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Authors: Abdulcabbar Yavuz, Sıtkı Aktaş, Salih Durdu

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Polypyrrole Modified Graphite Electrode for Supercapacitor Applications: The Effect of Cycling Electrolytes

Abdulcabbar Yavuz¹, Sıtkı Aktaş^{*2}, Salih Durdu³

Abstract

Graphite electrode was modified by polypyrrole (PPy) thin film. PPy was electrodeposited potentiostatically by applying -1.5 V from acidic aqueous solution having pyrrole monomers. The waiting time of deposition solution effect the surface coverage of resulted films. PPy modified electrodes fabricated by old solution have lower surface coverage than PPy obtained from freshly prepared solution. PPy films were transferred to aqueous (acidic, neutral, alkaline) and a non-aqueous (Deep Eutectic Solvent) solutions for cycling. Capacitance performance of PPy film in a choline chloride based ionic liquid (Ethaline) was compared with that of PPy films in aqueous solutions. As PPy film in salt solution (LiClO₄ and NaCl) was evolved because deposition electrolyte was different (H₂SO₄) than deposition electrolyte and salt ions are exchanged at the beginning of cycling. Film obtained in acidic media was transferred into alkaline solution or ionic liquid is electroinactive. PPy film is strongly electroactive in an acidic media for hundreds of cycles as acidic media can cause the highest charge which is directly related to capacitive performance. Upon increasing pH value of cycling electrolyte, current and charge value decreases. PPy film in a salt solution (NaCl or LiClO₄ in water) and acidic solution (H₂SO₄) is electroactive and can be used for supercapacitor application. As PPy film in ionic liquids and alkaline solution cannot be electroactive, they cannot be used for supercapacitor applications. Capacity retention of PPy in KOH and Ethaline is low (around 5%). However, PPy thin film in H₂SO₄ has 77% of capacitance retention after 500 scans.

Keywords: Electrodeposition, Polypyrrole, Graphite, Ionic Liquid, Supercapacitor

¹ Gaziantep University, Department of Metallurgical and Materials Eng., Gaziantep, Turkey. ORCID: <https://orcid.org/0000-0002-7216-0586>

* Corresponding Author: sitki.aktas@giresun.edu.tr

² Giresun University, Department of Mechanical Eng., Giresun, Turkey. ORCID: <https://orcid.org/0000-0002-9143-6752>

³ Giresun University, Department of Industrial Engineering, Giresun, Turkey. ORCID: <https://orcid.org/0000-0002-6288-0926>

1. INTRODUCTION

As fossil fuels can be consumed and cause environmental problems; sustainable, clean and highly efficient energy are researched in detail [1]. The storage of the sustainable energy required to be achieved is an important issue. Energy storage devices such as lead-acid batteries, nickel-metal hydride batteries, lithium-ion batteries and supercapacitors are used to meet high energy demands [2]. Supercapacitors are used in energy storage devices due to their high power densities (typically 20 kW kg^{-1}), long cycle life ($> 10,000$ cycles) and fast charge / discharge (within seconds) [3]. As high performance energy storage devices, both with high energy density and high power density, are required for energy storage devices, supercapacitors are suitable for these purposes and have recently been used in hybrid vehicles [4]. Depending on the energy storage mechanism, supercapacitors are grouped into two main types: electrical double layer capacitors (EDLC) and pseudo capacitors. EDLCs include non-faradaic processes where the charged particles adsorb at the electrode/electrolyte interface. EDLC consists of porous, conductive materials, such as activated carbons, which have a high surface area that allows for greater electrolyte accessibility and thus greater energy storage [5]. Various carbon based materials such as graphite, black carbon, carbon nanotubes which are main materials of technological applications are used as EDLC [6–8]. Pseudo capacitors have reversible Faradaic reactions where charge is obtained by redox reaction between electrochemically active materials and electrolyte [9]. Pseudo capacitors could be made of metal oxides/hydroxides or conductive polymers. Conducting polymers including mainly polyaniline, polypyrrole, polythiophene and their derivatives are used in supercapacitor applications [10]. Capacitors consisting of two or more electrode materials are called asymmetric supercapacitors or hybrid supercapacitors.

