

# Electrolyte and solvent effects on voltammetry behavior and surface morphology of Polypyrrole films deposited on glassy carbon electrode in the redox process

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## Abstract

Polypyrrole (PPy) films were electrochemically synthesized on glassy carbon electrode in different electrolytes and solvent media. Voltammetry studies of PPy films doped with  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  anions showed that the redox activity of the polymer is affected by the nature of the anions and solvent used in the electrochemical synthesis. The mobilities of the anions exhibited a well-defined order:  $\text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^-$ . The electrodeposited PPy films were characterized *ex situ* independently by atomic force microscopy (AFM) technique. The effect of solvent on the surface morphology of PPy films was clarified by AFM imaging. Our results showed that the level of doping will depend on the polarity of the solvent used. In polar solvent like DMSO, the doping of  $\text{Cl}^-$  anion is predominant. The results obtained suggested the presence of chemisorbed anions on the surface of PPy films.

**Keywords:** Polypyrroles, atomic force microscopy (AFM), thin films, morphology, electrolyte, glassy carbon.

## Introduction

Since the late 1970s, a great number of research groups have focused their interest on conducting polymers, such as polyacetylene, polypyrrole, poly(3,4-ethylenedioxythiophene), and so forth, studying them from several points of view including their synthesis, charac-

terization, and technological application (Skotheim *et al.*, 1998; Otero *et al.*, 1999; Gonzalez *et al.*, 2003). PPy is one of the most widely considered conducting polymers because pyrrole is easily synthesized, soluble in water, commercially available, and the most frequently used polymer in commercial applications. Also, PPy shows good long term stability of its electric conductivity, together with good redox properties (Diaz *et al.*, 1979; MacDiarmid *et al.*, 1985; Pasquali *et al.*, 1993; Sacak, 1999; Sarac *et al.*, 1999).

The electrochemical and mechanical properties of the electrochemically deposited polypyrrole (PPy) films are dependent on many variables such as the nature of the solvent used, the supporting electrolyte, temperature, and potential / current utilized during the electrodeposition process (Skotheim, 1986). PPy synthesis by electrochemical oxidation of pyrrole monomers is a well-known and well-controlled method. Anions of various sizes can be employed to dope PPy during the polymerization. Examples of these anions include (i) small inorganic anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ , (ii) medium sized anions like benzenesulfonate, dodecylsulfonate, p-toluenesulfonate, and (iii) large polymeric anions similar to polyvinylsulfonate and polystyrenesulfonate. The resulting polymer will exhibit different conductive, mechanical, or electrochemical properties depending on the incorporated anion (Shimidzu *et al.*, 1987; Bidan and Ehui, 1988; Lien *et al.*, 1991; Naoi *et al.*, 1991; Johanson, 2005; Fernandez Romero *et al.*, 2005). It is also well known that the mobility of ions in polypyrrole depends on the structure of the polymer.

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One good possibility for changing the structure of the polymer film is the variation of the potential / current used for the electrodeposition of the polymer (Bilger and Heinze, 1993; Heinze and Bilger, 1993).

On the other hand, the solvent must minimize the nucleophilic reactions. Aprotic solvents appear to be the best for PPy preparation. Among the solvents, acetonitrile is the most commonly used. Imanishi and co-workers (Imanishi *et al.*, 1988) have attempted to explain the strong influence of the solvent by drawing attention to its basicity and polarity. Film formation is influenced by the strength of the interactions between the solvent and the cation radicals. The basicity of the solvent is the principal factor influencing the selectivity in polymer formation. Additionally, the solvent polarity will affect the strength of the interactions between the solvent and the electrolyte anions. The ions interchanged with the solution during the redox switching are also influenced by the doping anion of the polymer. A more detailed study of the influence of the properties of the small anions on the electrochemical performance of the PPy films has been carried out in this work. The  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  anions were chosen for the investigation. The crystallographic radii of the selected anions are somewhat different:  $\text{NO}_3^-$  (0.129 nm),  $\text{Cl}^-$  (0.181 nm), and  $\text{ClO}_4^-$  (0.240 nm) (Marcus, 1997). The shape of these anions is also remarkably different: the halogenides are spherical, the nitrate is planar, and the perchlorate is a tetrahedral anion. Obviously, such differences should have some influence on their strength of interaction with polymer chains and also on their mobility in the polymer films. We also attempted to clarify the effect of solvent, including Acetonitrile (ACN), Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF), on surface morphology of PPy films by AFM.

