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PVF-PPy Composite as Support Material for Facile Synthesis of Pt@PVF-PPy Catalyst and Its Electrocatalytic Activity Towards Formic Acid Oxidation

Mutlu Sönmez Çelebí* and Ayşe Nur Yılmaz

Ordu University, Faculty of Science and Arts, Department of Chemistry, 52200, Ordu, Turkey

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Abstract: *Preparation and characterization of a Pt-based catalyst supported on poly(vinylferrocenium)-poly(pyyrole) conducting polymer composite (Pt@PVF-PPy) was described for electrocatalytic oxidation of formic acid. Pt precursor was aqueous solution of* K_2PtCl_4 *and electrochemical and chemical reduction methods were compared for optimum catalyst performance. Other experimental parameters such as polymer film thickness and Pt loading were also optimized with respect to the formic acid oxidation peak current values. Scanning electron microscopy, cyclic voltammetry and chronoamperometry methods were used for physical and electrochemical characterization of the catalyst system. When compared with similar Pt-based conducting polymer supported catalyst systems, the Pt@PVF-PPy catalyst revealed superior performance for formic acid electrooxidation.*

Keywords: Pt particles, Poly(vinylferrocenium), Poly(pyyrole), Formic acid electrooxidation, Supported catalyst

1. INTRODUCTION

In today's world, polymers are irreplaceable materials in the fields of science and technology. Their unique features such as light weight, high stability and mechanical resistance make them useful for improvement of advanced technological systems [1]. Conducting polymers which are also referred to as "synthetic metals" have the unique advantage of carrying both metal-like and polymer-like properties such as conductivity, magnetism, flexibility, processability and low toxicity. Among these polymers, polypyyrole (PPy), polyaniline (PANI) and polythiophene (PTh) and their derivatives are widely investigated. PPy, which can very easily be deposited on any electrode material via electrochemical deposition has many attractive properties such as high conductivity, excellent redox activity, easy processability, good thermal and electrochemical stability, low toxicity, etc. [2]. Poly(vinylferrocenium) (PVF) is a redox type conducting polymer which is preferred as a mediator in many catalytic reactions[3-5]. 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.

Fuel cells, which produce electrical energy with relatively low emissions are considered as one of the most promising alternative power sources to the traditional systems [6-7]. Polymer based support materials are widely used in low-temperature fuel cells in order to improve their electrocatalytical performance, durability and efficiency. Due to their unique properties such as gas and water permeability and proton and electron conductivity, conducting polymers are regarded as ideal catalyst supports. However, further development is still required for commercialization [8]. Recently, conducting polymers have been widely used as catalyst supports for metal nanoparticles [9-17].

Among the low-temperature fuel cells, direct formic acid fuel cell (DFAFC) has attracted great attention due to its low toxicity and low fuel cross-over rate compared to methanol [18]. Pt based metal catalysts are generally utilized for electrocatalytic oxidation of formic acid. Mono-metallic [18-24] or bimetallic [25-29] Pt based catalysts have been widely used for this purpose.

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. For example, replacing PVF or PPy with a PVF/PPy hybrid improves the electronic conductivity of the PVF film while eliminating insufficient exposure of PPy to the electrolyte due to relatively low porosity [30]. Herein, we describe utilization of PVF-PPy composite as support material for facile synthesis of Pt@PVF-

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*To whom correspondence should be addressed: Email: mutlucelebi@odu.edu.tr
Phone: +904522345010 ext.1672

PPy catalyst for electrooxidation of formic acid. 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-PPy catalyst prepared under optimum conditions was physically characterized using Scanning Electron Microscopy (SEM) and electrochemical characterization was performed by cyclic voltammetry and chronoamperometry. The prepared catalyst was also compared with Pt@PVF catalyst which was previously developed for formic acid electrooxidation [31].

2. EXPERIMENTAL

Poly(vinylferrocene) was obtained from Polysciences Inc. and pyrrole was purchased from Sigma-Aldrich. Tetra-N-butyl ammonium perchlorate (TBAP), methylene chloride (HPLC grade), sulfuric acid (H_2SO_4) 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 platinum disc electrode (Pt, 2 mm in diameter) as the working electrode. 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.

