

Electrocatalytic oxidation of formic acid using Pt nanocatalyst supported on PVF-PANI composite

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Abstract

Facile synthesis of Pt@PVF-PANI catalyst for electrooxidation of formic acid was described. Influence of experimental conditions, i.e. polymer film thickness, Pt loading and reduction time and potential, on the performance of the catalyst system was studied via cyclic voltammetry of formic acid solution in acidic medium. The catalyst prepared under optimum conditions was physically characterized using Scanning Electron Microscopy and elemental mapping. Electrochemical characterization was performed by electrochemical impedance spectroscopy

Anahtar kelimeler: PVF-PANI composite; Pt nanoparticles; Formic acid oxidation; Electrocatalysis

PVF-PANI kompozit destekli Pt nanokatalizörü kullanılarak formik asitin elektrokatalitik yükseltgenmesi

Öz

Bu çalışmada Pt@PVF-PANI katalizör sisteminin sentezi ve formik asitin elektroyükseltgenmesi için kullanımı anlatılmaktadır. Deneysel koşulların katalizör sisteminin performansı üzerine olan etkisi, asidik ortamda formik asit çözeltisinin dönüşümlü voltamogramları kaydedilerek saptanmıştır. Optimum koşullarda hazırlanan katalizörün fiziksel karakterizasyonu için taramalı elektron mikroskopu ve elementel haritalama ile gerçekleştirilmiştir. Elektrokimyasal karakterizasyon için ise elektrokimyasal empedans spektroskopisi yöntemi kullanılmıştır.

Keywords: PVF-PANI kompozit ; Pt nanopartikülleri ; Formik asit yükseltgenmesi ; Elektrokataliz

1. Introduction

Recently, polymer electrolyte membrane (PEM) fuel cells are accepted as candidates for current batteries especially in portable devices (Pekmez & Sönmez Çelebi, 2017). Despite being the most preferred fuel cells, there are still some limitations of hydrogen or methanol

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fueled systems. It is these limitations of hydrogen and methanol that have in recent years increased interest in direct formic acid fuel cells. Formic acid is safe and shows low toxicity compared to methanol; it is even used as a food additive (Ong et al., 2017). Compared with methanol, formic acid possesses some benefits such as allowance for high feed concentration of formic acid, high transportation of electron and proton within anode compartment and safety to human.

One of the most important factors to have higher cell efficiency in direct formic acid fuel cells is the activity of the anode material. Pt and Pd based catalysts display enhanced catalytic activity in formic acid electro-oxidation reactions (Hsieh et al., 2015; Ramírez et al., 2017). Catalytic activity of the catalyst depends on the support material used for incorporation of Pt and Pd particles and the surface properties of the catalyst. Metal particles supported on functional materials have many advantages over unsupported particles (Mutlu Sönmez Çelebi, 2016).

Because of their high accessible surface area, low resistance, and high stability together with their conductive and stable 3D structure, conducting polymers can be used as suitable supports for low-temperature fuel cells (Sharma & Pollet, 2012). The main advantage of conducting polymers as catalyst supports is improved catalytic activity due to high specific area as well as tolerance to CO formed during fuel oxidation. Polyaniline (PANI) is one of the most widely used conducting polymers for fuel cell catalyst preparation are heteroatom containing conjugated polymers (Lemos et al., 2015; Nagashree & Ahmed, 2008; Zhu et al., 2008).

Poly(vinylferrocenium) (PVF) is a redox type conducting polymer which is preferred as a mediator in many catalytic reactions (Akgül et al., 2012; M. S. Çelebi et al., 2008; Mutlu Sönmez Çelebi et al., 2008; Tian et al., 2015). Electrode surfaces can simply be modified with a PVF film via physical or electrochemical methods such as dip coating, droplet evaporation, oxidative deposition or cyclic voltammetric deposition. Combining redox polymers, with a conjugated conducting polymer overcomes limitations associated with the relatively low conductivity of the redox polymer compared to its conjugated analogue (Çelebi & Nur, 2018).

In this study, we performed electrooxidation of formic acid on Pt nanocatalyst supported on PVF- PANI composite immobilized on pencil graphite electrode (PGE). Influence of experimental conditions on the performance of the catalyst system was studied via cyclic voltammetry of formic acid solution in acidic medium. The Pt@PVF-PANI catalyst prepared under optimum conditions was physically characterized using Scanning Electron Microscopy (SEM). Electrochemical characterization of the catalyst system was also realized with electrochemical impedance spectroscopy (EIS).

