

ARAŞTIRMA MAKALESİ / RESEARCH ARTICLE

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SÜPERKAPASİTÖR AKTİF MALZEMESİ OLARAK POLİ(N-ETİLANİLİN) VE POLİ(ANİLİN-KO-N-ETİLANİLİN)'İN SUSUZ ORTAMDA KARAKTERİZASYONU

ÖZ

Poli(*N*-etilanilin) (PNEA) ve poli(anilin-*ko*-*N*-etilanilin) filmleri 0.1 M tetraetilamonyum tetrafloroborat (TEABF₄) içeren asetonitril (ACN) çözeltisi kullanılarak dönüşümlü voltametri (CV) yöntemiyle kalem grafit elektrot (PGE) yüzeyinde sentezlenmiştir. Elde edilen filmlerin elektrokimyasal karakterizasyonu monomersiz çözeltiler içerisinde CV yöntemi kullanılarak gerçekleştirilmiştir. Filmlerin yüzey morfolojileri taramalı elektron mikroskobu (SEM) ile görüntülenmiştir. Polimer filmi kaplı PGE'lerin (PGE/PNEA ve PGE/*co*-PNEA) elektrokimyasal enerji depolama özellikleri CV, elektrokimyasal empedans spektroskopisi (EIS), galvanostatik şarj-deşarj ve tekrarlanan kronopotansiyometri yöntemleriyle araştırılmıştır. PGE/PNEA ve PGE/*co*-PNEA için en yüksek spesifik kapasitans değerleri galvanostatik şarj-deşarj yöntemi ile 0.01 mA akımda sırasıyla 1112.72 and 1830.00 mF g⁻¹ olarak elde edilmiştir. Tekrarlanan kronopotansiyometri yöntemine göre, PGE/PNEA'un PGE/*co*-PNEA'tan daha yüksek şarj-deşarj kararlılığına sahip olduğu gözlenmiştir.

Anahtar Kelimeler: İletken polimer, Polianilin, Elektropolimerizasyon, Enerji depolama, Süperkapasitör.

CHARACTERIZATION OF POLY(*N*-ETHYLANILINE) AND POLY(ANILINE-*CO*-*N*-ETHYLANILINE) AS SUPERCAPACITOR ACTIVE MATERIALS IN NONAQUEOUS MEDIUM

ABSTRACT

Poly(*N*-ethylaniline) (PNEA) and poly(aniline-*co*-*N*-ethylaniline) (*co*-PNEA) films have been synthesized on a pencil graphite electrode (PGE) by using cyclic voltammetry (CV) in an acetonitrile (ACN) solution of tetraethylammonium tetrafluoroborate (TEABF₄). The electrochemical properties of the electrodeposited coatings have been characterized using CV method in monomer free solution. The surface morphologies of the films have been investigated by Scanning Electron Microscope (SEM). The electrochemical storage properties of polymer coated PGE (PGE/PNEA and PGE/*co*-PNEA) have been evaluated by CV, electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge and repeating chronopotentiometry tests. The highest specific capacitance values of PGE/PNEA and PGE/*co*-PNEA have obtained as 1112.72 mF g⁻¹ and 1830.00 mF g⁻¹ at 0.01 mA by using galvanostatic charge-discharge, respectively. According to repeating chronopotentiometry tests, it is observed that charge-discharge stability of PGE/PNEA is longer than PGE/*co*-PNEA.

Keywords: Conducting polymer, Polyaniline, Electropolymerization, Energy storage, Supercapacitor.

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1. GİRİŞ

Batteries and capacitors are regarded as traditional electrical energy storage devices (Michael and Prabakaran, 2000). Electrochemical capacitors also known as ultracapacitors or supercapacitors are a kind of energy storage devices between conventional capacitors and batteries (Sarangapani et al, 1996; Lota et al, 2004). Over the past few years, the supercapacitors have attracted a global attention due to their potential use as power source on the commercial scale in many low and high energy density applications such as electronic equipment, medical equipment, computer memory backup, electrical vehicles, etc. (Sarangapani et al, 1996; Kotz and Carlen, 2000; Nishino, 1996; Hashmi, 2004). Supercapacitors have many advantages in electrical devices by virtue of their large specific capacitance, high power and long cycle life (Ma et al, 1999). They have high power density compared to that of usual rechargeable batteries and they exhibit both high rate charge-discharge profile and long cycle life (Ganesh et al, 2008).

The materials studied as electrode active materials for supercapacitor applications have been mainly three types: (i) carbon; (ii) transition metal oxide; (iii) conducting polymers (Sarangapani et al, 1996; Prasad and Munichandraiah, 2002). Electrodes based on conductive polymers such as polypyrrole, PANi, polythiophene have been previously proposed for supercapacitor designs. These polymers utilize their π -conjugated backbones to transfer electrical charge from the current collector to the electrolyte. Conductive polymers are referred to as either n-doped or p-doped relative to their neutral state. The energy storage mechanism is proportional to the amount of electroactive species that can be absorbed by the electrode (Huggings and Parsons, 1996). This leads to much larger values of specific energy (SE) and specific capacitance (White and Slade, 2003). PANi and its derivatives have been considered promising materials in energy storage devices applications (Genies and Picart, 1995; Naoi et al, 1997). They have been widely used in supercapacitors as electrode active materials with high capacitance (Hu and Chu, 2009) due to the existence of several oxidation structures.

