# Investigation of Pulse-Electropolymerization of Conductive Polypyrrole Nanostructures

Hassan Karami<sup>1,2,\*</sup>, Azam Rahimi Nezhad<sup>1</sup>

<sup>1</sup>Nano Research Laboratory, Department of Chemistry, Payame Noor University, Abhar, Iran <sup>2</sup>Department of Chemistry, Payame Noor University, 19395-4697, Tehran, I.R. of Iran \*E-mail: <u>karami\_h@yahoo.com</u>

Received: 26 April 2013 / Accepted: 7 May 2013 / Published: 1 June 2013

We report here the electrochemical polymerization of polypyrrole (PPy) on platinum substrates by pulse galvanostatic method. The effects of variables as pulse height (current amplitude), relaxation time ( $t_{off}$ ), pulse time ( $t_{on}$ ), bath temperature, HCl and pyrrole concentrations were studied using SEM, UV-vis spectroscopy, Cyclic Voltammetry, and conductivity. The obtained results reveal the morphology and particles sizes of polypyrrole samples were strongly depended on the synthesis conditions. By changing the synthesis conditions, we can prepare nanoparticles, nanorods, nanoporous moss and nanotubes. The sample including nanotubes with 145 nm average outer diameter, 80 nm average inner diameter and 1600 nm average length selected as the best sample which can be synthesized on the conditions including 9 mA cm<sup>-2</sup> current density, 1 s relaxation time, 1 s pulse time, 30 °C solution temperature, 0.1 M pyrrole and 0.12 M HCl.

Keywords: Polypyrrole Nanostructures, Nanotube, Pulse Electropolymerization, Pulse Galvanostatic Method

# **1. INTRODUCTION**

Intrinsically conducting organic polymers such as polypyrrole (PPy), polyaniline and polythiophene were studied intensively during the last two decades. There are two main groups of applications for these polymers. One group utilizes their conductivity as its main property, and the other, their electroactivity [1-4]. Of all known Electrically conducting polymers (ECPs), polypyrrole (PPy) is by far the most extensively studied on account of the monomer (pyrrole) being easily oxidized [5], possibility of forming homopolymers or composites with optimal chemical and physical properties [6,7], water soluble [5], its high electronic conductivity [8], a relatively long period of stability [8-10], ease of preparation [9], and commercial applications including batteries [11-14], fuel cells [15],

supercapacitors [16-18], sensors [19-25,26], anhydrous electrorheological fluids [27], light emitting Diodes [28,29], corrosion protection [30-44], and thin film transistors [45-48].

There are two methods used to synthesize PPy, chemical and electrochemical polymerizations. Chemical methods can control morphology of PPy forming nanostructures [49-51], but they require relatively larger amounts of surfactants or other additives, which are rather tedious to recycle after polymerization. Moreover, it is difficult to attach nanosized polypyrrole onto a substrate without involving large contact resistance. Therefore, the nanosized polypyrrole synthesized by such methods is not suitable for electrochemical applications. A number of chemical methods for synthesis of polypyrrole in micro and nano scale are: in situ polymerization [52,53], two steps polymerization [54–64], emulsion polymerisation [65], and vapor phase polymerization [60,61]. The principal advantage of the electrochemical method is related to the better conducting properties and long time stability of conductivities [66,67]. As we know, the electrical conductivity of PPy is attributed to the electrons hopping along and across the polymer chains with conjugating bonds [68,69]. In the 1970s, Diaz and coworkers firstly synthesized conductive polypyrrole film via electropolymerization [70].

The reported electrochemical methods used in synthesizing polypyrrole include the constant potential (potentiostatic; PM) [71-80], constant current (galvanostatic; GM) [80-85], cyclic voltammetry (CV) [80,85-87], and pulse galvanostatic methods. Among these methods, pulse electrodeposition is a particularly interesting and reliable method to synthesize polyaniline with interest morphology such as nanowires and nanofibers. Pulse galvanostatic electrosynthesis is a powerful technique in controlling the size of the particles and the morphology of the samples. On the other hand, this method can be used in double electrode cells, allowing it to be applicable on laboratory and industrial scales.

Based on previous studies, there is a strong relationship between synthesis conditions and the morphology of the synthesized polypyrrole. The electropolymerization conditions that affect the polymerization processes include electrolyte anions, solvents, pH values of the aqueous solutions, and polymerization temperature, current/potential ratio and etc. To demonstrate this, during the optimization of pulse galvanostatic polymerization, the synthesis conditions were altered which resulted in considerable changes in the morphology of polypyrrole.

In this work, polypyrrole nanostructures were synthesized by applying the pulse current (pulse galvanostatic method) into a double-electrode electrochemical cell consisting of pyrrole and HCl. In this method, the parameters affecting the morphology of and the size of the polypyrrole particles include the pulse height, pulse time, relaxation time, pyrrole concentration, acid concentration and solution temperature. The effects of each parameter were fully investigated by means of the "one factor at a time method".