2. Materials and Methods

Poly(vinylferrocene) was obtained from Polysciences Inc. and aniline was purchased from Sigma-Aldrich. Tetra-N-butyl ammonium perchlorate (TBAP), methylene chloride (HPLC grade), sulfuric acid (H₂SO₄), perchloric acid (HClO₄) and formic acid (HCOOH) 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) as the working electrode. The connector of the PGE (0.5 mm HB Tombow) was a Tombow pencil. Silver/silver chloride (Ag/AgCl) and saturated calomel electrodes (SCE) were used as

reference electrodes in methylene chloride and aqueous media respectively. A platinum (Pt) wire was used as the counter electrode. Scanning electron microscopy (SEM) images were recorded with catalyst samples prepared on disposable pencil graphite electrodes (PGE) using JEOL model JSM-7001F. Electrochemical impedance spectroscopy studies were carried out using IVIUM Pocketstat (Ivium Technologies, Netherlands).

3. Results and Discussion

The preparation route of the Pt@PVF-PANI catalyst system involved three steps: (i) electrochemical formation of PVF-PANI composite film on the electrode surface, (ii) dispersion of PtCl_4^{2-} complex to the polymer composite matrix via cyclic voltammetric scans from aqueous solution, (iii) chemical or electrochemical reduction of the platinum complex. In order to get the best performance from the catalyst system, optimum experimental conditions were determined by recording the cyclic voltammograms (CVs) of 0.5 M HCOOH solution containing 0.5 M H_2SO_4 and comparing the formic acid oxidation peak current values. A representative CV recorded with the catalyst system prepared under optimum experimental conditions (15 cyclic voltammetric scans during polymer coating, 60 cyclic voltammetric scans during Pt loading, 30 minutes chemical reduction in hydrazine solution) is presented in Figure 1.

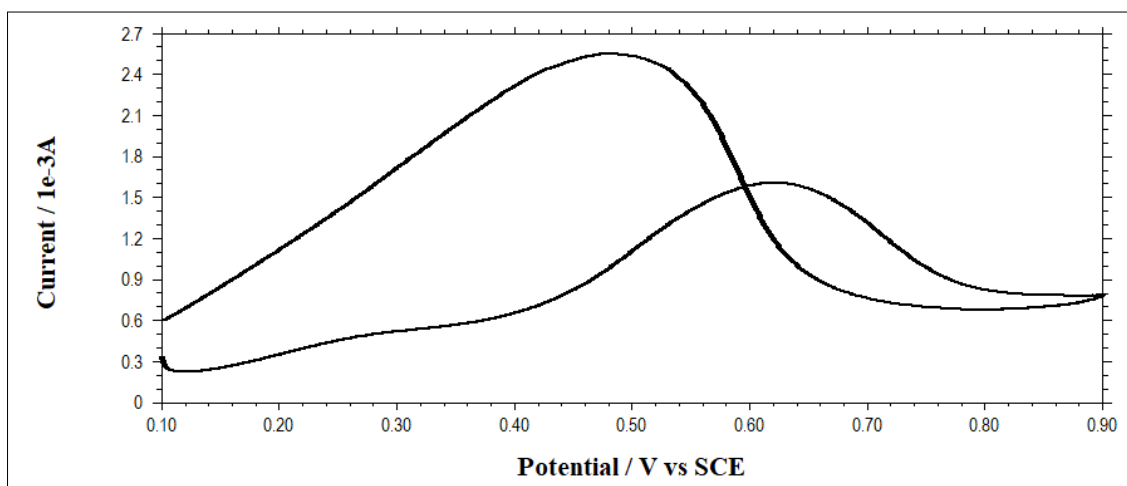


Figure 1. CV of 0.5 M HCOOH solution containing 0.5 M H_2SO_4 recorded with Pt@PVF-PANI catalyst prepared under optimum conditions. Scan rate: 50 mV s^{-1}

PVF-PANI composite film was electrochemically immobilized onto the working electrode by cyclic voltammetry according to the method described before (Kavanoz & Pekmez, 2012). For this purpose, cyclic voltammetric scans were applied to PGE in methylene chloride solution of PVF (1.00 mg mL^{-1}) and aniline (100 mM) containing HClO_4 (33.0 mM) and TBAP (100 mM). The potential window was between +0.2 V and +1.80 V vs. Ag/AgCl in this solution. In order to determine the optimum film thickness to get the best performance from the catalyst, polymer films prepared using cycle numbers between 5 and 25 have been prepared, loaded with PtCl_4^{2-} complex (via 70 cyclic voltammetric scans in 2 mM K_2PtCl_4) and treated with aqueous hydrazine solution for 30 min. Figure 2 presents influence of polymer composite film thickness on the oxidation peak current values of formic acid. As clearly seen from the figure, a PVF-PANI composite film prepared using 15 cycles is optimal.