The optical, electrochemical or mechanical properties of polymer electrodes can be altered by the interposition of ions between polymers as the conducting polymers are cycled in the electrolytes [11]. Depending on these mechanisms, conductive polymers could be used in the applications of sensors, organic light emitting diodes, electrochromic devices, organic solar cells, thin film transistors and electromagnetic devices [12]. In this study, polypyrrole, which is one of the main conductive polymers, is used for energy

storage devices. Polypyrrole has low cost, high capacitance, good environmental stability and good mechanical properties [13].

Generally, pyrrole monomer is chemically or electrochemically oxidized (polymerized) in various electrolytes to synthesize polypyrrole [14]. When polypyrrole is chemically produced, oxidants such as ammonium peroxydisulfate, iron chloride or iron perchlorate are used [15]. The chemically obtained polypyrrole depends on the conditions and the chemistry of the reaction mixture formed [16]. Various additives (such as carbon nanotubes) can be added to the electrolyte to form a polypyrrole-based composite [17]. The most practical method for obtaining polypyrrole is the electrochemical oxidation because its application is easy and the polypyrrole base properties (film morphology, thickness and electrical properties) can be tailored by the deposition conditions (by changing the electrolyte conditions and the applied potential) [18]. In the electrochemical polypyrrole growth method, a conductive substrate such as metal is used and PPy film is formed from an electrolyte [19]. During electrodeposition of thin PPy film, electrolyte (pH, temperature) and applied current (time, type) cause the optical, structural and electrical properties of the polymers to change [14]. It is possible to obtain polypyrrole having the desired properties by controlling the deposition conditions [20]. The effect of waiting time of deposition electrolyte and the effect of cycling composition are the objective of this work.

In this study, the effect of deposition bath left for different timescale from freshly prepared 36 hours for polypyrrole growth is analyzed. The effect of cycling electrolyte is also analyzed. The effect of various electrolyte and pH on the specific capacitance will be examined in this research.

2. EXPERIMENTAL DETAILS

Pyrrole (Merck, 99%) and all other reagents were used as bought from commercial sources. $0.5 \text{ M H}_2\text{SO}_4$ (Merck 95-97%), was used as the supporting agent in all pyrrole polymerizations. Purified water ($< 2 \text{ mS cm}^{-1}$) was used in the preparation of solutions and washing of the obtained polypyrrole electrodes. Polypyrrole electrodes were electrodeposited on graphite substrate potentiostatically from 0.3 M pyrrole and $0.5 \text{ M H}_2\text{SO}_4$ solution. Choline chloride (ChCl) was mixed with ethylene glycerol at a 1:2 mol ratio of ChCl to ethylene glycerol. The mixture called Ethaline was stirred at

50 °C until a homogenous and transparent liquid was formed.

All electrochemical tests were carried out using Ametek VERSASTAT 3-200 potentiostat connected to a computer. In the three electrode system, a platinum

flag was used as the counter electrode, Ag / AgCl as the reference electrode and graphite (0.5 cm diameter) as the working electrode (see Figure 1). All experiments were performed under room conditions (20 ± 2 °C).

