

Change in morphology of polyaniline/graphite composite: A fractal dimension approach

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Abstract

Polyaniline/graphite composites (PANi/G) with different graphite particle sizes were deposited on a platinum electrode by means of cyclic voltammetry. The surface morphology of PANi/G composites were studied by using the scanning electron microscopy (SEM) and the fractal dimension concept. This work presents the utilization of the cyclic voltammetry and electrochemical impedance spectroscopy to determine the fractal dimension. The results obtained from both these methods are in good agreement indicating the reliability of the estimated fractal dimension (D_f).

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1. Introduction

Polymers with π -conjugated double bonds in the chain show uncommon properties like low energy electronic transitions, low ionization potential and high electron affinity. These properties resulted in polymers that can be easily oxidized and reduced. In order to compensate the charge produced in the polymer matrix by such redox processes, there is usually incorporation/expulsion of ionic species (dopants) [1].

Among the conducting polymers, polyaniline has attracted much attention because of its multiple electronic states, high conductivity that occurs upon doping, as well as its easy and economic preparation, and good environmental stability [2]. The conducting polymers can therefore be used in many applications, including rechargeable batteries [3–5], sensors [6,7], electromagnetic shielding devices [8], biosensors [9], etc. However, the properties of these polymers depend on their microstructure and morphology, which are mainly determined by conditions of synthesis [10,11].

Investigation of surface roughness is an important issue in surface science. Electrode surface characteristics are exceptionally important for all electrochemical process because they can determine the adsorption and ion exchange behavior of the electrode [12].

Since the revolutionary discovery of fractal geometry by Mandelbort [13], it has been used for analysis of different objects in various branches of science and technology [14–16]. Fractal geometry is a mathematical concept that describes objects of irregular shape. Some natural geometrical shapes, that can be irregular, tortuous, and rough or fragmented, can be described using concepts of fractal geometry as long as the requirement of self-similarity is satisfied [17]. Moreover, fractal geometry provides a powerful opportunity to investigate surface roughness via geometrical models [13,18]. The term “fractal” indicates the fact that the material of interest has a fractional dimension, not a whole number value [19] and the term was specifically applied for temporal and spatial phenomena that exhibit partial correlations over many scales. Fractal dimension (D_f) is a quantitative parameter for analysis of fractal objects, which is widely used for different purposes. In addition, it is one of the most important and useful parameters for analysis of structure of rough surfaces.

Fractals have been characterized by several methods that can be classified as physical, chemical and electrochemical. Physi-

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cal methods for determination of fractal dimension are atomic force microscopy [20], scanning tunneling microscopy [21], X-ray reflectivity [22], electron diffraction [23] and small angle scattering of photons [24] or neutrons [25]. The most common chemical methods are based on physical adsorption [26], while electrochemical methods such as chronoamperometry [27], cyclic voltammetry [28], impedance spectroscopy [12] and hydrodynamics voltammetry (RDE) [29] have been introduced for the calculation of fractal dimension of electrode surfaces. Electrochemical methods have been supported by mathematical simulations and experimental evidences and are one of the most useful and reliable methods for the determination of fractal dimension of surfaces [19]. However, less attention has been paid to the use of these methods for real electrodes. Only a few reports on fractal studies of real electrodes are available, such as metal oxides coated electrodes [30], Li inserted electrodes [31], dispersed particles into polymeric film [32] and polyaniline composites [28].

The dependence of growing patterns on the polymerization condition was reported under fractal geometry approach [33] and it already established the possibility of the quantitative description of the degree of surface disorder in conducting polymers.

It has been proven difficult to characterize the structure of conducting polymers although its knowledge would form an elemental base for our understanding of their electronic and photonic properties. Electron micrographs of conducting polymers can also provide useful information on the structural behavior that depends on the technique used for preparation. However, it is difficult to extract quantitative information from the electron micrographs [34].

There are many advantages of using graphite in the composite materials. First, graphite has a high conductivity (>100 S/cm), high mechanical strength, and very good chemical stability. Second, graphite is cheap and available in large quantities [35].

