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Effects of hydrogen peroxide on the electrical conductivity of graphite/polyaniline composites

Aymen Mannaï *, Sami Saidi, Fethi Gmati, Abdellatif Belhadj Mohamed

Laboratory of Photovoltaic, Centre of Research and Technology of Energy, Technopole of Borj Cédria, B.P. 95, Hammam Lif 2050, Tunisia

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ABSTRACT

The effects of hydrogen peroxide (H_2O_2) on the direct current (dc) electrical conductivity of graphite (G)/polyaniline (PANI) composites are studied. It was found that the conductivity of G/PANI composite reacted with H_2O_2 decreases with increasing time. Results are confirmed by UV–vis, FTIR absorption measurements, X-ray diffraction analysis and Raman spectroscopy. From X-ray diffraction and Raman spectroscopy measurements we prove that H_2O_2 affects only PANI but not Graphite particles. After their treatment with H_2O_2 only G(10%)/PANI, G(20%)/PANI and G(30%)/PANI samples show a semi-conductor behavior. The charge transport mechanisms in these three samples are due to hopping and tunneling and are described by both Mott's three-dimensional variable range hopping model and Sheng's fluctuation induced tunneling model. The transition in the nature of charge transport in G(10%)/PANI, G(20%)/PANI and G(30%)/PANI samples after treatment with H_2O_2 is caused by disorder and localization, whereas the inverse semi-conductor-metal transition which occurs at above G(30%) in the same samples arises essentially from percolation in G/PANI composites.

1. Introduction

In the recent years, many researchers have focus their attentions towards on composites of conducting polymers, especially polyaniline with graphite, carbon black, graphite fibers and, recently carbon nanotube, like their potential applications such as antistatic coatings, anode and cathode in rechargeable batteries, solar cells, electronic devices, chemical sensors [1–5], etc. However, the use of these composites are limited due to undesirable properties of each at high temperature [1,5–10], due to electrical degradation with time under some environmental conditions [11–13]. The electrical degradation of these composites is a problem that must be reckoned, understand and resolved before the composites can deliver its potential role in suggested applications area [13]. For this reason, the degradation of polyaniline and its mechanisms via thermal, oxidation or reduction reaction has been studied by several workers [5–10,13]. The degradation process in conducting polymer interrupt the arrangement of the polymer chains and also change the extended electronic states by inducing localization of electronic states and thus leads to a charge in the dominating conducting mechanism [13].

The aim of this work is to understand, the effects of an oxidant agent; the hydrogen peroxide (H_2O_2) on the electrical properties of G/PANI composite. We have examined the variation of the dc electrical conductivity and the corresponding conduction mechanism of G/PANI composites with different G weight concentrations reacted separately by H_2O_2 at various times. We have used the ultraviolet–visible, the infrared and the Raman spececctroscopies and the X-ray diffraction (XRD) to control the changes in the molecular structure occurring in the composite during the actions of H_2O_2. The experimental measured dc conductivity data in the temperature range 298–403 K are analyzed by a number of different theoretical conduction models [13].

2. Experimental techniques

2.1. Sample preparation

G/PANI composites were prepared by mixing micro particles of G (with mean size of 15 μm) powder with conducting PANI obtained from PANIPLAST company (France) by mechanically grinding them in a mortar according to the protocol cited in Ref. [14]. We have prepared a series of G(y%)/PANI composite with different graphite weight concentrations *y*% (=10%, 20%, 30%, 40%, 50%, 60% and 70%). Samples are imputed in a solution of H_2O_2 (110 volumes) obtained from PARACHIMIC company (Tunisia) at the followings times; 0, 2, 4 and 24 h. These dispersions are placed in a closed medium and filtered at the end of the attack interval. Finaly powders were dried before using them for various

* Corresponding author. Fax: +216 98 968 521.
E-mail address: manaiaymen@yahoo.fr (A. Mannaï).

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characterizations.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out by using a PANalytical/X'Pert Pro MPD X-ray diffractometer using Cu Kα radiation ($\lambda=154$ Å) in the 2θ range of 15–80°. The ultraviolet and visible (UV–vis) spectra of the G/PANI composite powders were obtained in dimethylformamid (DMF) solution with a concentration of 0.1 g L^{-1} in the wave length range 190–1200 nm at room temperature by employing a Shimadzu 1800 spectrophotometer. Fourier-transform infrared (FTIR) spectra of G/PANI composites as pressed pellets in KBr were obtained with a Nicolet MAGNA-IR 560 E.S.P spectrometer. The morphologies of our samples have been studied using a JEOL840 scanning electron microscope (SEM). Micro-Raman scattering was used to characterize the graphite powder. The Raman spectra were performed at room temperature in backscattering configuration using the 488 nm Ar^{+} laser line as excitation. The dc conductivity was measured on pressed pellets of uniform thickness $t=2$ mm and diameter $d=13$ mm in the temperature range 298–403 K. The temperature of samples was controlled by a Memmert electric oven. We have made electrical contacts by depositing parallel metal electrodes of 13 mm diameter on both sides of these G/PANI pellets adopting the sandwich geometry. A voltage of 15 mV was applied across the samples; the resulting current and the corresponding bulk resistance R were measured using a KEITHLEY 2400 Source Meter. The dc conductivity was calculated by employing the formula $\sigma_{dc}=(1/R)\ (t/S)$, where, t and S are the thickness and the surface area of the sample respectively. The acquisition time of each measurement is about 60 s.

