

IMPEDANCE SPECTROSCOPY STUDIES ON DOPED POLYANILINES

D. Hui, R. Alexandrescu^a, M. Chipara^{b*}, I. Morjan^a, Gh. Aldica^c, M. D. Chipara, K. T. Lau^d

University of New Orleans, Department of Mechanical Engineering, USA

^aNational Institute for Lasers, Plasma and Radiation Physics, Laser Department, Bucharest, Romania

^bRadiation Effects Research Program, Indiana University Cyclotron Facility, 2401 Milo S Sampson Lane, Bloomington, Indiana, IN 47403-1398, USA

^cNational Institute of Materials Physics, Magurele, Bucharest, Romania

^dThe Hong Kong Polytechnic University, Department of Mechanical Engineering, Hong Kong, China

Impedance spectroscopy studies on polyaniline doped by various amounts of HCl are reported. The measurements were performed at room temperature, over a wide range of frequencies [1000 Hz to 45 MHz]. The experimental data shows that the resistance dominates the AC behavior of polyaniline confirming that the charge transport occurs through an one-dimensional hopping process.

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1. Introduction

Polyaniline, in its fully doped form, is among the conducting polymers with the highest conductivity. DC electrical conductivity of up to 6,000 S/m has been reported in heavily doped polyaniline [1-4]. Its poor mechanical properties, reduced solubility, and difficult processing balance the excellent electric and thermal stability of conducting polyanilines. Blending polyaniline with different polymers surpasses these drawbacks [5-8]. Nevertheless, the concentration, size, and shape of conducting particles controls the percolation threshold while the conductivity of polyaniline determines the highest conductivity of these composites. Hence, a detailed study of the doping process in conducting polymers is extremely important.

The charge transport mechanism in pristine and doped polyanilines has been investigated by electron spin resonance spectroscopy and DC conductivity in a previous contribution [1]. It was concluded that the charge transport mechanism occurs through electronic hopping (polarons) and the presence of metallic islands has been proved. The contribution of bipolarons to charge transport was ruled out. The temperature dependence of DC conductivity and electron spin resonance line width indicated that the electronic transport in doped polyanilines occurs through an one dimensional variable range hopping. However, the contribution of other transport phenomena has not been completely ruled out. The present study aims to a better understanding of the effect of dopants on the electrical features of polyanilines.

* Corresponding author: mchipara@iucf.indiana.edu: chipara@lycos.com

On leave from National Institute of Materials Physics, Magurele, Bucharest, Romania

2. Experimental methods

AC electrical measurements are used to investigate polyaniline samples doped during polymerization with various amounts of HCl. Details regarding the doping process and the methods used for estimation the doping level (Cl/N ratio) are given elsewhere [1,8] The conductivity measurements were performed on pressed pellets of polyaniline. To improve the electrical contact the faces of the pellet were painted with silver paste.

3. Experimental results

In Figs. 1A-2C are represented the Nyquist diagrams for pristine (Fig. 1A) and doped polyanilines. The frequency dependence of the phase shift, defined as the ratio between the imaginary and the real part of the impedance, is shown in Figs. 3A-4C. It is observed that the general trend is represented by the shift of the frequency at which the phase shift is maxim towards lower frequencies as the doping level is increased. For all samples, the phase shift is rather small indicating that the most important contributions are due to the sample resistance, both in pristine and doped polyanilines.

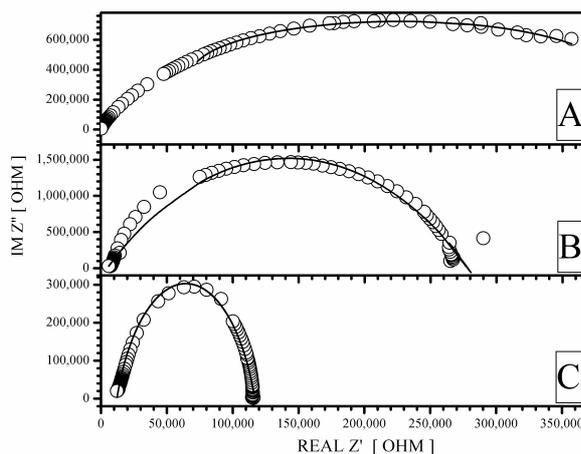


Fig. 1. Nyquist plot for the pristine polyaniline (A), polyaniline with Cl/N=1% (B), and polyaniline with Cl/N =2.0% (C). The line represents the best fit of experimental data by using equation (2). The size of experimental points reflects the experimental errors.