In the present work, graphite particles with different sizes were incorporated in polyaniline matrix to form polyaniline/graphite composites by electrochemical polymerization. The effect of graphite particle sizes on fractal structures of these composites were investigated by using electrochemical techniques, viz. cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

2. Experimental

Prior to use, aniline (Aldrich) was distilled under vacuum. Hydrochloric acid, sodium hydroxide, sodium dodecyl sulfate (SDS) and sulfuric acid were of analytical reagent grade chemicals prepared from Merck or Fluka. The water used for preparation of solutions was doubly distilled.

All electrochemical measurements were carried out in a conventional three electrode cell, powered by a potentiostat/galvanostat (EG&G 273A) and a frequency response detector (EG&G, 1025). An Ag/AgCl, Pt plates (5 cm \times 4 cm) and a Pt wire were used as reference, working and counter electrodes, respectively. Sieving was performed with a Retsch Analytical sieve shaker AS 200 control. Scanning electron microscopy (SEM) was performed with a Philips instruments, Model X-30.

pH measurements were made with a Metrohm pH-meter model 691.

The graphite particles of different sizes were prepared as follows. The graphite powder was first grinded, and then washed with 10% NaOH solution and concentrated H_2SO_4 , respectively, and dried. The resulting graphite powder with different particle sizes was then separated in the ranges of <20 , 20–25, 45–50 and >75 μm .

PANi/G composites were prepared by repeated potential cycling at the Pt electrode from -0.20 to 0.85 V for 100 cycles at a sweep rate of 50 mV s^{-1} in a stirring solution containing 1.0 M hydrochloric acid, 0.1 M aniline, 5.0×10^{-3} M SDS and 4% of graphite in suspension. SDS was used as an additive in order to suspend of graphite particles and to improve the stability and electroactivity of the resulting films [36]. The coated electrode with PANi/G composite was thoroughly washed with distilled water and dried.

Composites were analyzed by electrochemical impedance spectroscopy (EIS) measurements in 1.0 M HCl solution. The frequency range extended from 100 mHz to 100 kHz and an ac potential perturbation of 5 mV r.m.s. was used. The electrode potential was varied in steps of 50 mV in the potential range of 0.2 – 0.6 V, which is within the conducting range of PANi (emeraldine form) [37]. The impedance data were analyzed and fitted by Zplot/Zview software (Scribner Associate Inc.).

Cyclic voltammograms were obtained in 0.002 M $K_4[Fe(CN)_6]$ and 0.2 M $NaNO_3$ solution at different potential sweep rates varied from 50 to 500 mV s^{-1} .

3. Results and discussion

Fig. 1 shows the cyclic voltammograms for different PANi/G composites with a potential sweep rate of 50 mV s^{-1} between -0.2 and 0.85 V in 1.0 M HCl. As seen, the voltammograms show two well-defined peaks the corresponding peak currents of which increased upon increasing size of graphite particles in the composite. Another feature observable is that an increase in graphite particles size caused the anodic peaks to shift towards