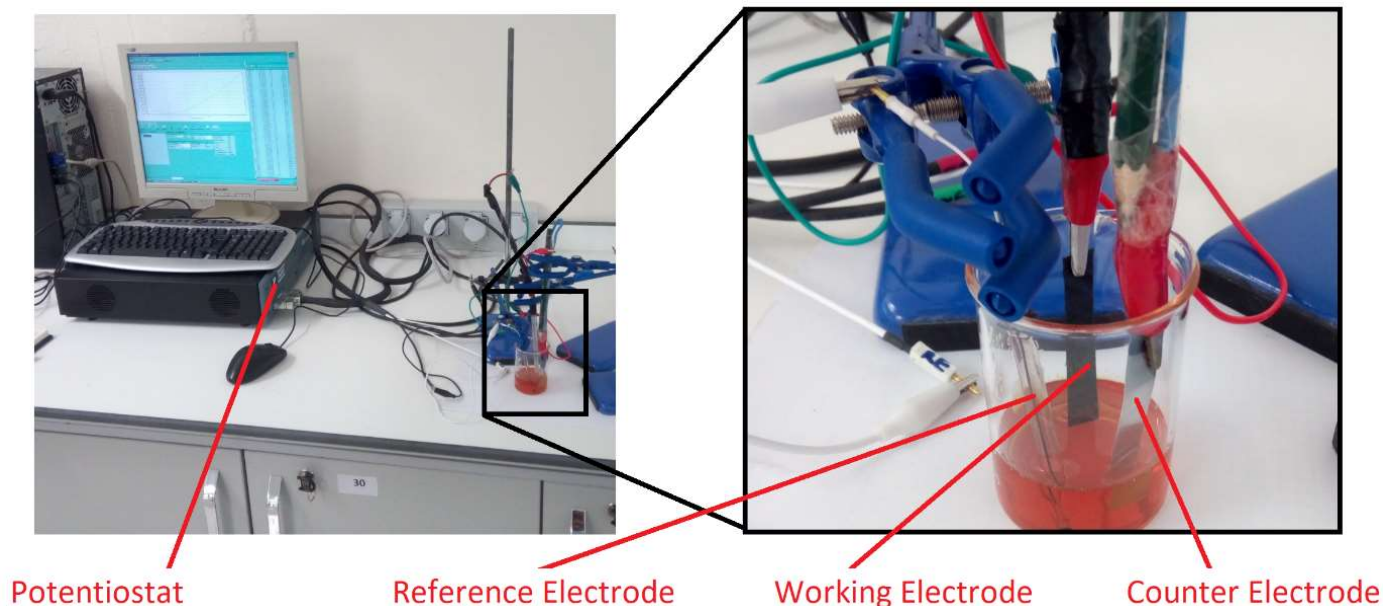


Figure 1: Experimental set-up of deposition of PPy on graphite. Platinum flag counter electrode, graphite working electrode and Ag/AgCl reference electrode were connected to a potentiostat.

3. RESULTS AND DISCUSSION

3.1. The Effect of Deposition Electrolyte

The chronoamperometric and chronocholometric responses of the polymerization of pyrrole in H_2SO_4 are shown in Figure 2a and 2b, respectively. Figure 2c illustrates waiting effect of deposition media. Beakers

shown in Figure 2c include 0.1 M Py and 1 M H_2SO_4 and these solutions are getting brown by time. The leftmost beaker is a fresh solution whose photo was taken immediately after preparation of it. The second beaker is the solution left for 6 hours. The photo of the third one which is yellowish was taken after 12 hours waiting. The other solutions in the beakers from left to right (yellow, darker yellow, orange and brown) were at room conditions for 18, 24, 30 hours and 36 hours, respectively.

