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Electrochemical Polymerization of a Novel Thiophene-Derived Monomer and Its Use as Support Material for Methanol Oxidation

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Abstract: This research, conductive polymer supported modified electrode system which was prepared for usage in direct methanol fuel cells. To test the behavior of these electrode system for methanol oxidation, cyclic voltammetry (CV), chronoamperometry (CHR) and electrochemical impedance spectroscopy (EIS) methods were used as electrochemical methods. As the working electrode, pencil graphite electrode (PGE) was preferred because of its porous structure, good ion conductivity, practicality in application and ease of preparation and obtaining. Thiophene derivative 4,4')-2,2'-(diazen-1,2 diylbis(4,1 phenylene))bis(4 (thiophene-2-ylmethylene) oxazol-5(4H)-one), (DiAzBiPhBiTyOx) monomer was prepared and electrochemically polymerized by CV method in 0.01M TBAP and 0.05 $HClO_4$ containing ACN solution on the surfaces of PGE. The spectroscopic characterization of the synthesized monomer was performed by NMR spectroscopy. Optimum polymerization conditions of monomer was determined according to scanning rate, potential range and acid density. The obtained modified electrode system (PGE/PDiAzBiPhBiTyOx) was doped with chloroplatinic acid hexahydrat-Pt2Cl6.6H2O (Pt) at different densities and the optimum catalyst density was determined as 3.25mM (PGE/3.25mMPt@PDiAzBiPhBiTyOx). The methanol oxidation performances of conductive polymer film, platinum and conductive polymer supported platinum catalyst systems were investigated separately. While the methanol oxidation responses of the conductive polymer film and platinum are almost similar, the methanol oxidation response of the platinum doped conductive polymer film catalyst system is higher. The modified electrode characterization was performed by CV, CHR and EIS methods. Furtheremore obtained modified electrode systems were characterized by FESEM/EDS, XRD to confirm the structures and morphologies. Also, the theoretical values such as electrochemical surface area (ECSA) and specific capacitance (Cs) were calculated in aqueous acidic solution with and without methanol. Cs values of the PGE/3.25mMPt@PDiAzBiPhBiTyOx electrode in aqueous acidic solution with and without methanol were 3.861 and 3x10-4Fg^{-1} respectively. Also, the electrochemical surface area values of the same electrode in aqueous acidic solution with and without methanol were 196.437 and 21.150m2g^{-1} respectively.

Keywords: Methanol oxidation, Platinum, Conductive polymer, Polythiophene, Fuel cell

Introduction

Highly efficient, renewable and environmentally friendly alternative energy sources are the focus of today's world and are still in the research and development process. Fuel cells are one of the systems worth investigating as an alternative energy source. Direct methanol fuel cells (DMFCs), a type of fuel cell, represent a promising energy source for a portable and clean environment that can be easily applied in modern life (Kamarudin et al., 2009; Andújar & Segura, 2009; Verma, 2000). Since they emit a low amount of pollutant, can be operated at a low working temperature and having high energy-conversion efficiency. Energy is generated by the exchange of ions at the interface of the active material coated on the working electrode surface and the electrolyte in fuel cells. Extensive application of DMFCs requires electrode materials based on dispersed electrocatalytic noble metals (mainly platinum or Pt-based alloys) on a conductive, stable, high surface area substrate (Spătaru et al., 2011; Zainoodin et al., 2010). Carbon-based materials with high conductivity and surface area such as activated carbon, carbon nanofibers, carbon nanotubes and graphene are widely used for DMFCs (Moussa et al., 2016). PGE was chosen as the carbon-based material for this research due to its porous structure, high ion conductivity, practicality in application, ease of preparation and low cost (Kilic et al., 2017; Arslan et al., 2019, Hur et al., 2013). On the otherhand the porous structure and high surface area of many conducting polymers have been led to their use as supporting materials in the development of new electrocatalytic materials. Conducting polymers have a single-electrone polaron state and are mechanically stable and they exhibit a low ohmic resistance across the electrode (Arico et al., 2000; Surampudi et al., 2003; Breiter, 1967; Lee et al., 2004; Raghuveer & Manthiram, 2005; Weidlich et al., 2005; Kitani et al., 2001; Liu et al., 2007; Kost et al., 1988; Rajesh et al., 2003). Electrode modification target with conducting polymers allows an easy flow of current during the electrochemical oxidation of methanol, increasing electrode conductivity, selectivity and reduce the poisoning of the electrode with intermediates. Methanol can be oxidized to carbon dioxide (CO_2) via a carbon monoxide (CO) or carboxylate ($HCOO^-$) reactive intermediates and the formation of strongly adsorbed linearly bonded CO leads to the self-poisoning of Pt electrocatalysts (Baldauf & Preidel, 1999). The biggest factors limiting the widespread use of fuel cells are; the high cost of the metallic catalysts used and the CO gas released during the reaction poisons the catalyst (Chen et al., 2003; Zhu et al., 2001; Herrero et al., 1995; Wu et al., 2004). Due to the relative high electric conductivity of some polymers, it is possible to transfer electrons through polymer chains, between the electrode and dispersed metal particles, where the electrocatalytic reaction occurs. Electrochemical deposition is adviced as an efficient method for the preparation of metal particles. Because of this, the conducting polymer used in this work was electrodeposited on PGE with CV (Domínguez-Domínguez et al., 2008).

In this work, 4,4')-2,2'-(diazen-1,2 diylbis(4,1-phenylene))bis(4 (thiophene-2-ylmethylene) oxazol-5(4H)-one) (DiAzBiPhBiTyOx), a new thiophene (Th) derivative, was chemically synthesized by our group. The advantage of this newly synthesized Th derivative monomer over Th in the electrochemical polymerization process is it's lower potential oxidation. This new polymer has been proposed as an alternative catalyst support material for use as a DMFC anode. Because of PDiAzBiPhBiTyOx is suitable medium for dispersing $H_2PtCl_6.6H_2O$ (Pt), Pt was elctrodeposited on the PGE/PDiAzBiPhBiTyOx modified electrode surface. In order to increase the catalytic effect of Pt with the supporting conductive polymer and to be more economical, it was investigated to decrease the amount of Pt catalyst. In order to eliminate self-poisoning of Pt by the effect of (CO) formed as an intermediate, which limits the common use of DMFCs, it is aimed to investigate the effect of PDiAzBiPhBiTyOx. This mechanism has shown at Figure 1.

