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Comparative Electrochemical Behavior of Poly (3-Aminobenzoic Acid) Films in Conventional and Non-Conventional Solvents

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Abstract. In this work we report the created films of poly derivatives of aniline by using electropolymerization on platinum (Pt) electrode surface in non-aqueous electrolyte (Ethaline). The electropolymerization process of poly (3-amino benzoic acid) was happened in two electrolytes H₂SO₄ and HClO₄ using a chronoamperometry (constant potential) technique for different times (50s, 100s, and 200s). All synthesized conducting polymer films were characterized by using FT-IR. Scanning electron microscopy (SEM) has been applied to study the morphologies of polymer samples. The electrochemical behaviour of prepared conducting films have studied by cyclic voltammetry. The overall findings shown that use a different electrolyte has led to the produce of various polymeric surface films as shown by scanning electron microscopy (SEM). Moreover, the charge consumed during the electropolymerization was calculated with time.

Keywords: Conducting polymer, Electropolymerization, Chronoamperometry, Cyclic voltammetry, Deep eutectic solvents.

INTRODUCTION

Electroactive films have been broadly used in several areas of electro-chemistry due to their attractive physiochemical features [1-3]. Studies have elucidated that conducting films such as polyaniline [4], polypyrrole [5,6], polythiophene [7] poly(3,4-ethylenedioxythiophene) (PEDOT) [8], and their derivatives [9-11] have interesting properties and potential applications in many technological fields where have attracted great research attention [2,6,12]. Electro-synthesis of conducting materials have many benefits such as ability to synthesis without use oxidizing agent and used various organic and inorganic ions also can control conditions of polymerization [5,13]. Chemical, mechanical, electronic and optical features which present in these materials have made to have potential applications in electrochromic devices [14,15], chemical sensors [16,17], corrosion inhibitors [18] and supercapacitors [19]. Derivatives of polyaniline may be synthesized using various means like chemical [20] and electro-chemical [21] methods and the second way can be considered more suitable and effective to prepare thin films and control on conditions of polymerization processes as well to examine the modified electrode [22].

Over the past twenty years, ionic liquids have attracted interest of scientific community in different fields. Green technological systems dynamically seek to employ eco-friendly influential solvents to be replaced of ordinary solvents that have several drawback like toxicity, volatility and high cost [23-25]. Ionic liquids are considered a new type of solvent electrolyte which prepared by combination of range of cations and anions [26] to produce compounds have melting points often below room temperature [27]. Their unique physicochemical properties of ionic liquids like density, viscosity and solubility have enabled these solvents to have a vital potential applications [28], in various

branch of chemistry like organic , inorganic , analytical and materials where use as media in batteries , energy storage [27,28], sensors, corrosion and formation of conducting polymers [28,30]. Moreover, Deep eutectic solvents (DES) are considered one of promising class of ionic liquids, which also have similar ionic features but with more features like lower cost, un-toxic and biodegradable [31,32]. These DES can be commonly prepared using choline chloride (quaternary ammonium salt) with urea, glycerol, ethylene glycol and succinic acid or other materials [33]. The green merits of deep eutectic solvents (DES) has enabled them to be considerable electrolytes in improvement of sustainable technologies [34]. Further, the use of these solvents have intensifying in polymer industry to open novel fields of applications where various monomers have been fabrication by using DES such as polythiophene, polyaniline, and polypyrrole. Herein, the current work were to formation and examine the electro-chemical behaviour of poly(3-aminobenzoic acid) (ABA) films with different thickness and preparation times [35-37]. The electrochemical technique (potential step) was applied to creation the polymer film from its monomer on platinum substrates. Prepared polymer films were investigated by cyclic voltammetry, FT-IR and SEM technique.