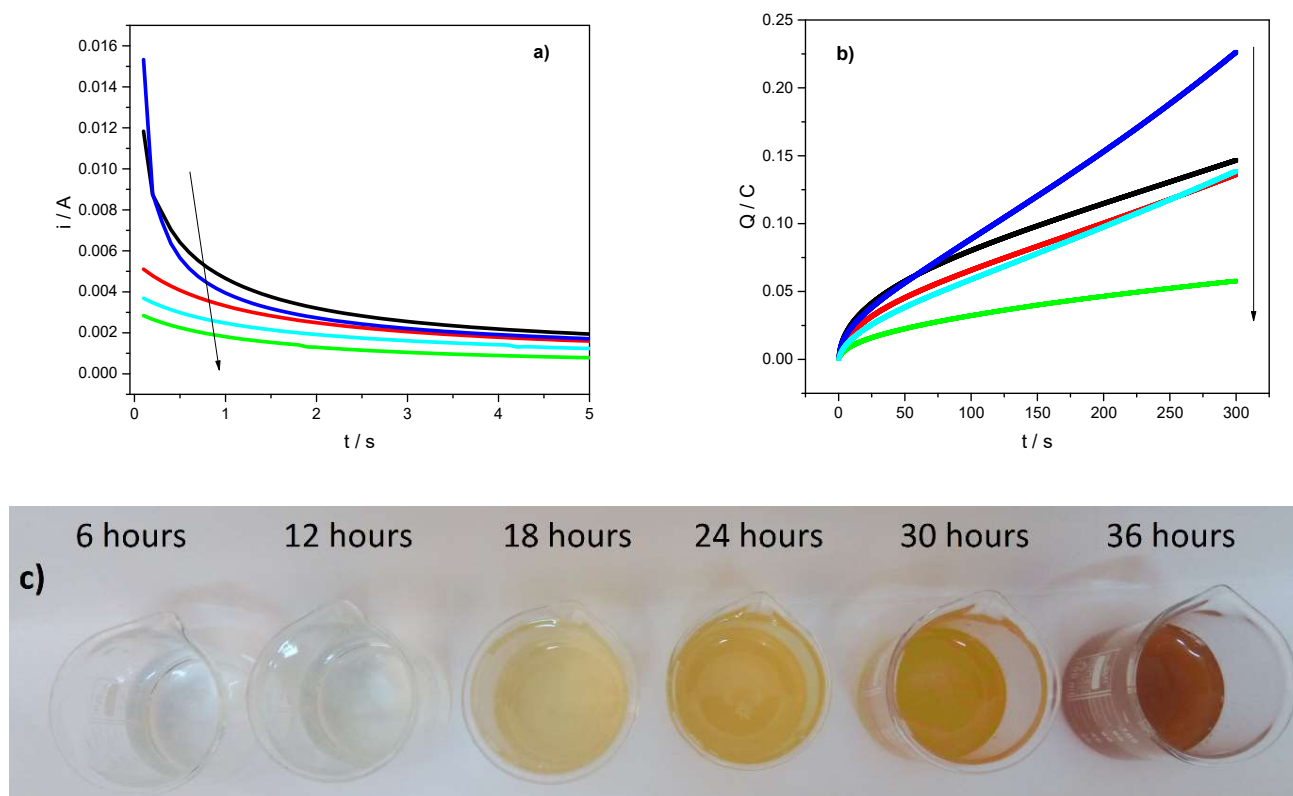


Figure 2: Potentiostatic response curves of the polymerization of PPy on graphite substrate with deposition bath left at room conditions for different time by applying 1.5 Volt. a) chronoamperometric response of first 5 seconds; b) chronochrometric responses of the film growth. c) the change of deposition electrolyte after. Arrows indicate how chronoamperometric and chronochrometric responses change when deposition electrolyte is wait.

While the deposition solution is left at room conditions, the films obtain from these solutions could be changed and have different thickness. Figure 2a shows current-time graph of PPy obtained from the deposition solutions left for different times. Blue lines in Figure 2a and 2b illustrate the potentiostatic response of a fresh deposition electrolyte prepared freshly just before PPy growth. Starting current point of fresh solution starts from the highest current value (15.3 mA) by compared with old solutions. When the deposition baths was left for 6 hours, current starting point decreases to 11.8 mA. Therefore, total charge for deposition is also decreased when old solution is used from 0.23 C to 0.15 C. Green line shows the current-time graph for the electrolyte left for 36 hours which has the lowest current starting point (2.8 mA) and also the lowest charge (0.05 C). It means the film obtained from old solution tends to be thinner and have lower surface coverage. The electrolyte preparation and storing conditions are crucial for a probable electrode for supercapacitor applications. As the film obtained from freshly prepared solution has

higher surface coverage, its current density is higher than the film deposited from old electrolyte (see Figure 3).

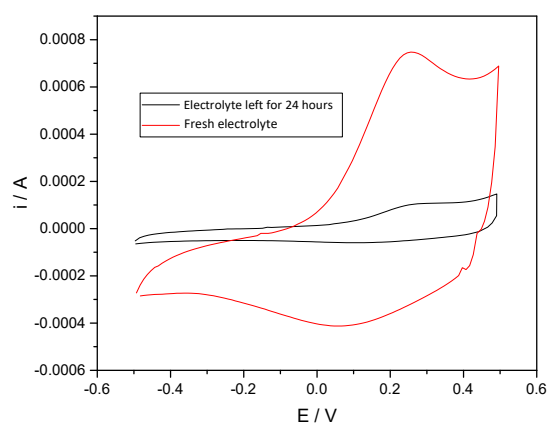


Figure 3: Cyclic voltammograms of PPy electrodes in monomer free (1 M H_2SO_4) solution at 50 mV s^{-1} . Red line: film obtained from fresh solution. Black line: film obtained from one day old solution by applying 1.5 V for 300 seconds.

After PPy films were obtained, they were transferred into different electrolytes to measure their capacitance performances.

3.2. The Effect of Cycling Electrolyte

PPy films electrodeposited on graphite surface by applying 1.5 V for 300 seconds were washed by deionized water and then transferred into different media to characterize their electrochemical behavior presented in Figure 4. Aqueous acidic, aqueous neutral, aqueous alkaline and non-aqueous ionic liquid solutions were used as cycling electrolyte. All films

were prepared with the same conditions in order to avoid growth conditions effect as growth conditions could effect electrochemical performance including specific capacitance, stability, energy density and power density [21,22]. Typical cyclic voltammogram of PPy films in neutral aqueous electrolyte (0.5 M LiClO₄) is shown in Figure 4a. It can be observed that after several scans cyclic voltammogram can be constant because electrolyte can enter into the electroactive material. As PPy film was grown in acidic media, it requires some cyclic for stabilization of the electrodes' electroactivity [23].

