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Araştırma Makalesi / Research Article

Conducting poly(thionine) film as a support material for Pt particles: Electrocatalytic activity towards methanol oxidation

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Abstract

Facile synthesis of Pt@PTH catalyst on pencil graphite electrode for electrooxidation of methanol was described. Influence of experimental conditions on the performance of the catalyst system was studied by recording cyclic voltammograms of methanol solution containing H_2SO_4 as the supporting electrolyte. The catalyst prepared under optimum conditions was physically characterized using Scanning Electron Microscopy, Energy Dispersive X-Ray Dispersion and Elemental Mapping methods. Electrochemical characterization was performed by cyclic voltammetry in H_2SO_4 solution.

Keywords: Poly(thionine), Conducting polymer, Pt particles, Methanol oxidation, Electrocatalysis

İletken poli(tiyonin) filminin Pt partikülleri için destek malzemesi olarak kullanılması: Metanol yükseltgenmesine karşı elektrokatalitik aktivite

Öz

Bu çalışmada kalem grafit elektrot üzerinde Pt@PTH katalizör sisteminin sentezi ve metanolün elektroyükseltgenmesi için kullanımı anlatılmaktadır. Deneysel koşulların katalizör sisteminin performansı üzerine olan etkisi, destek elektrolit olarak H_2SO_4 içeren metanol çözeltisinin dönüşümlü voltamogramları kaydedilerek saptanmıştır. Optimum koşullarda hazırlanan katalizörün fiziksel karakterizasyonu Taramalı Elektron Mikroskobu, Enerji Dağılımlı X-Işınları Spektroskopisi ve Elementel Haritalama ile gerçekleştirilmiştir. Elektrokimyasal karakterizasyon için ise H_2SO_4 çözeltisinde dönüşümlü voltametri yöntemi kullanılmıştır.

Anahtar kelimeler: Poli(tiyonin), İletken polimer, Pt partikülleri, Metanol yükseltgenmesi, Elektrokataliz

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1. Introduction

In recent years, energy-related research has focused especially on renewable energy sources, due to the rapidly increasing need for energy and the decrease in available energy resources. Therefore, fuel cells are of great concern as they are regarded as promising energy sources for the future to replace the traditional systems that use fossil fuels (Sönmez Çelebi 2016). In theory, a fuel cell using hydrogen as the fuel is the cleanest renewable energy source as it has zero toxic waste (Ong et al 2017). However, as methanol is easier to transport and store when compared with hydrogen and its energy density is higher, importance of direct methanol fuel cell (DMFC) among the studies on fuel cells has been increased dramatically in the last few decades (Sönmez Çelebi et al 2021; Li & Faghri 2013). On the other hand, electrooxidation of methanol is a slow and complex reaction in which many intermediates occur. Moreover, methanol crossover, which can be defined as diffusion of methanol from the anode to the cathode through the membrane, is one of the most notable technical barriers of DMFCs. Therefore, using an effective catalyst is crucial for obtaining optimum performance from DMFCs. The most commonly used catalysts for oxidation of methanol in acidic environment are Pt-based ones (Sönmez Çelebi et al 2008; Zhou et al 2010; Selvaraj & Alagar 2007).

The catalytic activity of the Pt particles in the electrocatalytic oxidation of methanol is particularly dependent on the support material used and the surface properties of the catalyst. Therefore, dispersing large surface area Pt particles on a suitable support material in order to develop the most efficient catalyst provides a significant increase on the activity of the catalyst. The use of conductive polymers as support material has been increasing in recent years (Lin et al 2012; Sönmez Çelebi & Pekmez 2017; Mondal & Malik 2016). The advantages of conductive polymers over other support materials are that they are mainly permeable to electroactive species, can be easily modified by different methods, and can easily be coated on many surfaces. Since these polymers have a porous structure and high surface area besides their high conductivity, they are ideal support materials for dispersion of metal particles. Thionine (TH) is a metachromatic dye belonging to the phenothiazine family and is a planar molecule having symmetrical -NH_2 groups on both sides. It dissolves easily in water and ethanol. Thionine is an excellent electronic mediator and has electrocatalytic activity as well. Electrochemical synthesis of poly(thionine) (PTH) can be performed by both cyclic voltammetry (CV) and constant potential electrolysis (Yang et al 1999; Ferreira et al 2006). In the literature, PTH has been successfully applied as a support material for fabrication of nanometal based sensor studies (Liu et al 2008; Liu et al 2018).