EXPERIMENTAL

Chemicals and Materials

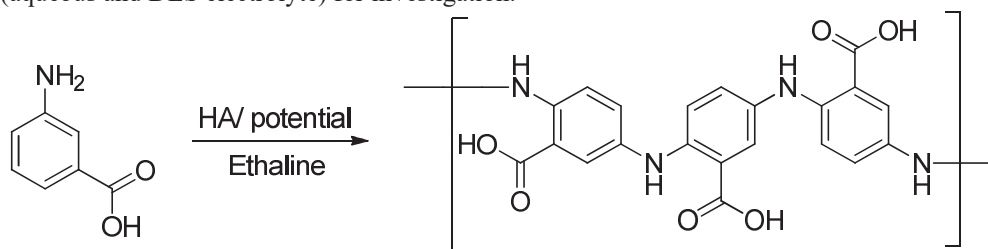
3-Amino benzoic acid monomer, choline chloride, ethylene glycol and perchloric acid (Sigma Aldrich 99%) was used as received. Sulphuric acid (Fisher Chemical, > 95%) was used as received. Ethaline electrolyte was synthesized by reacting ethylene glycol with choline chloride (ChCl) at 60 °C in 4: 1 ratio.

Instrumentation

Different techniques have been used in this paper, including cyclic voltammetry and chronoamperometry that were apply to study and examine the electropolymerization of polymer films and electrochemical behaviour of films in aqueous/ non-aqueous media. All experiments were happened in a standard cell containing three electrodes. The platinum electrode was used as the working electrode, the Pt sheet was used as the counter electrode and Ag/AgCl (or Ag wire) was used as the reference electrode (RE). Electrochemical studies were performed using an Autolab PGSTAT 20 potentiostat (Ecochemie, Holland). Analysis of morphology surface was accomplished using an FEI SIRION SEM. FT-IR spectra were recorded by using a Perkin Elmer Spotlight 400 FT-IR.

PROCEDURE

Monomers solution in DES media were synthesized from 3-amino benzoic acid (1 M) with H₂SO₄ (1.0 M) and HClO₄ (1.0 M). The electro-deposition of poly (ABA) films was accomplished potentiostatically with vary coverage polymer films due to different polymerization time.³⁸ The working electrode was disconnected, after electropolymerization processes was finalized and their rinsed with water and then transferred to monomer-free electrolyte (aqueous and DES electrolyte) for investigation.



SCHEME 1. General reaction schemes for electropolymerization of amino benzoic acid

RESULTS AND DISCUSSION

Electrodeposition of ABA from Ethaline Medium

Electropolymerization of 1 M solution of amino benzoic acid with 1M H₂SO₄ solution (in ethaline electrolyte) was achieved by means of potential step over diverse lengths of time (50, 100 and 200 seconds). The i-t curves are revealed in Fig 1 using a potential of 1.3 V. The same electrochemical method was used to electrodeposition of poly(ABA) from HClO₄ solution (in ethaline electrolyte) and use potential of 1.3 V as shown in Fig 2. It can be noted from these findings that chronoamperograms show a high current peak in the first seconds after voltage was applied; this was due to the charge double layer in polymer-solution interface. Then, the current was underwent of dropping due to the oxidation of ABA monomer and their convert to radical cations and their diffusion to electrodes. The next polymerization step shows an obvious current increase as result of coupling of radical cation and nucleation and growth of poly (ABA) on the electrode.²⁷ After this step, a gradual increase of current was noted due to deposition of polymer films.²⁶ Curve B exhibits that the electrodeposition charge increased with t^{1/2} due to diffusion control processes. The thickness of the ABA film (h/μm) was estimated from the electrical charge, Q, using equations 1 and 2 (n = 2). Tables 1 and 2 demonstrate the amount of charge and thickness of the ABA film at different times. The molar coverage of films per area can be calculated using Eq. 1

$$\Gamma = \frac{Q}{nFA} \dots\dots\dots (1)$$

where, F is the Faraday constant, Γ is the molar coverage, A is the electrode area and n is the number of electrons (2.3). The value of the molar coverage was useful to estimate the thickness of films from Eq. 2 when molar mass and density are known. Here, c is the density and concentration of the monomer units respectively, and M_r is the molecular weight. h is the thickness of polymer films.