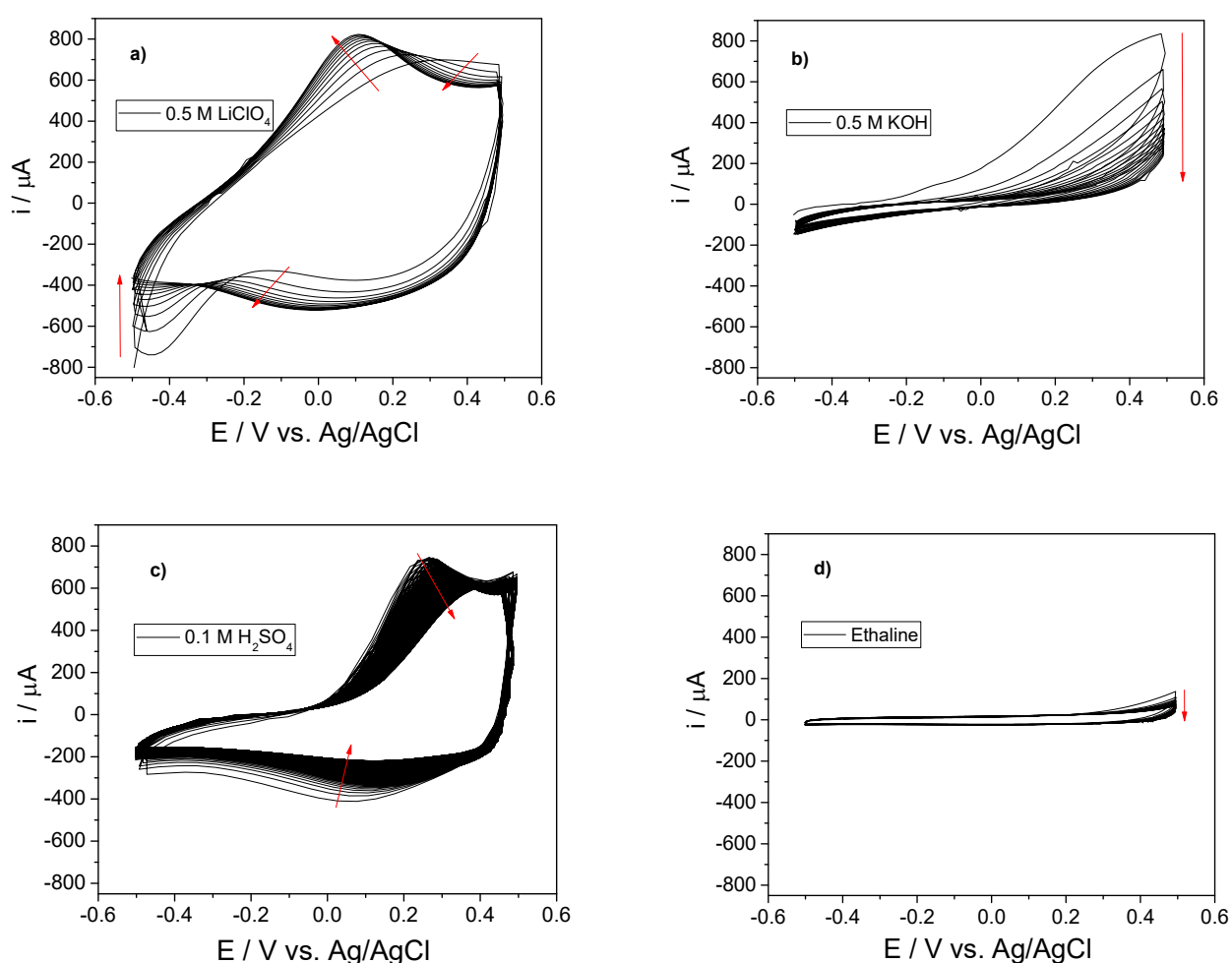


Figure 4: Cyclic voltammograms of PPy electrodes in a) 0.5 M LiClO₄; b) 0.5 M KOH; c) 0.1 M H₂SO₄; d) Ethaline ionic liquid. Red arrows indicate film evolution upon increasing cycle numbers