In this study, we prepared a Pt catalyst system using PTH conductive polymer as the support material and tested the efficiency of the obtained Pt@PTH catalyst for the electrocatalytic oxidation of methanol. A disposable pencil graphite electrode (PGE) has been used as the working electrode allowing the development of a catalyst system that is very inexpensive and easy to prepare. Optimization of the experimental conditions for the preparation of the Pt@PTH catalyst was done by recording the cyclic voltammograms of methanol solution in acidic medium. Characterization of the PTH supported Pt nanoparticles prepared under optimum conditions was done by electrochemical and physical methods.

2. Materials and Methods

Thionine acetate, H_2SO_4, K_2PtCl_4, and CH_3OH were obtained from Sigma-Aldrich and used as-received. Hydrazine solution was diluted from 80% hydrazine hydrate solution in water (Merck). All solutions were prepared using triple distilled water and purged with high purity nitrogen gas in order to remove the dissolved oxygen. All experiments were performed at ambient temperature.

Electrochemical experiments were recorded with CHI 600E electrochemical workstation. A three-electrode system glass cell was used with a pencil graphite electrode (PGE, area = 6.48 x 10^{-2} cm^2) as the working electrode. The connector of the PGE (0.5 mm HB Tombow) was a Tombow pencil. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum (Pt) wire was used as the counter electrode. Scanning electron microscopy (SEM) images and Energy Dispersive X-Ray Spectrum (EDS) were recorded with catalyst samples prepared on disposable PGE using JEOL model JSM-7001F.

3. Results and Discussion

The Pt@PTH catalyst system was prepared on the PGE via a simple procedure: (*i*) electrochemical formation of conducting PTH film on the electrode surface, (*ii*) dispersion of $PtCl_4^{2-}$ complex to the polymer matrix via cyclic voltammetric scans from aqueous K_2PtCl_4 solution, (*iii*) chemical or electrochemical reduction of the platinum complex. The methanol CV recorded with the catalyst system prepared under optimum experimental conditions is presented in Figure 1.

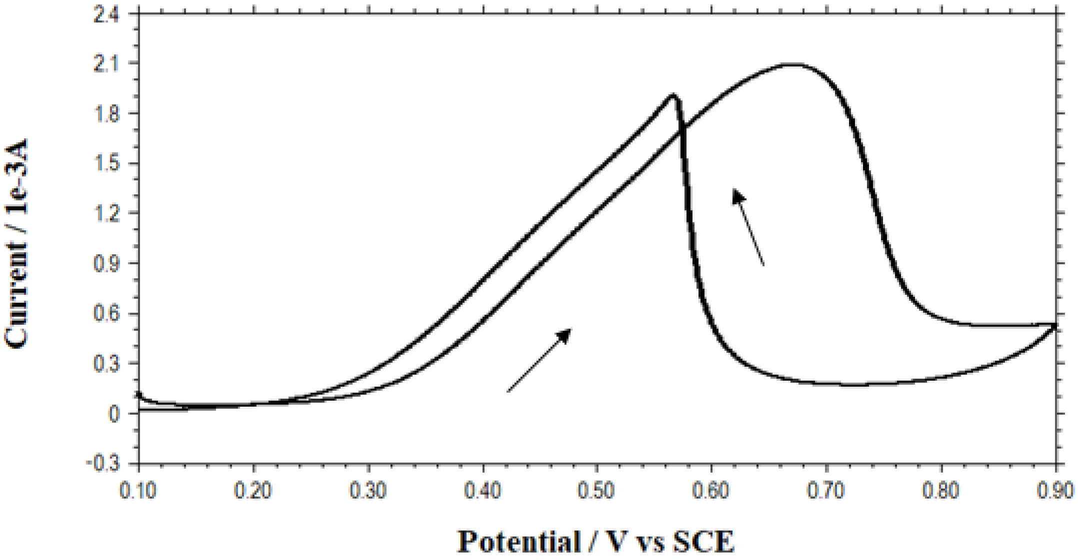


Figure 1 CV of 0.5 M CH_3OH solution containing 0.5 M H_2SO_4 recorded with Pt@PTH catalyst prepared under optimum conditions (Scan rate: 5 mV s^{-1})

3.1 Optimization of experimental parameters

In order to get the best performance from the catalyst system, we studied the optimization of the experimental parameters during the preparation of the Pt@PTH catalyst. For this purpose, CVs 0.5 M CH_3OH solution containing 0.5 M H_2SO_4 was recorded between potentials 0.1 – 0.9 V vs. SCE with a scan rate of 5 mV s^{-1}, and the oxidation peak current values were compared for different experimental conditions.