3. RESULTS AND DISCUSSION

The preparation route of the Pt@PVF-PPy catalyst was comprised of three facile stages: *(i)* electrochemical formation of PVF-PPy composite film on the electrode surface, *(ii)* loading $PtCl_4^{2-}$ complex ions to the polymer composite matrix via cyclic voltammetry, *(iii)* chemical or electrochemical reduction of the $PtCl_4^{2-}$ complex. The experimental preparation conditions were optimized 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.

3.1. Influence of thickness of polymer composite film

Electrochemical formation of PVF-PPy composite film on the electrode surface was carried out by cyclic voltammetry according to the method described before [32]. Cyclic voltammetric scans were applied to the solution containing 20 mM pyyrole (Py) monomer, 2.0 mg/mL PVF polymer and 100 mM TBAP (Figure 1a). Blank voltammogram of the resulting film in 0.5 M H_2SO_4 clearly indicates the existence of PVF (oxidation at 0.45 V and reduction at 0.29 V vs. SCE) and PPy (oxidation at 1.0 V vs. SCE) (Figure 1b).

Polymer film thickness was controlled by the number of cycles during the deposition of the polymer composite film. In order to investigate the influence of the polymer film thickness, Pt@PVF-PPy catalyst was prepared using polymer composites with different thicknesses and the performance of the catalysts were compared. 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 thin PVF-PPy composite film prepared using 15 cyclic voltammetric cycles is optimal.

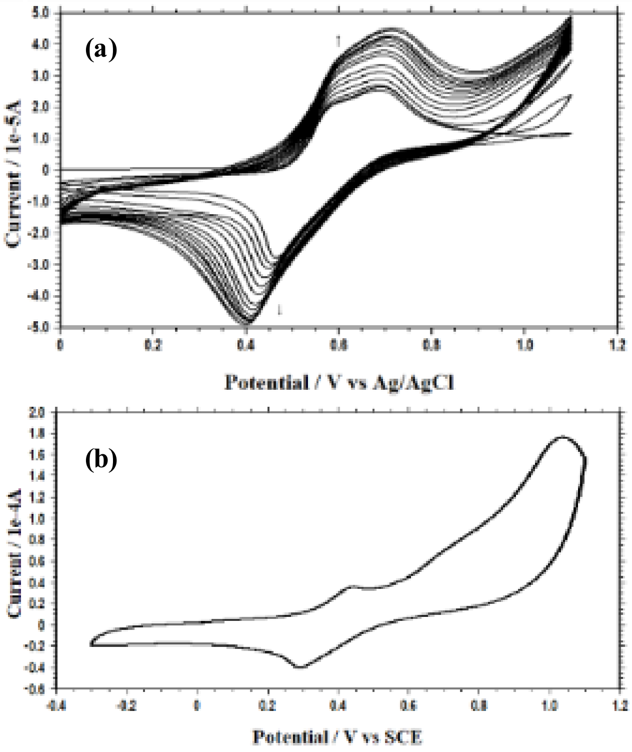

Figure 1. (a) Growth of PVF-PPy composite film by cyclic voltammetry from a solution containing 20 mM Py, 2.0 mg/mL PVF and 100 mM TBAP; (b) CV of PVF-PPy film recorded in 0.5 M H_2SO_4. Scan rate: 100 mV s^{-1}

3.2. Influence of amount of $PtCl_4^{2-}$ complex immobilized into the polymer composite film

Amount of the Pt complex immobilized into the polymer composite film was definitely the most important parameter influencing the performance of the Pt@PVF-PPy catalyst system. In order to optimize the amount of Pt in the catalyst, CVs of formic acid solution were recorded with catalyst systems prepared using various amounts of the $PtCl_4^{2-}$ complex. The amount of Pt was controlled by number of cycles during cyclic voltammetric deposition of the complex from 2.0 mM K_2PtCl_4 solution. As we know from previous studies, PVF film is well capable of accumulating negatively charged ions through anion exchange which is among the advantages of this polymer as a support material [4,33-34]. As the Pt precursor solution did not have any supporting electrolyte, the polymer film was loaded with $PtCl_4^{2-}$ anions through anion exchange with the ClO_4^- ions readily existed in the PVF-PPy film during the cyclic voltammetric cycles in K_2PtCl_4. Influence of the number of cycles in K_2PtCl_4 solution on the oxidation peak current of formic acid is given in Figure 3 and an optimal cycle number of 80 is clearly depicted from the figure.