## Materials and methods

### Materials

The monomer of pyrrole, (Fluka, purity  $\geq 98\%$ ), was distilled under reduced pressure prior to use. The solvents of acetonitrile (Aldrich, 99.93%), Tetrahydrofuran, (Merck, 99%), and Dimethyl sulfoxide, (Merck, 99%) and the supporting electrolytes of sodium nitrate, (Merck, 98%), sodium perchlorate (Fluka, 99%), and sodium chloride, (Merck, 99%), were used as received. The solutions of pyrrole were freshly prepared for each deposition. Other reagents were in analytical grade.

### Instrumentation

A glassy carbon electrode (GC) was used as working electrode and a platinum wire employed as counter electrode in the measurements. All potentials were determined and reported respect to the reference electrode of Ag/AgCl (saturated KCl). The working electrode surface was cleaned by polishing pretreatment using 0.05  $\mu\text{m}$  alumina slurry successively. After polishing, the GC electrode was cautiously washed with distilled water.

Electropolymerization and cyclic voltammetry (CV) studies were carried out using a Potentiostat / Galvanostat EG&G Model 263 A; USA with a PC and electrochemical set up that controlled with M 270 software. A Nanosurf Easy Scan 2 AFM apparatus (ST Instruments, Liefstal, Switzerland) was used to scan and surface morphology of the deposited films at nanometer scale in various electrolytes and solvents. This AFM apparatus was mounted on TS – 150 tables from TableStable LDT® and confined using a noise reduction hood to avoid any vibration influence during measurements. The device was used in contact mode and silicon tips with Al coated cantilevers were selected. These cantilevers have a length of  $225 \pm 10 \mu\text{m}$ , a thickness of  $3.0 \pm 1 \mu\text{m}$  and a width of  $28 \pm 7.5 \mu\text{m}$ . The tip radius is supposed to be below 10 nm and in average around 7 nm. Scans were performed with 256 lines at a speed of 0.7 s per line. Image analysis was performed using the Scanning Image Probe Processor version 4.2.2.0 software.

### Synthesis of PPy films on glassy carbon electrode

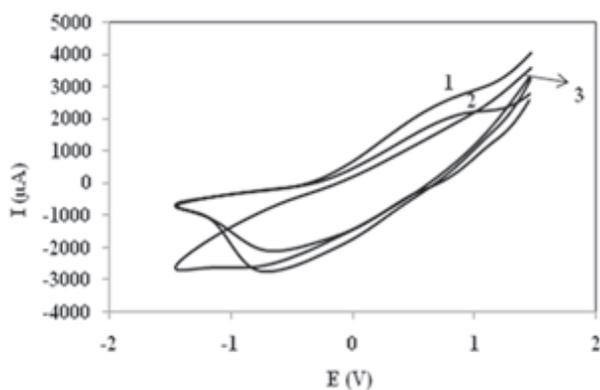
PPy films were electrochemically grown in a conventional three-electrode cell, at potentiostatic conditions of 0.8 V in aqueous solution having 50 mM pyrrole in 0.1 M of several supporting electrolytes including  $\text{NaClO}_4$ , NaCl and  $\text{NaNO}_3$ . Prior to the measurements, the solutions were deaerated by bubbling high purity (>99.9%) and dried  $\text{N}_2$  for 20 min. After polymerization, the films were electrochemically characterized in the same electrolyte solution used in the growth process but without monomer (0.1 M of supporting electrolyte in aqueous solution + 10% the solvents) in the potential range between  $-1.5$  to  $1.5 \text{ V}$  at  $v = 100 \text{ mV s}^{-1}$ .

A spin coating deposition technique was used to prepare the samples for AFM observations. About 4-5 drops of the homogeneous blends in THF was placed on micro cover glasses to produce very thin films of the compositions using a spin coater.