PTH film was electrodeposited onto the PGE via cyclic voltametric scans from 0.05 M thionine acetate solution containing 0.5 M H_2SO_4. The potential window was between potentials -0.2 V - +1.15 V vs. SCE (Figure 2a). Formation of the polymer film on the electrode surface was confirmed by CV of the resulting film in 0.5 M H_2SO_4 solution. Figure 2b indicates the formation of the polymer as the oxidation and reduction peaks are apart from the peaks of the monomer when compared with the peaks observed in Figure 2a. It is also worth noticing that the polymer is stable on the electrode surface as the oxidation and reduction peaks do not decrease in the polycyclic voltammogram.

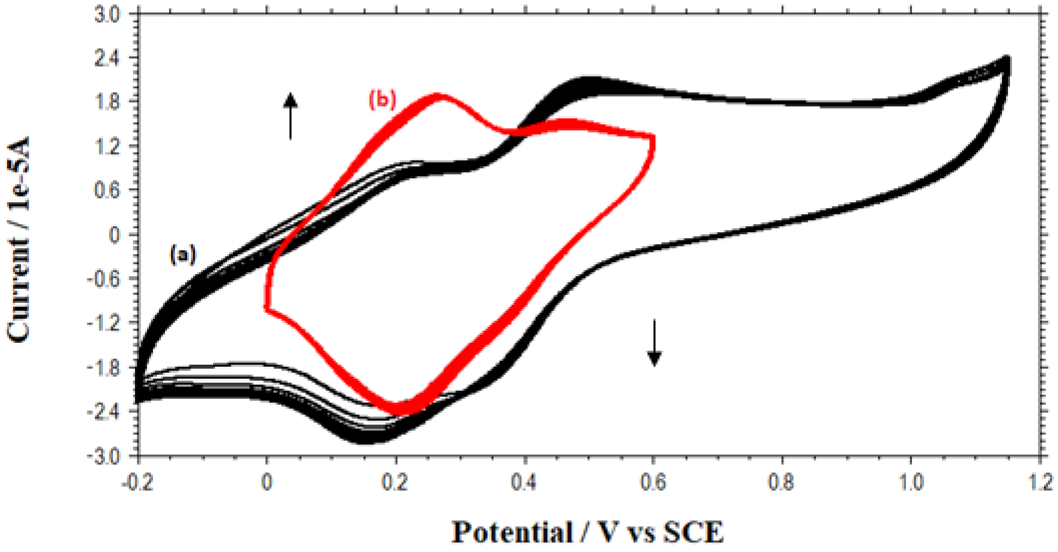


Figure 2 (a) Electrochemical formation of PTH film on PGE from 0.05 M thionine acetate solution containing 0.5 M H_2SO_4 (b) CV of PTH film in 0.5 M H_2SO_4 (Scan rate: 100 mV s^{-1})

In order to control the thickness of the polymer film, number of cycles performed during the CV in the monomer solution was used. Figure 3 compares the oxidation peak current values for 0.5 M CH_3OH solution recorded using polymers with different thicknesses. As clearly seen from the figure, maximum peak current was observed with the film prepared using 10 cycles.