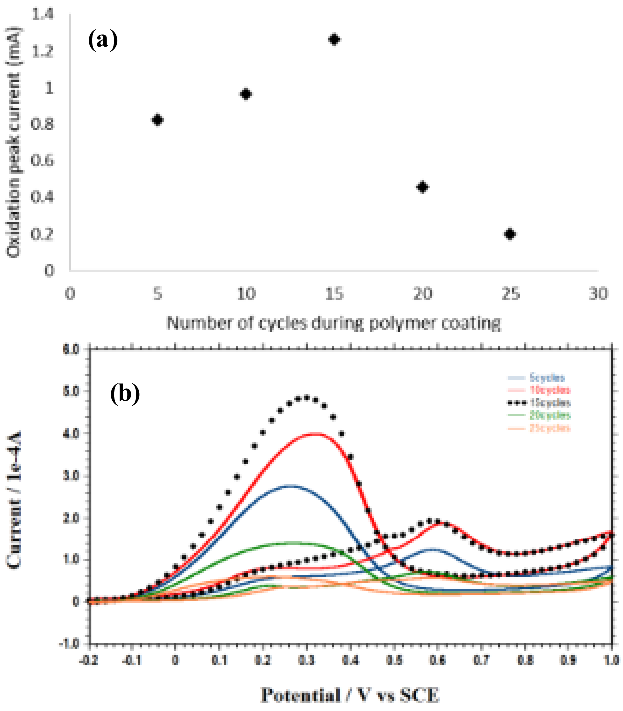

Figure 2. (a) Influence of polymer composite film thickness on the oxidation peak current values of formic acid; (b) Corresponding CVs recorded in 0.5 M HCOOH + 0.5 M H_2SO_4. Scan rate: 50 mV s^{-1} (Other experimental conditions are 60 cycles during Pt loading from K_2PtCl_4 and 60 minutes chemical reduction time.)

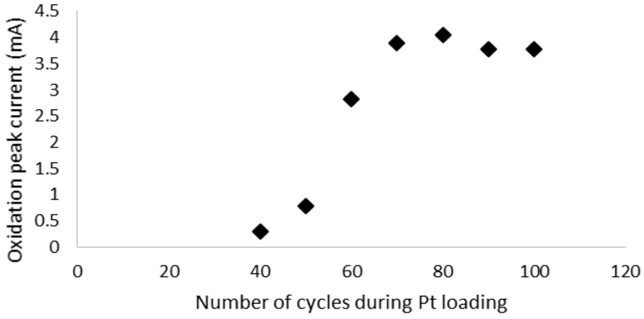

Figure 3. Influence of Pt loading on the oxidation peak current values of formic acid. (Other experimental conditions are 15 cycles during polymer coating and 60 minutes chemical reduction time.)

3.3. Comparison of electrochemical and chemical methods for the reduction of $PtCl_4^{2-}$ complex

Electrochemical and chemical reduction methods were both studied and compared for the reduction of $PtCl_4^{2-}$ complex immobilized into the polymer composite film. Electrochemical reduction was performed by constant potential electrolysis method 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 and the optimum conditions were determined as -0.3 V (vs. SCE) for electrolysis potential and 5 min for electrolysis time. 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-PPy composite film in stirred 0.1 M hydrazinium hydrate solution. The optimum reduction time for chemical reduction process were found as 30 min. When the performance of the two reduction methods were compared towards electrooxidation of formic acid, chemical reduction was chosen as the preferred reduction method by means of oxidation peak current (Figure 4).

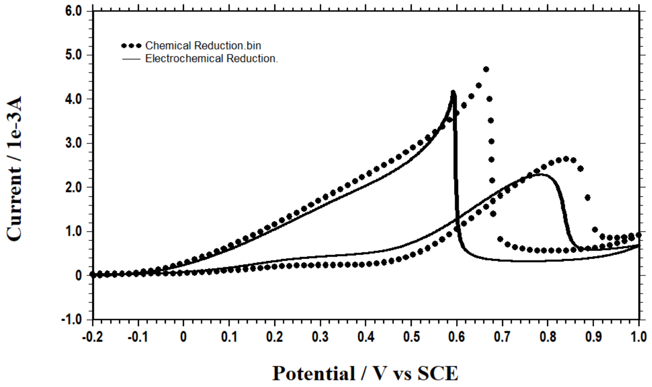

Figure 4. CVs of 0.5 M HCOOH + 0.5 M H_2SO_4 solution recorded with Pt@PVF-PPy catalyst prepared by chemical () and electrochemical (—) reduction methods. Scan rate: 50 mV s^{-1}