$$\text{Pt} + \text{CH}_3\text{OH} \longrightarrow \text{Pt-(CH}_3\text{OH)}_{\text{ad}} \tag{1}$$

$$\text{Pt-(CH}_3\text{OH)}_{\text{ad}} + \text{Pt} \longrightarrow \text{Pt-(CH}_2\text{OH)}_{\text{ad}} + \text{Pt-H}_{\text{ad}} \tag{2}$$

$$\text{Pt-(CH}_2\text{OH)}_{\text{ad}} + \text{Pt} \longrightarrow \text{Pt-(CHOH)}_{\text{ad}} + \text{Pt-H}_{\text{ad}} \tag{3}$$

$$\text{Pt-(CHOH)}_{\text{ad}} + \text{Pt} \longrightarrow \text{Pt-(COH)}_{\text{ad}} + \text{Pt-H}_{\text{ad}} \tag{4}$$

$$\text{Pt-(COH)}_{\text{ad}} + \text{Pt} \longrightarrow \text{Pt(CO)}_{\text{ad}} + \text{Pt-H}_{\text{ad}} \tag{5}$$

$$\text{Pt-H}_{\text{ad}} \longrightarrow \text{H}^+ + \text{Pt} + \text{e}^- \tag{6}$$

$$2\text{Pt} + \text{H}_2\text{O} \longrightarrow \text{Pt(OH)}_{\text{ad}} + \text{Pt-H}_{\text{ad}} \tag{7}$$

$$\text{Pt-(CO)}_{\text{ad}} + \text{Pt-(OH)}_{\text{ad}} \longrightarrow \text{CO}_2 + \text{H}^+ + 2\ \text{Pt} \tag{8}$$

The oveall reaction is :

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \tag{9}$$

Figure 1. Pt-catalyzed methanol oxidation mechanism

Method

Materials

All the chemicals and the solvents used for this experiment were of analytical purity and used without further purification. NMR spectra was recorded on Bruker NMR equipment in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard for ^1H (500MHz). Electrochemical measurements including CV, EIS and CHR methods were performed in a conventional three electrode system. PGE, platinum sheet and silver (Ag) wire (for unaques solutions experiments) and Ag/AgCl (for aques solution experiments) were used as working, counter and reference electrodes, respectively. Pencil graphide electrode (PGE) used for preparation of the working electrode. 2cm of 0,50mm of PGE (0,48cm^2) were used in tests. Before use, PGE washed in an ultrasonic bath (with distilled pure acetone, pure ethanol and acetonitrile respectively at room temperature, for 2 minutes each). Electrochemical measurements were performed on potentiostat-galvanostat system (Gamry 3000 potentiostat/galvanostat/ZRA) and were analyzed by software (Gamry CMS-300 (version 5.50b) framework/analysis). All electrochemical measurments were repeated three times. All experiments were performed at room temperature.

The structural and morphological characterization of conducting polymer and Pt doped conducting polymer were done by X-ray diffraction (XRD) and by field emission-scanning electron micrograph (FE-SEM/EDS). The devices used for FESEM and XRD are Hitachi Regulus 8230 FE-SEM and RIGAKU brand SmartLab model X-ray Diffractometer equipped with Cu target respectively.

Synthesis of Monomer

Synthesis of DiAzBiPhBiTyOx monomer was conducted according to our previous procedure and summarized in Figure 2 (Arslan et al., 2019)

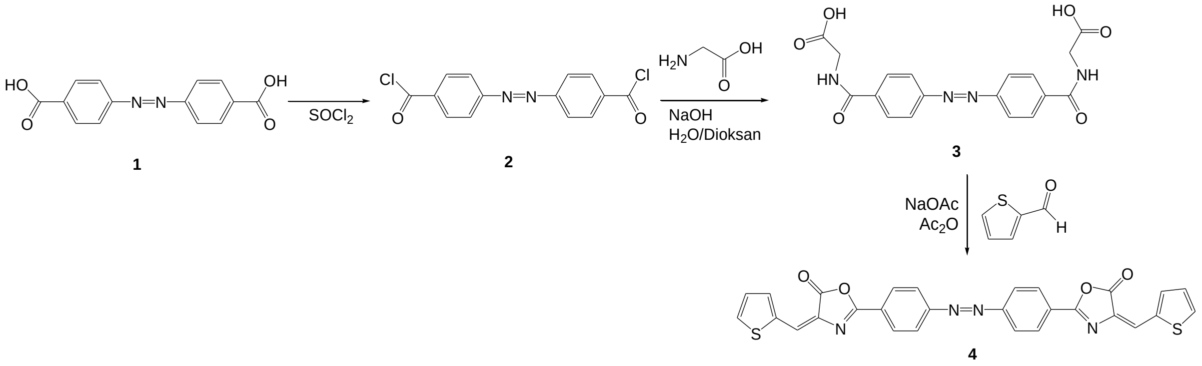

Figure 2. Chemical synthesis of DiAzBiPhBiTyOx monomer

Synthesis of (4,4')-2,2'-(diazen-1,2-diylbis(4,1-phenylene))bis(4-thiophen-2 ylmethylene)oxazole-5(4H)-on), DiAzBiPhBiTyOx, 4

4-[2-(4-carboxyphenyl)diazen-1-yl]benzoic acid, 1 (1 eq. mol) was refluxed in thionyl chloride ($SOCl_2$, excess) in the presence of a catalytic amount (1.2 drops) of DMF under nitrogen atmosphere for 5 hours. At the end of the reaction, excess $SOCl_2$ was evaporated under vacuum distillation. Thus, the carboxy functions were chlorinated to obtain 4-[2-(4-carboxyphenyl)diazen-1yl]benzoyl chloride, 2 in 95% yield and used in the next reaction without any purification. Glycine (2 eq. mol) and NaOH (4 eq mol) were dissolved in 40 mL of water. To this mixture, a solution of 4-[2-(4-carboxyphenyl)diazen-1-yl]benzoyl chloride, 2, (1 eq. mol) in dioxane (80mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 hours. At the end of the reaction time, the dioxane was evaporated under vacuum. The remaining reaction mixture was diluted with water and extracted with ethyl acetate (EtOAc) (3x30mL). 10% HCl (aqueous) solution was added to the collected water phase until pH=2. This solution was extracted with EtOAc again and the amide compound formed was taken to the organic phase. The organic phase was dried with Na_2SO_4 and filtered. The filtrate was evaporated in vacuo to remove EtOAc and diglycinamide, 3, was obtained in, 72% yield. Oxazolone rings were formed by boiling diglycinamide, 3 (1 eq. mol) in acetic anhydride (10mL) under reflux for 2 hours with thiophene-2-carbaldehyde (2 eq. mol) and sodium acetate (NaOAc, 2 eq. mol). The reaction mixture was evaporated under vacuum and ethanol (10mL) was added to the obtained residue, and it was kept in the refrigerator at 5^{o}C overnight. The product, DiAzBiPhBiTyOx, 4, was obtained in 67% yield as a dark red precipitate.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ ppm: 9.58 (d, J= 1.67 Hz, 1H), 8.60 (dd, J= 2.06, 8.30 Hz, 1H), 8.49 (s, 1H), 8.47 (s, 1H), 7.86-7.85 (m, 2H), 7.75 (d, J= 3.33 Hz, 1H), 7.72 (d, J= 3.62 Hz, 1H), 7.69 (s, 1H), 7.65 (s, 1H), 7.25 (d, J= 3.85 Hz, 1H), 7.24 (d, J= 3.82 Hz, 1H) ppm.