There has been more interest in two types of supercapacitors. One is the electrical double-layer capacitor, and the other is the redox capacitor (pseudo-capacitor). In the former, energy storage arises mainly from the ionic

charge separation at the electrode electrolyte interface (Nishino, 1996). Graphitic, activated, templated and carbide derived carbons, carbon fabrics, fibers, nanotubes and nano-horns have been tested as highly conducting, open porous, electrochemically stable and cost effective electrical double-layer capacitor materials for charge storage (Pandolfo and Hollenkamp, 2006; Portet et al., 2008; Yang et al., 2007). In the latter type, a faradaic process, due to redox reactions, takes place at the electrode materials at characteristic potentials (Arbizzani et al., 1996; Hashmi et al., 1997). Metal oxides and conducting polymers constitute pseudo-capacitive electrodes with high capabilities. Although conducting polymers have high specific capacitance, pseudo-capacitive materials have disadvantages that include a lower cyclic-life in the charge-discharge duty than carbon-based electrodes because the redox sites in the polymer backbone are not sufficiently stable for many repeated redox process (Wang et al., 2008). To overcome the challenges of carbon materials and pseudo-capacitive materials, electrodes which are used as supercapacitor active materials containing carbon and pseudo-capacitive materials have been synthesized, and have demonstrated improvement in the electrical performance (Sharma et al., 2007; Devaraj and Munichandraiah, 2007). In these electrodes, carbon has been used as a support material to achieve electrical conductivity, large active surface area and mechanical stability (Sharma et al., 2007; Kim and Popov, 2003; Sharma et al., 2008). Therefore, combination of these materials provides more stable electrodes.

This work is an extension of our previous work. In our previous work (Arslan and Hür, 2012), we synthesized polyaniline (PANi) and poly(*N*-methylaniline) (PNMA) on PGE to investigate availability of these materials as an electrode active material for supercapacitor applications. PANi and PNMA coated PGE presented the highest specific capacitances of 35.30 mF g⁻¹ and 44.27 mF g⁻¹, respectively. Then, in this work, to suggest as new supercapacitor electrode active materials and to

improve the electrochemical storage properties of electrodes, we synthesized PNEA and *co*-PNEA on PGE by CV method in nonaqueous medium. The electrochemical properties and the stabilities of these films were investigated by using CV. The surface morphologies of the electrodes were characterized by SEM. Electrochemical storage properties of the electrodes were determined by

CV, EIS, galvanostatic charge-discharge and repeating chronopotentiometry methods. The goal of this study is to evaluate the capacitive performances, to calculate the specific capacitance values of these electrodes as well as to investigate availability of the electrodes as supercapacitor electrode active materials.

2. EXPERIMENTAL

Aniline (ANi) (99.5%) and *N*-ethylaniline (NEA) (98.0%) were purchased from Aldrich Chemical Company. All monomers have been vacuum-distilled and maintained under nitrogen atmosphere before use. ACN (99.0%) and TEABF₄ (99.0%) were purchased from Sigma Aldrich and Fluka, respectively.

The all electrochemical experiments except galvanostatic charge-discharge have been realized in three-electrode system consisting of PGE as working electrode, platinum wire as counter and pseudo Ag/AgCl as reference electrode. PGE is Tombo lead with a diameter of 0.50 mm. The PGE has been prepared by cutting the leads into 3 cm long sticks and 1 cm (area 0.16 cm²) was dipped in electrolyte. A Rotring Tikky pencil model was used as a holder for PGE. Electrical contact with the PGE was obtained by soldering a metallic wire to the metallic part of the holder. All electrodes were cleaned in ACN using ultrasonic bath (Bandelin Sonarex) and dried before each experiment. The all electrochemical experiments were performed using A Gamry 3000 potentiostat/galvanostat/ZRA system (Wilmington, USA) and obtained datas were analyzed using Gamry CMS-300 (version 5.50b) framework/analysis software. The surface morphologies of homopolymer and copolymer films coated PGE were investigated via a Zeiss Ultra Plus Field Emission Scanning Electron Microscope. All experiments were carried out at 25 °C and at open air atmosphere.

Electrochemical polymerizations have been carried out by using CV. Electrochemical characterizations of PNEA and *co*-PNEA have been investigated in monomer free solution. Electrochemical storage properties of the electrodes have been determined by CV, EIS, galvanostatic charge-discharge and repeating

chronopotentiometry methods. The specific capacitance (C_s) values of electrodes which suggested as supercapacitor electrode active materials have been calculated.

3. RESULTS and DISCUSSION

3.1. Electrochemical Synthesis of PNEA and *Co*-PNEA Films on PGE

Electrochemical methods are generally employed for polymerization of ANi and its derivatives under: (i) a constant current (galvanostatic); (ii) a constant potential (potentiostatic); and (iii) a potential scanning/cycling or sweeping (potentiodynamic). The electrooxidation of aniline and its derivatives by continuous cycling between the predetermined potentials produces even polymeric films which firmly adhere on the electrode surface (Genies and Tsintavis, 1985; Genies et al., 1985). The films of PANi and its derivative films can then either be reduced or oxidized to control conductivity (Bhadra et al., 2008; Bhadra et al., 2009). Because of these advantages of the potentiodynamic method, we have preferred CV which is a potentiodynamic method as an electrochemical synthesis technique.

Electrochemical synthesis of PNEA were performed on PGE in ACN solution which contains 0.1 M NEA and 0.1 M TEABF₄ using CV. Fig. 1 shows cyclic voltammogram of PNEA in the potential range between -0.20 and +0.90 V, at a scan rate of 50 mV s⁻¹ for 15 cycles. In the first cycle of the cyclic voltammogram of PNEA, oxidation wave attributed to the oxidation of monomers appears starting at about +0.66 V for NEA. The intensity of oxidation waves gradually decreases during subsequent scans. Starting with the second cycle, new one oxidation and one reduction peaks which belong to polymer formation were seen from CV. The oxidation peaks were observed at +0.43 V, while the reduction peaks were observed at +0.16 V for PNEA. The oxidation peaks belong to the formation of the leucoemeraldine cation radical from leucoemeraldine (Şahin et al., 2003a; Şahin et al., 2003b; Şahin et al., 2004). As can be seen from our previous work (Arslan and Hür, 2012), the presence of alkyl substituent in the benzene ring of NEA provokes to shift leucoemeraldine cation radical/leucoemeraldine redox couple to more positive potentials. This result can be

related to the basis of steric and electronic effects of the $-C_2H_5$ group.