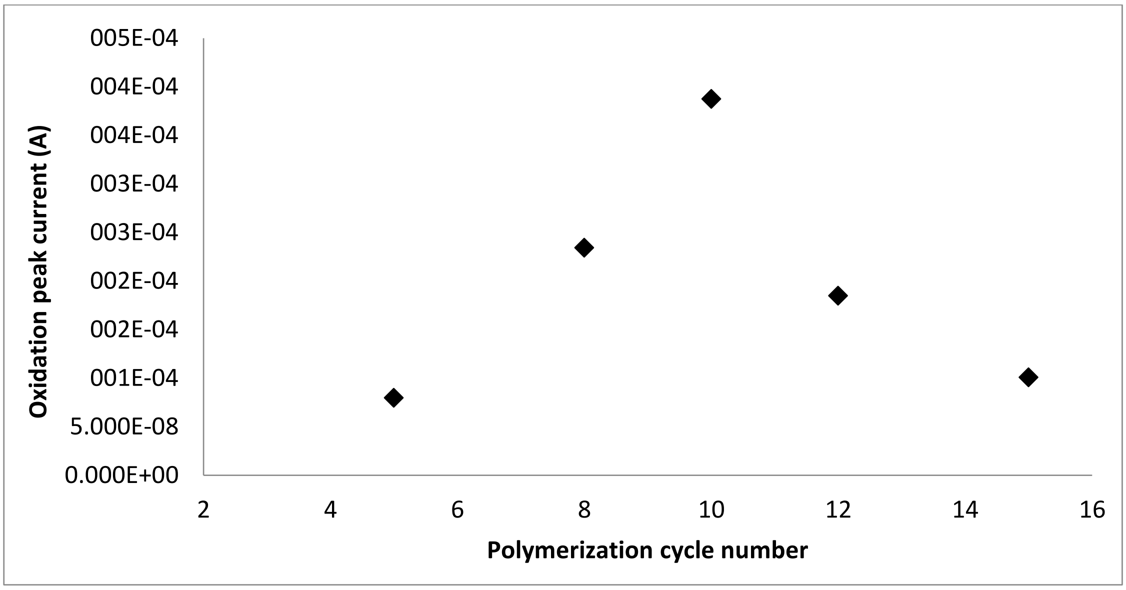
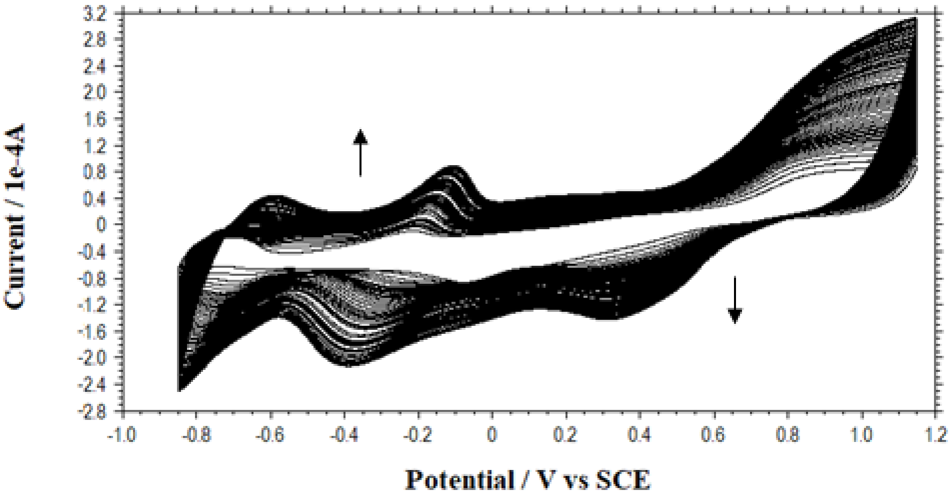


Figure 3 Influence of polymer film thickness on oxidation peak current of methanol

Amount of the Pt complex immobilized into the polymer film was controlled with the number of cyclic voltametric scans in the K_2PtCl_4 solution. A representative polycyclic voltammogram of Pt loading is given in Figure 4a. In figure 4b, influence of the Pt loading on the oxidation peak current of methanol is presented. As clearly seen from the plot of peak current vs. cycle number, best performance was obtained when the number of cycles in the Pt complex was 60.

(a)



(b)