## Results and Discussion

### Effect of supporting electrolyte on voltammetry behavior of PPy films in 10% DMSO solution

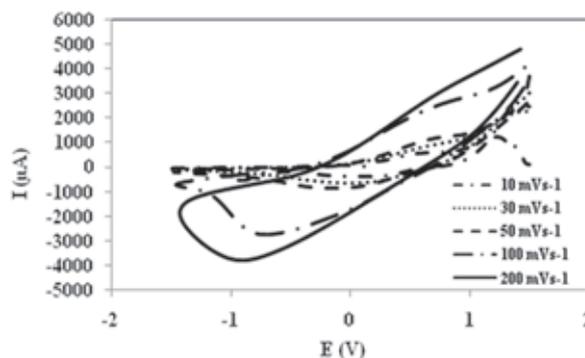
Polypyrrole has been formed by using of aqueous solution consist of 0.1 M pyrrole and 0.1 M of NaCl, NaClO<sub>4</sub>, and NaNO<sub>3</sub> as supporting electrolyte. Figure 1 shows the voltammograms of PPy films deposited in the presence of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> anions. The shape of the CV curves is apparently similar. The most essential differences were observed in the case of the Cl<sup>-</sup> anions. The charge needed for the reduction or oxidization of the PPy/Cl<sup>-</sup> film is remarkably larger than those obtained for the other anions. The reason for this phenomenon may be related to the differences in doping level or in the efficiency of the electrodeposition. It is essential to state that the differences in redox activity virtually do not depend on the nature of the anions used during the measurements. Therefore, the structure of the polymer does not change considerably since the used anions are relatively similar in size.



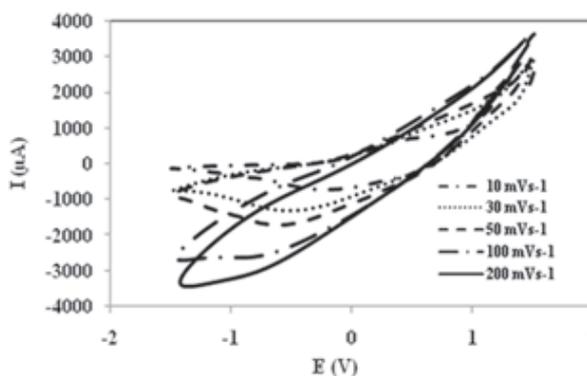
**Figure 1.** Voltammograms of the PPy films deposited and measured in aqueous solution consist of 10% Dimethyl sulfoxide solvent of the same anions: (1) Cl<sup>-</sup>, (2) NO<sub>3</sub><sup>-</sup>, (3) ClO<sub>4</sub><sup>-</sup> Scan rate 100 mVs<sup>-1</sup>.

As it was reported previously (Latonen *et al.*, 2002; Pigani *et al.*, 2004; Refaey, 2004) the dependence between level of doping and the nature of the anion is clear because the anions stabilizes the positive charged centers in the polymer chains. A good possibility to compare the mobilities of the anions in the polymer film is to study the influence of the scan rate  $\nu$  on the shape of the CV curves. Typical results were presented in Figures 2 and 3. The voltammograms in these figures are presented enabling good comparison.

From the comparison of the results, presented in Figures 2 and 3, it follows that doping of Cl<sup>-</sup> anion in PPy/Cl<sup>-</sup> system is conquering in comparison to PPy/ClO<sub>4</sub><sup>-</sup> system. Obviously, the shift of the peak on the oxidation curve in the case of PPy/Cl<sup>-</sup> is more pronounced, especially at higher scan rates.



**Figure 2.** Voltammograms of the PPy/Cl<sup>-</sup> films (current divided by scan rate) in 0.1M NaCl at scan rate  $\nu$ : (1) 10 mVs<sup>-1</sup>; (2) 30 mVs<sup>-1</sup>; (3) 50 mVs<sup>-1</sup>; (4) 100 mVs<sup>-1</sup>; and also (5) 200 mVs<sup>-1</sup>.



**Figure 3.** Voltammograms of the PPy/ClO<sub>4</sub><sup>-</sup> films in 0.1M LiClO<sub>4</sub>. The same scan rates as in Figure 2.