$$h = \frac{\Gamma}{c} \dots\dots\dots (2)$$

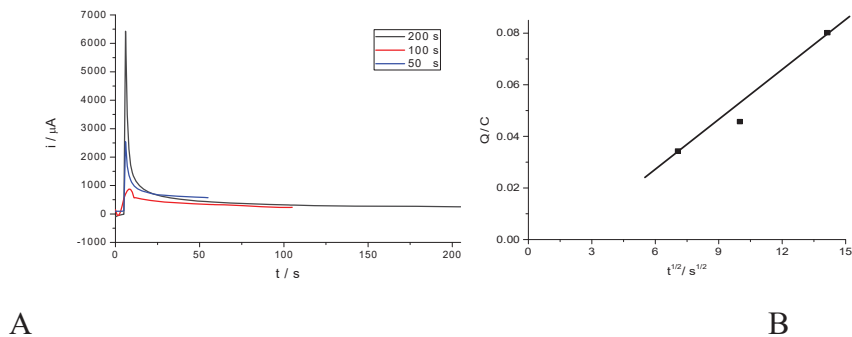


FIGURE 1. A. Current-time transients for potentiostatic electrodeposition of 1 M 3-amino benzoic acid in 1 M H₂SO₄/Ethaline solution at 1.3 V vs. an Ag wire over 50, 100 and 200 seconds. B. Plot of charge vs. square root of time.

TABLE 1. Electrical charge due to electropolymerisation of 1 M 3-amino benzoic acid films during 50, 100 and 200 seconds.

Monomer conc.(M)	Time / s	Charge Q / C	Thickness / cm
1	50	0.0345	2.05x 10 ⁻⁴
1	100	0.0461	2.83x 10 ⁻⁴
1	200	0.0795	4.92x 10 ⁻⁴

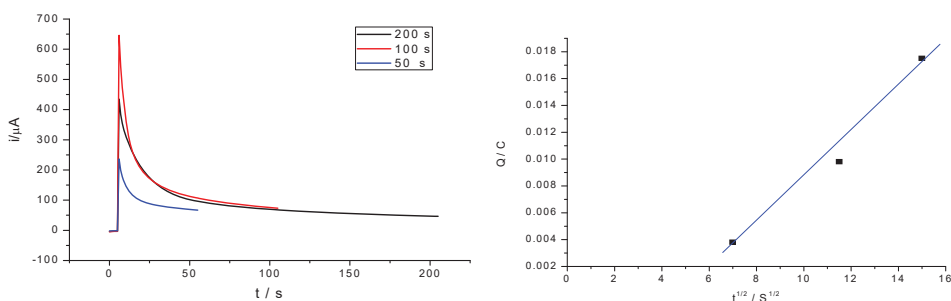


FIGURE 2. A. Current-time transients for potentiostatic electrodeposition of 1 M 3-amino benzoic acid in 1 M HClO₄/ Ethaline solution at 1.3 V vs. an Ag wire over 50, 100 and 200 seconds. B. Plot of charge vs. square root of time.

TABLE 2. Electrical charge due to electropolymerisation of 1M 3-amino benzoic acid films during 50, 100 and 200 seconds

Monomer conc.(M)	Time / s	Charge Q / C	Thickness / cm
1	50	0.0044	2.02×10^{-5}
1	100	0.0115	4.76×10^{-5}
1	200	0.0158	8.07×10^{-5}

Fourier Transformation Infrared Spectrum (FT-IR) Analysis

It is important to understand the poly(APA) chemical structures created from DES electrolyte. In this paper, FT-IR method was applied to determine the structures of two poly(APA) films. Fig. 3 indicate that FT-IR spectra of poly(APA) obtained from 1 M of H₂SO₄ and 1 M of HClO₄ in ethaline solutions. The broad peak at 3250–3080 cm⁻¹ is the distinctive peak of OH moieties which apparent for two poly(APA) samples. The C-H stretch of the aromatic system which located at the range 3050 cm⁻¹. The sharp peak located at 1745 cm⁻¹ was due to the ν(C=O) stretch of the CO₂H. Peak at 1565 cm⁻¹ which is indicative of quinoid rings in ABA structure, as will the peak at 1472 cm⁻¹ assigned to the C=C stretch of aromatic rings and the 1255 cm⁻¹ band corresponds to C–N stretching of its aromatic amine groups.³⁹