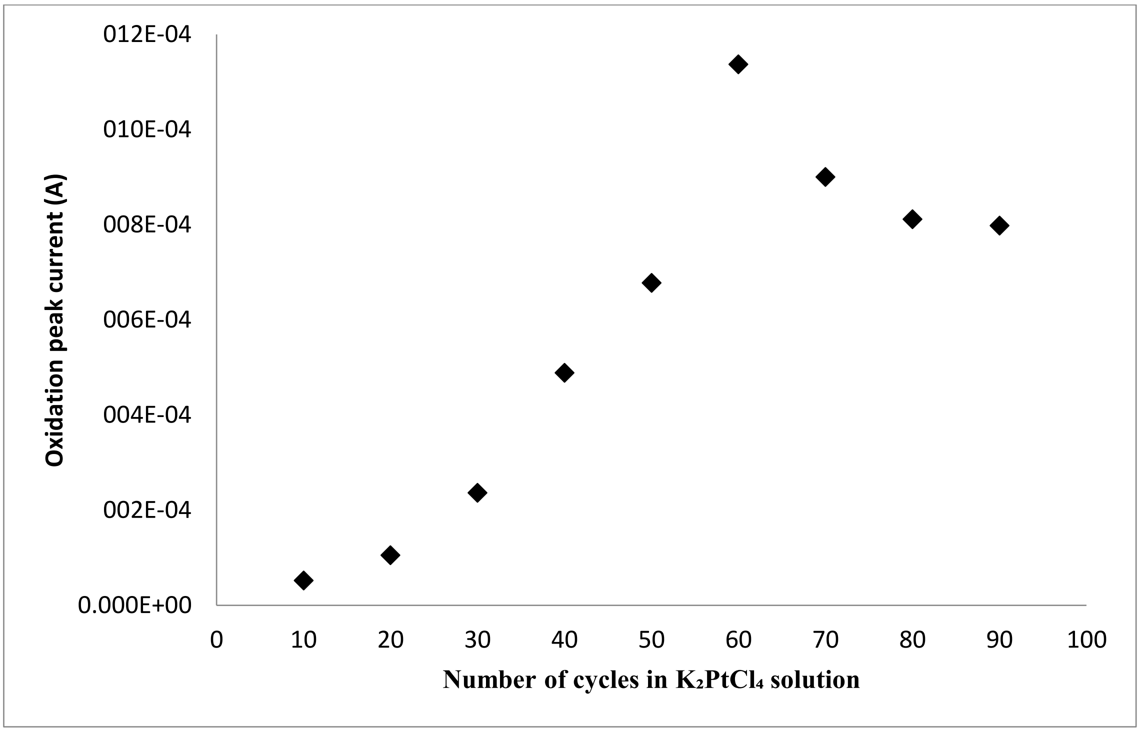


Figure 4 (a) Electrochemical loading of Pt complex onto the PTH coated PGE from 2 mM K_2PtCl_4 solution (Scan rate: 100 mV s^{-1}) (b) Influence of Pt loading on oxidation peak current of methanol

Electrochemical and chemical reduction methods were both optimized and compared for the reduction of $PtCl_4^{2-}$ complex immobilized into the polymer film. Constant potential electrolysis was used for electrochemical reduction in 0.5 M H_2SO_4 solution. Influence of both reduction potential and reduction time on the oxidation peak current of formic acid were studied (CVs not shown) and the maximum performance was obtained at 15 min electrolysis time at -0.3 V vs. SCE. Chemical reduction was performed in aqueous hydrazine solution by simply dipping the $PtCl_4^{2-}$ incorporated polymer film in stirred 0.1 M hydrazinium hydrate solution. The optimum reduction time for chemical reduction process were found as 30 min (CVs not shown). When the performance of the two reduction methods were compared, chemical reduction was superior according to the oxidation peak current values obtained (Figure 5).

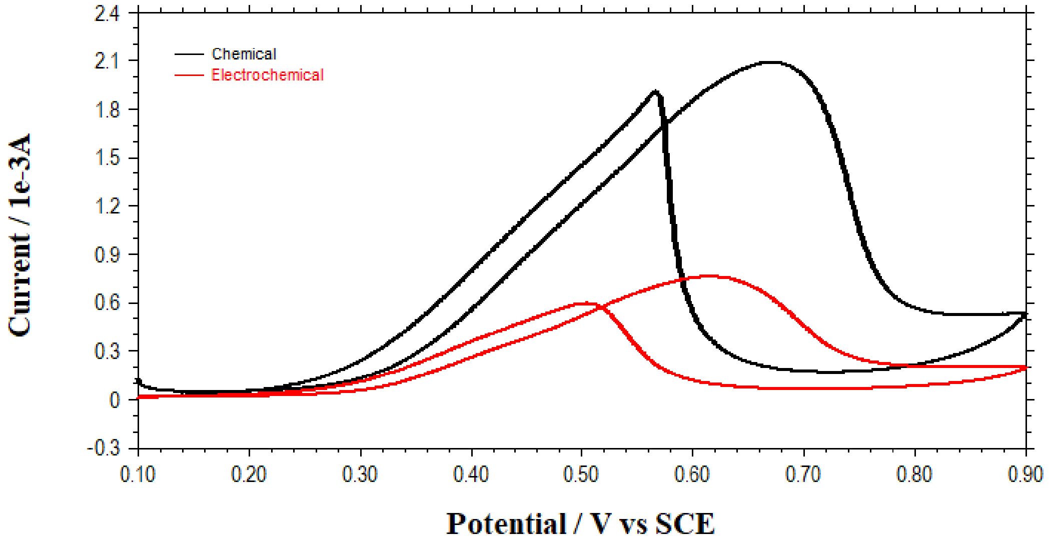


Figure 5 Comparison of electrochemical and chemical reduction methods for the reduction of Pt complex