More information could be obtained from the comparison of the voltammograms measured in the presence of different anions with PPy films synthesized in the same solution. In these cases, the structures of the PPy films are identical or at least very similar, and the changes in the shape of the CV curves are more directly associated to the mobility of anions. It is clear that the mobility of all the anions studied is rather close together. Only at more positive potentials, some differences in the shape of the CV curves become evident as addressed in Figure 4.

The dependence of the peak of current of the anodic branch on the scan rate is presented in Figure 5. This figure shows that the dependencies of  $i_{p,a}$  on  $v$  that well described by straight lines (correlation coefficients are 0.90 or higher) and the mobility of anions does not differ too much, but remarkably in the sequence:  $\text{ClO}_4^- < \text{Cl}^- < \text{NO}_3^-$ .

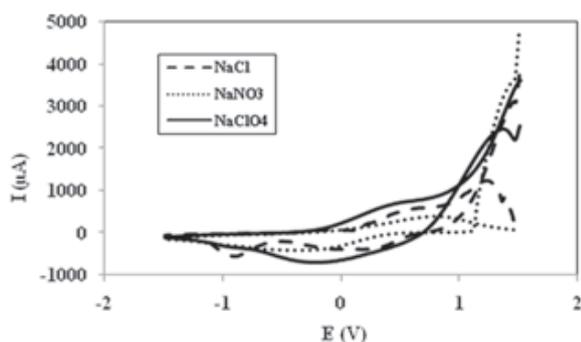


Figure 4. Voltammograms of the PPy films at scan rate  $10 \text{ mVs}^{-1}$  measured in: (1) NaCl; (2)  $\text{NaNO}_3$ ; (3)  $\text{NaClO}_4$ .

Presumably, the mobility of the  $\text{ClO}_4^-$  anion is lower due to its larger crystallographic radius, and causes essential deviation of the points from the straight line at higher scan rates. On the other hand, the interaction of the  $\text{Cl}^-$  ions with the PPy chain is stronger as indicated by inspection the results in Figure 5 and Table 1.

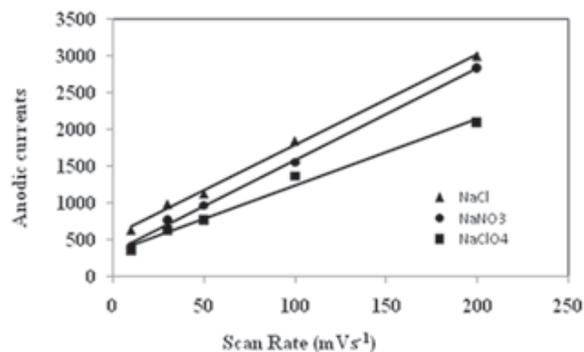


Figure 5. Dependence of the peak of current density  $j_{p,c}$  on the scan rate  $v$  of the PPy films in: (1) NaCl; (2)  $\text{NaNO}_3$ ; (3)  $\text{NaClO}_4$ .

Table 1. Current increment values (I) during the doping process of PPy formed upon GC by the using of different Supporting electrolytes at different scan rate ( $v$ ).

NaClO <sub>4</sub>		electrolytes NaNO <sub>3</sub>		NaCl	
$v$ (mVs <sup>-1</sup> )	I (µA)	$v$ (mVs <sup>-1</sup> )	I (µA)	$v$ (mVs <sup>-1</sup> )	I (µA)
10	346	10	410	10	630
30	624	30	760	30	985
50	765	50	976	50	1127
100	1363	100	1560	100	1847
200	2100	200	2850	200	3000