Fig. 2 illustrates the successive scans during the electrochemical copolymerizations of ANi and NEA on PGE in ACN solution which contain 0.1 M TEABF₄, 0.1 M ANi and 0.1 M NEA.

The potential was scanned from -0.20 V to +0.90 V at a scan rate of 50 mV s⁻¹ for 15 cycles. The formation and growth of the copolymer film can

be seen in this figure. The oxidation and reduction peaks of the film were observed at +0.24 V and +0.17 V. The peak current values of oxidation peaks were decreased while the peak current values of reduction peaks were increased with increasing scan number. These results indicate that *co*-PNEA films can be coated on PGE under these conditions according to electrochemical process.

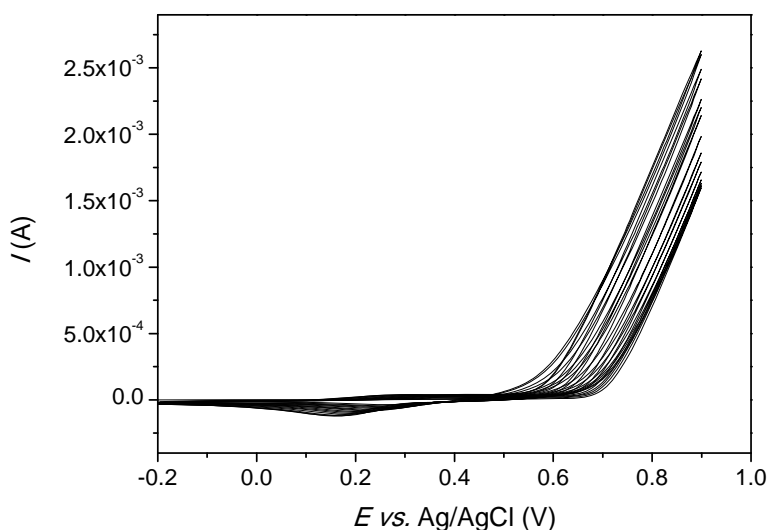


Figure 1. Cyclic voltammograms of the ACN solution containing 0.1 M TEABF₄ and 0.1 M NEA (scan rate: 50 mV s⁻¹, cycles: 15).

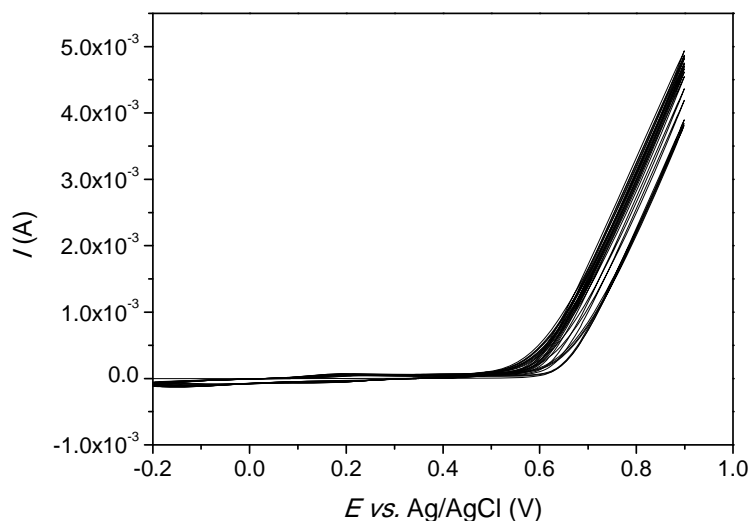


Figure 2. Cyclic voltammograms of the ACN solution containing 0.1 M TEABF₄, 0.1 M ANi and 0.1 M NEA (scan rate: 50 mV s⁻¹, cycles: 15)

3.2. Electrochemical Characterization of PNEA and Co-PNEA Films

After electrodeposition, PNEA and *co*-PNEA films were electrochemically characterized in monomer free solution at different scan rates (50 mV s^{-1} to 350 mV s^{-1}) using CV in the potential range between -0.20 and 0.90 V (Fig. 3a-b). Anodic and cathodic peak currents obtained from Fig. 3a-b were plotted against both the square root of scan rate and scan rate (Fig. 4a-d). A linear relationship was obtained between the peak currents of anodic-cathodic peaks and the square root of scan rates.

Additionally, calculated linear regression coefficient values in the plot of current vs scan rate (v) are smaller than that of plot of current vs square root of scan rate ($v^{1/2}$). These mean that all electrochemical processes are diffusion-controlled. Also, the peak currents of anodic-cathodic peaks are found to have a linear dependency on the scan rate (v), according to Fig. 4c-d. This demonstrates that both homopolymer and copolymer films are well adhered (Cebeci et al., 2007). Apart from all these results, as can be seen from Fig. 4, electroactivities of homopolymer and copolymer films which are associated with the slopes of the lines varies as *co*-PNEA > PNEA. Electro-activities of PNEA can be increased by forming copolymer with ANi and NEA.