## 2. EXPERIMENTAL

# 2.1. Materials

To begin with, pyrrole and hydrochloric acid (HCl) were purchased from Merck. Next, pyrrole was distilled prior to being used and subsequently stored in the dark. Double distilled water was used in all experiments.

#### 2.2. Instrumental

All the electrochemical experiments were carried out by means of an electrolyzer equipped with a pulse system (BTE 04, Iran). Cyclic voltammetry (CV) experiments were done by Autolab (Eco Chimie, PGSTAT-10). The pores of porous graphite electrode were mechanically filled with the synthesized polypyrrole nanopowder and used as the working electrode in all CV experiments. A platinum electrode and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. The morphology of the samples was characterized by scanning electron microscopy (SEM, Philips, XL-30, Netherland). UV-Visible absorption spectra were measured using a double-beam spectrophotometer (Shimadzu 2550).

#### 2.3. Electrosynthesis of polypyrrole nanostructure

Before each deposition, one pair of cylindrical platinum grid electrodes was boiled in HNO<sub>3</sub> for 15 minutes and then rinsed with distillated water so that any surface species in contact with air would be removed. Two cylindrical platinum grid electrodes were coupled together in coaxial form into the electrochemical cell. The smaller electrode was connected to the positive pole of the electrolyzer to act as the anode. The cell was filled with a solution containing 0.1 M pyrrole and 0.12 M hydrochloric acid at a temperature of 30  $^{\circ}$ C. The nitrogen gas was passed through the electropolymerization solution so that the dissolved oxygen would be removed. A 9 mA cm<sup>-2</sup> pulsed current with 1 s of pulse time and 1 s of relaxation time was inserted into the cell for 3 h while the solution was stirred. The precipitate of polypyrrole nanostructure was filtered and washed first using 0.12 M hydrochloric acid and finally distilled water. The filtered paste was then dried at 80  $^{\circ}$ C for 90 minutes. The values of the effective parameters including the pulse amplitude (pulse height or current density), pulse time (t<sub>on</sub>), relaxation time (t<sub>off</sub>), solution temperature, pyrrole and HCl concentrations were varied and optimized through the "one factor at a time" method. At last, the samples were characterized by SEM, CV, UV-Vis spectrophotometer and conductivity.

### **3. RESULTS AND DISCUSSION**



Figure 1. DC current pulse diagram

Polypyrrole nanostructures were synthesized by means of the pulsed current method on the pt grid electrode from a solution including pyrrole and HCl. Figure 1 illustrates the used dc current pulse diagram. The pulse diagram reveals that a current pulse has at least three variables includes pulse height (pulsed current amplitude or pulse current density), pulse time ( $t_{on}$ ) and relaxation time ( $t_{off}$ ).

In addition to the pulse variables, the present study takes into account several other variables such as the solution temperature, pyrrole and HCl concentrations, whose values were specified via the "one factor at a time" method. In the following sections, the optimization process will be described.

# 3.1. Effects of Pulsed Current Amplitude



**Figure 2.** SEM images of different polypyrrole samples synthesized at different pulsed current densities; (a) 2 mA cm<sup>-2</sup>, (b) 4 mA cm<sup>-2</sup>, (c) 6 mA cm<sup>-2</sup>, (d) 9 mA cm<sup>-2</sup> and (e) 12 mA cm<sup>-2</sup>.

The chronopotentiometric experiments in the electropolymerization suggest that the substrate electrode polarizes. By exerting a current pulse, the surface of the platinum anode and cathode is polarized and the cell voltage is increased up to the sufficient degree so that the oxidation of pyrrole starts.

In the first step, the effects of the pulse amplitude (current density) on the morphology and the particles sizes of the synthesized polypyrrole were investigated. The pulse amplitude was varied from 2 mA cm<sup>-2</sup> to 12 mA cm<sup>-2</sup>, while the other parameters were kept constant (temperature:  $25 \, {}^{0}$ C, pyrrole: 0.1 M, HCl: 0.12 M, t<sub>on</sub>: 1 s and t<sub>off</sub>: 1 s). The obtained samples were studied by SEM (Fig. 2). As it can be observed in Fig. 2, the pulse amplitude (surrent density) of 9 mA cm<sup>-2</sup> leads to more uniform in intertwined nanorods (or intertwined short nanowires) with average diameters of 5 nm and average lengths of 15 nm. Increasing the density of the currents from 9 mA cm<sup>-2</sup> brings about a transformation in the morphology of the polypyrrole samples from short nanowires into an amorphous bulk form. To find a probable reason, the electrochemical reactions of the pyrrole electropolymerization are useful. The mechanism of the pyrrole polymerization reactions has been studied by a number of researches. The oxidative polymerization of pyrrole has been shown to proceed via the formation of dimer molecules during the nucleation process, followed by the oligomerization reaction [88-91]. Based on the previous reported reactions, pyrrolium cation radical is the main initiator of electropolymerization. Therefore, the product and the size of its particles.