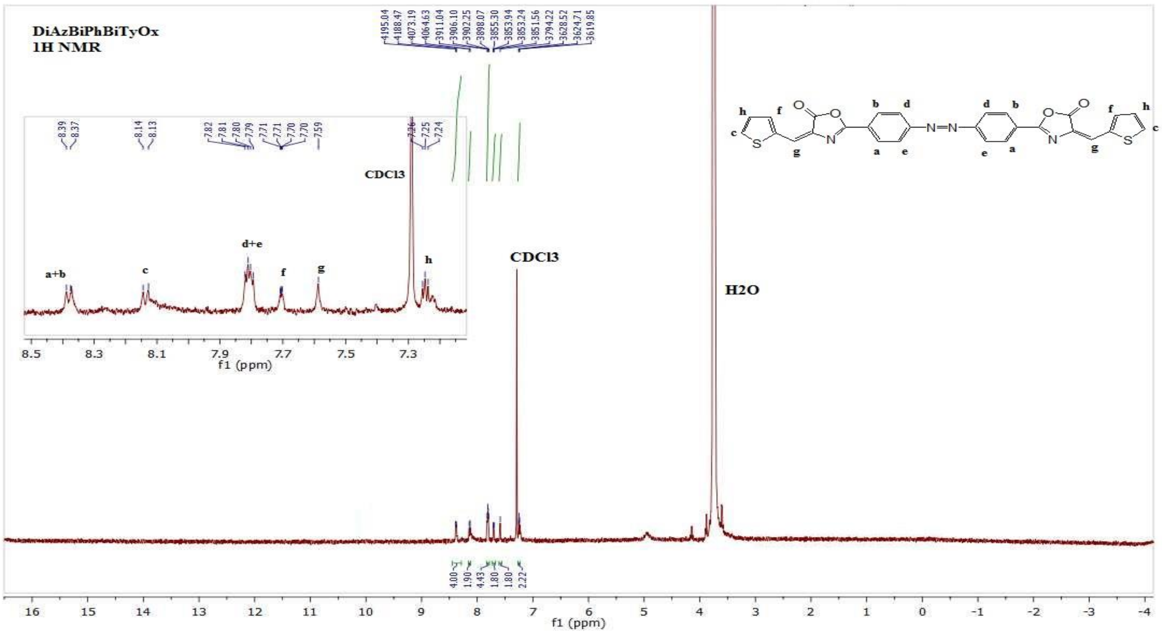

Figure 3. ^{1}H NMR spectrum of DiAzBiPhBiTyOx

Preparation of the Catalyst Support Material

The catalyst support material was formed by electrochemical deposition of PDiAzBiPhBiTyOx on PGE in ACN solution which contains 1.00 x 10^{-4}M DiAzBiPhBiTyOx, 0.10M TBAP and 0.05M $HClO_4$ using CV method. Electropolymerization was performed in the potential range of +0.20 to +2.00 V at a scan rate of 30 mVs^{-1} for 40 cycles. After electropolymerization, the modified electrode (PGE/PDiAzBiPhBiTyOX) was rinsed with ACN and air dried after the electrochemical polymerization.

Platinum Electrodeposition onto Support Material

The electrodeposition of platinum onto the PGE/PDiAzBiPhBiTyOx electrode was carried out in a conventional electrochemical cell consisting of 3 electrode at room temperature. An aqueous solution containing 0.5 M H_2SO_4 (Sigma-Aldrich) and 5mM $H_2PtCl_6.6H_2O$ (Sigma-Aldrich) was used as the electrodeposition solution. Electrodeposition was applied in the potential range of -0.10 to +0.80 V at a scan rate of 50 mVs^{-1} for 50 cycles.

Methanol Oxidation Analysis

The electrochemical properties of the prepared Pt-supported electrode (PGE/3.25mMPt@PDiAzBiPhBiTyOx) was tested form methanol oxidation, which was measured in a 0.5 M CH_3OH + 0.5 M H_2SO_4 solution by cyclic voltammetry, over a potential range of -0.30, +1.00 V with a scan rate of 50 mVs^{-1}, CHR was taken at 0.50 V potential for 300 seconds and EIS was taken between 10^{-2} and 10^{4} frequency range.

Results and Discussion

Electrochemical preparation and characterization of PGE/PDiAzBiPhBiTyOx

PGE/PDiAzBiPhBiTyOx was prepared by forming PDiAzBiPhBiTyOx on PGE using CV technique. The optimization measurement were utilized to determine the effect of potential range, scan rate and acid concentration on the preparation of the electrodes. Firstly, PDiAzBiPhBiTyOx films were formed on PGE carrying out different potential ranges at $50mVs^{-1}$ for 10 cycles. Single cycle voltammograms of the electrodes were recorded in ACN solution which contains 0.1M TBAP in the potential range where polymerization was done at $50mVs^{-1}$. The highest anodic peak current was obtained for the potential range between +0.20 and +2.10V (Figure 4a). Different scan rates were applied to determine the optimum scan rate. Thus, films were formed in the ACN solution which contains 0.10M TBAP+ 1.00×10^{-4}M on PGE in the potential range between +0.20 and +2.10V for 10 cycles. The highest current was obtained for $30mVs^{-1}$ from single cycle voltammograms (Figure 4b). In order to examine the effect of acid concentration on PDiAzBiPhBiTyOx formation, measurements were conducted by changing the $HClO_4$ concentration and taking 40 cycles at 30 mV in the potential range of +0.20 to +2.10V. Single cycle voltammograms of the electrodes were recorded under the same conditions. The highest current was obtained for 0.03M acid from single cycle voltammograms (Figure 4c). According to optimization measurements, optimum conditions for PGE/PDiAzBiPhBiTyOx electrode were found using CV in the potential range between +0.20 and +2.10V for 40 cycles at $30mVs^{-1}$ in ACN which contains 1.00×10^{-4}M monomer, 0.10 M TBAP and 0.03M $HClO_4$.