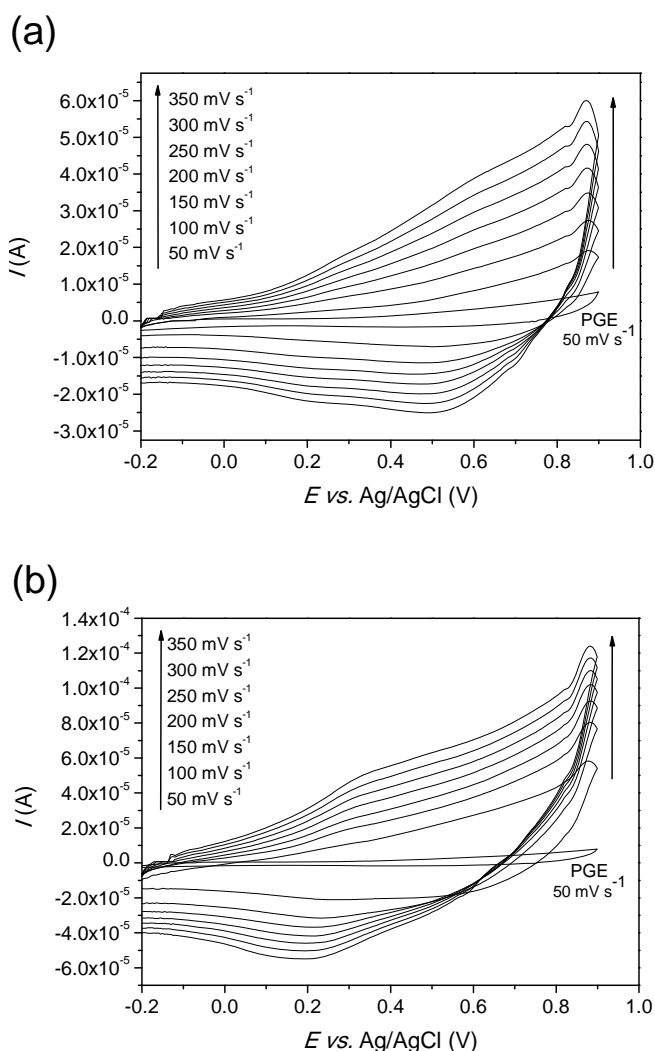


Figure 3. Cyclic voltammograms of (a) PNEA and (b) *co*-PNEA films at different scan rates in ACN solution containing 0.1 M TEABF_4 .

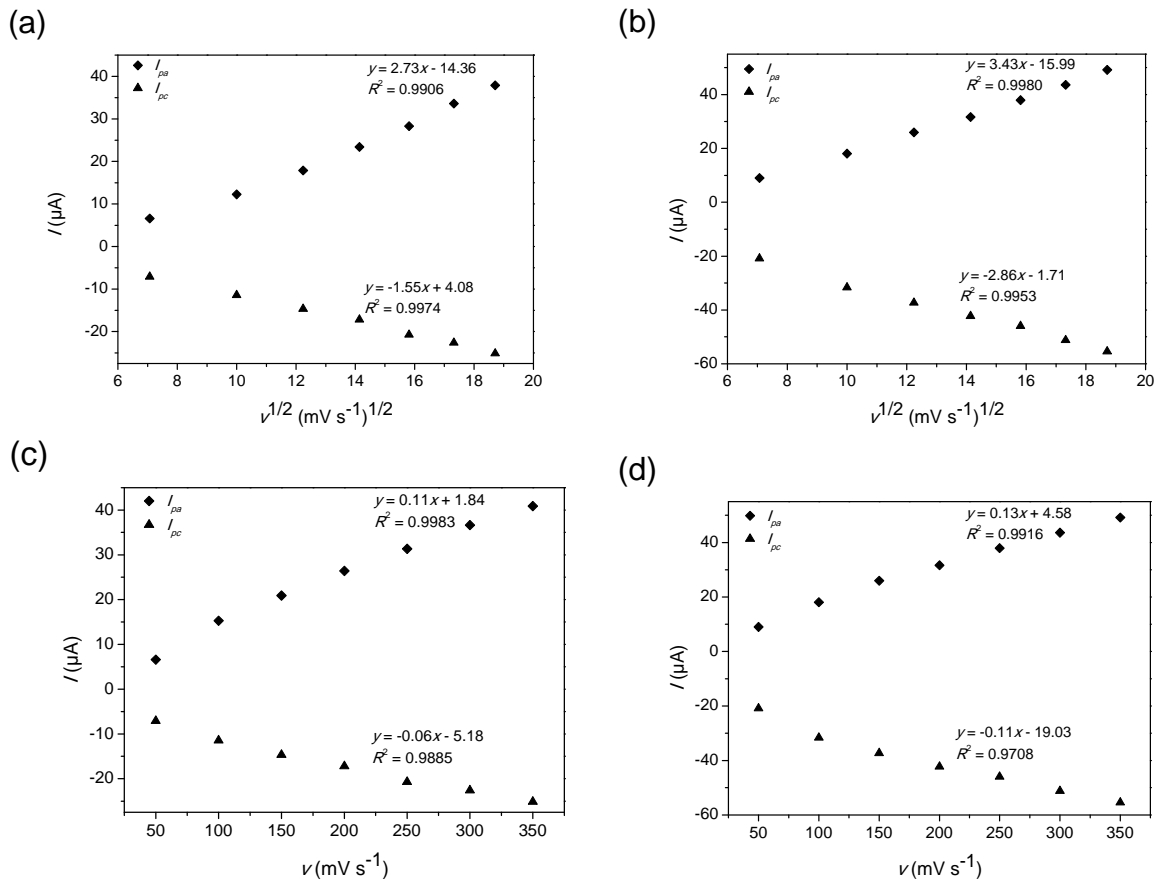


Figure 4. Plots of anodic (I_{pa}) and corresponding cathodic (I_{pc}) peak currents versus the square root of scan rate of the (a) PNEA and (b) *co*-PNEA films up to 350 mV s^{-1} in ACN solution containing 0.1 M TEABF_4 . Plots of anodic (I_{pa}) and corresponding cathodic (I_{pc}) peak currents versus the scan rate of the (c) PNEA and (d) *co*-PNEA films up to 350 mV s^{-1} in ACN solution containing 0.1 M TEABF_4 .