For all the reaction media, the electropolymerization potential of pyrrole increased with increasing applied current density and a linear relationship was observed in acidic medium [92]. At high current densities, the production rate of pyrrolium cation radicals as the initiator of pyrrole polymerization is more than that in low current densities, where the synthesized polymer have a specific and uniform morphology and particles are finer. At much higher current densities, the amount of the synthesized polypyrrole during each pulse will be large. As the amount of the synthesized polypyrrole increases on the surface of anode, the anion insertion and de-insertion becomes a limiting parameter [93]. Clearly, the process of ion insertion/de-insertion is easier in small particles than in big particles.

## 3.2. Optimization of Relaxation Time $(t_{off})$

To investigate the effects of relaxation time on the morphology and the structure of the synthesized polypyrrole, the value for this parameter was varied from 0.25 to 2 s while the values of the other parameters were kept constant. All experiments were conducted at 25  $^{0}$ C. Figure 3 shows the SEM images of polypyrrole samples which were synthesized at different relaxation times. SEM images indicate when the t<sub>off</sub> is 1 s, it leads to more uniform nanorods (4 nm average diameter and 10 nm average length) which connected together. Pulse on time plays an important role in controlling chain size and chain defects [94]. The relaxation time in pulse elctropolymerization is the main factor affecting the mechanism of the particle growth. At low relaxation times, for instance, polypyrrole short nanorods are shorter and more agglomerated; further, they are not completely isolated because the

relaxation between two consequent pulses is so short that before the short nanorods formation is completed in the first pulse, the next pulse is applied and another nanorods begins to be formed and, as a result, gets connected to the last nanorods. At relaxation times longer than 1 s, the short nanorods formed during each pulse can be isolated from others. Thus, the structure becomes more regular and comes from the disorganization.



**Figure 3.** SEM images of different polypyrrole samples synthesized at different amounts of relaxation times (t<sub>off</sub>); 0.25 (a) , 0.5 s (b) , 0.75 s (c) , 1 s (d) , 1.5 s (e) and 2 s (f).



**Figure 4.** SEM images of polypyrrole samples that synthesized at different pulse times (t<sub>on</sub>), 0.25 s (a), 0. 5 s (b), 0.75 s (c), 1 s (d) and 1.5 s (e).

The effects of pulse time were investigated on the structure and morphology of polypyrrole samples. In this step, we apply different pulse times (0.25 s, 0.5 s, 0.75 s, 1s and 1.5 s). In these experiments, the pulse current,  $t_{off}$ , temperature, pyrrole and HCl are 9 mA cm<sup>-2</sup>, 1 s, 25 °C, 0.1 M and 0.12 M respectively. Fig. 4 displays the SEM images of the polypyrrole samples. As can be seen in Fig. 4, the pulse time of 1 s brings more uniform short nanowires. Pulse on time plays an important role in controlling chain size and chain defects [94]. Ordered pyrrole polymerization is shown by pulsed current deposition and these films demonstrate a relationship in increasing electrical conductivity and anisotropy with decreasing on time of the current pulse [95]. Each current pulse

contains a calculable number of electrons whose number varies depending on the pulse time. As the pulse time decreases, so do the electrons of each pulse. During the application of the pulse, polypyrrole short nanowires are formed. Any variation in the number of electrons can affect the morphology and the size of the sample particles. At the beginning of each pulse, the nucleation process is faster than the particle growth [96]. Conversely, at the end of each pulse, it is the particle growth that is faster than the nucleation process. Therefore, the pulse time is an important parameter affecting the morphology of and the size of the particles in the samples.

When a current pulse is exerted into the cell, there is big impedance against electron transmission which causes the cell potential to increase and overcome this impedance. Once the cell potential has reached the suitable degree, the oxidation of pyrrole will start. In each pulse, a major part of the pulse time is spent on increasing the potential. Therefore, the effective period of the optimized pulse time is 1 s.

#### 3.4. Effects of Pyrrole Concentration



**Figure 5.** SEM image of polypyrrole samples which synthesized at different pyrrole concentration: 0.01 M (a) , 0.0.05 M (b) , 0.1 M (c) ,0.25 M (d) and 0.5 M (e).

