.
21. Sayari, A.; Karra, V. R.; Reddy, J. S.; Moudrakovski, I. L.; *J. Chem. Soc. Chem. Commun.* **1996**, 411.
22. Peralta-Zamora, P.; Moraes, S. G.; Reynes, J.; Durán, N.; *Polymer Bull.* **1996**, *37*, 531.
23. Huang, W. -S.; MacDiarmid, A. G.; *Polymer* **1994**, *34*, 1833.
24. Rao, C. N. R.; *J. Chem. Soc. Chem. Commun* **1996**, 2217.
25. Gates, B. C., *Catalytic Chemistry*, John Wiley & Sons, New York, 1992.
26. Durán, N., Espósito, E., Rodrigues, J. J.; *Photochem. Photobiol.* **1991**, *62*, 269.
27. Durán, N.; Espósito, E.; Inocentini-Mei, L. H.; *Biodegradation* **1994**, *5*, 13.
28. Farias, R. F. de; Souza, J. M. de; Melo, J. V. de; Airoidi, C.; *J. Colloid Interf. Sci.* **1999**, *212*, 123.
29. Farias, R. F. de; Souza, J. M. de; Melo, J. V. de; Airoidi, C.; *J. Colloid Interf. Sci.* **2000**, in press.
30. Geniès, E. M.; Boyle, A.; Laokowski, M.; Tsintavis, C.; *Synth. Met.* **1990**, *36*, 139.
31. Kulszewicz-Bajer, I.; Pron, A.; Abramowicz, J.; Jeandey, C.; Oddou, J. -L.; Sobczak, J. W.; *Chem. Mater.* **1999**, *11*, 552.
32. Chan, H. S. O.; Teo, M. Y. B.; Khor, E.; Lim, C. N.; *J. Thermal Anal.* **1989**, *35*, 765.
33. Neoh, K. G.; Kang, E. T.; Tan, K. L.; *Thermochim. Acta* **1990**, *171*, 279.
34. Farias, R. F. de; Airoidi, C.; *J. Thermal Anal.* **1998**, *53*, 751.
35. Farias, R. F. de; Nunes, L. M.; Airoidi, C.; *J. Thermal Anal.* **2000**, in press.