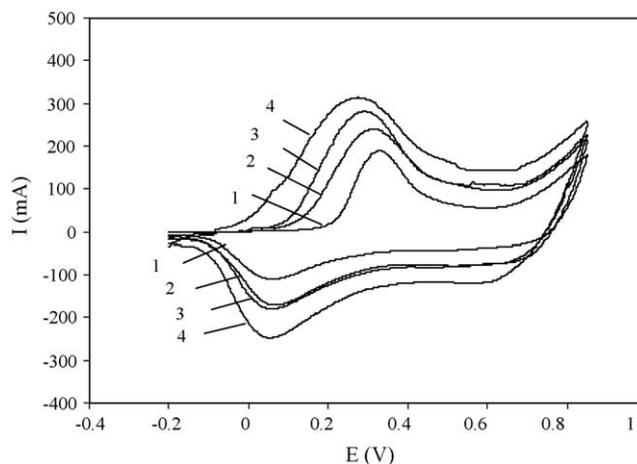
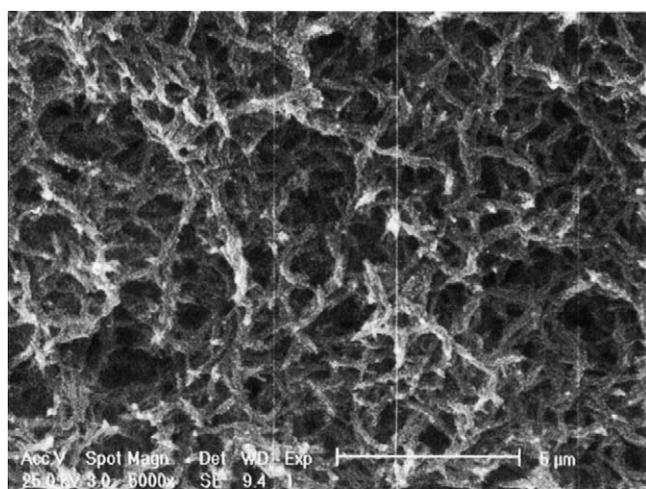
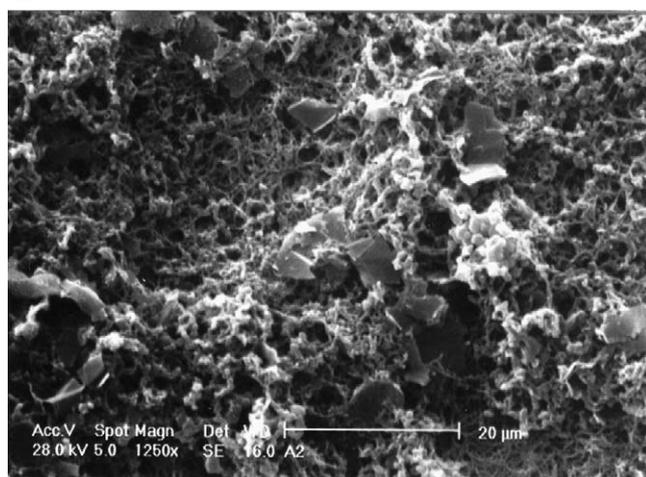


Fig. 1. Cyclic voltammograms for PANi/G composites with different sizes of graphite particles obtained in 1.0 M HCl. $\nu = 50$ mV s^{-1} . Curves: (1) <20 μm ; (2) 20–25 μm ; (3) 45–50 μm ; (4) >75 μm .



(a)



(b)

Fig. 2. (a) SEM micrograph of PANi film synthesized in the presence of SDS. (b) SEM micrograph of PANi/G composite film with graphite particle size of <20 μm.

negative potentials. Also, the peak potential separation lowered upon raising the graphite particle size. Therefore, it can be concluded that the electrochemical kinetics of redox transition of PANi/G composites have been enhanced. This feature is related to the enhancement of the conductivity of composites, ionically and/or electronically. Probably, the graphite particles in the composites act as electronic conductors, which connect the polyaniline chains and improve the film conductivity. Moreover, the graphite particles with different size can affect the morphology of PANi/G composite and improved the diffusion rate of dopant anions of electrolyte species via changing the diffusion path.

As shown in Fig. 2, the films prepared with and without graphite distinctly show differences in polymer morphology. The morphology of the film obtained from a solution containing aniline and SDS, without graphite, is defined by fibular structures (Fig. 2a). In contrast, in the presence of graphite, a porous globular structure is observed (Fig. 2b). The graphite powders are crystalline particles, some with sharp edges which can be clearly observed in Fig. 2b. It is interesting to note that the morphology

of PANi films obtained by similar electrochemical procedures is also known to be strongly determined by the nature of electrolyte or by the potential limits used during the synthesis [38]. These parameters usually affect the nucleation and growth mechanism for polymer formation and, consequently, its morphology.

The surface morphology of PANi/G composites were studied by using the fractal concept. It has been reported [39] that for a diffusion controlled redox transition, which occurred via diffusion of an electroreactant species to a target surface, followed by heterogeneous electron transfer, there is a power dependence between the peak current (I_{pc}) in cyclic voltammograms and the corresponding potential sweep rate (ν):

$$I_{pc} \propto \nu^\alpha \quad \text{or} \quad I_{pc} = \sigma'_F \nu^\alpha \quad (1)$$

where α is the fractal parameter and σ'_F is a proportionality factor.