To investigate the effect of aniline concentration, five samples were synthesized at 25 <sup>o</sup>C in the following concentrations: 0. 01, 0.05, 0.1, 0.25, and 0.5 M. Fig. 5 shows the SEM image of the synthesized samples. According to the SEM images, the concentration of 0.1 M results in the most uniform short nanowires and ought to be selected as the optimized concentration. The electropolymerization potential, decreased slightly with increasing monomer concentration. This phenomenon may be associated with the process of an electrochemical reaction. The electropolymerization of pyrrole generally consists of two continuous steps. The first step is the diffusion of pyrrole monomer to the electrode surface, the rate of this step is determined by the pyrrole concentration. The second step is the oxidation reaction of pyrrole at the interface between the electrode and electrolyte solution. Since the applied current density and the electrolyte concentration were kept constant, the rate of the reaction was determined by the amount of monomer available at the interface at unit time. For higher monomer concentration the positive charge at the working electrode is rapidly consumed by pyrrole, the accumulation of the charge at the electrode is lower, thus the corresponding reaction potential is lower. At lower monomer concentration, the positive charge cannot be consumed by pyrrole immediately, thus some charge will be accumulated at the working electrode, resulting in a higher reaction potential [92].

# 3.5. Effects of HCl concentration



**Figure 6.** SEM images of polypyrrole samples which synthesized at different HCl concentration: 0.048 M (a), 0.12 M (b), 0.48 M (c), 2.02 M (d) .

To achieve uniform polypyrrole short nanowires, six samples were synthesized in different concentrations of HCl. In these experiments, the current density, relaxation time, pulse time, temperature and pyrrole concentration were 9 mA cm<sup>-2</sup>, 1 s, 1 s, 25 °C and 0.1 M, respectively. Figure 6 shows the effect of HCl concentration on the morphology and the size of the particles of polypyrrole. As the SEM images in Fig. 6 demonstrate, an HCl concentration of 0.12 M as dopant acid is a suitable medium to synthesize uniform polypyrrole short nanowires. One important parameter affecting the physical characteristics and morphology of PPy is the nature and the concentration of the dopant that represents about 30% of the weight of the polymer film. The choice of an electrolyte is made by considering its solubility and its nucleophilicity. Moreover, the anion oxidation potential should be higher than the monomer.

The size of the anion controls the microstructure and the porosity of the polymer. Indeed, this determines the ability of the polymer to undergo an easier diffusion of the dopants during the redox process [97]. The nature of the anion has an impact on the quality of the film produced which depends on the hydrophobic character of the anion, and the interactions between the polymer and the dopant [98]. Anion's hydrophobic interaction with water, one of the roles played by these organic anions is to orient the polymer chain parallel to the electrode surface. This chain orientation increases the order in the polymer structure[99]. basicity of the anion plays a role in polymer growth. The higher basicity of the anion, causes the lower conductivity of the polymer. This phenomenon is due to an increase in the interactions between the positive charges of the polymer and the anions. Conversely, anion acidity leads to an increase in the conductivity of polypyrrole [100]. The electrolyte concentration is also important although the effect is not entirely understood. The electropolymerization potential decreased gradually with increasing electrolyte concentration. This phenomenon is expected since the increasing electrolyte concentration can reduce the overall resistance of the system [92]. The polymers of the highest conductivity are produced when elevated concentrations of electrolyte are used [100]. Optimization of the pH results in the formation of a uniform surface with very few defects [101]. A low pH or acid solution generally favors polymerization. However, a very low pH will equally be responsible for weak conductivity because of the acid catalyzed formation of none conjugated trimers which further react to form a partly conjugated PPy or are incorporated into the film, or even diffuse into the solution. This reaction is presented in Figure 7 [102].

## 3.6. Optimization of Synthesis Temperature

As demonstrated by our previous studies [103-109], the temperature of electrosynthesis solution is an important parameter that can affect the morphology and the size of the particles of the final yield. To this end, seven samples were synthesized at different temperatures (4  $^{\circ}$ C, 10  $^{\circ}$ C,20  $^{\circ}$ C,30  $^{\circ}$ C, 40  $^{\circ}$ C and 50  $^{\circ}$ C).

Figure 8 shows the SEM images of polypyrrole samples which were synthesized at 4 °C, 10 °C, 20 °C, 30 °C, 40 °C and 50 °C. By varying the synthesis temperature, a wonderful change is seen at 30 °C. The SEM images indicate that 30 °C is the suitable temperature to form uniform polypyrrole nanotubes.



Figure 7. Electrochemical synthesis mechanism of partly conjugated PPy.



**Figure 8.** SEM images of polypyrrole samples synthesized at temperatures of 4 °C (a), 10 °C (b), 20 °C (c), 30 °C (d), 40 °C (e) and 50 °C (f).

Electropolymerization temperature has a substantial influence on the kinetics of polymerization as well as on the conductivity, redox properties and mechanical characteristics of the films [110]. In polypyrrole electrosynthesis, the temperature controls two effective factors: the generation rate of cation radicals, and the particle growth. The average activation energy of the polymerization process on platinum is between 15 and 20 kJ mol<sup>-1</sup> [111]. It should be noted that a decrease in the redox properties is observed as the temperature increases. Spectral analysis of the material prepared at the lower temperature shows a more regular structure. At higher temperatures, side-reactions such as solvent discharge and nucleophilic attacks on polymeric radicals cause the formation of more structural defects, resulting in lower conducting films. In general, higher conductivities are obtained at lower temperatures [112,113]. In acidic medium, the overall process is favored by lower reaction temperatures [114].