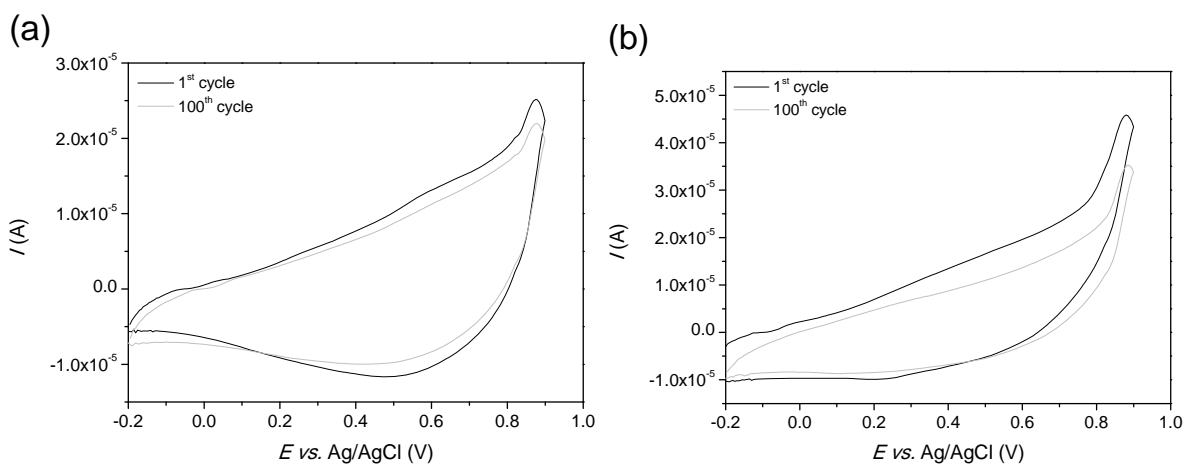


Figure 5. Stability tests for (a) PNEA and (b) *co*-PNMA in ACN solution containing 0.1 M TEABF_4 (scan rate: 50 mV s^{-1} , cycles: 100).

The electrochemical stabilities of the obtained films were evaluated using CV in monomer free solution at a scan rate of 50 mV s^{-1} in the potential range between -0.20 V and $+0.90 \text{ V}$ for 100 cycles (Fig. 5a-b). Differences between initial and final anodic peak current (ΔI_{p_a}) values were determined from CV curves of stability tests of the homopolymer and copolymer films (Fig. 5a-b). If the homopolymer or copolymer film exhibits minimum decrease in I_{p_a} on repetitive cycling, the films are electrochemically most stable (Sarac et al., 2006). ΔI_{p_a} values of the obtained films calculated from Fig. 5a-b are $1.87 \mu\text{A}$ for PNEA and $3.68 \mu\text{A}$ for *co*-PNEA. The decreases ΔI_{p_a} values are about 16% and 31.0% for PNEA and *co*-PNEA, respectively. It can be said that PNEA film is most electrochemically stable than *co*-PNEA.

3.3. Surface Morphology of PGE/PNEA and PGE/*co*-PNEA

Surface morphologies of the uncoated and coated electrodes were investigated by SEM (Fig. 6a-c). Fig. 6a shows the morphology of uncoated PGE, it exhibits the presence of regularly ordered graphite layers. Its surface is uniform and smooth. As can be seen from Fig. 6b-c, the surface of the PGE is uniformly covered by PNEA and *co*-PNEA. On the other hand, the structure of PNEA has similarity with that of *co*-PNEA. PNEA and *co*-PNEA has a homogeneous and close structure.