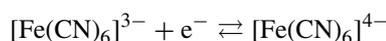
Thus, the fractal parameter can be obtained easily by plotting the peak current against sweep rate in a log–log scale. On the other hand, the fractal parameter is related to the fractal dimension ' D_f ' of the electrode surface as [27]:

$$\alpha = \frac{D_f - 1}{2} \quad (2)$$

Eq. (2) is applicable to electrochemical methods, as it has been successfully used for calculating the fractal dimension of electrode surfaces.

Based on this information, cyclic voltammograms for PANi composites in solution of 0.2 M NaNO₃ containing 0.002 M [Fe(CN)₆]³⁻, were recorded at different potential sweep rates in the range of 50–500 mV s⁻¹. Here, the electrochemically reversible redox couple ferri/ferrocyanide was used as a suitable probe to examine the morphology of composite films.

For analytical purposes, it was assumed that the diffusion of oxidized, [Fe(CN)₆]³⁻, and reduced species, [Fe(CN)₆]⁴⁻, in the electrolyte is semi-infinite and one-dimensional. The solution initially contains only oxidized species, the bulk concentration of these species being constant away from the electrode, while the corresponding concentration of reduced species is zero. The supporting electrolyte, NaNO₃, is assumed to present at a sufficient concentration so that the contribution of the redox couple to migration can be neglected. Since the PANi synthesized in acid solution is electroactive when the pH of the medium is less than 4 and is electroinactive when the pH is neutral or basic [37], under the experimental conditions used, i_{peak} was background corrected so that the only reversible reaction occurring with the redox couple is



Typical cyclic voltammograms of PANi/G composite (with graphite particle size >75 μm) in [Fe(CN)₆]³⁻ solution, recorded at different potential sweep rates, are shown in Fig. 3. Fig. 4 represents the relationship between the anodic peak current and potential sweep rate in a log–log scale, obtained for the PANi/G composites films with different graphite particle sizes. The slope of the lines gives the α value for each composite. Substituting α values in Eq. (2), gives the fractal dimensions of 2.97 ± 0.03 , 2.80 ± 0.05 , 2.70 ± 0.03 and 2.63 ± 0.03 for

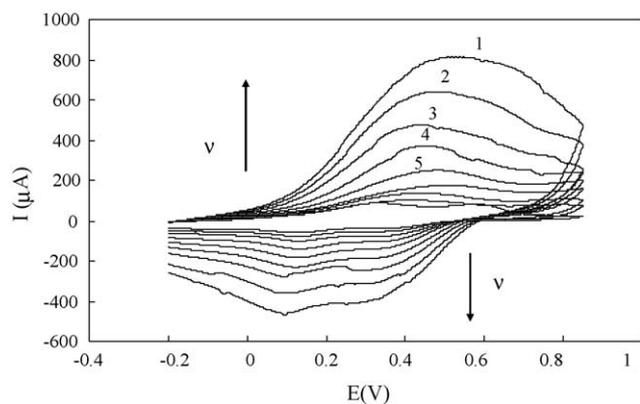


Fig. 3. Cyclic voltammograms for PANi/G composite (with graphite particle size $>75 \mu\text{m}$) in 0.2 M NaNO_3 and 0.002 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. Curves: (1) 500 mV/s; (2) 400 mV/s; (3) 300 mV/s; (4) 250 mV/s; (5) 200 mV/s.

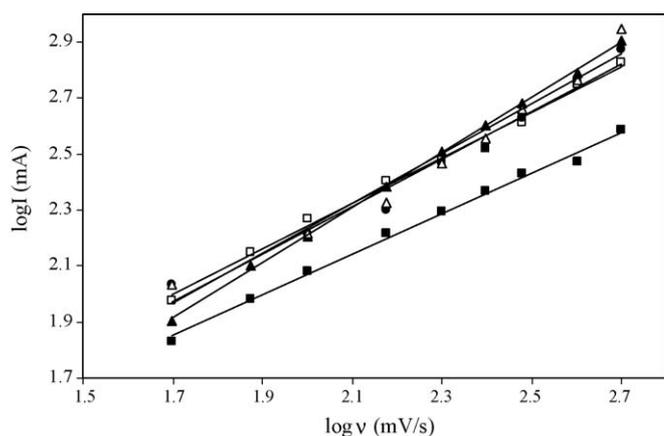


Fig. 4. Log–log scale presentation of the plot of the peak current vs. potential sweep rates for PANi and PANi/G composites with different sizes of graphite particles. Curves: (■) PANi; (□) $<20 \mu\text{m}$; (◆) $20\text{--}25 \mu\text{m}$; (△) $45\text{--}50 \mu\text{m}$; (▲) $>75 \mu\text{m}$.