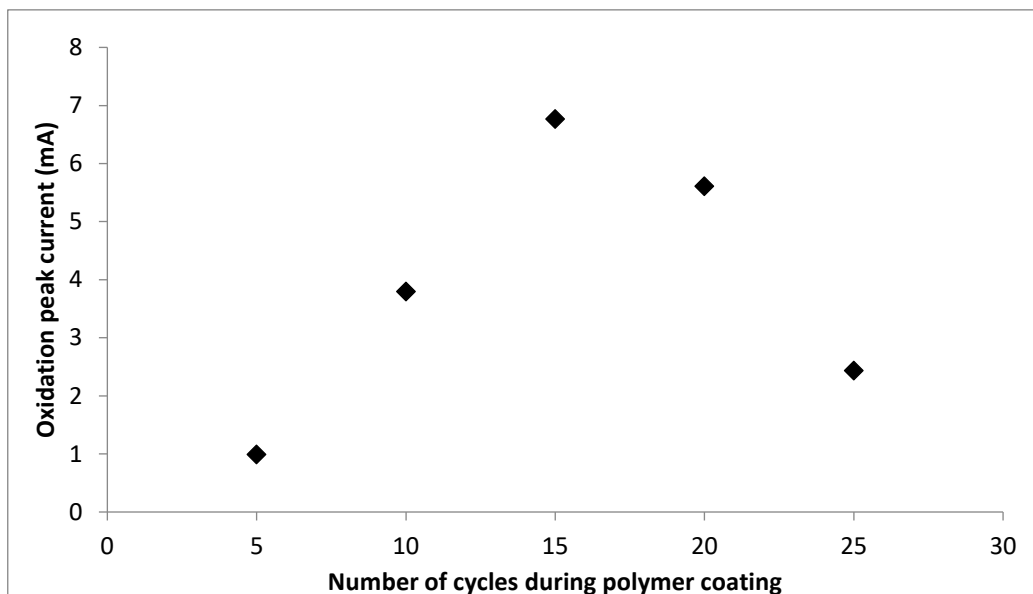


Figure 2. Influence of polymer composite film thickness on the oxidation peak current values of formic acid.

Amount of the Pt complex immobilized into the polymer composite film is an important parameter influencing the performance of the Pt@PVF-PANI catalyst system. After coating the working electrode with the polymer composite film, the amount of Pt was controlled by number of cycles during cyclic voltammetric deposition of the complex from K_2PtCl_4 solution. In this step, aqueous solution of K_2PtCl_4 was used without supporting electrolyte in order to avoid accumulation of any ionic species other than the Pt complex into the polymer matrix. Polycyclic voltammogram of the composite coated PGE in 2.0 mM K_2PtCl_4 solution is given in Figure 3(a). Influence of the number of cycles in K_2PtCl_4 solution on the oxidation peak current of formic acid is given in Figure 3(b) and maximum current was obtained with an optimal cycle number of 60.

For reduction of the Pt complex immobilized into the polymer composite film, we performed and optimized both electrochemical and chemical reduction methods. Electrochemical reduction was performed by constant potential electrolysis method in 0.5 M H_2SO_4 solution. Experimental studies revealed that the optimum reduction potential was -0.1 V vs. SCE and the maximum oxidation peak current for formic acid oxidation was obtained for 20 min electrolysis. Hydrazine was used as the reducing agent for the chemical reduction of the Pt complex and the reduction was carried out by simply holding the $PtCl_4^{2-}$ incorporated PVF-PANI composite film in stirred 0.1 M hydrazinium hydrate solution. The optimum reduction time for chemical reduction process was 30 min. When the two reduction methods were compared, chemical reduction was preferred according to the oxidation peak current values for electrooxidation of formic acid.