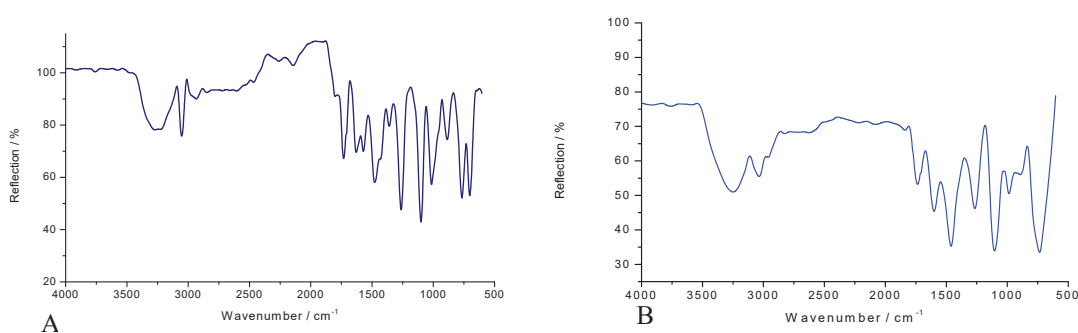


FIGURE 3. FT-IR spectra of poly 3-amino benzoic acid film in (A) 1 M H₂SO₄/ Ethaline solution and (B) 1 M HClO₄/ Ethaline solution.

Morphologies of Poly (ABA)

The morphologies of the poly(ABA) films which produced with two types of DES were examined using SEM technique. From Fig 4 and 5, it can be noted that use different DES solution led to affected the micro-structures of polymer lattice of poly(ABA) films samples. The homogenous and fibrous morphology was found for poly (ABA)/ H₂SO₄, as shown in Fig 4. However, the morphology of poly(ABA)/ HClO₄ as shown in Fig 5 indications a uniform structure with small fibrous regions and it seems these polymer films have a less porous surface compared to poly(ABA)/ H₂SO₄ samples. We suppose that variation in morphology of film surface and electrochemical behaviors are associated to the different media electrolytes performance resulting in produce of polymer films with vary structural characteristics. previous researchers have mention that are polymer films which prepared in H₂SO₄ electrolytes have conductivity more than other dopants which exactly as found in this paper; the conductivity of poly(ABA)/ H₂SO₄ is larger than that films of poly(ABA)/HClO₄, as shown in the next section.³

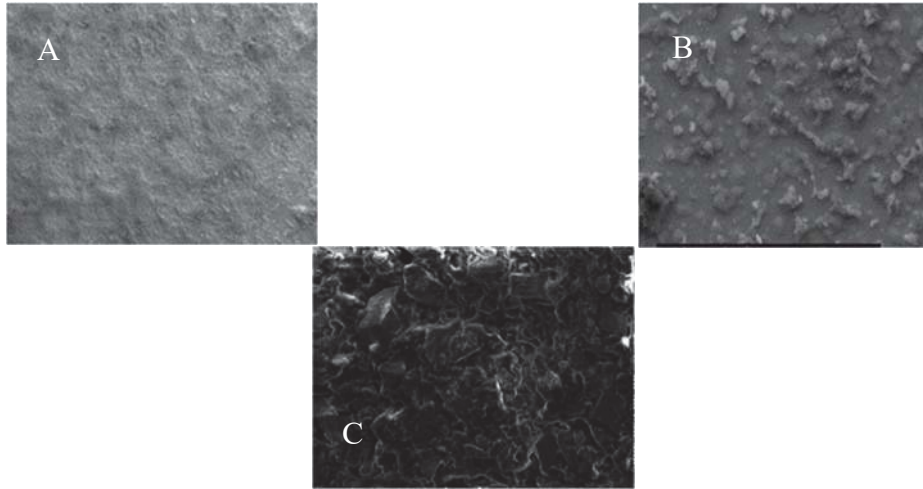


FIGURE 4. SEM images of surface polymers deposited via 1 M concentrations of poly(ABA)in solutions of Ethaline/ H₂SO₄ at A-50 s, B-100 s and C-200 s.