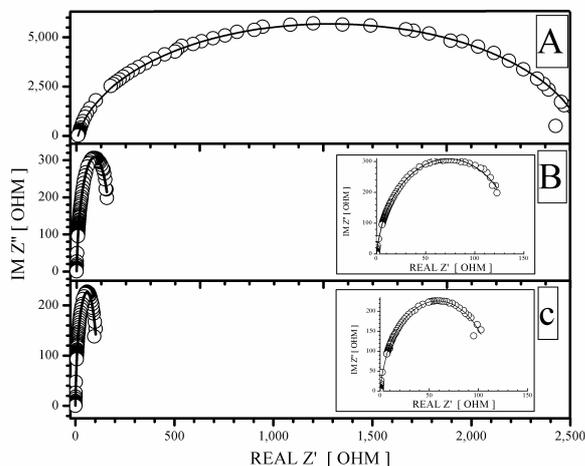


Fig. 2. Nyquist plot for the polyaniline with Cl/N=3% (A), polyaniline with Cl/N=10% (B), and polyaniline with Cl/N =15.0% (C). The line represents the best fit obtained of experimental data by using equation (2). The size of experimental points reflects the experimental errors.

The frequency dependence of the real part of the sample impedance, which is governed by the resistance of pristine and doped polyanilines is shown in Figs. 5A-6C. It is observed that the real part of the impedance is starting to decrease even from low frequencies and reaches an asymptotic value in the high frequency range and that the HCl doping is decreasing the impedance of the sample.

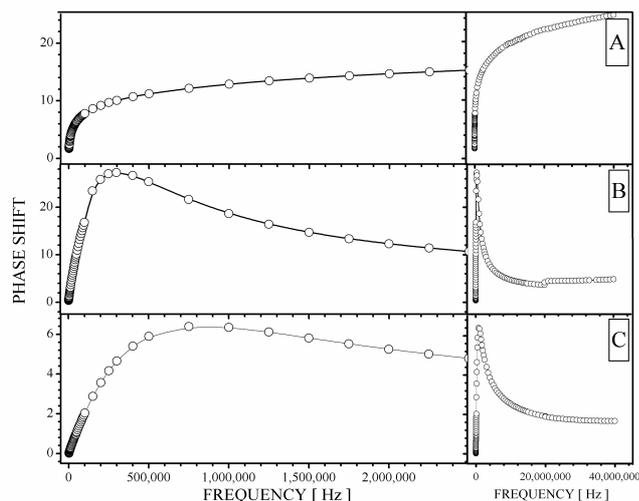


Fig. 3. Bode plot for the pristine polyaniline (A), polyaniline with Cl/N=1% (B), and polyaniline with Cl/N =2.0% (C). The size of experimental points reflects the experimental errors.

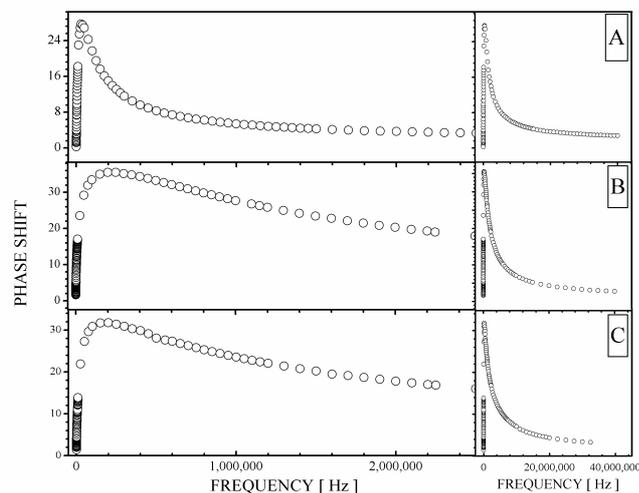


Fig. 4. Bode plot for the polyaniline with Cl/N=3% (A), polyaniline with Cl/N=10% (B), and polyaniline with Cl/N =15.0% (C). The size of experimental points reflects the experimental errors.