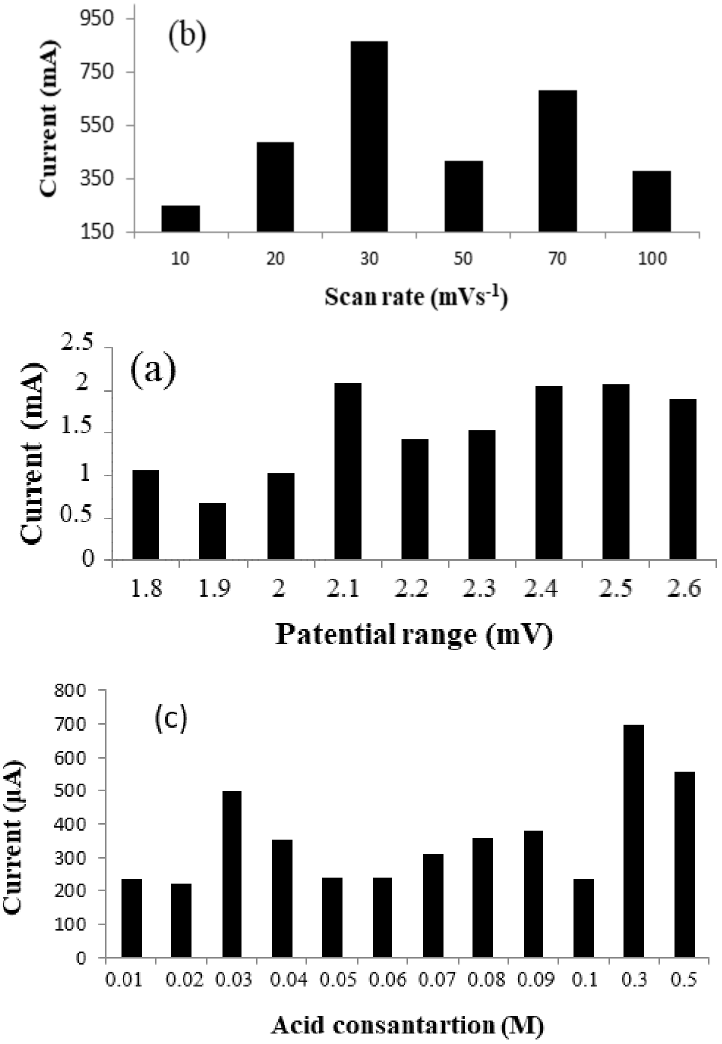

Figure 4. The effect of (a) potential range, (b) scan rate and (c) acid consantration on the formation of PDiAzBiPhBiTyOx on PGE at a scan rate of $30mV s^{-1}$ in ACN which contains 1.00×10^{-4}M monomer, 0.10 M TBAP

DiAzBiPhBiTyOx monomer was polymerized on the PGE electrode under optimum conditions determined by the CV method (in the potential range of +0.20V to +2.10V, scan rate of $30mVs^{-1}$ for 40 cycles). The multi-cycle voltammogram of the electropolymerization and the voltammograms of the first and last cycles are given in Figure 5 respectively.

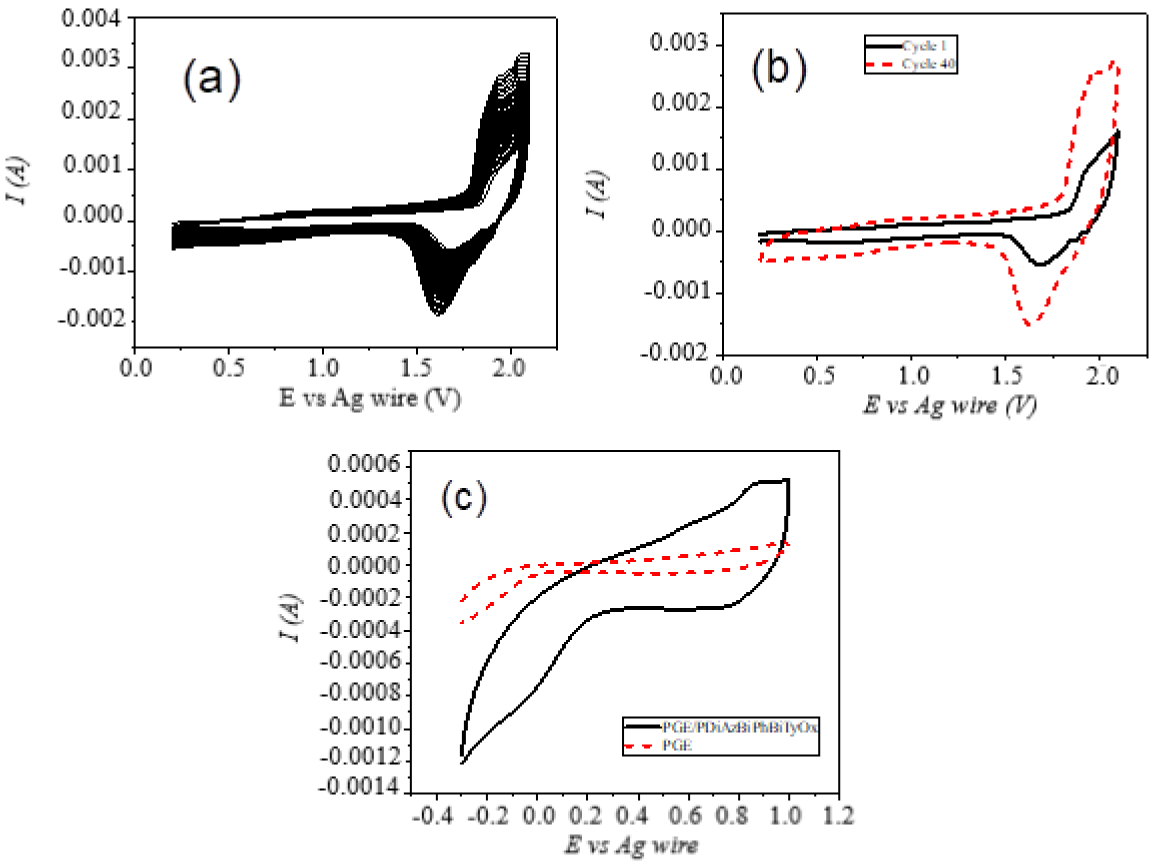

Figure 5. Cyclic voltammograms of PDiAzBiPhBiTyOx polymer film (a) 40 cycles, (b) first and last cycle (c) electrochemical characterization of PGE and PGE/PDiAzBiPhBiTyOx at a scan rate of 50mVs^{-1} in monomer free solution