### Effect of solvent on the redox behavior of PPy films

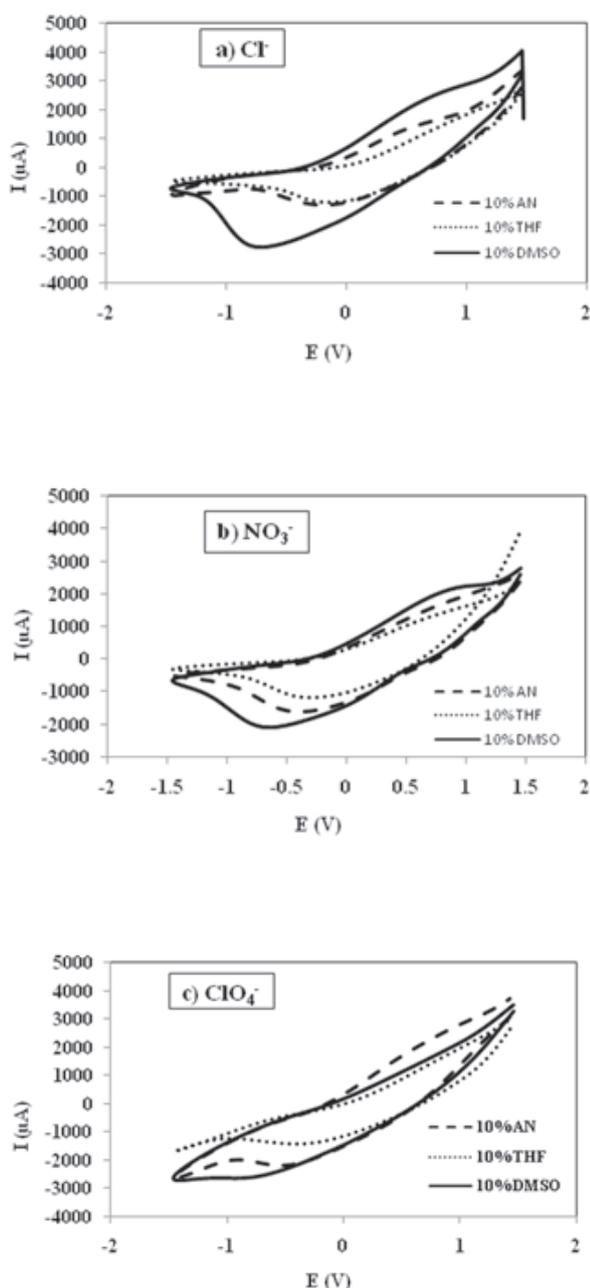
To elucidate how the solvent nature affects the redox capacitance, we studied Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF) and acetonitrile (ACN) those have substantially different polarities. In the general case, the solvent interaction with the species which take part the electronic process (dopant ions, charged and neutral film fragments) may influence the charge transport processes in the polymer films. It was found that cyclic voltammograms of 0.1 M electrolyte solutions containing different anions of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  in DMSO, ACN and THF had a similar form and very close anodic and cathodic peak currents. As shown in Figure 6a to c, we can observe that

the level of doping is depending on the type of anion and the used solvent. Our results demonstrated that in polar solvent, such as DMSO, doping of  $\text{Cl}^-$  anion is predominant whiles  $\text{ClO}_4^-$  doping is conquering in non-polar solvents of THF and ACN.