The frequency dependence of the real impedance R_{INF} is shown in Fig. 7. It is observed R_{INF} decreases as the doping level is increased. However, a small maximum of R_{INF} has been observed at 1% Cl/N. The characteristic frequency at which the phase shift is maximum, f_C , decreases as the doping level (see Fig. 7) is increased suggesting that this effect is eventually determined by the capacitance component of the equivalent electric circuit. The projection on the real axis of the center of the circle in the representation imaginary impedance versus real impedance, defined by R_0 , has a

smooth decrease as the doping level is increased (see Fig. 7). The parameters R_{INF} and R_0 for some simple equivalent electrical circuits are shown in Fig. 8A-8C.

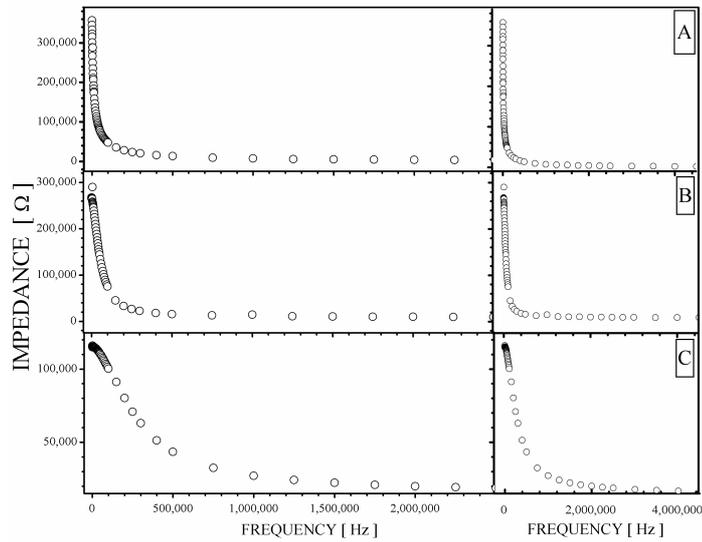


Fig. 5. The frequency dependence of the impedance for the pristine polyaniline (A), polyaniline with Cl/N=1 % (B), and polyaniline with Cl/N = 2.0 % (C). The size of experimental points reflects the experimental errors.

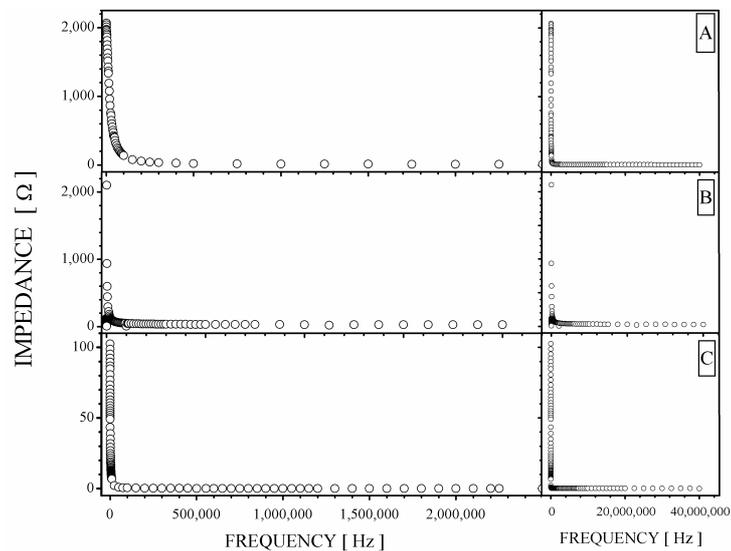


Fig. 6. The frequency dependence of the impedance for the polyaniline with Cl/N=3% (A), polyaniline with Cl/N = 10 % (B), and polyaniline with Cl/N = 15.0 % (C). The size of experimental points reflects the experimental errors.