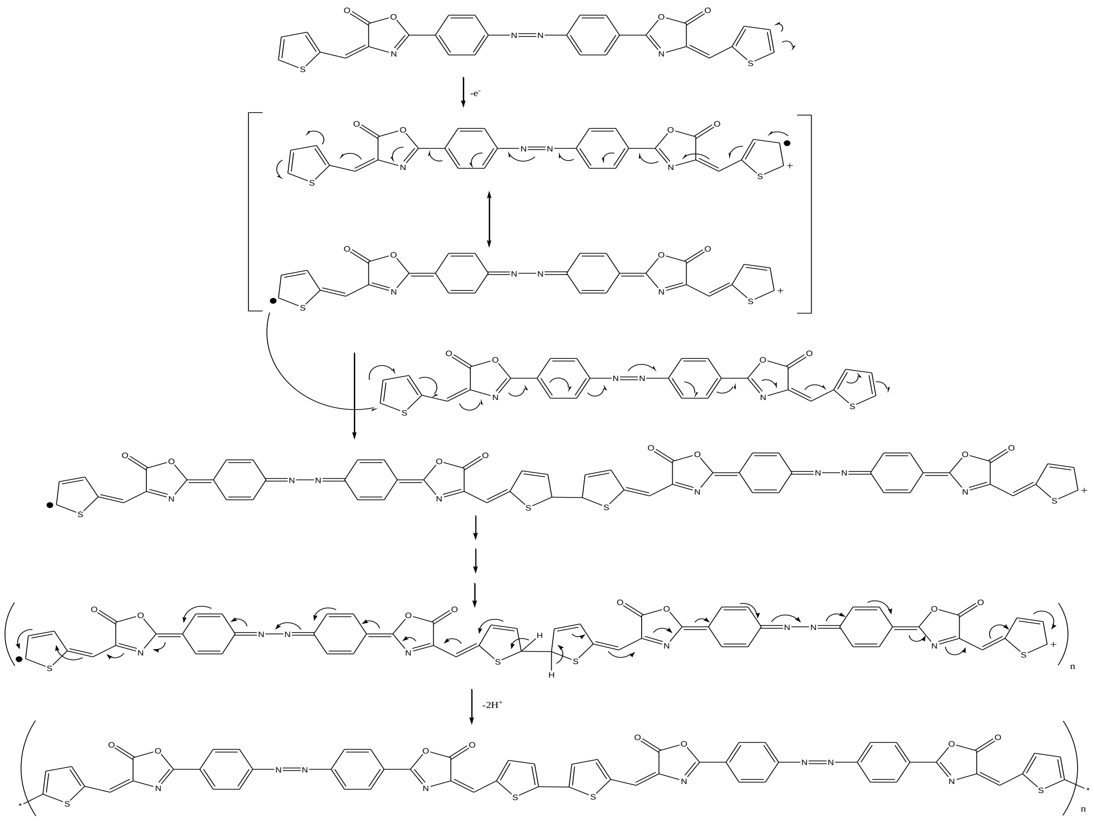

Figure 6. Proposed polymerization mechanism of DiAzBiPhBiTyOx

During polymerization process of DiAzBiPhBiTyOx monomer on PGE by CV method, recorded first cycle was belong to oxidation of monomer. The oxidation peak of the monomer (forward peak) was around +1.80V (+915µA) and the reduction peak (backward peak) was observed around +1.60V (-533µA) in the first cycle. In the last cycle, forward and backward peaks can be seen around +1.95V (at +2.560 mA) and +1.62V (-1.514mA) potentials, respectively. As the number of loops increases, the oxidation peak current increases significantly, indicated that the modified PGE electrode has a higher capacitance. This shows that the amount of monomer decreases in the solution medium, therefore, while the transferred ions decrease, polymer is formed on the electrode surface. In addition, the increase in current with the number of cycles proves that the modified electrode has higher capacitance than the PGE electrode (Fu et al., 2012; Lai et al., 2011; Montilla et al., 2011;Data et al., 2014). The polymer mass was determined as 0.24mg/cm^2 by a precision balance after keeping under reduced pressure. Proposed polymerization mechanism of DiAzBiPhBiTyOx is given in Figure 6.

Electrochemical characterization of PGE and PGE/PDiAzBiPhBiTyOx electrodes were investigated in the potential range of -0.30 V to +1.00 V at 50 mVs^{-1} scan rate, in 10 ml of ACN solution containing 0.10 M TBAP and 0.05 M $HClO_4$ by CV method (Figure 5.c). According to voltammograms, it is seen that the PGE/PDiAzBiPhBiTyOx has higher current value than the PGE electrode. As a result, it can be said that the PGE/PDiAzBiPhBiTyOx electrode has a higher surface area than the PGE electrode, therefore it has higher electrical conductivity and specific capacitance values (Li et al., 2010; Chen et al., 2006).

Platinum Electrodeposition and Electrochemical Characterization of PGE/ PDiAzBiPhBiTyOx

The optimum amount of catalyst (Pt) to be used with the polymer support for methanol oxidation was determined. The PGE/PDiAzBiPhBiTyOx electrode surface was doped with Pt in the potential range of -0.10 V to +0.80 V for 25 cycles at 50 mVs^{-1} in 10 ml distilled water containing 0.50 M H_2SO_4 and 3mM $H_2PtCl_6.6H_2O$ as 3.25, 3.50 and 3.75 mM. Obtained electrodes described as PGE/3mMPt@PDiAzBiPhBiTyOx, PGE/3.25mMPt@PDiAzBiPhBiTyOx,PGE/3.50mMPt@PDiAzBiPhBiTyOx,PGE/3.75mMPt@PDiAzBiPhBiTyOx, respectively. Single-cycle voltammograms of the electrodes were taken in 10 ml distilled water containing 0.50 M H_2SO_4 and 0.50 M CH_3OH at the scan rate of 50 mVs^{-1}. The optimum catalyst density was determined by electrochemical characterization of modified electrodes doped with platinum at different densities using the CV method. The obtained results are given as CV voltammograms and, current value graphic in Figure 7a and 7b, respectively.

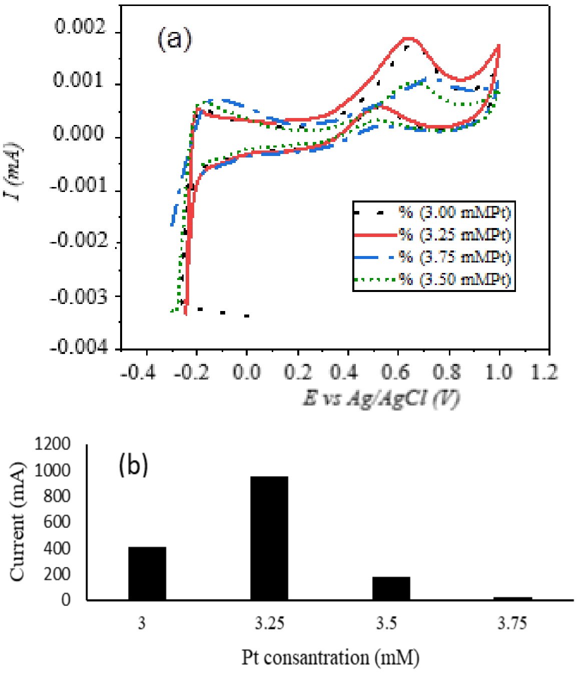

Figure 7. (a) The cyclic voltammograms of Pt density effect, (b) graph of current values versus pt density on PGE/Pt@PDiAzBiPhBiTyOx

In addition, the electrochemical active surface area (ECSA) values of the modified electrodes were calculated using the data obtained from the integration of single-cycle voltammograms in 10ml distilled water containing

0.50M H_2SO_4 and 0.50M CH_3OH. Atomic adsorption of hydrogen which obtained from voltammograms was used to estimate the surface area of the catalysts. It can be said that the presence of cathodic and anodic peaks in the potential range of -0.15V and 0.20V is due to H-adsorption and H-desorption in acidic medium. The ECSA value of the polymer supported catalyst can be calculated using the Q_h charge value from H desorption (Liu et al., 2016). ECSA values was calculated by the following equation;

$$ECSA = \frac{QH}{m.c} \qquad \text{(Eq. (1))}$$

Where; Q_H is the charge of hydrogen desorption ($mCcm^{-2}$), m is the weight of deposited catalyst on the electrode ($mgcm^{-2}$) and c is the charge required to oxidize a single layer of hydrogen on the polymer supported catalyst, respectively. The calculated ECSA values for each modified electrode are given at Table 1.