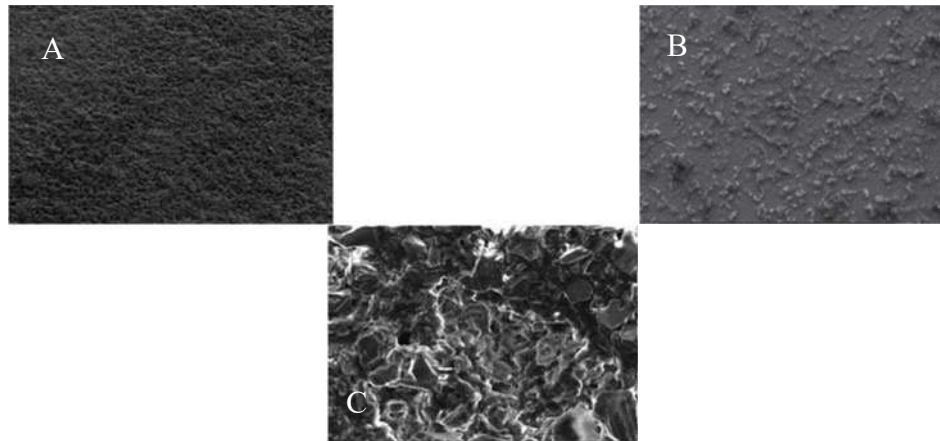


FIGURE 5. SEM images of surface polymers deposited via 1 M concentrations of poly(ABA)in solutions of Ethaline/ HClO₄ at A-50 s, B-100 s and C-200 s.

Electrochemical Study

In this section electrochemical characterization and behaviour of polymers in two monomer free electrolytes (in water and DES) with 1 M H₂SO₄ were examined. The idea here is to monitor any electro-chemical changes of polymer films. As we mentioned in previous sections that the polymer films have various thickness, thus we will obviously

expect affecting of their stabilities and electrochemical properties in the water and DES media. The potential windows of the CVs responses for these films were -0.2 V to 1.2 V versus Ag/AgCl (sat. KCl) in aqueous electrolyte, and -0.2 V to 1.4 V versus Ag wire in Ethaline solution. According to the voltammetric findings shown in Fig 6-9, it can be seen that there are two peaks due to the redox process. These current peaks of films cycled in acidic solution (water) were sharper and clearer than current peaks shown that the oxidation peaks in Ethaline using the same acid media. From these findings, it can be seen that the rate of electro-response in the polymer films have declined during consecutive voltage cycling and that electrochemical behaviour of polymers in DES electrolytes was lower than of aqueous electrolyte due to increasing of viscosity of DES compared with viscosity of water

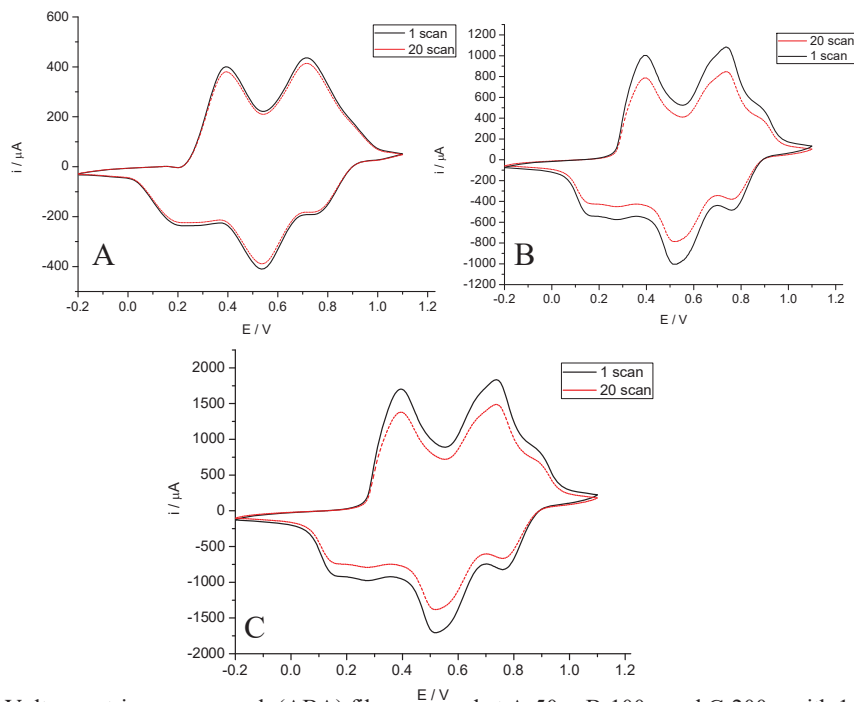


FIGURE 6. Voltammetric response poly(ABA) film prepared at A-50 s, B-100 s and C-200 s with 1 M H₂SO₄ (FIGURE 1) exposed to 1M H₂SO₄ aqueous solution (monomer free) at -0.2 - 1.2 V.