Film electrodeposited in acidic pyrrole media was transferred into alkaline solution (0.5 M KOH) in order to observe whether there is the evolution of the film which could be indicated by means of a cyclic voltammetry in alkaline electrolyte because the film evolution performance is directly related to charge

storage capacity. Figure 4b presented that there is an oxidation peak for the first scan but reduction peak does not appear as the electroactivity of the film decrease in alkaline media. After each cycles, current values decrease and film loses its electroactivity significantly. However PPy film is electroactive in

acidic media (0.5 M H₂SO₄) illustrated in Figure 4c and this electroactivity is stable after even hundreds of cycles. PPy film evolves in acidic media as shown by an arrow in Figure 4a. Current peak of PPy film in LiClO₄ and H₂SO₄ is at 0.11 V and 0.25 V, respectively. This difference is due to the interaction of PPy modified electrode with different electrolytes [24].

Film deposited in aqueous acidic media was transferred to a deep eutectic solvent (Ethaline) to characterize the film behavior in an ionic liquid. Ethaline consist on only ions of choline chloride and ethylene glycol. As Ethaline does not have water, PPy film was washed by deionized water and Ethaline before transferring into Ethaline solution. Figure 4d illustrates the cyclic voltammogram of PPy electrode in Ethaline and the film in Ethaline evolves similar to the film in LiClO₄. First cycles of all PPy films in various electrolytes are demonstrated in Figure 5. This figure clearly show that acidic media (H₂SO₄) can cause highest current peak and also highest charge which is directly related to capacitance (calculated below). The current curve of PPy film in KOH is very small by comparison with that in H₂SO₄. The current value of PPy film in a salt (either NaCl or LiClO₄) is less than that of PPy film in H₂SO₄ but more than that of PPy film in KOH. This graph shows that when pH value of cycling electrolyte increases, current value and charge value (area of current-time graph) decreases. PPy film in a salt solution (NaCl or LiClO₄ in water) is electroactive and can be used for supercapacitor. However, PPy film in ionic liquids which has salts but does not have water cannot be electroactive strongly as can be observed by comparison of green lines (belonging to LiClO₄ and NaCl) with black line (belonging to Ethaline) in Figure 5. Among them the cyclic voltammogram of PPy film in NaCl electrolyte is given in Figure 6.

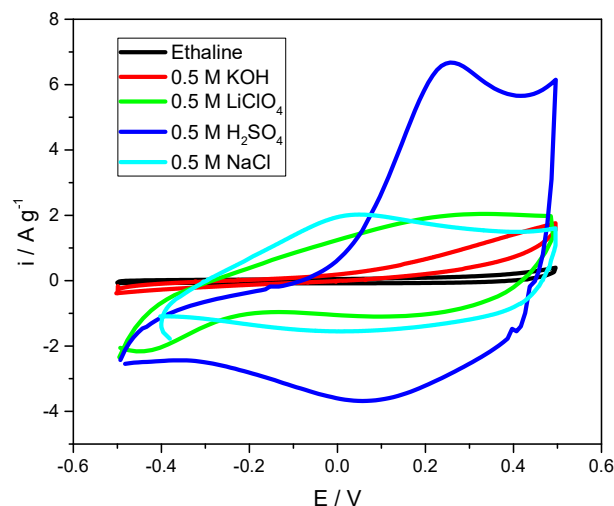


Figure 5: cyclic voltammograms of PPy in various electrolytes.

The specific capacitance was calculated from cyclic voltammetric curves by the Equation 1

$$C_s = \frac{i_a dt}{dV/dt}$$

where i_a is the area under the curve given in the cyclic voltammetry already divided by active mass of the material and dV/dt is the scan rate. Specific capacitance of the films given in Figure 3 is 39.0 F/g and 12 F/g for the film deposited from a fresh electrolyte and the film deposited from an old electrolyte (left for one day), respectively due to structural differences of growth.