Table 1. Calculated ECSA values for each modified electrode

Modified Electrode System	ECSA value calculated for the PGE modified electrode (m^2/g)
PGE/3mMPt@PDiAzBiPhBiTyOx	89.571
PGE/3.25mMPt@PDiAzBiPhBiTyOx	196.437
PGE/3.50mMPt@PDiAzBiPhBiTyOx	5.126
PGE/3.75mMPt@PDiAzBiPhBiTyOx	140.300

It can be seen that the ECSA value of the PGE/3.25mMPt@PDiazBiPhBiTyOx electrode is quite high when compared to the available literature (Liu et al., 2016; Karim & Yahya, 2018; Tian et al., 2017). The modified electrode systems in which Pt is used as a catalyst form methanol oxidation and the ECSA values compiled from the literatüre are given in Table 2.

Table 2. Comparison of ECSA values of modified electrode systems using Pt as a catalyst in the oxidation of methanol according to available literature

Electrode/ Catalyst System	ECSA (m^2/g)	Reference
Pt/C	38.900	(Liu et al., 2016)
Pt/rGO	8.700	(Liu et al., 2016)
Pt/GO	64.480	(Karim & Yahya, 2018)
Pt/CNT	33.680	(Karim & Yahya, 2018)
PtAu/rGO	13.120	(Karim & Yahya, 2018)
PtFe/rGO	18.000	(Karim & Yahya, 2018)
P/CNT@TiCoN	55.900	(Karim & Yahya, 2018)
Pt/CNTs@TiN	50.500	(Karim & Yahya, 2018)
Pt/G	45.800	(Tian et al., 2017)

The optimum catalyst amount was determined as 3.25 mM as can be seen from Figure 7a, b and Table 1. According to this results, the methanol oxidation response of the PGE/3.25mMPt@PDiAzBiPhBiTyOx modified electrode was investigated by CV, CHR and EIS methods. The current and resistance values obtanined from these methods in aqueous solution with and without methanol are given in Table 3 comparatively.

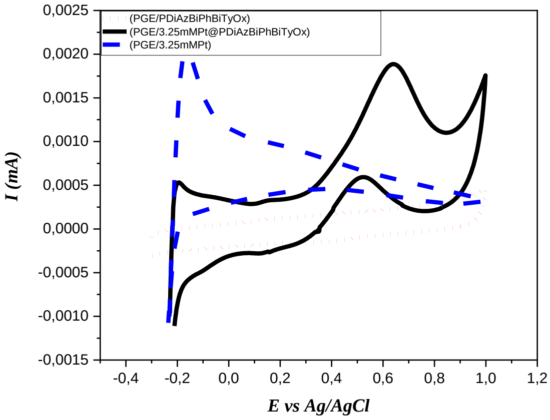

Figure 8. Cyclic voltammograms of PGE/3.25mMPt@PDiAzBiPhBiTyOx, PGE/PDiAzBiPhBiTyOx and PGE/3.25mMPt in methanol containing 0.5M H_2SO_4 aqueous solution at scan rate $50mVs^{-1}$

The methanol oxidation performance of the PGE/3.25mMPt@PDiAzBiPhBiTyOx electrode was compared with single cycle voltammograms of PGE/PDiAzBiPhBiTyOx and PGE/3.25mMPt in 0.50 M H_2SO_4 solution with and without methanol. As can be seen from Figure 8, the CO_2 peak belonging to the methanol oxidation of the PGE/3.25mMPt@PDiAzBiPhBiTyOx electrode has the highest current value. The CO_2 peak, which is expected to be observed in the 0.60 - 0.80V potential range, is not evident in the single-cycle voltammograms of the PGE/PDiAzBiPhBiTyOx and PGE/3.25mMPt electrodes.

The methanol oxidation response of the PGE/3.25mMPt@PDiAzBiPhBiTyOx electrode was investigated in with and without methanol containing 0.50 M H_2SO_4 aqueous solutions. According to the CV method, it was observed that the CO2 peak current increased in the methanol solution. Maximum peak currents were obtained at with and without methanol 0.50 M H_2SO_4 aqueous solutions as 350 µA and 955.2 µA, respectively (Figure 9a).

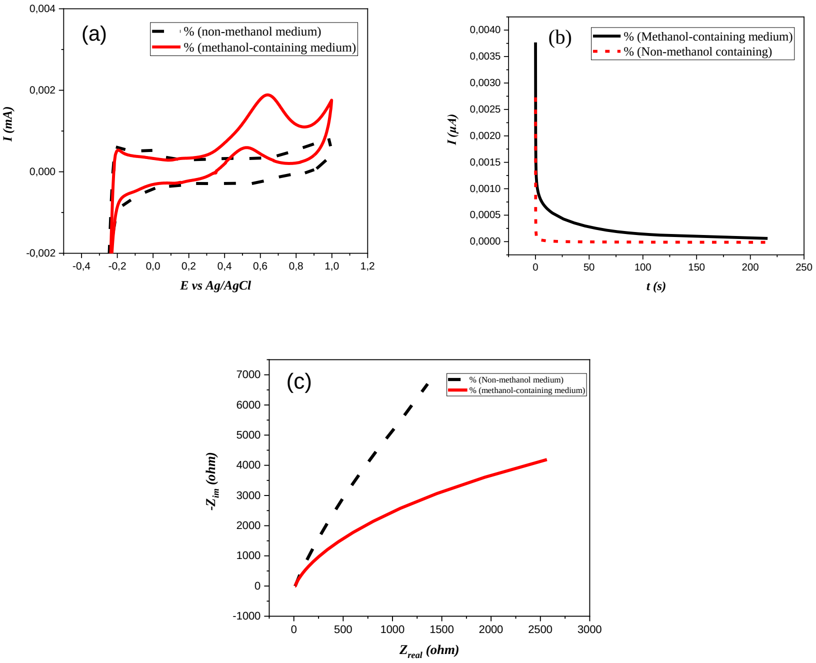

Figure 9. Graphical comparison of methanol oxidation behavior of PGE/3.25mMPt@DiAzBiPhBiTyOx electrode in aqueous solution with and without methanol using by a) CV, b) CHR, c) EIS methods

The methanol oxidation performance of PGE/3.25mMPt@DiAzBiPhBiTyOx conductive polymer supported catalyst system was investigated by chronoamperometry method in aqueous solution with and without methanol. According to the obtained results, for PGE/3.25mMPt@DiAzBiPhBiTyOx system the current value was recorded at 56.15µA in methanol-free medium, while it was recorded 148.90µA in methanol-containing medium (Figure 9b) The sharp current decrease was seen in chronoamperograms, can be explained by the formation of intermediate products such as CO etc. Stabilization of PGE/3.25mMPt@PDiAzBiPhBiTyOx modified electrode at higher current in methanol containing aqueos medium shows that it has the higher tolerance limit against CO poisoning (Xing, 2010; Prabakar, 2016).