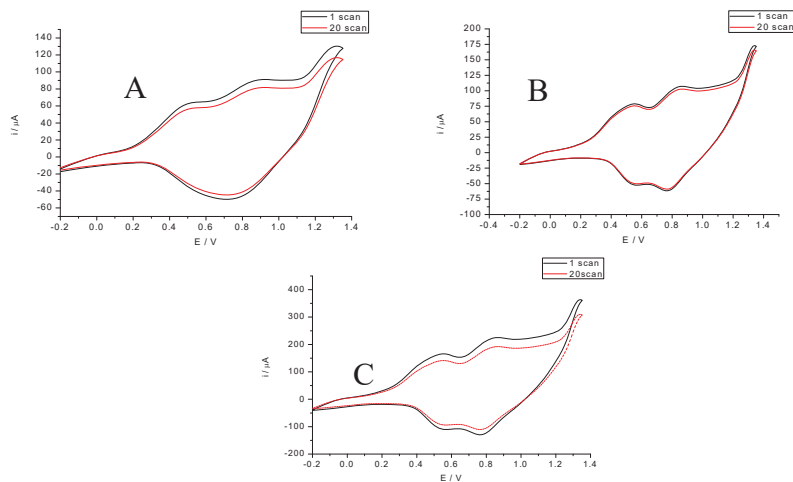


FIGURE 7. Voltammetric response poly(ABA) film prepared at at A-50 s, B-100 s and C-200 s with 1 M H₂SO₄ (Figure 1) exposed to 1M H₂SO₄ /Ethaline solution (monomer free) at -0.2 - 1.4 V.

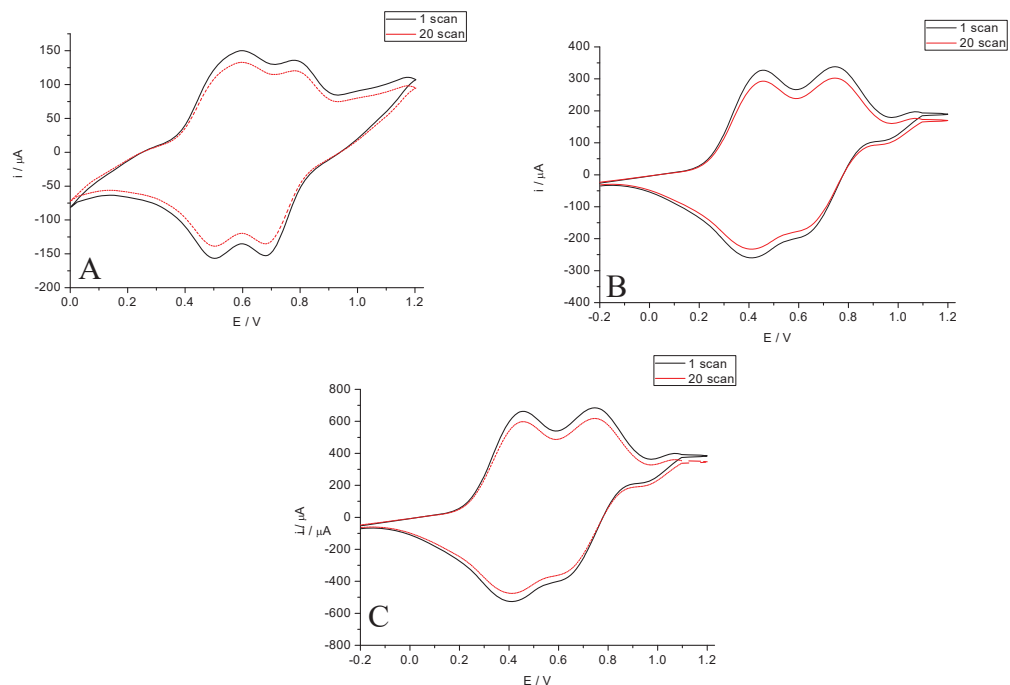


FIGURE 8. Voltammetric response poly(ABA) film prepared at at A-50 s, B-100 s and C-200 s with 1 M HClO₄ (FIGURE 2) exposed to 1M H₂SO₄ aqueous solution (monomer free) at -0.2 - 1.2 V.