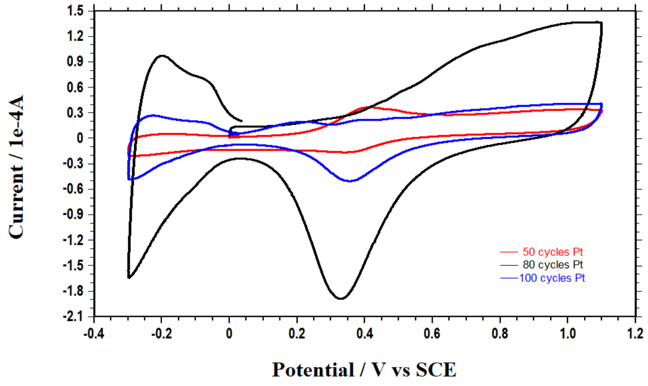

Figure 5. CVs of 0.5 M H_2SO_4 recorded with Pt@PVF-PPy catalysts with Pt loadings corresponding to 50 (—), 80 (—) and 100 (—) cycles in K_2PtCl_4 solution. Scan rate: 100 mV s^{-1}

3.4. Electrochemical characterization of the Pt@PVF-PPy catalyst

3.4.1. Electrochemical characterization by cyclic voltammetry

Electrochemical characterization of the catalyst system was performed by recording CVs of 0.5 M H_2SO_4 solution and comparing the hydrogen adsorption/desorption peaks for different Pt loadings. For this purpose, Pt@PVF-PPy catalysts with 50, 80 and 100 cylic voltammetric scans in K_2PtCl_4 solution has been compared (Figure 5). As seen from the CVs, the best performance was achieved for 80 cycles of Pt loading which supports the finding that this loading

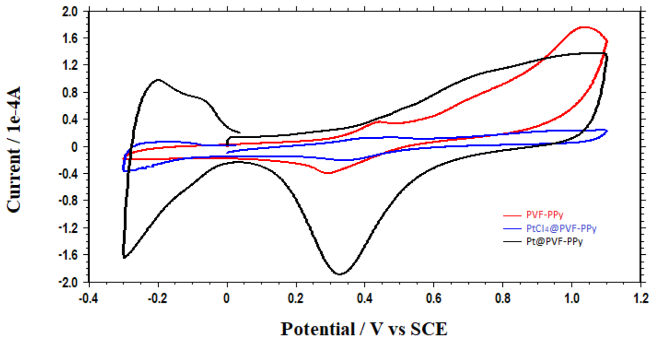

Figure 6. CVs of 0.5 M H_2SO_4 recorded with Pt electrode coated with PVF-PPy (—), $PtCl_4^{2-}$ incorporated PVF-PPy (—) and Pt@PVF-PPy (—).Scan rate: 100 mV s^{-1}

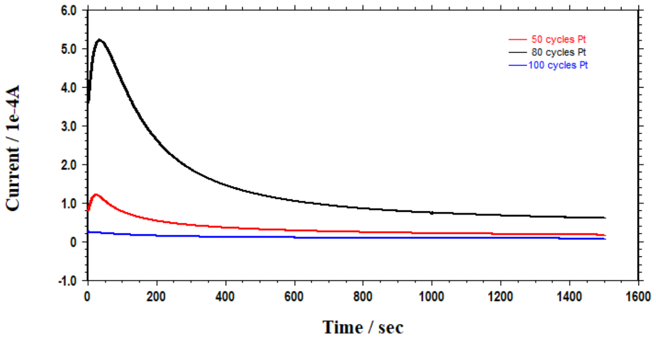

Figure 7. Chronoamperometry curves recorded in 0.5 M HCOOH + 0.5 M H_2SO_4 solution with Pt@PVF-PPy catalysts having Pt loadings corresponding to 50 (—), 80 (—) and 100 (—) cycles in K_2PtCl_4 solution at 0.5 V vs. SCE.