4. Discussions

The Nyquist diagrams for simple electrical circuits consisting of resistors and capacitors are shown in Figs. 8A-8C. The presence of a single semicircle and the shift of its centre along the real axis indicate that the circuit shown in Fig. 8B describes better the actual features of pristine and doped polyanilines. Dyre [9] proved that such an electrical circuit is a simpler representation of an amorphous semiconductor in which charge transport occurs through hopping. The hopping

contribution are included in the real part of the impedance while the capacitor collects unrelated purely imaginary contributions from the atomic polarizability given by the high frequency dielectric constant. The fast decrease in the radius of these circles reflects the decrease in the resistance of polyanilines due to HCl doping. As shown in [10-14] the observation of a single circle reflects the fact that our system is equivalent with a collection of elements such as the one shown in Fig. 8B, coupled in series. The distribution of R, R₁, C and C₁ values is eventually narrowed. This behaviour is consistent with an one dimensional hopping process as the transfer of the electron from one chain to an adjacent chain is negligible. A careful inspection of Figs. 1A to 2C reveals that actually the circles are distorted. This deformation was explained by assuming that a constant phase element is in series with the capacitor [12-14].

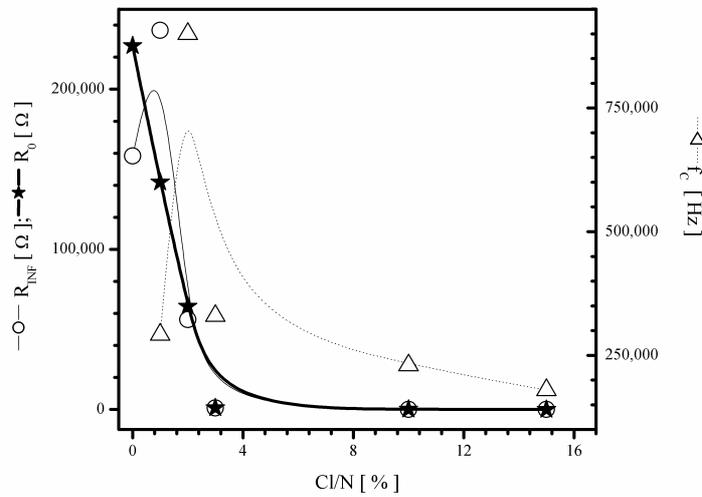


Fig. 7. The dependence of R_{INF}, R₀, and f_C on the doping level.

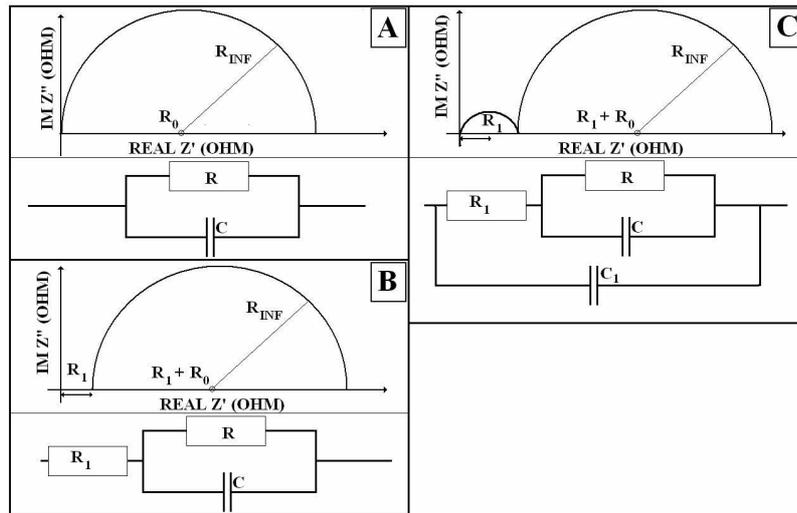


Fig. 8. Simple equivalent circuits in impedance spectroscopy.

Such an element is characterized by complex impedance, Z [12-14]:

$$Z = \frac{1}{(j\omega)^n Q} \tag{1}$$

Where $j = \sqrt{-1}$ and $Q\omega^{n-1}$ is a capacitance (measured in Farads). For $n = 1$ the element is an ideal capacitor. Such a contribution may reflect the contribution of diffusion processes [12-14].