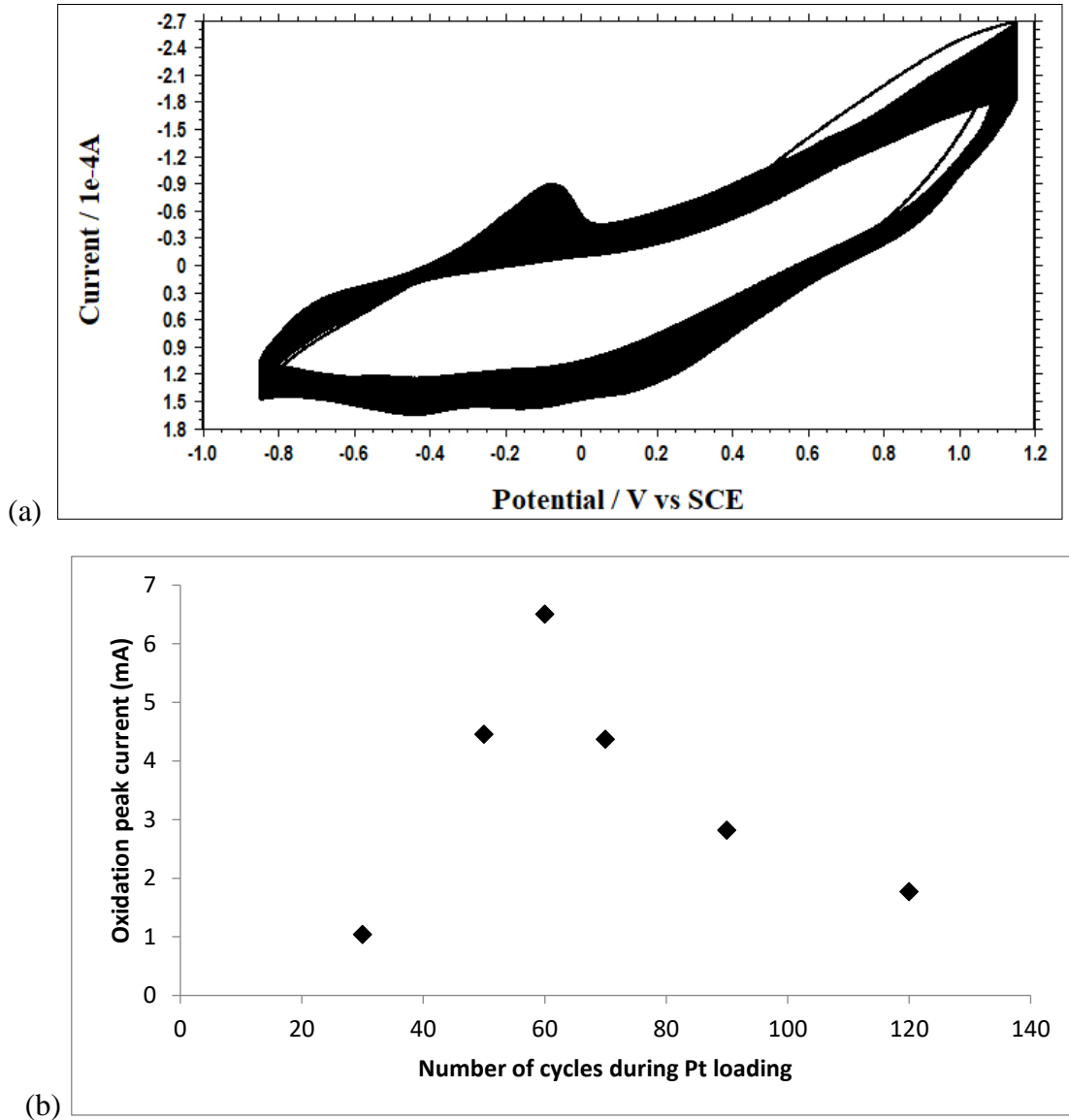


Figure 3. (a) Polycyclic voltammogram of PVF-PANI coated PGE recorded in 2 mM K_2PtCl_4 solution (Scan rate: 100 mV s^{-1}). (b) Influence of Pt loading on the oxidation peak current values of formic acid. (Other experimental conditions are 15 cycles during polymer coating and 30 minutes chemical reduction time.)