3. Results and discussion

3.1. UV–vis absorption study

Fig.1 shows the UV–vis spectra of G(20%)/PANI pristine composite and those reacted with H_2O_2 at various times.

The absorption bands observed in the UV–vis spectrum of G/PANI pristine composites are characteristic of conducting form of PANI. In fact the absorption bands at about 320 and 470 nm correspond to the transitions π–π^{*} and polaron band-π^{*}, respectively. The broad band in the form of tail situated at around 900 nm is assigned to mobile polarons in the doped PANI [15–17]. This free charge carrier tail is consistent with delocalization of electrons in the polaron band [18]. The absence of both the 470 nm band and the free charge carrier band, and the appearance of a band at about 620 nm in the UV–vis spectrum G/PANI reacted with H_2O_2 suggest that H_2O_2 causes a deprotonation of PANI in the composite. The progressive increases in the absorption band at about 620 nm when the attack time with H_2O_2 increases, indicates that H_2O_2 dedoped PANI and converts it to the non conducting emeraldine base by a progressive deprotonation of imines nitrogen atoms [13,19–22]. The absorption bands obtained from the UV–vis are in good agreement with that reported in the literature [13,19–22]. These results are the same for all our G/PANI samples.

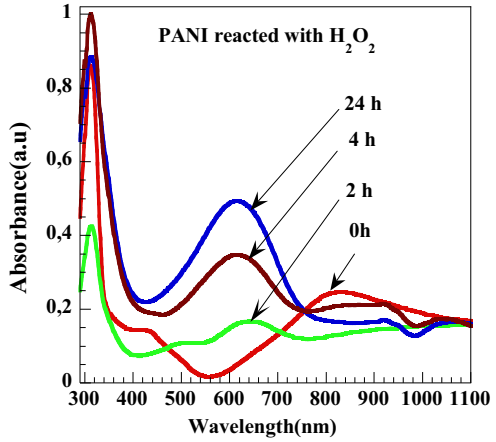

Fig. 1. UV–vis spectra of G (20%)/PANI reacted with H_2O_2 at 0, 2, 4 and 24 h.

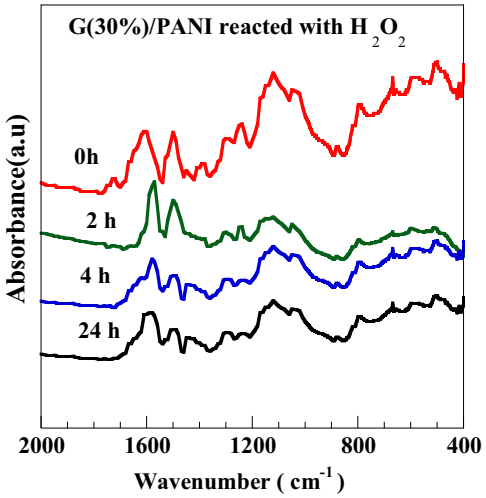

Fig. 2. FTIR spectra of G (30%)/PANI composites reacted with H_2O_2 at 0, 2, 4 and 24 h.

3.2. FTIR absorption study

Fig. 2 shows the FTIR spectrum of G (30%)/PANI composites reacted with H_2O_2 at various times.

By comparing the FTIR spectrum of pristine G(30%)/PANI and those reacted with H_2O_2, one can see that when G/PANI composites are treated with H_2O_2, the absorption bands positioned at about 1140 and 1245 cm^{-1}, which are characteristic of the protonated form of PANI [9,10], are gradually suppressed with increasing time. These results indicate that H_2O_2 dedope PANI by a deprotonation reaction [13,23].

3.3. Raman spectroscopic study

The molecular structures of pure graphite and graphite reacted with H_2O_2 at various times were analysed by Raman spectroscopy (Fig. 3). The spectrum of graphite exhibits tow sharp peaks situated at 1580 cm^{-1} (band labeled "G" for ordered graphite) and 1350 cm^{-1} (band labeled "D" for disordered form of graphite) [24,25]. These bands do not shift when the graphite is reacted with H_2O_2. These results prove the absence of graphite oxide (GO).

3.4 X-ray diffraction study

We present in Fig. 4 the X-ray diffraction patterns of pristine G (30%)/PANI composite and those reacted with H_2O_2 for 24 h. For the three samples we distinguish the crystalline structure of Graphite by the presence of diffraction peaks at $2\theta=26.55°$, 42.18°, 44.67°, 50.7°, 54.68°, 60° and 70.69° [26]. From these results we prove also that H_2O_2 affect only PANI but not Graphite particles. The X-ray patterns of pristine G(30%)/PANI shows the presence of a peak at $2\theta=20{,}22$ which is attributed to the PANI doped with