Under these circumstances, using the following expression has been used to fit the experimental data:

$$\alpha(\text{Im}Z - \text{Im}Z_0)^2 + (\text{Real}Z - \text{Real}Z_0)^2 = R_{\text{INF}}^2 \quad (2)$$

Where $\text{Im}Z_0$ and $\text{Real}Z_0(=R_0)$ are the coordinates of the center, and R_{INF} the radius of the circle. The bold line in Figs. 1A-2C represents the best fit obtained by assigning the experimental data to the circuit represented in Fig. 8B. In Fig. 8 are represented the dependence of the resistance (R_{INF}) and value of the projection of the circle origin onto the real axis (R_0). It is observed from Fig. 7 that both R_{INF} and R_0 are decreasing as polyaniline is doped. However, R_{INF} presents an unexpected jump for 1% Cl/N. Such behaviour cannot be assigned to R_1 as in this case it should have a negative value. We tentatively assign this behaviour to the appearance of conducting islands at nanometer scale. The reduced size of these islands makes surface effects extremely important and probably may result in a more complex equivalent circuit.

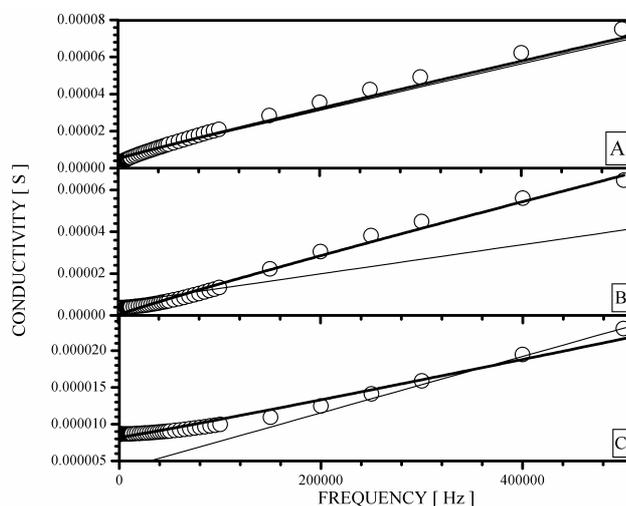


Fig. 9. The frequency dependence of the impedance for the pristine polyaniline (A), polyaniline with Cl/N=1% (B), and polyaniline with Cl/N =2.0% (C). The bold line represents the best fit obtained by using the expression (4) and the narrow line the best fit corresponding to the equation (3). The size of experimental points reflects the experimental errors.

The Bode plots, shown in Figs. 3A-4C shows a maximum in the frequency dependence of the phase shift, expected for simple electrical circuits as such shown in Figs. 8A and 8B [13]. At low frequencies, the phase shift is negligible, as expected for a simple electric circuit that has a capacitor in parallel with a resistor. By increasing the frequency, the phase shift is increased up to a maximum value, observed at a characteristic frequency, f_c . Higher frequencies ($f > f_c$) will result in a decrease of the phase shift. As it is observed from Fig. 7, the characteristic frequency is decreased as the doping level is increased. It is supposed that for the pristine polyaniline f_c is too high to be observed by our experimental set up. However, the value of f_c for the samples doped at 1% Cl/N is unexpectedly low, supporting the complex behaviour of this sample. Fig. 7 shows that for all samples R_0 decreases monotonously as the doping level is increased. The relatively low value of the phase shift indicates that the electric behaviour is dominated by the resistive component. The presence of an inductive component has been reported [15] in polyaniline by electrochemical impedance spectrometry. We were not able to identify an important contribution due to the presence of an inductive element.

Under these circumstances, it is justified to try to fit the frequency dependence of the resistance by a power law as predicted by the Mott localization and scaling theories [16]:

$$\sigma = \sigma_0 + Bf^s \quad (3)$$

Where B and s are constants. The theory predicts $s=2.00$ for $f < f^*$ and $s=0.3$ for $f > f^*$, where f^* is the cross over frequency. A more complex expression for the frequency dependence of the conductivity was obtained within the extended pair approximation [16];

$$\sigma(f) = \sigma(0) + k\sigma(0)(f / f_0)^s \quad (4)$$

Where $\sigma(f)$ is the sample conductivity for an AC current excitation of a frequency f , f_0 is a critical frequency that describes the conductivity crossing, $\sigma(0)$ is the DC conductivity of the sample, K is a parameter and the exponent s is correlated to the charge transport mechanism. This model predicts that if $1 > s > 0.8$, the charge transport occurs through hopping.