After determining the optimum experimental conditions for Pt@PVF-PANI catalyst system, we characterized the modified electrode using AC impedance spectroscopy. In the Nyquist plot of impedance spectra, the diameter of the semicircle represents the charge-transfer resistance (R_{ct}) at the electrode surface (Kuralay et al., 2013; Lin et al., 2013). Reduction of the R_{ct} value as the result of a modification indicates that the electron transfer has been easier due to the increase in the conductivity. Figure 4 presents the impedance spectra of uncoated, PVF-PANI coated and Pt/PVF-PANI modified PGE at different magnifications. As clearly seen from the spectra, coating the surface with the PVF-PANI composite results in significant decrease in the R_{ct} value. A further decrease is observed in the R_{ct} value when the

composite film is decorated with the Pt particles. Therefore, it can be concluded that, as expected, the conductivity of the film is increased as a result of the modification.

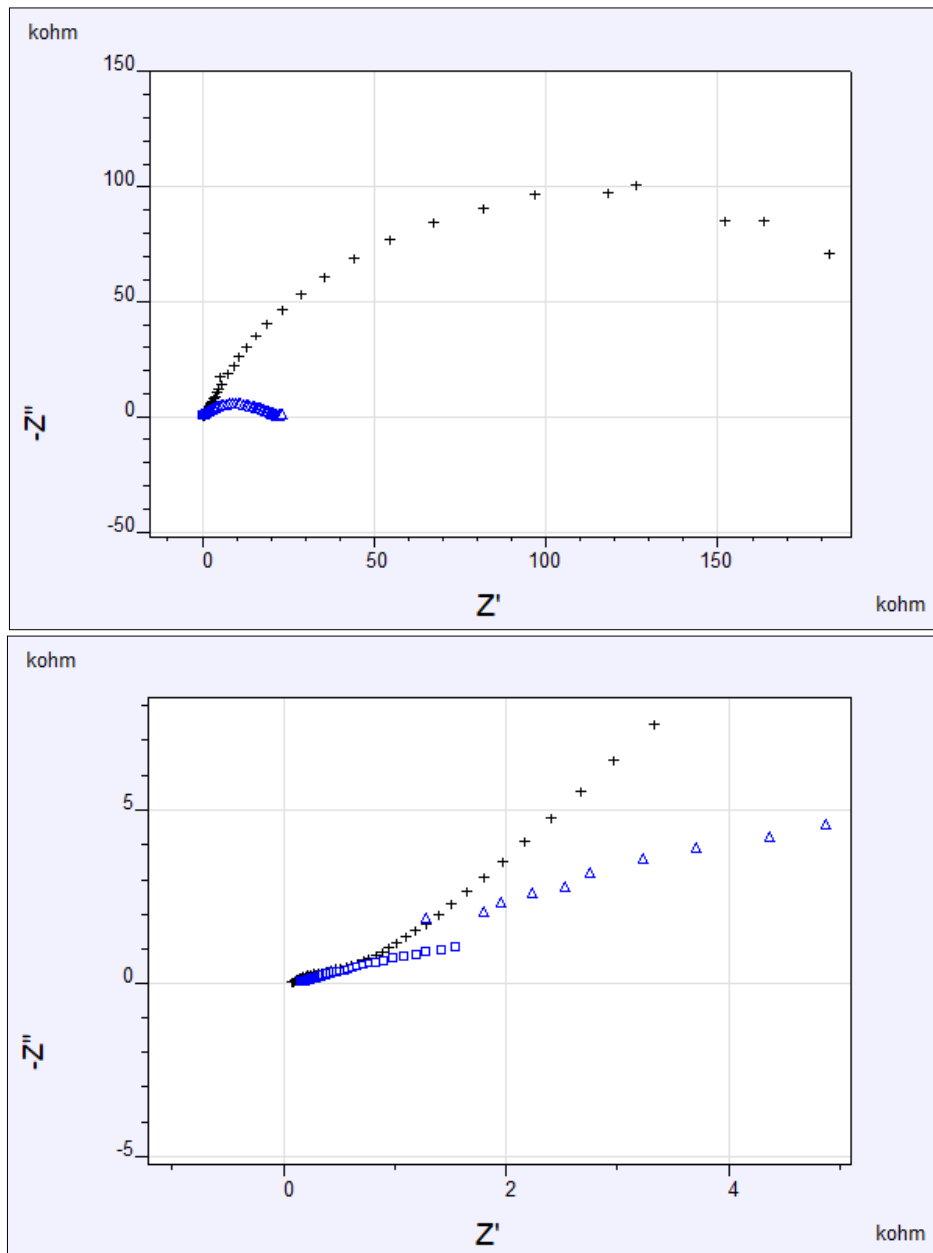


Figure 4. Impedance spectra of uncoated PGE (+), PVF-PANI coated PGE (Δ) and Pt/PVF-PANI modified PGE (\square) at two different magnifications.