The methanol oxidation performance of the PGE/3.25mMPt@DiAzBiPhBiTyOx conductive polymer supported catalyst system was investigated by EIS method. Nyquist plot of phase angle-log Freq and log Z-log Freq obtained in aqueous solution containing 0.05M H_2SO_4, 0.50M CH_3OH for 1 hour exposure time for PGE/3.25mMPTDiAzBiPHBiTyOx electrode and corresponding Bode plots are given in Figure 9c. R values calculated from Bode plots were obtained in in aqueous solution with and without methanol as 3.223kohm and 6.758kohm, respectively.

Resistance is an important performance indicator in energy storage devices, and it can be said that the performance of the low resistance device is higher (Morali & Erol, 2020). The resistance value obtained from Nyquist curves of the PGE/3.25mMPTDiAzBiPHBiTyOx electrode in aqueous methanol solution show that, because of methanol oxidation performance of this electrode, its use in methanol fuel cells is promising.

Table 3**.** Comparison of methanol oxidation behavior of PGE/3.25mMPt@DiAzBiPhBiTyOx electrode in aqueous solution with and without methanol using CV, CHR, EIS methods.

Method/Parameter/Unit	0.05 M H_2SO_4 PGE/3.25mMPt@PDiAzBiPhBiTyOx
CV/ I/ µA	350
CHR/ I/ µA	67.890
EIS/ R/ Ω	49.510
	0.05 M H_2SO_4 + 0.50 M CH_3OH
CV/ I/ µA	955.200
CHR/ I/ µA	58.260
EIS/ R/ Ω	$1x10^{-6}$

In addition, the theoretical specific capacitance (C_s) value was calculated from the Nyquist plot obtained from 0.50M H_2SO_4 aqueous solution containing 0.50M CH_3OH (aqueous solution with methanol) of the modified electrode (Eq. (2)). The inverse of the slope, obtained from the Z_{im} plot drawn against the $1/(2\pi f)$ value, calculated from the frequency value which was obtained from this curve gives the capacitance value (Xing et al., 2010). Methanol fuel cells can transfer energy as much as the power they store while being charged in the discharge process. Accordingly, as the Cs value of the modified electrode system, which is related to the energy storage capacity, increases, the energy storage capacity of the methanol fuel cell will also increase (Snook et al. 2011; Li et al., 2010).

$$C_s = -\frac{1}{2\pi f Zim.m} \qquad \text{(Eq. (2))}$$

The calculated theoretical Cs values of the PGE/3.25mMPt@PDiAzBiPhBiTyOx electrode in aqueous medium with and without methanol are 3.8613 and $3x10^{-4}Fg^{-1}$ respectively. Therefore, the higher specific capacitance of the modified electrode in aqueous solution with methanol is an advantage for energy storage systems. The Cs value of the PGE electrode calculated in the aqueous solution with methanol is higher than in the methanol-free one, shows it's properity for use in methanol fuel cells.

Morphological and Structural Characterization of Pt Doped PGE/ PDiAzBiPhBiTyOx

The methanol oxidation performance of the modified electrode was not change in direct proportion to the amount of catalyst doped on the catalyst support layer according to the results obtained by the electrochemical measurements (CV, CHR and EIS). This can be related to the fact that the maximum amount of catalyst that catalyst support can take, is limited. This suggestion supported by FESEM/EDS analyses.

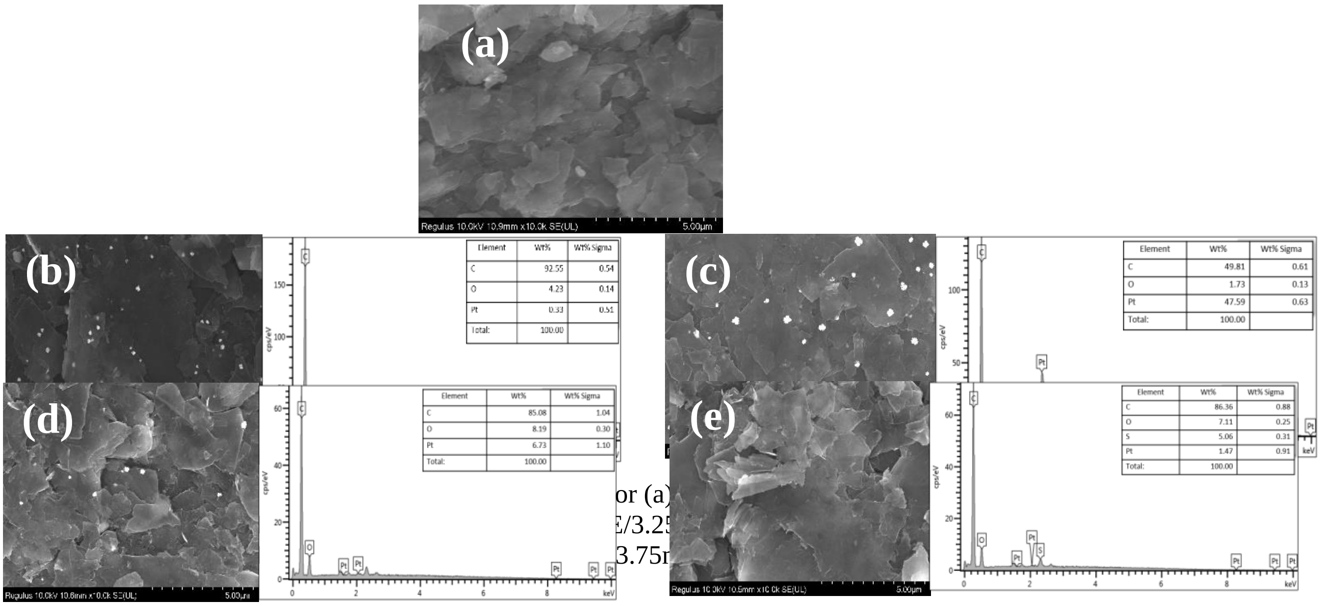

Figure 10 shows typical SEM images and EDS obtained for PGE/PDiAzBiPhBiTyOx, PGE/3.00mMPt@PDiAzBiPhBiTyOx, PGE/3.25mMPt@PDiAzBiPhBiTyOx, PGE/3.50mMPt@PDiAzBiPhBiTyOx and PGE/3.75mMPt@PDiAzBiPhBiTyOx electrodes. For comparison, micrographs of the five modified electode systems, obtained at the same magnification (X10.k).