3.2 Electrochemical characterization

For electrochemical characterization of the catalyst system, CV of 0.5 M H_2SO_4 solution was recorded using Pt@PTH coated PGE with different amounts of Pt loading (Figure 6). When the hydrogen adsorption/desorption peaks at the potential region 0.0 V – -0.25 V were compared, it was observed that the best performance was with 60 cycles of Pt loading. This behavior also supports the fact that the catalyst prepared under optimum experimental conditions has the maximum catalytic activity towards methanol oxidation.

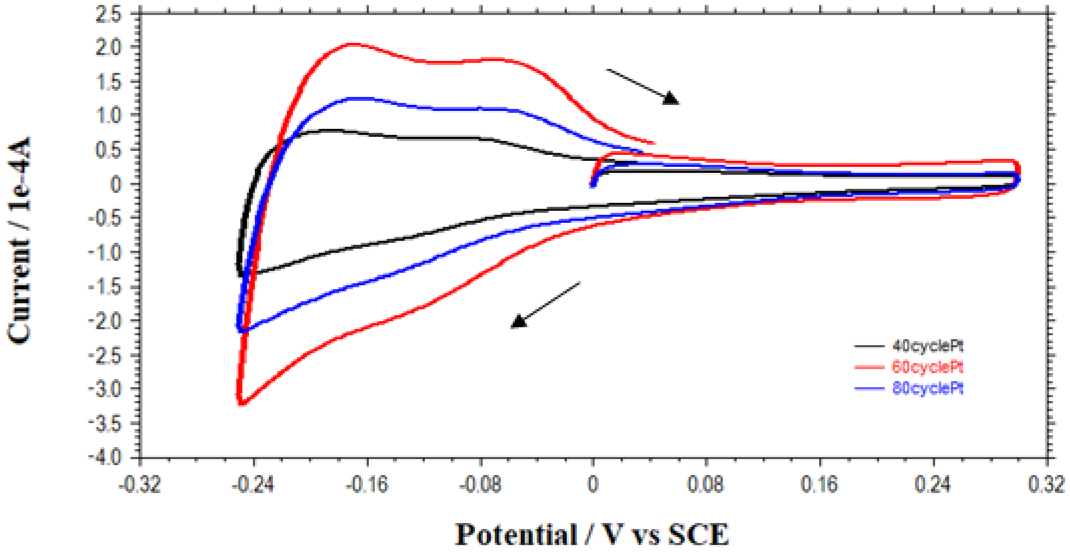


Figure 6 CVs of 0.5 M H_2SO_4 recorded with Pt@PTH catalysts with Pt loadings corresponding to 40, 60 and 80 cycles in K_2PtCl_4 solution (Scan rate: 100 mV s^{-1})

3.3 Physical characterization

In order to evaluate the morphological features of the catalyst, SEM images have been recorded. In Figure 7, SEM images of uncoated PGE, PTH coated PGE and Pt@PTH catalyst prepared on PGE are presented. It is seen from the SEM images that, PTH coating has been formed on the electrode surface and the Pt loading is well dispersed on the polymer composite film.