In order to further characterize the catalyst, SEM images of the Pt@PVF-PANI catalyst has been recorded. In Figure 5, SEM images of uncoated PGE, PVF-PANI coated PGE and Pt@PVF-PANI catalyst prepared on PGE are presented. It is seen from the SEM images that, PVF-PANI coating has been formed on the electrode surface and the Pt loading is well dispersed on the polymer composite film.

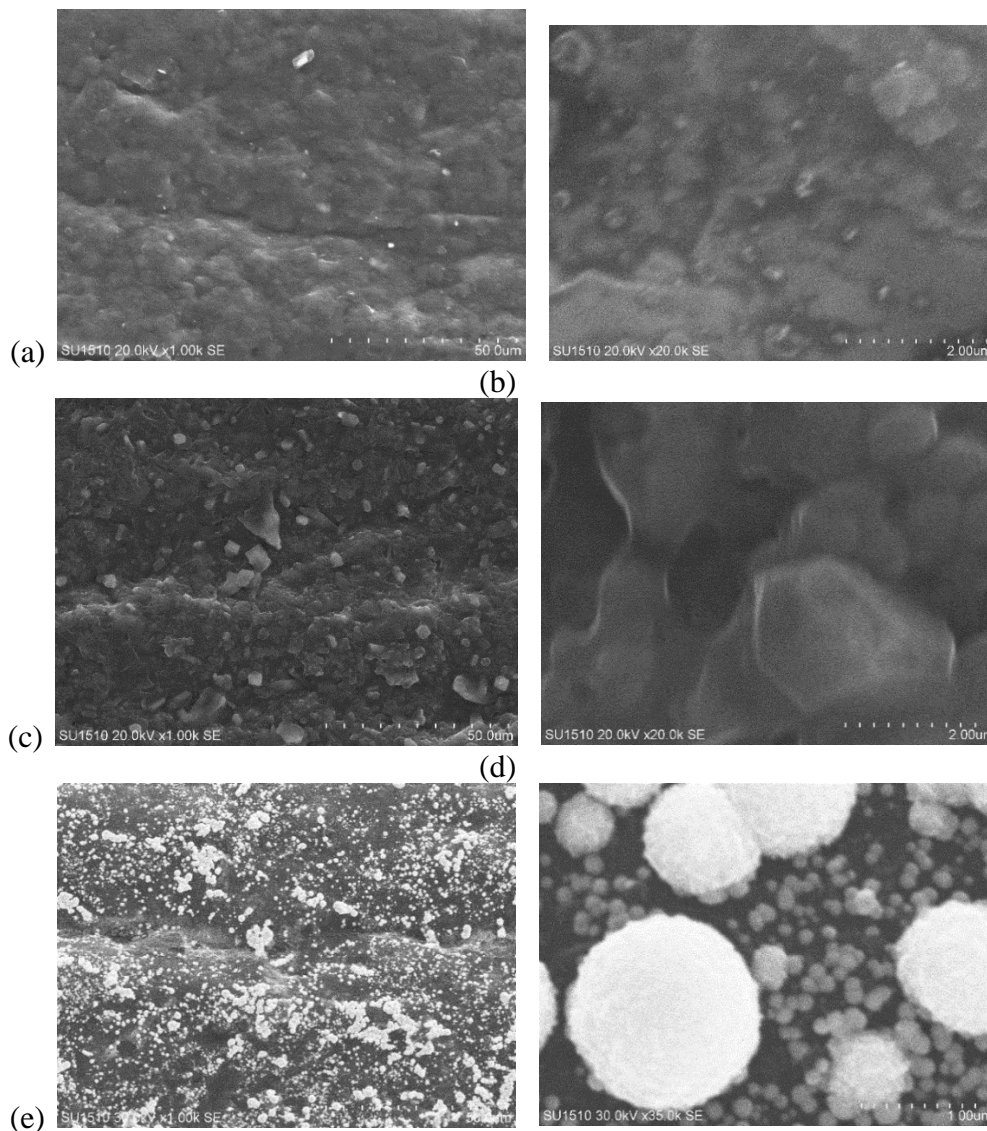


Figure 5. SEM images of uncoated PGE (a), PVF-PANI coated PGE (b) and Pt/PVF-PANI modified PGE (c) at different magnifications.