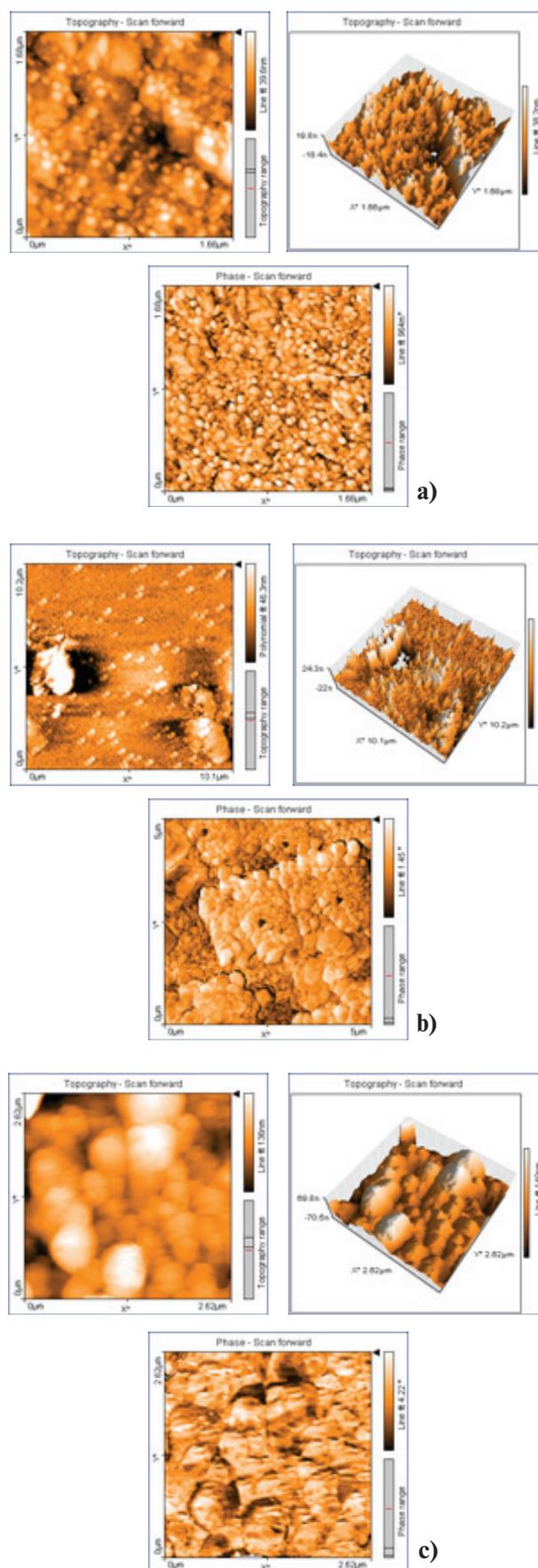
### Analysis of surface morphology using AFM

The surface morphological structure of the PPy films deposited in various solvents and supporting electrolytes were depicted in Figures 7 and 8, respectively. The particle size will be different based on the solvent polarity and the size of the used anions. Further that we observed a well dispersed morphology of the anions in the film matrixes as indicated by AFM photographs. Figure 7 presents the typical AFM topography

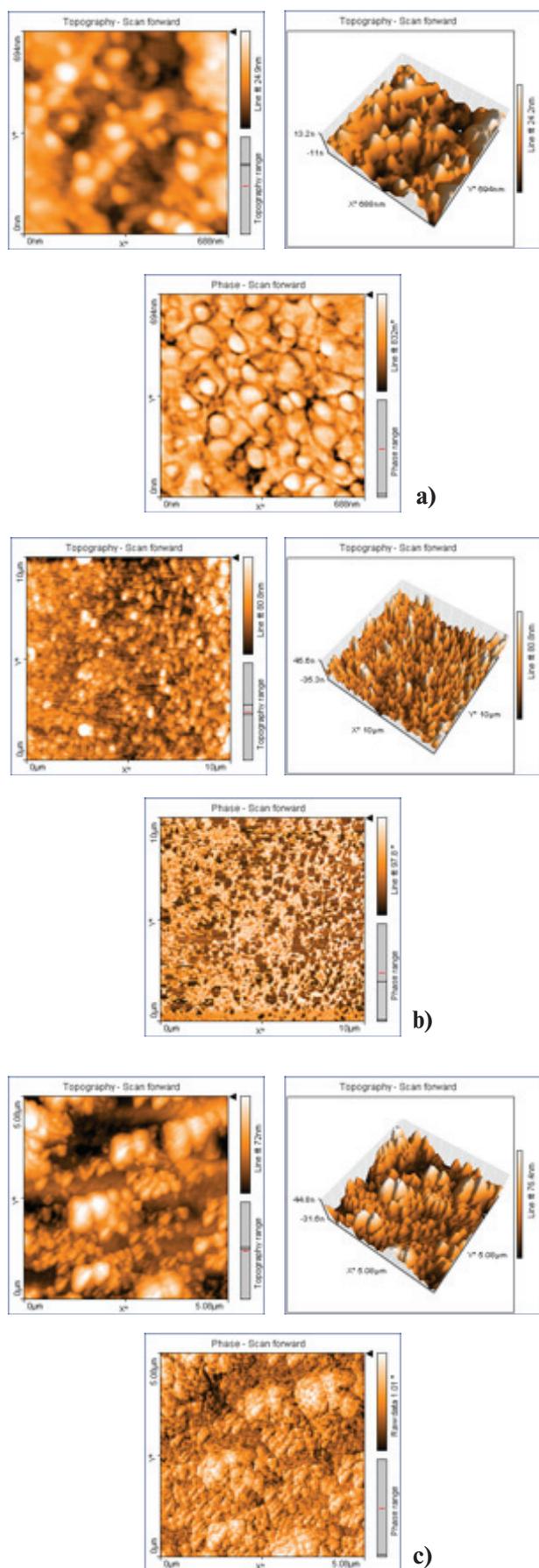
of a PPy / NaCl system in ACN, THF, and DMSO. The PPy films appear to be partially crystallized with many nano-crystals with diameters around 40 nm and height values below 120 nm. The mean height value was the minimum, around 13 nm, for the deposition in ACN. Sample prepared in DMSO was found to be more amorphous. Our studies also showed the volume fraction of the crystalline phase is strongly influenced by the polarity of solvent. The most important parameter is the composition of the PPy films, i.e. anion size: the smaller size of the anion results in the crystallized fraction.