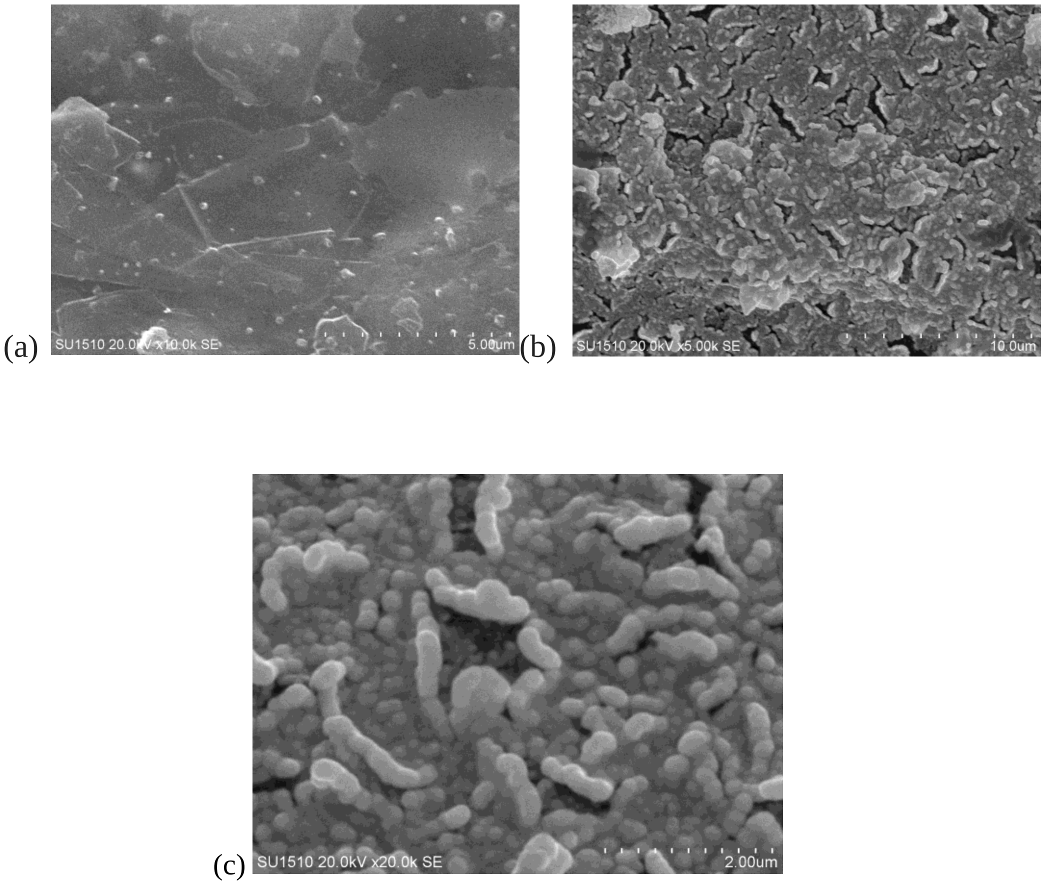
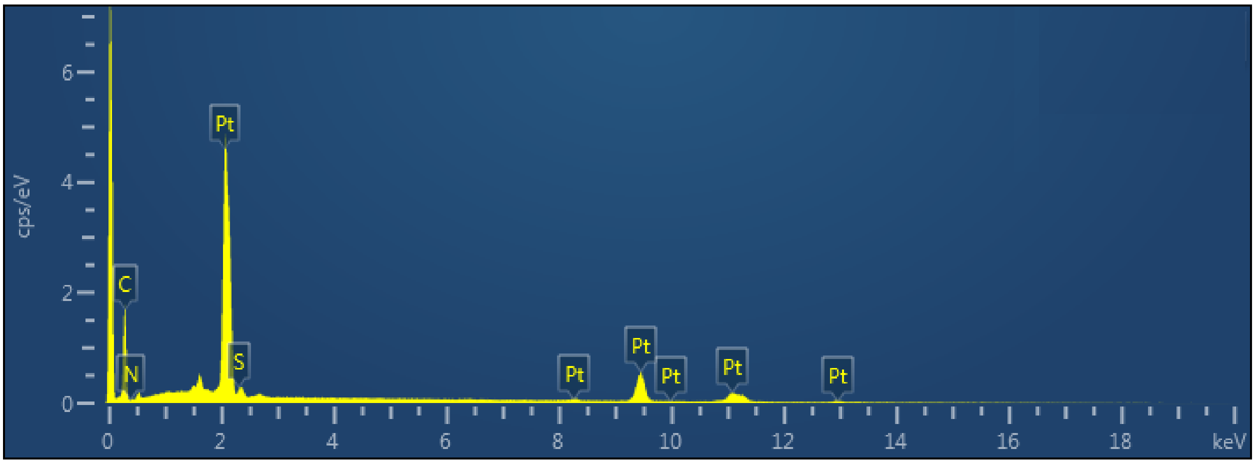


Figure 7 SEM images of uncoated (a) PGE, (b) PTH coated PGE and (c) Pt@PTH modified PGE