As an indication of even dispersion of the polymer composite film and the Pt in the catalyst system, elemental mapping of the Pt@PVF-PANI catalyst is given in Figure 6. The elemental mapping reveals that the catalyst system has an even distribution and the Pt nanoparticles and the polymer composite film has been well dispersed on the PGE surface.

4. Conclusions

Pt@PVF-PANI catalyst system was prepared and used for electrooxidation of formic acid in acidic medium. Three simple steps were followed during the preparation route: electrodeposition of the polymer composite film onto PGE, incorporation of Pt complexes into the polymer matrix from K_2PtCl_4 solution, and reduction of Pt complexes. Optimum experimental conditions were determined according to the performance of the catalyst towards electrochemical oxidation of formic acid. The catalyst system prepared under optimum conditions were characterized with electrochemical impedance spectroscopy and scanning electron microscopy techniques.

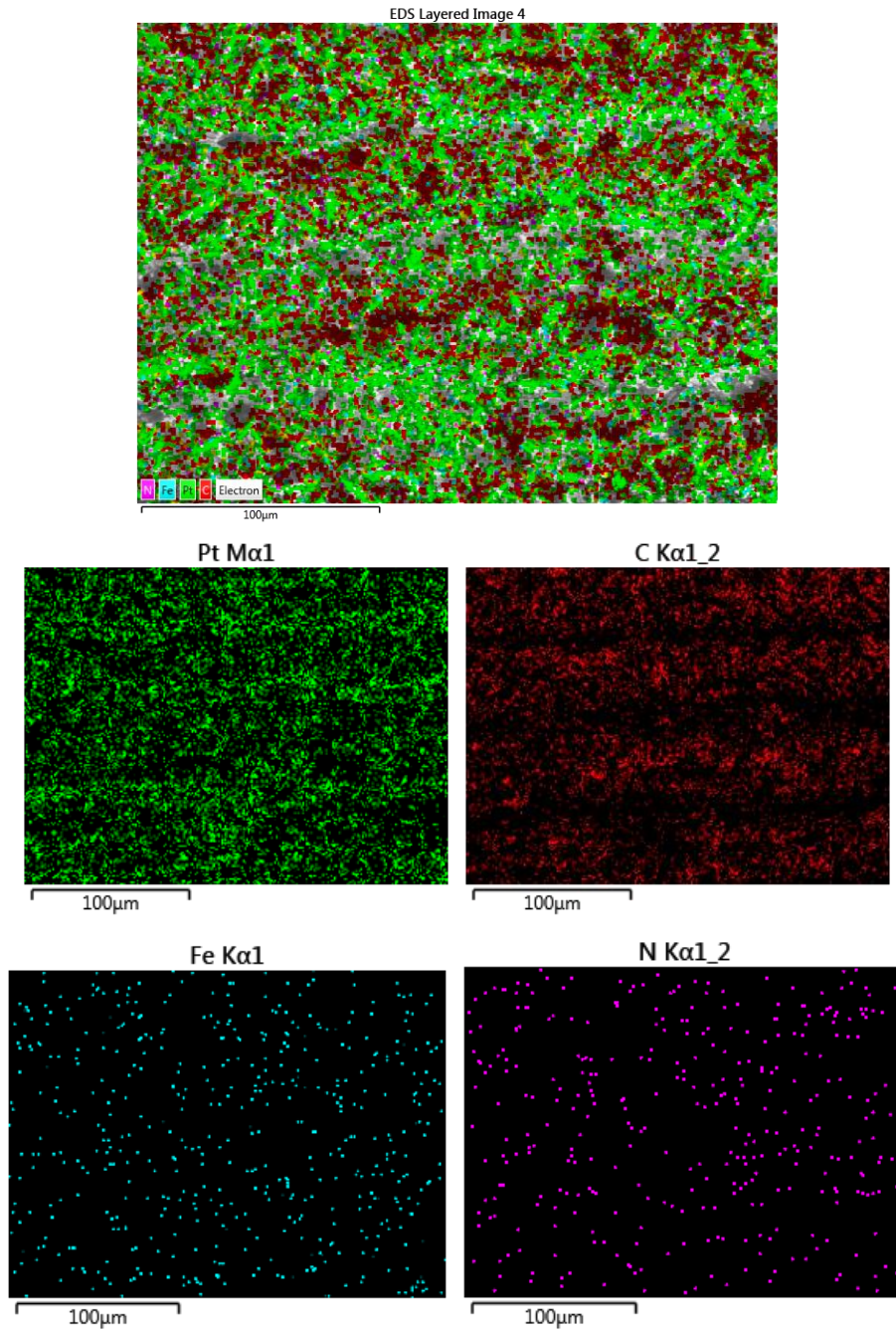


Figure 6. Elemental mapping of Pt@PVF-PANI for Pt,C, Fe, and N atoms.