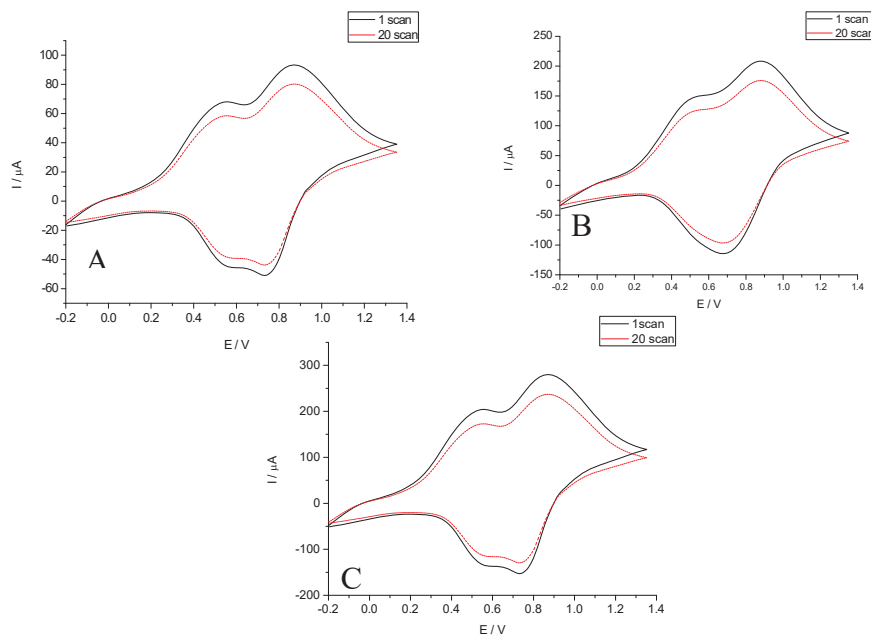


FIGURE 9. Voltammetric response poly(ABA) film prepared at at A-50 s, B-100 s and C-200 s seconds with 1 M HClO₄ (Figure 2) exposed to 1M H₂SO₄/ Ethaline solution (monomer free) at -0.2 - 1.4 V.

CONCLUSIONS

This paper has studied the electrochemical polymerization of 3-amino benzoic acid in DES solution at different times on platinum electrode surface. This study explains electropolymerization of poly(ABA) in two electrolytes, H₂SO₄ and HClO₄ by using a chronoamperometry technique for different times (50s, 100s, and 200s). FTIR and SEM techniques have used to examine various polymer films. The film thickness of poly(ABA) was estimated from the electrical charge (Q) by using Faraday's Law. The electrochemical study of conducting films have indicated that films have various electrochemical response due to use different doping ions (H₂SO₄ and HClO₄). The overall findings shown that use a different electrolyte has led to the produce of various polymeric surface films and the films which have prepared in H₂SO₄ electrolyte have electrochemical response more than other polymer films.