PANi/G composites with graphite particle sizes of >75 , $45\text{--}50$, $20\text{--}25$ and $<20 \mu\text{m}$, respectively, as summarized in Table 1.

Fractal dimensions can also be obtained from impedance spectra. The standard model used to model the frequency response of the film is an equivalent analog electric circuit where, for each distinct dielectric component in a mixture of dielectrics, a parallel path comprising of a resistor (R) and a capacitor (C) in series is included; each RC element represents

Table 1
Comparison of fractal dimension of PANi and PANi/G composites with different sizes of graphite particles using CV and EIS techniques^a

Composite	CV		EIS	
	α	D_f	n	D_f
PANi	0.73	2.45 (0.04)	0.68	2.47 (0.02)
(PANi/G) $<20 \mu\text{m}$	0.82	2.63 (0.03)	0.61	2.65 (0.02)
(PANi/G) $20\text{--}25 \mu\text{m}$	0.85	2.70 (0.03)	0.57	2.76 (0.03)
(PANi/G) $45\text{--}50 \mu\text{m}$	0.90	2.80 (0.05)	0.55	2.82 (0.02)
(PANi/G) $>75 \mu\text{m}$	0.98	2.97 (0.03)	0.52	2.90 (0.02)

^a The values in parentheses are standard deviations calculated based on three replicate series of experiments.

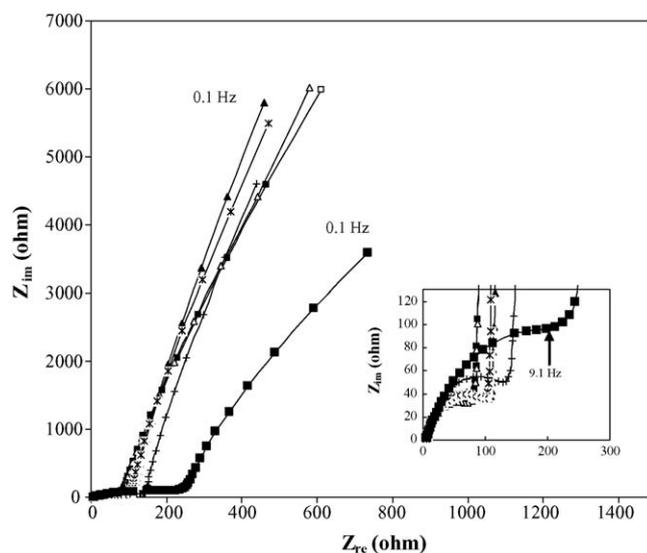


Fig. 5. The electrochemical impedance spectra of PANi/G composite (with graphite particle size $>75 \mu\text{m}$) in the potential range (0.2–0.6 V) vs. Ag|AgCl. The electrode potential was varied in steps of 50 mV in 1.0 M HCl electrolyte. Curves: (■) 0.45 V; (+) 0.4 V; (*) 0.35 V; (▲) 0.3 V; (△) 0.25 V; (□) 0.2 V. Inset: the main panel which is enlarged the high frequencies range.

a Debye relaxation [40]. However, ideal elements are not usually sufficient to account for the interpretation of impedance spectra unless the so-called constant phase elements (CPE), or ‘fractal’ capacitors, were substituted for the capacitors in the model. A review of CPEs and their association with rough and porous electrodes is available [40]. The CPE is an empirical circuit element that was introduced to account for the apparent distribution. The impedance of a CPE is given by [41]:

$$Z_{\text{CPE}} = \frac{1}{A(j\omega)^n} \quad (3)$$

where j is the square root of negative one, ω is the angular frequency of the applied ac signal in the impedance experiment, A is a capacitance parameter and $0 < n < 1$.