For further characterization of the catalyst, we present the EDX Spectrum and the elemental mapping profile of the catalyst system prepared under optimum conditions (Figure 8). The elemental mapping reveals that the catalyst system has an even distribution and the Pt particles and the polymer film has been well dispersed on the PGE surface.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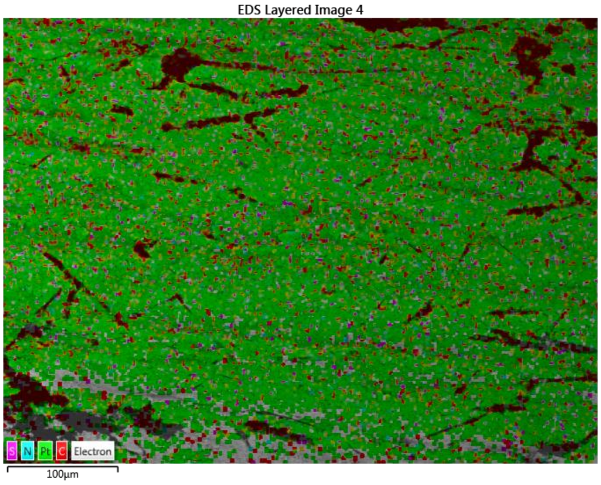
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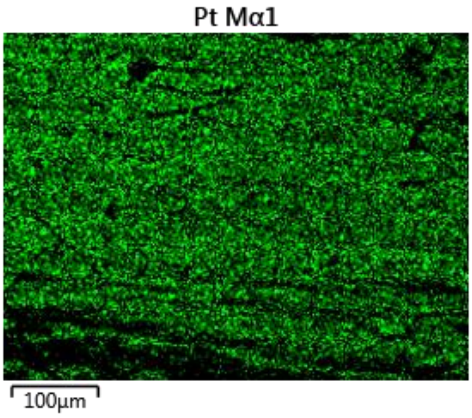
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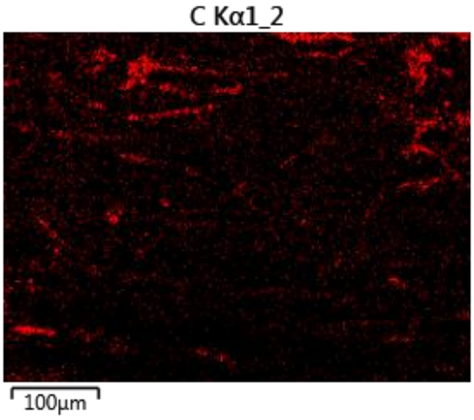
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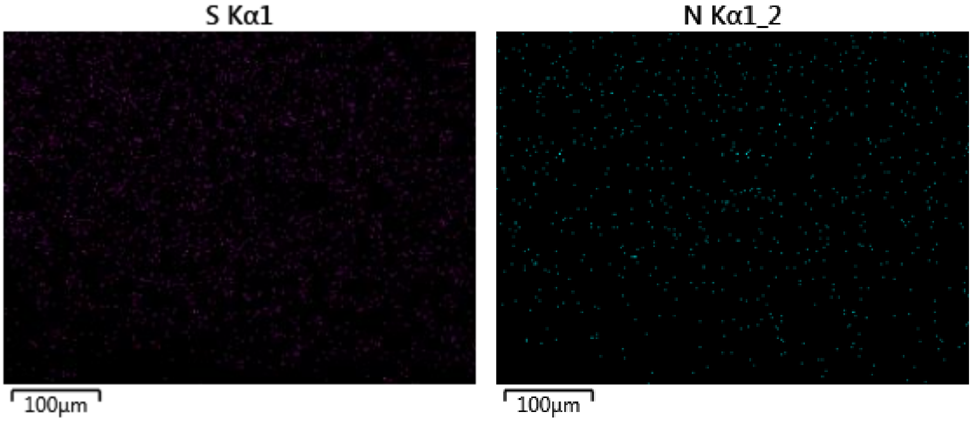

Figure 6 EDX spectrum and elemental mapping of Pt@PTH catalyst for Pt, C, S, and N atoms.

4. Conclusions

Pt@PTH catalyst system was synthesized and tested for its electrocatalytic activity towards methanol oxidation in acidic medium. Optimum experimental conditions were determined according to oxidation peak current of methanol obtained during cyclic voltammetry. The catalyst system prepared under optimum conditions was characterized with cyclic voltammetry and SEM-EDX methods.

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