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REFERENCES

1. C. I. Awuzie, *Mater.* 4 (4, Part E), 5721-5726 (2017).
2. Guo and P. X. Ma, *Biomacromolecules* 19 (6), 1764-1782 (2018).
3. B. M. Jokić, E. Džunuzović, B. N. Grgur, B. Z. Jugović, T. L. Trišovic, J. S. Stevanović and M. Gvozdenović, *J. Polym. Res.* 24 (9), 146 (2017).
4. K. Lee and T.-H. Kim, *Electrochim. Acta.* 283, 260-268 (2018).
5. V. C. Tran, S. Sahoo, J. Hwang, V. Q. Nguyen and J.-J. Shim, *J. J. Electroanal. Chem.* 810, 154-160 (2018).
6. A. Slimane, A. Al-Hossainy and M. Zoromba, *J Mater Sci - Mater El.* 29 (10), 8431-8445 (2018).
7. J. Roncali, *Chem. Rev.* 92 (4), 711-738 (1992).
8. L. V. Kayser and D. J. Lipomi, *Adv. Mater.* 31 (10), 1806133.(2019).
9. E. h. Y. Thiam, A. Dramé, S. Sow, A. Sene, C. R. Szczepanski, S. Y. Dieng, F. Guittard and T. Darmanin, *ACS Omega.* 4 (8), 13080-13085 (2019).
10. J. Husson, S. Lakard, S. Monney, C. C. Buron and B. Lakard, *Synt.Met.* 220, 247-254 (2016).
11. S. Lakard, J. Husson, S. Monney, C. C. Buron and B. Lakard, *Prog. Org.* 99, 429-436 (2016).
12. L. Shen and X. Huang, *Synt.Met.* 245, 18-23 (2018).
13. E. Muthusankar and D. Ragupathy, *Nano-Str. & Nano-Obj.* 20, 100390.(2019)
14. F. Wolfart, B. M. Hryniewicz, M. S. Góes, C. M. Corrêa, R. Torresi, M. A. O. S. Minadeo, S. I. Córdoba de Torresi, R. D. Oliveira, L. F. Marchesi and M. Vidotti, *J Sold State Electr.* 21 (9), 2489-2515 (2017).
15. M. Gicevičius, A. Ramanavičienė, L. Mikoliūnaitė and A. Ramanavičius, *IEEE 7th Proc. NAP Conference,* (2017).
16. T. F. Otero and S. Beaumont, *Sens. Actuators B Chem.* 253, 95.(2017).
17. J. Ibanez, M. Rincón, S. G.Granados, M. Chahma, O. Quintero and B. A. Uribe, *Chem. Rev.* 118 (9), 4731-4816 (2018).
18. M. Ates, *J Adhes Sci. Technol.* 30 (14), 1510-1536 (2016).
19. Q. Meng, K. Cai, Y. Chen and L. Chen, *Nano Energy.* 36, 268-285 (2017).
20. Y. Wang, Y. Chen and Q. Wen, *Environ. Chem. Lett.* 16 (1), 319-326 (2018).
21. H. M. Mousa, J. R. Aggas and A. Guiseppi-Elie, *Mater.* 238, 267-270 (2019).
22. E. Kim, N. Kang, J.-J. Moon and M. Choi, *Bull. Korean Chem. Soc.* 37 (9), 1445-1452 (2016).
23. A. Abbott, G. Frisch, H. Garrett and J. Hartley, *Chem. Comm.* 47 (43), 11876-11878 (2011).
24. C. Chiappe and D. Pieraccini, *J. Phys. Org.Chem.* 18 (4), 275-297 (2005).
25. A. Abbott, G. Capper, D. Davies, R. Rasheed and V. Tambyrajah, *Chem. Comm.* (1), 70-71 (2003).
26. R. Sheldon, *Chem. Comm.* (23), 2399-2407 (2001).
27. D. Mecerreyes, *Prog. Polym. Sci.* 36 (12), 1629-1648 (2011).
28. R. L. Vekariya, *J. Mol. Liq.* 227, 44-60 (2017).
29. D. Wei and A. Ivaska, *Anal. Chim. Acta.* 607 (2), 126-135 (2008).
30. Q. B. Zhang and Y. X. Hua, *Electrochim. Acta.* 54 (6), 1881-1887 (2009).
31. J. Lu, F. Yan and J. Texter, *Prog. Polym. Sci.* 34 (5), 431-448 (2009).

32. Q. Zhang, K. Vigier, S. Royer and F. Jérôme, [Chem. Soc. Rev.](#) 41 (21), 7108-7146 (2012).
33. E. L. Smith, A. P. Abbott and K. S. Ryder, [Chem. Rev.](#) 114 (21), 11060-11082 (2014).
34. Y. Dai, J. van Spronsen, G. Witkamp, R. Verpoorte and Y. H. Choi, [Anal. Chim. Acta.](#) 766, 61-68 (2013).
35. L. Janiszewska, [J. Electrochem. Soc.](#) 134 (11), 278.(1987).
36. A. Krishna, C. Laslau, G. Waterhouse, Z. Zujovic and J. Travas-Sejdic, [Chem. Pap.](#) 67,995-1002 (2013).
37. T. A. Zawodzinski, L. Janiszewska and R. A. Osteryoung, [J. Electroanal. Chem. Interf. Electrochem.](#) 255 (1), 111-117 (1988).