The power-law dependence of the CPE impedance suggests a possible relationship between CPE behavior and the fractal interface geometry of the electrode [40]. The value of fractal dimension (D_f) can be obtained using the average of n values at different offset potentials according to the following equation:

$$D_f = \left(\frac{1}{n}\right) + 1 \quad (4)$$

in which n is close to 1 for very smooth and clean surfaces like liquid mercury. However, the relation between the fractal dimension and the exponent n (Eq. (4)), was found to be valid in some, but not all, systems studied so far [40,42].

Thus, we used impedance spectra to determine the fractal dimension of PANi composites. Impedancemetrics of composite films immersed in 1.0 M HCl solution were performed at dc-offset potential range of 0.2–0.6 V.

The impedance spectra of PANi/G composite (with graphite particle size $>75 \mu\text{m}$) at different dc-offset potentials are shown in Fig. 5. The resulting impedance spectra represent two

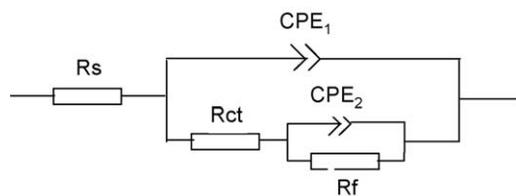


Fig. 6. Schematic representation of an equivalent circuit model.

depressed semicircles for the composite at each applied voltage, one at low frequencies and another at high frequencies (enlarged in the inset of Fig. 5). It is noteworthy that, in each case, the dots show the experimental points and the line is the fitted experimental point to the equivalent circuit model. As seen, there is an excellent agreement between the experimental data points and the calculated line. The high frequencies semicircle characterizes the polyaniline substrate interface and the low frequencies semicircle characterizes the polyaniline|solution interface. The appearance of the depressed semicircles (i.e., impedance dispersion) in the high frequency region is also ascribed to the blocking properties of a rough electrode, which render extremely slow the faradaic process of the ionic exchange at the polymer|electrolyte interface [43].

Interpretation of Nyquist diagrams is usually done by fitting the experimental impedance spectra to an electrical equivalent circuit. That is, an electric circuit combined by some physical elements can be built that has an impedance spectrum identical to that of the electrochemical system under investigation. However, it is often difficult to find an unambiguous physical meaning for particular circuit elements. Moreover, the situation is further complicated in the case of conducting polymers by different opinions concerning the mode of transport of charge carriers within the polymer film [44].

Based on Nyquist diagrams represented in Fig. 5, an equivalent circuit can be suggested (Fig. 6). In this circuit, R_s is the electrolyte solution resistance, R_f is interpreted as the film resistance of the polyaniline film (resulting from the penetration of the electrolyte), CPE_1 is the capacitance of the polyaniline film|metal interface, R_{ct} denotes the charge transfer resistance and CPE_2 is the double layer capacitance related to the polyaniline film|electrolyte interface.

In order to determine the fractal dimension, Nyquist diagram's were analyzed and fitted via complex non-linear least square procedure based on the equivalent circuit represented in Fig. 6, which gave the exponent n values for each dc potential. By substituting the average n values in Eq. (4), we obtained the fractal dimensions of 2.90 ± 0.02 , 2.82 ± 0.02 , 2.76 ± 0.03 and 2.65 ± 0.02 for PANi/G composites with graphite particle sizes of >75 , 45–50, 20–25 and <20 μm , respectively.

As it is obvious, PANi/G composites have more porosity than PANi film, while with increase in graphite particle size, the fractal dimension, porosity level is increased, and the size of these pores and spaces becomes larger, so that the diffusion of dopant ions can occur much easier. In addition, here is a satisfactory agreement between the fractal dimensions obtained by using CV and EIS techniques (Table 1).

4. Conclusion

The surface morphology of PANi/G composites with different graphite particle sizes were studied by using the fractal dimension concept. The fractal dimensions evaluated from the cyclic voltammetry and impedance spectroscopy measurements do indeed coincide. As shown by using SEM and fractal dimension, the PANi/G composites possess more porous structure with an increase in graphite particle size. However, one needs to pay attention to each single measurement made with a film, as the exact reproducibility of the matrices and polymeric composites is very difficult. The results indicated that the electrochemical methods described in this work could be used as a simple tool for analyzing the fractal structure of conducting polymers and their composites.

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