Based on the optimization experiments presented in sections 3-1 to 3-6, the optimum conditions for the electropolymerization of pyrrole in nanotube form are 9 mA cm<sup>-2</sup> for the current density, 1 s for the relaxation time, 1 s for the pulse time, 30 °C for the solution temperature, 0.1 M for the pyrrole and 0.12 M for the HCl.

## 3.7. More characterizations

Synthesis conditions can change the morphology of polypyrrole samples. Accordingly, four polypyrrole samples were synthesized under various conditions (Table 1), and they were tested by means of Uv-Vis spectroscopy and conductivity measurements. Figure 9 shows the SEM images of the selected samples to more characterizations.

sample	palse current(mAcm <sup>-2</sup> )	t <sub>on</sub> (s)	t <sub>off</sub> (s)	pyrrole(mol dm <sup>-3</sup> )	HCl(mol dm <sup>-3</sup> )	temperature(°c)
а	9	1	1	0.1	0.48	25
b	9	1	1.5	0.1	0.12	25
с	9	1	1	0.1	0.12	25
d	9	1	1	0.1	0.12	30

Table 1. Experimental conditions to synthesize the selected samples

As Fig. 9 shows, the morphologies of the selected samples are very different. It can be expected that they shows very different behaviors in Uv-Vis spectrum and electrical conductivity.

As a first study, the light absorbance of the samples was investigated by Uv-Vis spectroscopy. Figure 10 shows the Uv-Vis absorbance of the selected samples. As it can be seen in Fig. 10, the samples a, b and c shows similar behaviors. They have maximum absorbance ( $\lambda_{max}$ ) 255 nm. The same spectrum is related to the similar morphologies. But, the sample d has very different morphology. Therefore, it is expected that the sample d has different Uv-Vis spectrum. Based on the spectrums shown n Fig. 10, the sample d shows  $\lambda_{max}$  at 270 nm. Then, the sample d shows 15 nm red shift.



**Figure 9.** SEM images of different polypyrrole nanostructures. The samples (a, b, c, d and e) were synthesized under conditions noted in Table 1.

The electrical conductivity is one of the important parameters of charge/discharge ability of polypyrrole in lithium batteries. The results of conductivity measurements by direct two probe method were summarized in Table 2. As it can be seen in Table 2, the electrical conductivities of the samples are high. Between the samples, sample c shows higher conductivity. This result can be related to the good connectivity of the smaller particles of the sample c. The unexpected lower conductivity of sample d can be related to its week connectivity of pyrrole nanotubes together.



Figure 10. Uv-Vis spectrums of the selected samples which synthesized according to Table 1.

Table 2. Electrical conductivity results of the selected sample according to the Table 1.

Sample	a	b	С	d
Conductivity (mS cm <sup><math>-1</math></sup> )*	110	580	20800	20

\*The results were obtained by two probe methods.

# 4. CONCLUSIONS

Polypyrrole nanostructures can be prepared by using the pulsed current electrochemical method. In this method, the pulse height (pulse current amplitude), relaxation time, pulse time, synthesis temperature, pyrrole and HCl concentrations are the most important factors affecting the morphology of and the size of particles in polypyrrole samples. The suitable values of the effective parameters can be determined by the "one-at-a-time" method. By changing the synthesis conditions, the polypyrrole samples with different morphologies such as nanoparticles, nanorods, short nanowires and nanotubes can be synthesized can be prepared.

## ACKNOWLEDGEMENTS

We gratefully acknowledge the support of Abhar Payame Noor University Research Council.