Figure 10(a) shows conductive polymer coated PGE. A porous surface morphology is desirable for electrodes used for fuel cell applications, as the porous structure morphology provides easy access for Pt ions to be used as catalysts to enter the electrode/electrolyte interface.

Figure 10 (b, c, d and e) shows SEM/EDS images of different Pt doped electrodes that named as PGE/3.00mMPt@PDiAzBiPhBiTyOx, PGE/3.25mMPt@PDiAzBiPhBiTyOx, PGE/3.50mMPt@PDiAzBiPhBiTyOx, PGE/3.75mMPt@PDiAzBiPhBiTyOx, respectively. As can be seen from the figures, it is clear that PGE/PDiAzBiPhBiTyOx is doped on its surface. It is seen that the concentration of Pt particles on the surface is the highest on the surface of PGE/3.25mMPt@PDiAzBiPhBiTyOx, while the least on the surface of the PGE/3.75mMPt@PDiAzBiPhBiTyOx electrode.

Element contents for Pt catalyst of all modified electrode systems were determined by EDS detection. The EDS results show that different amounts of Pt are doped on the surface of the PGE/PDiAzBiPhBiTyOx electrodes. Pt metal loadings were 0.33, 47.59, 6.73 and 1.47 wt.% in PGE/3.00mMPt@PDiAzBiPhBiTyOx, PGE/3.25mMPt@PDiAzBiPhBiTyOx, PGE/3.50mMPt@PDiAzBiPhBiTyOx, PGE/3.75mMPt@PDiAzBiPhBiTyOx respectively.

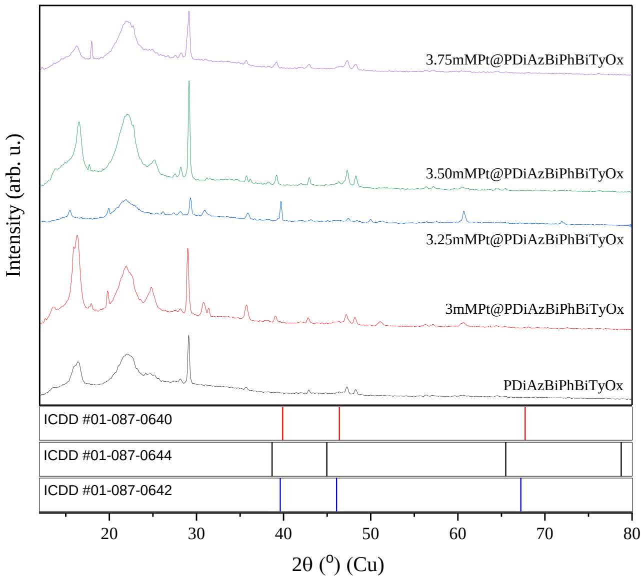

Figure 11. XRD patterns of PGE/PDiAzBiPhBiTyOx and Pt doped PGE/PDiAzBiPhBiTyOx XRD patterns in the range of 2θ=10-80° and characteristic Pt patterns (ICDD # 01-087-0640, ICDD # 01-087-0644, ICDD # 01 087-0642) to determine the presence of Pt within the structure of PDiAzBiPhBiTyOx and Pt@PDiAzBiPhBiTyOx are given in Figure 11.

As it can be seen from the Figure 11, two broad bands observed around 12° and 22° in the 2θ=10-40° region. XRD patterns are known to belong to the PDiAzBiPhBiTyOx polymer and these regions are known to correspond to different structures belonging to C (ICDD # 00-050-0926) and S (ICDD # 00-042-1278) and in addition, the sharp and intense peak around 29° is known to correspond to N (ICDD # 96-901-477).

In XRD pattern of PDiAzBiPhBiTyOx, the absence of a distinct diffraction peak around 2θ=39°, which was observed in other samples, indicated the presence of Pt in Pt@PDiAzBiPhBiTyOx samples. These peaks in the XRD patterns correspond to Pt that has crystalline parameters belonging to cubic crystal system (a=b=c=3.911Å) in cubic Fm-3m space group.

According to three different reference patterns, cubic Pt has diffraction peaks within the range of 38.5-40°, 45-46.5°, 65.5-67.5° and also at 78.6°. However, among the peaks seen in the patterns of Pt@PDiAzBiPhBiTyOx samples, the peak in the 2θ=39° de (111) orientation is observed as the dominant peak, the diffraction peak belonging 2θ=39° (200) is barely present. In reference patterns belonging to cubic Pt, 65° (220) and 78° (311) peaks that are known to have low intensity could not be encountered (Arbizzani et al., 2008). The most distinct and intense diffraction peak (111) at 2θ=39° was observed in the pattern belonging to PGE/3.25mMPt@PDiAzBiPhBiTyOx sample.

Conclusion

PDiAzBiPhBiTyOx, a new thiophene-based conductive polymer, was prepared and investigated for the first time in this study as a catalyst support material for Pt catalyst to be used directly in methanol fuel cells. Methanol oxidation performance of modified electrode (PGE/PDiAzBiPhBiTyOx) was tested by using CV, CHR and EIS methods. In addition, theoretical calculations were done using the values obtained from these methods. ECSA and C_s values were obtained as a result of theoretical calculations. PDiAzBiPhBiTyOx monomer, which is the Th derivative synthesized for this study, is oxidized at a lower potential than Th and can be polymerized more easily. The fact that the calculated ECSA values for PDiAzBiPhBiTyOx, which is used as a catalyst support for Pt, are higher than that of PTh and Pt in the literature, indicates that catalytic activity of is PDiAzBiPhBiTyOx also high. Moreover, the new modified electrode system proposed in this study was also effective in elimination of CO poisoning. Another novelty of this study in terms of literature is that C_s value, which is related to the energy storage capacity of the modified electrode systems, was calculated for the first time in this study according to EIS analysis results. This approach can be considered as a new proposal to the literature for future researches on methanol fuel cells. Electrochemical characterization methods show that the electrode with the best methanol oxidation performance is the 3.25mM Pt doped modified electrode system. The structural and surface analysis results of these electrodes with FESEM/EDS and XRD also show that the optimum amount of Pt added to the catalyst support is 3.25mM.

Scientific Ethics Declaration

The authors declares that the scientific ethical and legal responsibility of this article published in EPSTEM Journal belongs to the authors.

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