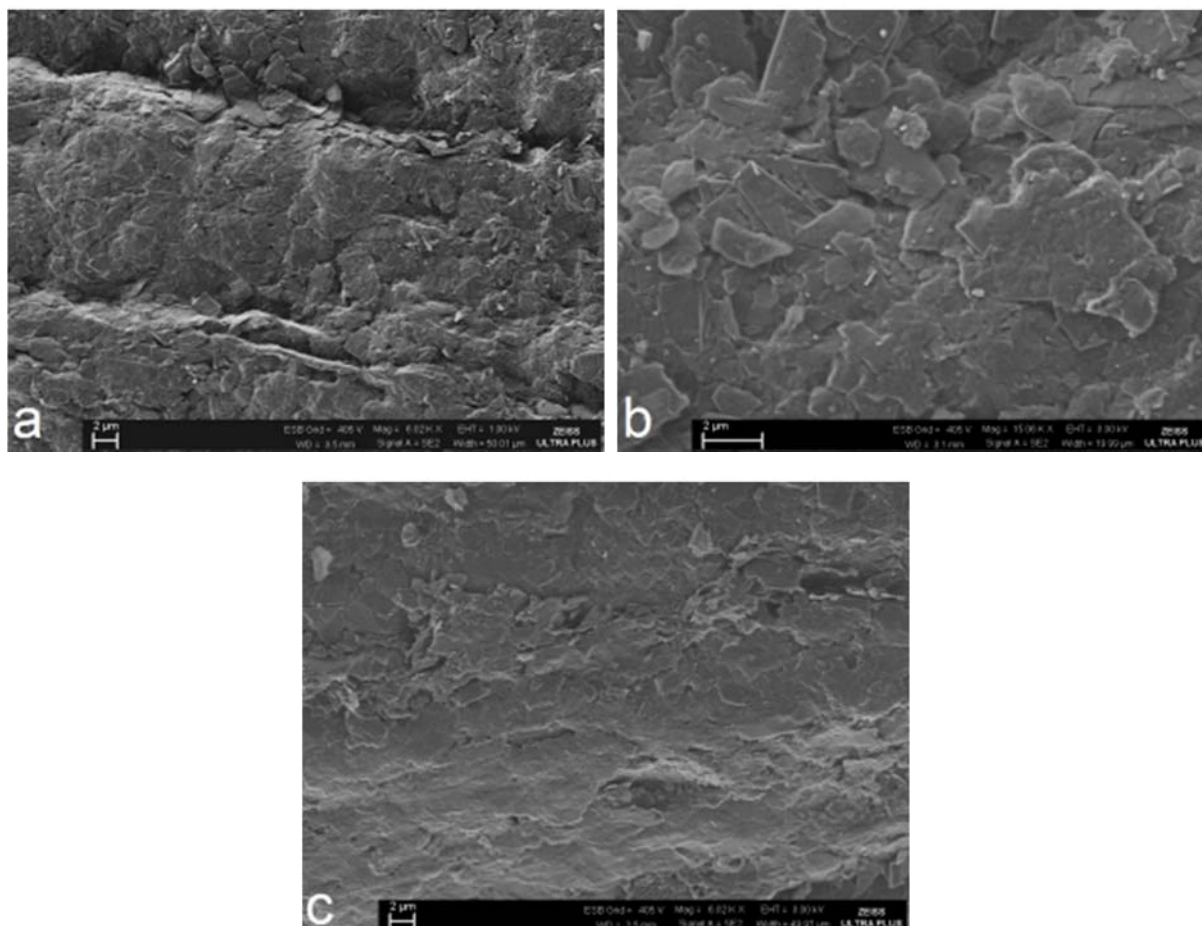


Figure 6. SEM micrograph of the PGE/conducting polymers under different magnification (a) uncoated PGE, (b) PGE/PNEA and (c) PGE/*co*-PNEA.

Table 1. Specific capacitance values of PGE/PNEA and PGE/*co*-PNEA in ACN solution containing 0.1 M TEABF₄ at the different scan rates.

ν	PGE/PNEA	PGE/ <i>co</i> -PNEA
	C_s	C_s
(mV s ⁻¹)	(mF g ⁻¹)	(mF g ⁻¹)
50	239.27	411.36
100	222.91	410.45
150	216.97	392.88
200	212.73	359.09
250	205.96	344.73
300	203.81	330.53
350	196.39	319.22

3.4. Electrochemical Storage Properties of PGE/PNEA and PGE/*co*-PNEA

CV, EIS, galvanostatic charge-discharge and repeating chronopotentiometry methods were employed in monomer free solution to investigate the electrochemical storage properties of PGE/PNEA and PGE/*co*-PNEA. C_s values of PGE/PNEA and PGE/*co*-PNEA were calculated.

Cyclic voltammograms of the electrodes were recorded at different scan rates from monomer free solution (Fig. 3 a-b). As can be seen, PGE/PNEA and PGE/*co*-PNEA exhibit a larger current response when compared to PGE in the same electrolyte at a scan rate of 50 mV s⁻¹. This proves that the coated electrodes have larger surface area than that of PGE and lead to an enhancement of charge storage capability of PGE. C_s values at different scan rates for PGE/PNEA and PGE/*co*-PNEA were calculated from obtained CV results by using the following relationship

$$C_s = \frac{I}{sm}$$

where s is the scan rate, I is the constant current and m is the deposited weight of the polymer films (Hu et al., 2011). C_s values calculated from voltammetric curves for PGE/PNEA and PGE/*co*-PNEA are presented in Table 1. As can be seen from Table 1, both C_s values are ranged as PGE/*co*-PNEA > PGE/PNEA at all scan rates and the specific capacitance values of PGE/PNEA could be enhanced with formed copolymer NEA with ANi. Specific capacitance values of polymer coated electrodes were changed as inverse

proportion with scan rates. The decrease in the specific capacitance is related to transfers of electrolyte ions are limited during oxidation-reduction process and parts of the surface of the electrodes become inaccessible at high scan rates (Patil et al., 2011). It must be known that, the specific capacitances of the polymer coated electrodes are higher than that of PGE (7.40 mF g⁻¹) at the same scan rate.

On the other hand, EIS was also studied to prove the electrochemical storage performance at the OCP in the frequency range of 10⁵ to 10⁻² Hz with potential amplitude of 10 mV. OCP values of PGE/PNEA, PGE/*co*-PNEA and PGE were measured as -0.10, -0.10 and +0.70 V, respectively. Fig. 7a-b represents the Nyquist plots of PGE/PNEA, PGE/*co*-PNEA and PGE. Obtained Nyquist plots for supercapacitor electrode active materials have generally a semicircle and inclined straight line (Hu and Chu, 2001). The high frequency semicircle which is combination of the charge transfer resistance and the double-layer capacitance is related to the faradaic process occurred at the polymer or copolymer film/electrolyte interface (Heli et al., 2012), while the inclined straight line at low frequency is characteristics of diffusion limiting step in electrochemical processes. In our case, Nyquist diagrams of PGE/*co*-PNEA have no semicircle at high frequency region, only a near vertical line is observed in the all range of scanned frequencies. It can be said that the PGE/*co*-PNEA have shown low charge transfer resistance (Laforgue, 2011). This behavior is close to an ideal electrical double layer capacitor and this can be related that no any redox process occurred at -0.10 V for PGE/*co*-PNEA (Heli et

al., 2012; Laforgue, 2011; Sharma and Zhai, 2009). However, both of the electrodes represent an ideal capacitive behavior with a near vertical line parallel to the imaginary axis in the low frequency region (Khomeenko et al., 2008). The slope of the low frequency curve is nearly vertical and dominated by pseudocapacitive process (Laforgue, 2011; Sharma and Zhai, 2009). On the other hand, PGE just exhibits a vertical line at scanned frequencies, demonstrating an ideal electrochemical double layer capacitor. For electrochemical capacitors, the majority of their capacitance is only available at low frequency, so attention should be paid to the data in this range (Bakhmatyuk et al., 2008). C_s values of electrodes which were calculated from Bode plots belong to EIS at 10^{-2} Hz were given in Table 2. As can be seen from Table 2, all capacitance values have varied as PGE/*co*-PNEA > PGE/PNEA > PGE. C_s values of the electrodes have been calculated from Bode plots belong to EIS using below equations:

$$C_s = -\frac{1}{2\pi f Z_{im} m}$$

where f , Z_{im} and m represent frequency, imaginary part of EIS and the deposited weight of the polymer films (Wang et al., 2007).