## References

- 1. C. Pratt, Conjugated Polymers: Electronic Conductors, London: Kingston Univ. (2003).
- 2. J. Margolis, Conductive Polymers and Plastics, London: Chapman & Hall (1989) p. 33.
- 3. D.W. Salaneck, R.T. Clark, and E.J. Samuelsen, *Science and Application of Conducting Polymers*, Bristol: IOP (1991) p. 168.
- 4. H. Naarmann, Polymers to the Year 2000 and Beyond, New York: Wiley, 1993.
- 5. J. Zhang, L. B. Kong, H. Li, Y. C. Luo, L. Kang, Mater. Sci. 45 (2010) 1947.
- 6. M. Hughes, M.S.P. Shahher, A.C. Renouf, C. Singh, G.Z. Chen, D.J. Fray, A.H. Windle, *Adv. Mater.* 142 (2002) 382.
- 7. Y.C. Liu, C.J. Tsai, Chem. Mater. 15 (2003) 320.
- R. Ansari Khalkhali, Rus. J. Electrochem, 41 (9) (2005), pp. 950–955. From Elektrokhimiya, 41 (9) (2005), pp. 1071–1078.
- 9. Benjamin L. Fletcher, Timothy E. McKnight, Jason D. Fowlkes, David P. Allison, Michael L. Simpson, Mitchel J. Doktycz, *Synth. Met.* 157 (2007) 282.
- 10. Y.C. Liu, J.M. Huang, C.E. Tsai, T.C. Chuang, C.C. Wang, Chem. Phys. Lett. 387 (2004) 155.
- 11. D.G. Shchukin, K. Kohler, H. Mohwald, Am. Chem. Soc. 128 (2006) 4560.
- 12. Q. Zhou, C.M. Li, J. Li, X. Cui, D. Gervasio, Phys. Chem. C 111 (2007) 11216.
- 13. R.P. Ramasamy, B. Veeraraghavan, B. Haran, B. N. Popov, Power Sources. 124 (2003) 197.
- 14. S. Kuwabata, M.J. Tomiyori, *Electrochem. Soc.* 149 (2002) A988.
- M.A. Smit, A.L. Ocampo, M.A. Espinosa-Medina, P. J. Sebastia'n, *Power Sources*. 124 (2003) 59.
- 16. M.D. Ingram, H. Staesche, K.S. Ryder, Power Sources. 129(2004) 107.
- 17. K.H. An, K.K. Jeon, J.K. Heo, S.C. Lim, D.J. Bae, Y.H. Lee, *Electrochem. Soc.* 149 (2002) A1086.
- 18. K. Jurewicz, S. Delpeux, V. Bertagna, F. Beguin, E. Frackowiak, Chem. Phys. Lett. 347 (2001) 36.
- 19. S. Sabah, M. Aghamohammadi, N. Alizadeh, Sens. Actuators. B 114 (2005) 489.

- 20. S. Cosnier, R.E. Ionescu, S. Herrmann, L. Boufer, M. Demeunynck, R.S. Marks, *Anal. Chem.* 78 (2006) 7054.
- J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P. L. Burns, A.B. Holmes, *Nature*. 347 (6293) (1990) 539.
- 22. O.A. Sadik, *Electroanal*. 11 (12) (1999) 839.
- 23. Y.C. Liu, B.J. Hwang, W.C. Hsu, Sens. Actuators. B 87 (2002) 304.
- 24. L. Ruangchuay, A. Sirivat, Schwank, Synth. Met. 140 (2004) 15.
- 25. V.M. Schmidt, D. Tegtmeyer, J. Heitbaum, Electroanal. Chem. 385 (1995) 149.
- 26. D.u. Kim, B. Yoo, Sens. Actuators. B 160 (2011) 1168.
- 27. J.W. Goodwin, G.M. Markham, B.J. Vinent, Phys. Chem. B 101(1997) 1961.
- R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Bredas, M. Loglund, W.R. Salaneck, *Nature*. 397 (6715) (1999) 121.
- 29. S.R. Forrest, Nature. 428 (6986) (2004) 911.