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References

1. Akgül E, Gülce A & Gülce H (2012). Electrocatalytic oxidation of methanol on poly(vinylferrocene) modified Pt electrode. *Journal of Electroanalytical Chemistry* 668: 73–82.

2. Çelebi M S & Yılmaz A N (2018). PVF - PPy Composite as Support Material for Facile Synthesis of Pt @ PVF - PPy Catalyst and Its Electrocatalytic Activity Towards Formic Acid Oxidation. *Journal of New Materials for Electrochemical Systems* 162: 157–162.
3. Çelebi M S, Pekmez K, Özyörük H & Yıldız A (2008). Electrochemical synthesis of Pd particles on poly(vinylferrocenium). *Catalysis Communications* 9(13): 2175–2178.
4. Çelebi M S (2016) in *Advanced Electrode Materials*, Edited by A. Tiwari, F. Kuralay, and L. Uzun, Wiley-VCH, Weinheim, pp. 397–434.
5. Çelebi M S, Pekmez K, Özyörük H & Yıldız A (2008). Preparation and physical/electrochemical characterization of Pt/poly(vinylferrocenium) electrocatalyst for methanol oxidation. *Journal of Power Sources* 183(1): 8–13.
6. Hsieh C T, Hsiao H T, Tzou D Y, Yu P Y, Chen P Y & Jang B S (2015). Electro-oxidation of methanol and formic acid on platinum nanoparticles with different oxidation levels. *Materials Chemistry and Physics*, 149: 359–367.
7. Kavanoz M & Pekmez N Ö (2012). Poly(vinylferrocenium) perchlorate-polyaniline composite film-coated electrode for amperometric determination of hydroquinone. *Journal of Solid State Electrochemistry* 16(3): 1175–1186.
8. Kuralay F, Erdem A, Abacı S & Özyörük H (2013). Electrochemical characterization of redox polymer modified electrode developed for monitoring of adenine. *Colloids and Surfaces B: Biointerfaces*, 105: 1–6.
9. Lemos H G, Santos S F & Venancio E C (2015). Polyaniline-Pt and polypyrrole-Pt nanocomposites: Effect of supporting type and morphology on the nanoparticles size and distribution. *Synthetic Metals*, 203: 22–30.
10. Lin H, Yang J, Liu J, Huang Y, Xiao J & Zhang X (2013). Properties of Pd nanoparticles-embedded polyaniline multilayer film and its electrocatalytic activity for hydrazine oxidation. *Electrochimica Acta*, 90: 382–392.
11. Nagashree K L & Ahmed M F (2008). Electrocatalytic oxidation of methanol on Pt modified polyaniline in alkaline medium. *Synthetic Metals*, 158(15): 610–616.
12. Ong B C, Kamarudin S K & Basri S (2017). Direct liquid fuel cells: A review. *International Journal of Hydrogen Energy* 42(15): 10142–10157.
13. Pekmez K & Sönmez Çelebi M (2017). Electrooxidation of Formic Acid Using Pt Nanoparticles Supported on Conducting Poly(Vinylferrocene) Polymer Support. *Hacettepe Journal of Biology and Chemistry*, 3(45): 351–358.
14. Ramírez M R A, del Valle M A, Armijo F, Díaz F R, Angélica Pardo M & Ortega E. (2017). Enhancement of electrodes modified by electrodeposited PEDOT-nanowires with dispersed Pt nanoparticles for formic acid electro-oxidation. *Journal of Applied Polymer Science* 134(16): 1–7.
15. Sharma S & Pollet B G (2012). Support materials for PEMFC and DMFC electrocatalysts - A review. *Journal of Power Sources*, 208: 96–119.

- 16.** Tian W, Mao X, Brown P, Rutledge G C & Hatton T A (2015). Electrochemically Nanostructured Polyvinylferrocene/Polypyrrole Hybrids with Synergy for Energy Storage. *Advanced Functional Materials*, 25(30): 4803–4813.
- 17.** Zhu Z Z, Wang Z & Li H L (2008). Functional multi-walled carbon nanotube/polyaniline composite films as supports of platinum for formic acid electrooxidation. *Applied Surface Science* 254(10): 2934–2940