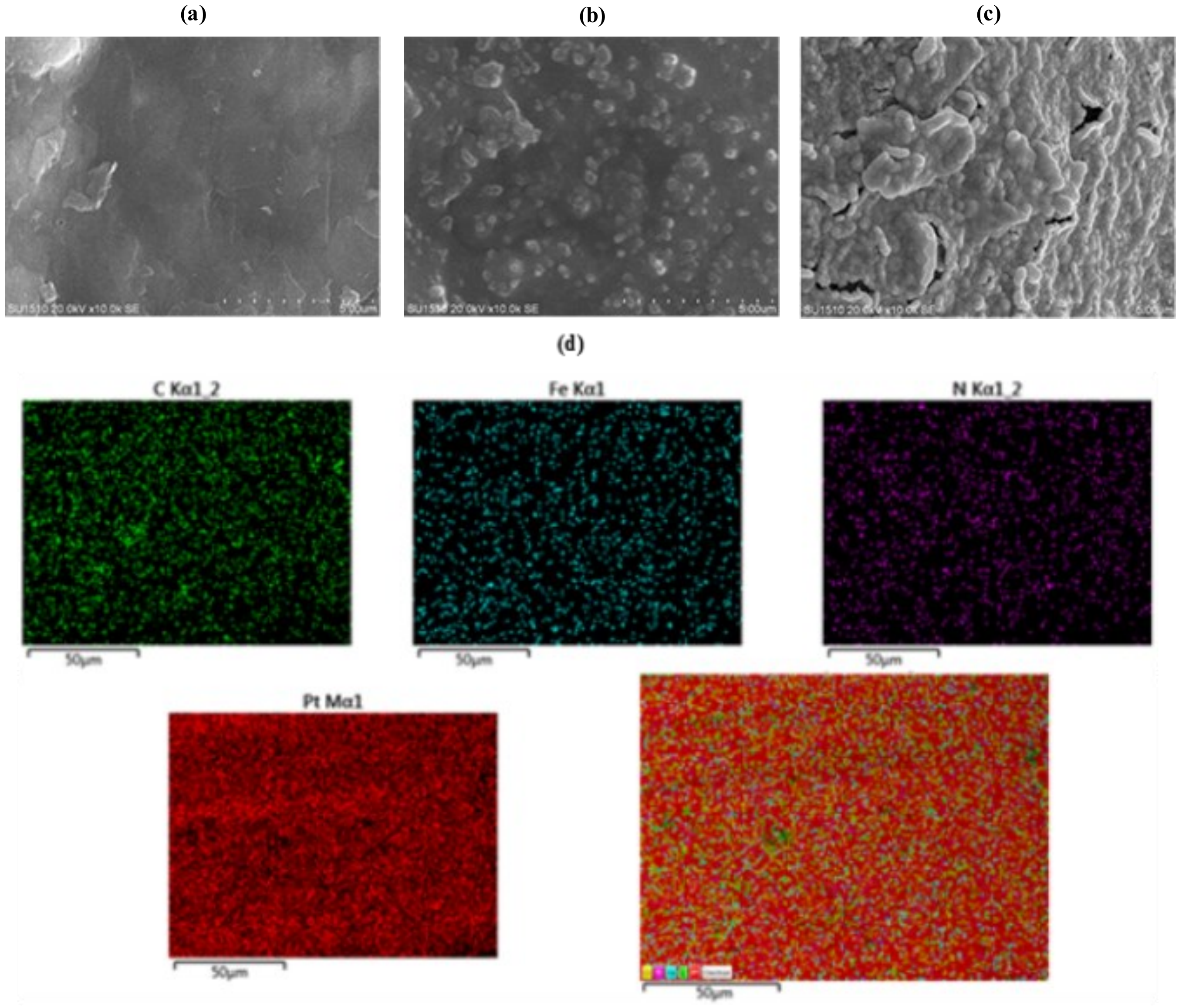

Figure 8. SEM images of (a) uncoated PGE, (b) PVF-PPy coated PGE, (c) Pt@PVF-PPy coated PGE. (d) Elemental mapping of Pt@PVF-PPy for C, Fe, N and Pt atoms.