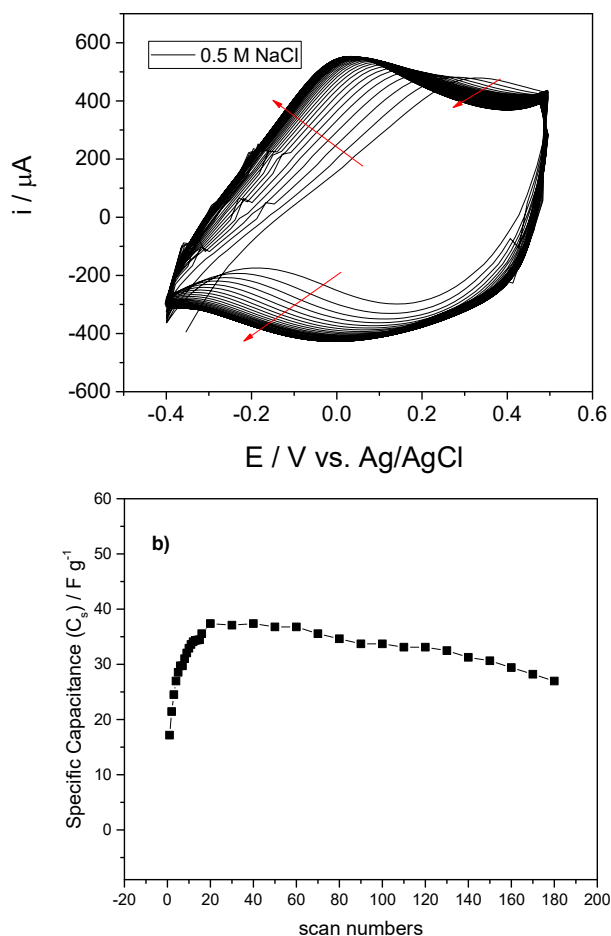


Figure 6: Specific capacitance retention specific capacitance of the PPY film in NaCl solution was calculated from cyclic voltammetric curves.

When the film was immersed in LiClO_4 electrolyte, it need to have several cycle to evolve and the specific capacitance values depending on cycle numbers are shown in Table 1. For first scan it has 31 F g^{-1} . The it inceases to 38 at 10 th scan as film evolves. The same trend is observed for PPy film in a different salt solution (0.5 M NaCl). As electroactivity of KOH is lost, specific capacitance of film in alkaline media (KOH) decreases. Specific capacitance of film in KOH is tabulated in Table 1. While capacitance of PPy film in KOH was 15 F g^{-1} for the first cycle, its capacitance decreases to 2.4 F g^{-1} after 10 cycles. Capacitance value of PPy in acidic media ($0.5 \text{ M H}_2\text{SO}_4$) was higher than others and the change of capacitance was not significant as it was 39 F g^{-1} for the first scan and 38 for the tenth scan because PPy film was obtained and cycled in the same acidic electrolyte. Film evolution was not significant. The only difference is that there was pyrrole monomers in deposition electrolyte for PPy growth. As PPy film was electrodeposited in acidic

media ($0.5 \text{ M H}_2\text{SO}_4$) and transferred to the same acid (momomer free acidic solution), film can evolve quickly (typically few scans). When PPy film electrodeposited in acidic media was immersed in Ethaline solution, the specific capacitance of this electrode-electrolyte is very low (around 1.5 F g^{-1}) compared with PPy film in acidic or neutral aqueous electrolyte

Table 1: Specific capacitance values of PPy films depending on scan numbers in various electrolyte.

Scan Numbers	Specific Capacitance (F g^{-1})				
	LiClO_4	NaCl	KOH	H_2SO_4	Ethaline
1	31	17	15	39	1.9
2	35	21	8.7	39	1.7
3	36	25	6.1	39	1.6
4	37	27	5.1	38	1.6
5	37	29	4.2	38	1.5
6	38	30	3.7	38	1.5
7	38	31	3.4	38	1.5
8	38	31	2.9	38	1.5
9	38	32	2.6	38	1.4
10	38	32	2.4	38	1.4

Cyclic stability is an important parameter to compare the performance of electrochemical supercapacitor. Cyclic stability of PPy in different electrolyte was tested by repeating cycling between selected potential window at a scan rate of 50 mV s^{-1} . Capacity loss of PPy in KOH, Ethaline were not continued for hundreds of scans as they are not electroactive after several scan illustrated in Figure 7a. This figure cleary provesthe capacitance decreases of PPy film in KOH and Ethaline (shown by red and black lines, respceviely in Figure 7a). PPy thin film in H_2SO_4 is the most stable by compare to the other electrolyte presented in blue line of Figure 7. Capacitance retation of PPy in H_2SO_4 after 500 scans is 77% (from 39 F g^{-1} to 30 F g^{-1}). PPy modified electrode in NaCl has a different behaviour: firstly its capacitance increases from 17 F g^{-1} to a the specific capacitance of 22 F g^{-1} due

to film evolution. Capacitance retention of PPy in NaCl (by compare with maximum capacitance) increases after 200 scans because film was deposited in acidic media and transferred to neutral electrolyte. However, after around 70 cycles specific capacitance tend to decrease (see cyan line in Figure 7b).