**Figure 6.** Voltammograms of the PPy films in 0.1 M electrolyte solutions containing different anions: (a)  $\text{Cl}^-$ , (b)  $\text{NO}_3^-$ , and (c)  $\text{ClO}_4^-$  solutions in DMSO, ACN and THF.



**Figure 7.** AFM topography represents height image (left), 3D image (right), and phase scan (below) of PPy films deposited using NaCl electrolyte in a) ACN, b) THF, and c) DMSO.



**Figure 8.** AFM topography represents height image (left), 3D image (right), and phase scan (below) of PPy films deposited in ACN using a) NaCl, b) NaClO<sub>4</sub>, and c) NaNO<sub>3</sub> electrolytes.

Although, all the PPy films show some crystalline structure with regularly shaped nano-crystals but the sizes are different. Typical AFM images of the PPy films deposited in various supporting electrolytes in ACN were shown in Figure 8.

One can observe that the grain sizes increase with the anion size. The PPy/ NaCl system contains small grains on the order of 40 nm. The maximum grain size appeared to be about 80 nm in the case of ClO<sub>4</sub><sup>-</sup> anion. It can be seen that the AFM image reveals more details of the morphology of the films. The interfaces between the grains in AFM images are not very sharp. This is due to the achievable resolution which is dependent on the curvature of the tip. The experimental results of AFM investigations of the PPy films indicate that some agglomeration of the doped anions may be occurred depend on the solvent polarity.

However, figure 8 indicate nearly uniform matrix with some small lighter regions within the matrix, which may arise from the more elastic soft segment domains, i.e. PPy, and will also possess some crystallinity whereas the darker areas are indicative of more particulate hard material region. The extensive agglomeration on the PPy film surface in DMSO may be explained by considering the reactions between the doped anions and the polymeric chains.

## Conclusions

The electropolymerization of ppyrole was studied in different organic solvents and supporting electrolytes on glassy carbon electrode. The effects of solvent, supporting electrolyte type were examined. The two tendencies affecting the mobility of anions – the size and the strength of interaction with the chains – are not proportional for all the anions. The perchlorate anions are least “bound” to the polymer chains but their mobility is still low due to their largest radius and bulkier shape. The chloride anions have good mobility due to their favorable shape but also have rather strong interaction with the polymer as suggested by calculations and the tendency for increased participation of cations in the redox cycling. In case of singly charged small inorganic anions, the redox activity of the polymer film is almost completely determined by the nature of the anions used during the electrodeposition and is virtually independent of the nature of the anions used in the electrochemical studies. The AFM images revealed a surface characterized by a network of cylindrical-like features with lengths of several hundreds of nanometers and much smaller width. The

height and phase contrast images showed that the presence of some voids and zones of different packing density.