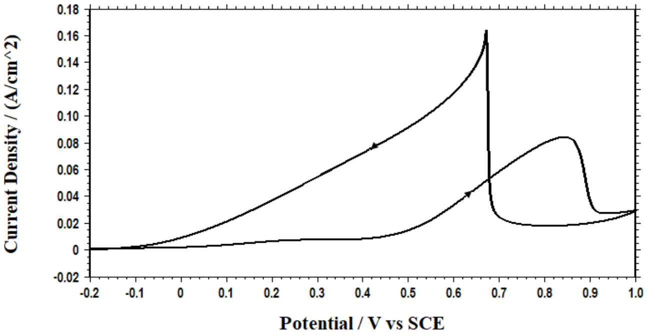

Figure 9. CV of 0.5 M HCOOH + 0.5 M H_2SO_4 solution recorded with Pt@PVF-PPy catalyst prepared under optimum conditions. Scan rate: 50 mV s^{-1}

supplies the optimum Pt amount. The role of reduction of the Pt complexes was also confirmed by cyclic voltammetry. In Figure 6, CVs of 0.5 M H_2SO_4 recorded with the catalyst before and after reduction of the $PtCl_4^{2-}$ complex are presented clearly indicating the increase in the performance of the catalyst after the reduction process.

3.4.2. Electrochemical characterization by chronoamperometry

Electrochemical characterization of the catalyst system was also performed by chronoamperometry for catalyst systems with different Pt loadings. In Figure 7, chronoamperometry curves in formic acid solution recorded with Pt@PVF-PPy catalysts with 50, 80 and 100 cylic voltammetric scans in K_2PtCl_4 solution has been compared and, as expected, the best performance was obtained for the optimum Pt loading.

3.5. Physical characterization of the Pt@PVF-PPy catalyst

Physical characterization of the catalyst was practiced by recording the SEM images of the catalyst prepared on disposable PGE. In Figure 8, SEM images of uncoated PGE (Figure 8a), PVF-PPy coated PGE (Figure 8b) and Pt@PVF-PPy catalyst prepared on PGE (8c) are given. It is clear that a thin PVF-PPy coating has been formed on the electrode surface and the Pt loading is well dispersed on the polymer composite film. As an indication of even dispersion of the polymer composite film and the Pt in the catalyst system, elemental mapping of the Pt@PVF-PPy catalyst is also given in Figure 8d.

3.6. Performance of the Pt@PVF-PPy catalyst prepared under optimum conditions

Figure 9 presents CV of 0.5 M HCOOH solution recorded with the Pt@PVF-PPy catalyst prepared under optimum conditions. As a comparison, performances of some conducting polymer-supported Pt based catalysts towards electrooxidation of formic acid in terms of oxidation peak current density are given in Table 1.

4. CONCLUSIONS

Facile synthesis of a Pt based electrocatalyst was described using PVF-PPy conducting polymer composite as the support material. Three simple steps were followed during the preparation route: electrodeposition of the polymer composite film onto the electrode material, incorporation of Pt complexes into the polymer matrix via cyclic voltammetric scans in 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 characterization of the catalyst system was carried out using both physical and electrochemical methods and the performance of the Pt@PVF-PPy catalyst system was compared with former conducting polymer supported Pt based catalysts indicating that the developed catalyst was better than majority of the similar ones in the literature.

5. ACKNOWLEDGEMENT

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Table 1. Comparison of Pt@PVF-PPy catalyst with previously reported conducting polymer-supported Pt based catalysts towards electrooxidation of formic acid.

Supported Catalyst	E_f, V	J_f, mA cm^{-2}	E_r, V	J_r, mA cm^{-2}	Reference
Pt-SWNT/PANI	0.21[a]	49	0.68[a]	78	[14]
Pt-MWNT/PANI	0.69[a]	350	0.46[a]	420	[15]
Pt/PCZ	0.62[a]	14.38	0.30[a]	14.84	[16]
Pt/PAIn	0.68[a]	11.8	0.35[a]	7.5	[17]
Pt/PCI	0.40[a]	37.04	NA	NA	[18]
Pt│PEDOT,PEDOT-nw/NP-Pt	0.600[b]	3.200	0.731[b]	1.500	[23]
Pt│PEDOT-nw/Pt-np	0.237[c]	0.1250	0.335[c]	0.110	[24]
Pt/PVF	0.659[a]	20.508	0.494[a]	52.375	[31]
Pt@PVF-PPy	0.838[a]	61.22	0.672[a]	150.37	This work

E_f and E_r: Potentials of the forward and reverse peaks ; J_f and J_r: Current density values for the forward and reverse peaks [a]SCE ; [b]SHE ; [c]Ag/AgCl ; NA: Not Available

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