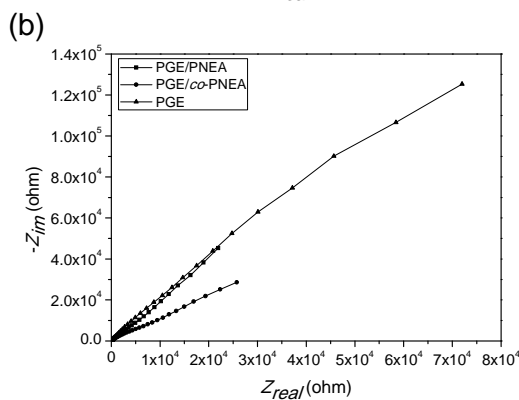
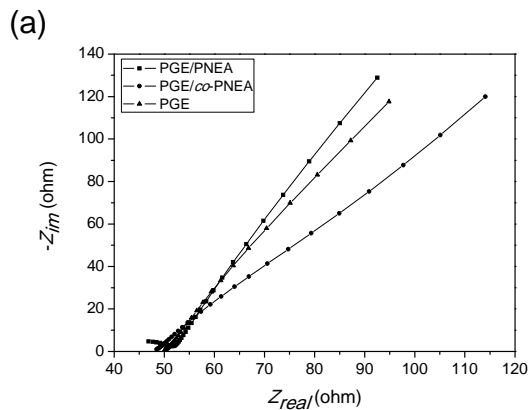


Figure 7. (a) Enlarged version of low-resistance state of Nyquist plots of PGE/PNEA, PGE/*co*-

PNEA and PGE measured at OCP in ACN solution containing 0.1 M TEABF₄. (b) Nyquist plots of PGE/PNEA, PGE/*co*-PNEA and PGE measured at OCP in ACN solution containing 0.1 M TEABF₄.

Charge-discharge profiles of the electrodes were evaluated by using galvanostatic charge-discharge methods in two-electrode system at a current of 0.01 mA in the potential range between 0.00 and 1.00 V (Fig. 8). As can be seen, the charge-discharge curves of the electrodes deviated from the typical linear curve, indicating the pseudocapacitive character at this voltage range (Sen and De, 2010). C_s , specific power (SP) and specific energy (SE) values of the electrodes were calculated and given in Table 3. C_s , SP and SE values of the electrodes can be calculated by following equations:

$$C_s = \frac{I \Delta t_d}{\Delta V m}$$

$$SP = \frac{I \Delta V}{m}$$

$$SE = \frac{I \Delta t_d \Delta V}{m}$$

where I is the discharge current, Δt_d is the time of discharge, ΔV is the potential range during the discharge and m is the deposited weight of polymer films (Mujawar et al., 2011).

Table 2. Specific capacitance values of PGE/PNEA, PGE/*co*-PNEA and PGE in ACN solution containing 0.1 M TEABF₄ using EIS.

Electrode	C_s (mF g ⁻¹)
PGE/PNEA	575.01
PGE/ <i>co</i> -PNEA	940.23
PGE	10.95

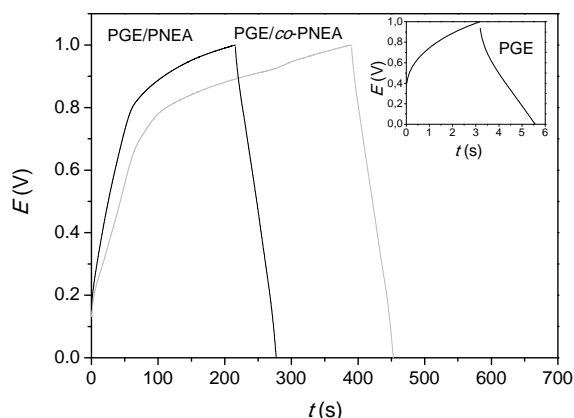


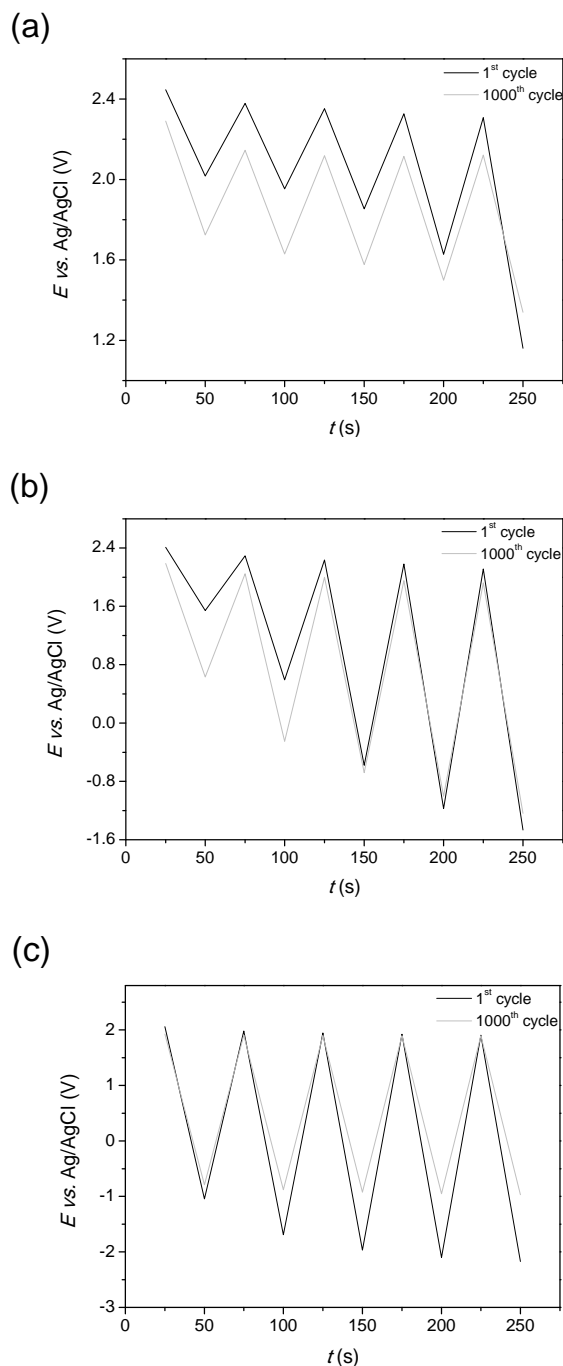
Figure 8. Galvanostatic charge-discharge curves for PGE/PNEA and PGE/co-PNEA in two-electrode system. Inset: Galvanostatic charge-discharge curves for PGE in two-electrode system.