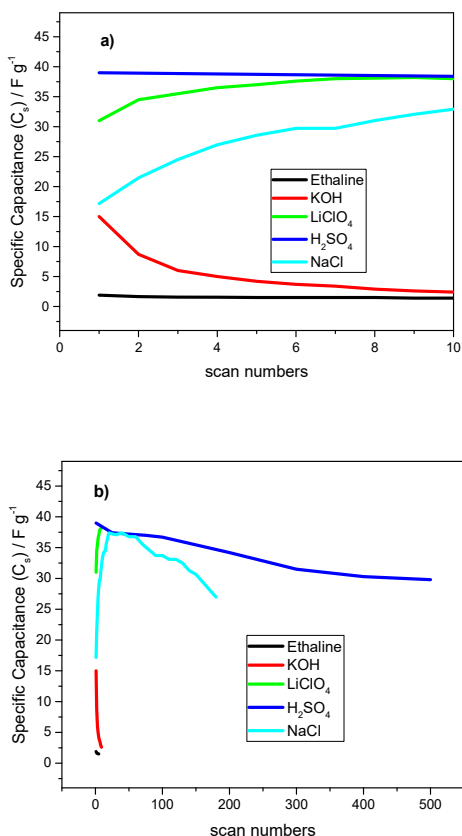


Figure 7: Specific capacitance values of PPy film cycled in different electrolytes a) for first ten scans; b) for further scans.

4. CONCLUSION

The preparation of the deposition electrolyte for an electrode which could be used in a supercapacitor application is crucial and hence the effect of pyrrole electrolyte for PPy films were left at room conditions before deposition of PPy. The thin films of PPy was electrodeposited potentiostatically on the graphite substrates by applying -1.5 V from acidic aqueous solution of 0.5 M H_2SO_4 having 0.1 M pyrrole. The more deposition solution left at room conditions, the thinner films obtained. Starting current point of fresh solution has the highest current value and the starting current value decreases upon leaving deposition

solution at room conditions. Therefore, the films obtained from old solution have lower surface coverage.

Aqueous (acidic, neutral, alkaline) and non-aqueous (ionic liquid) solutions were used as cycling electrolyte of PPy modified graphite. All films in various electrolyte were prepared potentiostatically. After several scans, cyclic voltammogram of PPy film in salt solution ($LiClO_4$ and NaCl) was constant because a new electrolyte enters into the electroactive PPy material. PPy film grown in acidic media requires less scans for stabilization of the cyclic voltammogram. Film obtained in acidic media was transferred into alkaline solution has an oxidation peak for the first scan but reduction peak of that film does not appear because the PPy film in alkaline bath is electroactive. PPy film is strongly electroactive in an acidic media (0.5 M H_2SO_4) for hundreds of cycles. When PPy film was deposited in aqueous acidic media and transferred to a deep eutectic solvent (Ethaline), the film in Ethaline has not electroactivity. Acidic media (H_2SO_4) can cause the highest current peak and also has the highest charge which is directly related to capacitive performance. The current curve of PPy film in KOH is very small by comparison with that in H_2SO_4 . The current value of PPy film in a salt (either NaCl or $LiClO_4$) is less than that of PPy film in H_2SO_4 but more than that of PPy film in KOH. Upon increasing pH value of cycling electrolyte, current and charge value decreases. PPy film in a salt solution (NaCl or $LiClO_4$ in water) and acidic solution (H_2SO_4) is electroactive and can be used for supercapacitor application. On the other hand, PPy film in ionic liquids and alkaline solution cannot be electroactive. Capacity loss of PPy in KOH, Ethaline were not continued for hundreds of scans as they are not electroactive after several scan. PPy thin film in H_2SO_4 is the most stable by compare to the other electrolyte. Capacitance retention of PPy in H_2SO_4 after 500 scans is 77%. PPy modified electrode in NaCl has a different behavior: firstly its capacitance increases due to film evolution. However, after around 70 cycles specific capacitance decreases.

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