- 30. N. Attarzadeh, K. Raeissi, M.A. Golozar (2008) Prog Org Coat 63:167
- 31. K.K. Kanazawa, A.F. Diaz, R.H. Geiss, W.D. Gill, J.F. Kwak, J.A. Logan, J.F. Rabolt, G.B. Street, *Chem. Soc. Chem. Comm.* (1979) 854.
- 32. A.F. Diaz, K.K. Kanazawa, G.P. Gardini, J. Chem. Soc. Chem. Comm. (1979) 635.
- 33. A.F. Diaz, Chem. Scripta. 17 (1981) 142.
- 34. G. Tourillon, F. Garnier, Electroanal. Chem. 135 (1982) 173.
- 35. A.F. Diaz, J.A. Logan, *Electroanal. Chem.* 111 (1980) 111.
- A.G. MacDiarmid, J.C. Chiang, M. Halpern, H.S. Huang, S.L. Mu, N.L.D. Somasiri, W.Wu, S.I. Yaniger, *Mol. Cryst. Liq. Cryst.* 121 (1985) 173.
- 37. W. Janssen, F. Beck (Eds.), Polymer. 30 (1989) 353.
- C.A. Ferreira, B. Zaid, S. Aeiyach, P.C. Lacaze, in: P.C. Lacaze (Ed.), Organic Coatings, AIP Press, Woodbury, NY, 1996, pp. 159.
- 39. D.W. DeBerry, Electrochem. Soc. 132 (1985) 1022.
- 40. R. Gasparac, R. Martin, Electrochem. Soc. 149 (2002) B409.
- 41. C.K. Tan, D.J. Blackwood, Corros. Sci. 45 (2003) 545.
- 42. A.M. Fenelon, C.B. Breslin, *Electrochim. Acta.* 47 (2002) 4467.
- 43. H.N.T. Le, B. Garcia, C. Deslouis, Appl. Electrochem. 32 (2002) 105.
- 44. J. Petitjean, S. Aeiyach, J.C. Lacroix, P.C. Lacaze, *Electroanal. Chem.* 478 (1999) 92
- 45. O. Mermer, G. Veeraraghavan, T.L. Francis, Y. Sheng, D.T. Nguyen, M. Wohlgenannt, A. Kohler, M.K. Al-Suti, M.S. Khan, *Phys. Rev.* B 72 (20) (2005).
- 46. C.D. Dimitrakopoulos, Adv. Mater. 14 (2) (2002) 99.
- 47. D.J. Gundlach, Y.Y. Lin, T.N. Jackson, IEEE Electron. Dev. Lett. 18 (3) (1997) 87.
- 48. M. Shtein, J. Mapel, J.B. Benziger, S.R. Forrest, Appl. Phys. Lett. 81 (2) (2002) 268.
- 49. K.A. Noh, D.W. Kim, C.S. Jin, K.H. Shin, J.H. Kim, J.M. Ko, Power Sources. 124 (2003) 593.
- 50. H.Y. Mi, X.G. Zhang, X.G. Ye, S.D. Yang, Power Sources. 176 (2008) 403.
- 51. S.J. Hawkins, N.M. Ratcliffe, Mater. Chem. 10 (2000) 2057.
- 52. D. Kincal, A. Kumar, A. Child, J. Reynolds, Synth. Met. 92 (1998)53.
- 53. H. SeungLee, J. Hong, Synth. Met. 113 (2000) 115.
- 54. J. Wu, D. Zhou, C.O. Too, G.G. Wallace, Synth. Met. 155 (2005) 698.
- 55. K. Wha, H. Jin, S. Hun, Appl. Polym. Sci. 88 (2003)1225.
- 56. N.V. Bhat, D.T. Seshadri, M.N. Nate, A.V. Gore, Appl. Polym. Sci. 102 (2006) 4690.
- 57. E. Hakansson, A. Kaynak, T. Lin, S. Nahavandi, T. Jones, E. Hu, Synth. Met. 144 (2004) 21.
- 58. T. Lin, L. Wang, X. Wang, A. Kaynak, Thin Solid Films. 479 (2005) 77.
- 59. F. Ferrero, L. Napoli, C. Tonin, A. Varesano, Appl. Polym. Sci. 102 (2006)4121.
- 60. S.H. Hosseini, A. Pairovi, Iran Polym. 14 (2005)934.
- 61. L. Dall'Acqua, C. Tonin, A. Varesano, M. Canetti, W. Porzio, M. Catellani, *Synth. Met.* 156 (2006)379.