The frequency dependence of the AC electrical resistance is shown in Figs. 9A-10C. The predictions based on equation (3) are represented in Figs. 9A-10C by narrow lines. By analyzing the results, it is observed that the best predictions are obtained by using the relationship (4) (see the bold lines in Figs. 9A-10C). As observed from Table 1 the exponent values corresponding to the best fit of experimental data (using equation 4) confirm that the charge transport occurs through hopping.

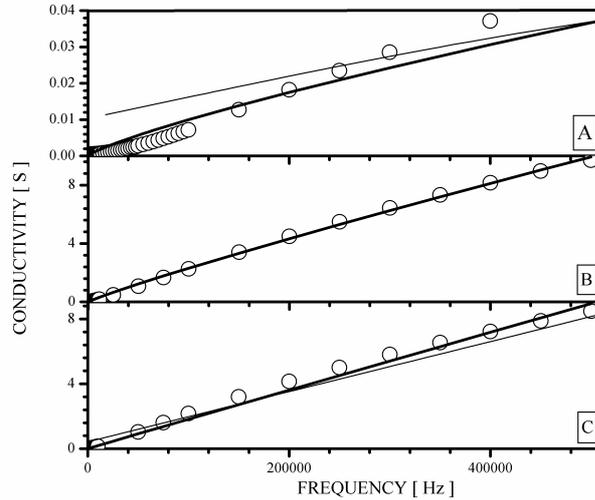


Fig. 10. The frequency dependence of the impedance for the polyaniline with Cl/N=3% (A), polyaniline with Cl/N=10% (B), and polyaniline with Cl/N =15.0% (C). The bold line represents the best fit obtained by using the expression (4) and the narrow line the best fit corresponding to the equation (3). The size of experimental points reflects the experimental errors.

Table 1. The values of the exponent, s , obtained by fitting the frequency dependence of the conductivity with the equation (4), for polyanilines doped with different amounts of chlorine.

Doping level Cl/N (%)	Exponent s
0	0.96
1	0.94
2	1.04
3	0.81
10	0.91
15	0.99

5. Conclusions

The electrical conductivity of conducting polymers is enhanced by several orders of magnitude by manipulating the pH and the applied potential on the polymer. The electrical conductivity on conducting polymers is increased by both protonic and electronic doping. The doping introduces states within the forbidden gap. As the doping level is increased, these states collapse into a band and finally at high doping levels the band gap disappears and the polymer exhibits metallic conducting features. As the pristine (not doped) conducting polymers have rather modest electrical conductivities, the doping step is extremely important in the synthesis of a polymer with a high electrical conductivity. This contribution is focused on the protonic doping of polyaniline with chlorine. The AC behavior of pristine and doped polyaniline was investigated. Experimental results indicate that the electrical equivalent circuit is represented by a resistor in parallel with a capacitor. Such an equivalent electric circuits describes the variable range hopping of electrons. A small contribution due to another resistor, R_0 , in series with this element has been observed. The value of R_0 decreases as the doping level is increased, suggesting that R_0 represents the resistance between adjacent conducting islands (characterized by a resistance in series with a capacitor). As expected this additional resistance is decreasing as the doping level is increased as more conducting islands are produced and eventually some of these conducting islands collapsed into bigger conducting islands. The increase in the size of conducting islands due to chlorine doping was confirmed by the analysis of the shape of electron spin resonance spectra [1].

The observed distortion of Nyquist diagrams indicates the contribution of a phase constant element. It is speculated that this additional term may reflect the granular structure of our conducting composite. The experimental data show that within the experimental errors the equivalent electric circuit contains no inductive element. In the whole frequency range investigated by us, the resistive character was found to be dominant. The frequency dependence of the conductivity proved that the charge transport mechanism is an one dimensional hopping, in agreement with the temperature dependence of the DC conductivity and with electron spin resonance data [1].

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