Table 3. Specific capacitances, *SP* and *SE* values of PGE/PNEA, PGE/co-PNEA and PGE calculated from galvanostatic charge-discharge curves.

Electrodes	$C_s / \text{mF g}^{-1}$	$SP / \text{W kg}^{-1}$	$SE / \text{Wh kg}^{-1}$
PGE/PNEA	1112.72	18.18	1112.78
PGE/co-PNEA	1830.00	22.73	1830.00
PGE	1.87	0.79	1.88

The charge-discharge cycle durability is one the most important properties of electrochemical performance of supercapacitor in practical applications. Therefore, the long-term cycle stabilities of the electrodes have been studied. The charge-discharge behaviors of the electrodes have been also investigated by repeating chronopotentiometry tests at two different currents ($\pm 2 \text{ mA}$) for 1000 cycles. Fig. 9a-c show first five cycles and last five cycles charge-discharge behaviors of PGE/PNEA, PGE/co-PNEA and PGE. The variation of the charge cut-off potential values of the electrodes versus number of charge-discharge cycles are shown in Fig. 9c. The decreases in the charge cut-off potential were observed as 14.00, 24.00 and 8.00% for PGE/PNEA, PGE/co-PNEA and PGE, respectively. These results demonstrate that PGE/PNEA is more stable than PGE/co-PNEA. These results are compatible with stability tests measured by using CV. On the other hand,

charge-discharge stability of PGE hasn't significantly changed but specific capacitance of PGE can be enhanced by the formation of polymer and copolymer films on PGE, according to electrochemical measurements.



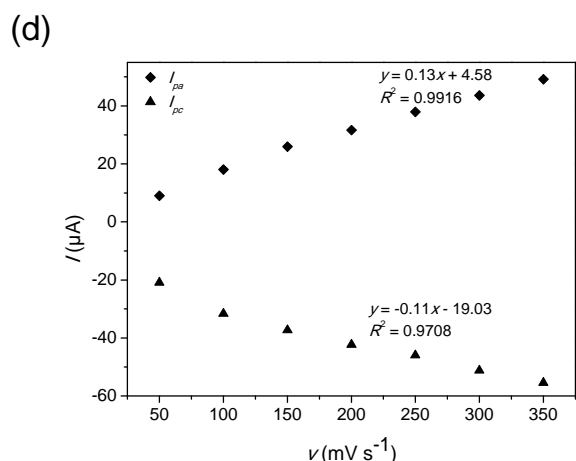


Figure 9. First 5 cycles and last 5 cycles of charge-discharge behaviors of (a) PGE/PNEA, (b) PGE/*co*-PNEA and (c) PGE in 1000 cycles charge-discharge tests. (d) Variation of the charge cut-off potential of the electrodes versus number of charge-discharge cycles.

4. CONCLUSIONS

In this study, we have been able to characterize PNEA and *co*-PNEA on PGE which is renewable and cheap pencil writing device and to investigate the utility of these electrodes as supercapacitor electrode active material. PGE/PNEA and PGE/*co*-PNEA electrodes were obtained by electrochemical polymerization of monomers in non-aqueous medium. The morphological properties of the electrodes have been determined by SEM. Results show that surface of PGE can be coated with polymer films in our parameters. Characterizations of polymer and copolymer films were done by CV. According to CV results, polymer and copolymer films have an electro-active behavior. The electrochemical storage properties of PGE/PNEA and PGE/*co*-PNEA were investigated by CV, EIS, galvanostatic charge-discharge and repeating chronopotentiometry. Results of CV, EIS and galvanostatic charge-discharge methods which were used to calculate the capacitance values of electrodes are same trend and these results change as PGE/*co*-PNEA > PGE/PNEA. The highest specific capacitance values of PGE/PNEA and PGE/*co*-PNEA have obtained as 1112.72 mF g⁻¹ and 1830.00 mF g⁻¹ at 0.01 mA by using galvanostatic charge-discharge, respectively. The results of repeating chronopotentiometry have presented that PGE/PNEA has a longer cycle life than PGE/*co*-PNEA.

When all these obtained results are compared to results of our previous work (Arslan and Hür, 2012), it can be said that PNEA and *co*-PNEA are more electroactive than PANi and PNMA, according to CV measurements. On the other hand, the specific capacitance values of PGE/PANi (35.30 mF g⁻¹) and PGE/PNMA (44.27 mF g⁻¹) can be enhanced with formation of PGE/PNEA and PGE/*co*-PNEA. Although, PGE/PANi has not charge-discharge stability, PGE/PNEA and PGE/*co*-PNEA have good charge-discharge stabilities.

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