## References

- Bidan G., Ehui B., 1988. Conductive polymers with immobilized dopants: ionomer composites and auto-doped polymers—a review and recent advances. *J. Phys. D: Appl. Phys.* 21:1043-1054.
- Bilger R., Heinze J., 1993. Role of the formation potential on the redox processes of polypyrrole studied by an electrochemical quartz microbalance. *Synth. Met.* 55:1424-1429.
- Diaz A.F., Kanazawa K.K., Gardini G.P., 1979. Electrochemical polymerization of pyrrole. *J. Chem. Soc. Chem. Commun.* 14:635-636.
- Fernandez Romero A.J., Lopez Cascales J.J., Fernandez Otero T., 2005. Perchlorate interchange during the Redox Process of PPy/PVS Films in an acetonitrile medium. A voltammetric and EDX study. *J. Phys. Chem. B.* 109:907-914.
- Gonzalez J., Fernandez A.J., Otero T.F., Hotta S., 2003. In *Electronics and Optical Properties of Conjugated Molecular Systems in Condensed Phases*, Ed., Research Signpost: Kerala, India, Chapter 5.
- Heinze J., Bilger R., 1993. Ion movements during redox switching of polypyrrole - experiment and simulation. *Phys. Chem.* 97:502-506.
- Imanishi K., Satho M., Yasuda Y., Tsushima R., Aoki S., 1988. Solvent effect on electrochemical polymerization of aromatic compounds. *J. Electroanal. Chem.* 242:203-208.
- Johanson U., Marandi M., Tamm T., Tamm J., 2005. Comparative study of the behavior of anions in polypyrrole films. *J. Electrochim. Acta.* 50:1523-1528.
- Latonen R.M., Kvarnstrom C., Grzeszczuk M., Ivaska A., 2002. Study of electrolyte effects on electrochemical synthesis and p-doping of poly(thienyl biphenyl) films. *Synth. Met.* 130:257-269.
- Lien M., Smyrl W.H., Morita M., 1991. Cation and anion insertion in separate processes in poly(pyrrole) composite films. *J. Electroanal. Chem.* 309:333-340.
- MacDiarmid A.G., Chiang J.C., Halphen M., Huang W.S., Mu S.L., Somasli N.L., Wu W., Yaniger S.L., 1985. Polyaniline: interconversion of metallic and insulating forms. *Mol. Crystal & Liq. Crystal.* 121:173-180.
- Marcus Y., 1997. *Ion Properties*, Marcel Dekker, New York.
- Naoi K., Lien M., Smyrl W.H., 1991. Quartz crystal microbalance study: ionic motion across conducting polymers. *J. Electrochem. Soc.* 138:440-445.
- Otero T.F., White R.E., Bockris J.M., 1999. In *Modern Aspects of Electrochemistry*, Kluwer Academic: New York, 33, Chapter 3.
- Pasquali M., Pistoia G., Rosati R., 1993. Storage characteristics of polyanilines. an investigation by cyclic voltammetry and impedance spectroscopy. *Synth. Met.* 58:1-15.
- Pigani L., Seeber R., Terzi F., Zanardi C., 2004. Influence of the nature of the supporting electrolyte on the formation of poly[4,4'-is(butylsulphanyl)-2,2'-bithiophene] films. A role for both counter-ion and co-ion in the polymer growth and p-doping processes. *J. Electroanal. Chem.* 562:231-239.
- Rafaey A.A.M., 2004. Electrochemical impedance studies on the electrochemical properties of poly(3-methylthiophene) in aqueous solutions. *Synth. Met.* 140:87-94.
- Sacak M., 1999. Electrochemical synthesis of poly(N-vinyl carbazole) doped with  $\text{HSO}_4^-$  and  $\text{NO}_3^-$  anions. *J. Appl. Polym. Sci.* 74:1792-1796.
- Sarac A.S., Sonmez G., Ustamehmetoglu B., 1999. Electrochemical polymerization of pyrrole in acrylamide solution. *Synth. Met.* 98:177-182.
- Shimidzu T., Ohtani A., Yyoda T., Honda K., 1987. Charge-controllable polypyrrole/polyelectrolyte composite membranes part II. Effect of incorporated anion size on the electrochemical oxidation-reduction process. *J. Electroanal. Chem.* 224:123-135.
- Skotheim T.A., Elsenbaumer R.L., Reynolds J.R., 1998. *Handbook of Conducting Polymers*, Eds., Marcel Dekker, New York.
- Skotheim T.A., 1986. *The Handbook of Conducting Polymers*, Marcel Dekker, New York, p. 1.