- 62. D. Beneventi, S. Alila, S. Boufi, D. Chaussy, P. Nortier, Cellulose. 13 (2006)725.
- 63. L. Dall'Acqua, C. Tonin, R. Peila, F. Ferrero, M. Catellani, Synth. Met. 146(2004)213.
- 64. E. Gasana, P. Westbroek, J. Hakuzimana, K. De Clerck, G. Priniotakis, P. Kiekens, D. Tseles, *Surf Coat Technol.* 201 (2006)3547.
- 65. P. Lekpittaya, N. Yanumet, B.P. Grady, E.A. O'Rear, Appl. Polym. Sci. 92 (2004) 2629.
- 66. H.H. Kuhn, A.D. Child, W.C. Kimbrell, Synth. Met. 71 (1995) 2339.
- 67. N. Balci, E. Bayramli, L.J. Toppare, Appl. Polym. Sci. 64 (1997) 667.
- 68. B. Scrosati, Application of Electroactive Polymers, first ed, Chapman & Hall, London, 1993, p. 33 (Chapter 2).
- 69. R. Erlandsson, O. Inganas, I. Lundstron, W.R. Salaneck, Synth. Met. 10 (1985) 303.
- 70. A.F. Diaz, K.K. Kanazawa, G.P. Gordini, Chem. Soc. Commun. 13 (1979) 635.
- 71. M. Nakayama, J. Yano, K. Nakaoka, K. Ogura, Synth. Met. 128 (2002) 57.
- 72. Y.C. Liu, J.M. Huang, C.E. Tsai, T. C. Chuang, C.C. Wang, Chem. Phys. Lett. 387 (2004) 155.
- 73. A. E. Taouil, F. Lallemand, L. Hallez, J-Y. Hihn, *Electrochim. Acta*. 55 (2010) 9137.
- 74. M. Bazzaoui, J.I. Martins, S.C. Costa, E.A. Bazzaoui, T.C. Reis, L. Martins, *Electrochim. Acta*. 51 (2006) 2417.
- 75. M.B. González, S.B. Saidman, Electrochem. Communs. 13 (2011) 513.
- 76. Z. Mekhalif, D. Cossement, L. Hevesi, J. Delhalle, Appl. Surf. Sci. 254 (2008) 4056.
- 77. Y.C. Liu, K. H. Yang, *Electrochim. Acta*. 51 (2006) 5376.
- 78. D.U. Kim, B. Yoo, Sensors. Actuators. B 160 (2011) 1168.
- 79. D. Kowalski, M. Ueda, T. Ohtsuka, Corr. Sci. 50 (2008) 286.
- 80. P. Herrasti\*, L. D'1az, P. Ocón, A. Ibáñez, E. Fatas, Electrochim. Acta. 49 (2004) 3693.
- 81. T. Kobayashi, H. Yoneyama, H. Tamura, Electroanal. Chem. 161(1984) 419.
- 82. J. Petitjean, J. Tanguy, J.C. Lacroix, K.I. Chane-Ching, S. Aeiyach, M. Delamar, P.C. Lacaze, *Electroanal. Chem.* 581 (2005) 111.
- 83. M. Deepa, Shahzada Ahmad, Eur. Polym. 44 (2008) 3288.
- 84. M. Bazzaoui, E.A. Bazzaoui, L. Martins, J.I. Martins, Synth. Met. 128 (2002) 103.
- 85. M. Sharifirad, A. Omrani, A.A. Rostami, M. Khoshroo, Electroanal. Chem. 645 (2010) 149.
- 86. S. Geetha, D.C. Trivedi , Mater. Chem. Phys. 88 (2004) 88.
- 87. P. A. Mabrouk, Synth. Met. 150 (2005) 101.
- 88. B. L. Funt, A. F. Diaz, Organic Electrochemistry: an Introduction and a Guide, Marcel Dekker, New York, (1991), 1337.
- 89. E. M. Genies, G. Bidan and A. F. Diaz, Electroanal. Chem. 149 (1983) 101.
- 90. R. J. Waltman, J. Bargon, Can. Chem. 64 (1985) 76.
- 91. R. J. Waltman, J. Bargon, Tetrahedron. 40 (1984) 3963.
- 92. W. Su, J.O. Iroh, Synth. Met. 95 (1998) 159.
- 93. S. Asavapiriyanont, G.K. Chandler, G.A. Gunawardena and D. Pletcher, *Electroanal. Chem.* 177 (1984) 229.
- 94. R.K. Sharma, A.C. Rastogi, S.B. Desu, Electrochem. Commun. 10 (2008) 268.
- 95. M.S. Kiani, N.V. Bhat, F.J. Davis, G.R. Mitchell, Polymer. 33 (1992) 4113.
- 96. S. Y. Cui, S. M. Park, Synth. Met. 105 (1999) 91.
- 97. E. Beelen, J. Riga and J. J. Verbist, Synth. Met. 41 (1991) 449.
- 98. A. Kassim, F. J. Davis and G. R. Mitchell, Synth. Met. 62 (1994) 41.
- 99. L. F. Warren, D. P. Anderson, *Electrochem. Soc.* 134 (1987) 101.
- 100.Y. Li and J. Yang, Appl. Polym. Sci. 65 (1997) 2739.
- 101.J. Unsworth, P. C. Innis, B. A. Lunn, Z. Jin and G. P. Norton, Synth. Met. 53(1992) 59.
- 102.T. F. Otero, J. Rodriguez, Electrochim. Acta. 39 (1994) 245.
- 103.H. Karami, M. Alipour, *Electrochem. Sci.* 4 (2009) 1511.
- 104.H. Karami, B. Kafi and S.N. Mortazavi, Int. Electrochem. Sci. 4 (2009) 414.
- 105.H. Karami, A. Kaboli, int. Electrochem. Sci. 5 (2010) 706.

- 106.H. Karami, E. Mohammadzadeh, Electrochem. Sci. 5 (2010) 1032.
- 107.H. Karami, O. Rostami-Ostadkalayeh, Clust. Sci. 20 (2009) 587.
- 108.H. Karami, S. Mohammadi, Clust. Sci. 21 (2010) 739.
- 109.H. Karami, M. Ghale Asadi, M. Mansoori, Electrochim. Acta. 61 (2012) 154.
- 110.J. Rodriguez, H. J. Grande and T. F. Otero, in Handbook of Organic Conductive Molecules and Polymers, ed. H. S. Nalwa, John Wiley & Sons, New York, (1997) 415.
- 111.T. F. Otero, J. Rodriguez, E. Angulo and C. Santamaria, Synth. Met. 43(1991) 2831.
- 112.M. Satoh, K. Kaneto and K. Yoshino, Synth. Met. 14(1986) 289.
- 113.M. Ogasawara, K. Funahashi, T. Demura, T. Hagiwara and K. Iwata, Synth. Met. 14(1986) 61.
- 114.S.U. Rahman, M.S. Ba-Shammakh, Synth. Met. 140 (2004) 207.

© 2013 by ESG (www.electrochemsci.org)