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Electrooxidation of Formic Acid Using Pt Nanoparticles Supported on Conducting Poly(vinylferrocene) Polymer Support

Poli(vinilferrosen) İletken Polimer Destekli Pt Nanopartikülleri Kullanarak Formik Asitin Elektroyükseltgenmesi

Research Article

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ABSTRACT

Methanol as a fuel has some disadvantages such as toxicity and low electrocatalytic oxidation rate, therefore, alternative liquid fuels are of interest for fuel cell applications. Formic acid has been considered as an alternative which fulfilled the requirements such as ease of transportation and handling and high theoretical open circuit voltage. Platinum supported on poly(vinylferrocenium) (Pt/PVF) is a promising catalyst for use in direct formic acid fuel cells. This work deals with electrooxidation of formic acid on Pt/PVF catalyst system and comparison of methanol and formic acid. According to the scanning electron microscopy (SEM) images, Pt particles are well dispersed over the polymer support. The Pt/PVF catalyst displays enhanced catalytic activity towards formic acid oxidation. When compared with methanol electrooxidation at the identical conditions, better results are achieved for formic acid oxidation.

Key Words
Poly(vinylferrocene), Pt nanoparticles, formic acid, fuel cell.

ÖZ

Yakıt olarak metanolün toksisite ve düşük elektrokatalitik yükseltgenme hızı gibi bazı dezavantajları olduğu için yakıt pili uygulamalarında alternatif yakıtlar ilgi çekmektedir. Diğer taraftan, taşıma ve kullanım kolaylığının yanı sıra yüksek teorik açık devre potansiyeli gibi özellikleriyle dikkat çeken formik asit metanole alternatif olarak ortaya çıkmaktadır. Poli(vinilferrosen) destekli platin (Pt/PVF) doğrudan formik asit yakıt hücrelerinde kullanım için gelecek vadeden bir katalizördür. Bu çalışmada Pt/PVF katalizör sistemiyle formik asitin elektroyükseltgenmesi ile metanol ve formik asitin karşılaştırılması yer almaktadır. Taramalı elektron mikroskobu görüntülerine göre, Pt tanecikleri polimer destek üzerinde düzgün dağılmıştır. Pt/PVF katalizörü formik asit yükseltgenmesi için yüksek katalitik aktivite göstermiştir. Aynı koşullarda metanolün elektroyükseltgenmesiyle karşılaştırıldığında, formik asit için daha iyi sonuçlar elde edilmiştir.

Anahtar Kelimeler
Poli(vinilferrosen), Pt nanopartikülleri, formik asit, yakıt pili.

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INTRODUCTION

Recently, direct fuel cells which use liquid fuels attract much more attention than the hydrogen based ones mainly because of the high cost of miniaturized hydrogen containers and the potential dangers in the transport and use of hydrogen. Among various liquid fuels, methanol has been extensively investigated due to its impressive energy density. However, because of its toxicity, low electrocatalytic oxidation rate and limited compatibility with Nafion® membranes (hence use of low methanol concentrations), alternatives to direct methanol fuel cell (DMFC) have been investigated [1,2]. Direct formic acid fuel cell (DFAFC) has been the focus of such investigations because of its advantages over DMFC such as higher theoretical open circuit potential and lower fuel crossover [3-5]. Formic acid is a non-toxic liquid which is inflammable, thus its storage and transportation is relatively easy and safe. It is well known from the previous studies that Pt-based catalysts show good catalytic activity towards electrooxidation of formic acid [1,5-9].

Incorporation of metal nanoparticles onto suitable supporting materials greatly enhances the catalytic properties of the metals allowing the generation of metal nanoparticles with a controlled size and size distribution [10]. Many supporting materials were investigated for metal nanoparticles such as conducting polymers [11-14], carbon nanotubes [15-17], graphene [18-20] and various hybrid materials [21-23].

Poly(vinylferrocene) (PVF) is a conducting polymer featuring redox properties which is commonly used as a favorable agent for preparing modified electrodes with desired surface properties [24]. Upon the advantages of using PVF for modification, simple electrochemistry with a reversible one-electron process, high stability, and ease of deposition of thin films using a variety of methods are the most outstanding ones. PVF oxidizes from methylene chloride to give the less soluble ferrocenium form of the polymer (PVF+) precipitating onto the electrode surface. Owing to these characteristics, PVF modified electrodes have been widely applied to many applications such as electroanalysis [25-27], biosensors [28-30] and preparation of polymer supported metal catalysts [11,12,31].

In this work, electrooxidation of formic acid was studied on Pt nanoparticles supported onto PVF conducting polymer matrix. Structural characterization of the Pt/PVF catalyst system was evaluated by scanning electron microscopy (SEM) technique. Catalytic activity of the electrocatalyst was examined via cyclic voltammetry experiments performed in formic acid solutions in acidic medium. The system was tested using a homemade single DFAFC configuration in terms of fuel cell performance and open circuit voltage (OCV). Cyclic voltammograms (CVs) and OCV values were also compared with methanol electrooxidation at identical conditions.

MATERIALS and METHODS

Reagents and Instruments

PVF was prepared by chemical polymerization of vinylferrocene at 70°C for 24 h using 2,2-asobis(2-methylpropionitrile) (AIBN) as the initiator [32]. Vinylferrocene and tetra-n-butyl ammonium perchlorate (TBAP) was purchased from Sigma-Aldrich. AIBN was obtained from Alfa. Methylene chloride (HPLC grade), formic acid, H_2SO_4 and K_2PtCl_4 were obtained from Merck and used as-received. Hydrazine solution was prepared using hydrazinium sulfate ($NH_2{\cdot}NH_2{\cdot}H_2SO_4$, Merck). All solutions were deoxygenated by bubbling pure nitrogen gas (BOS) prior to use in the electrochemical experiments.

The potential-controlled coulometric and cyclic voltammetric studies were carried out with CH Instruments System, Model 608B. The catalyst system was examined using a Gemini scanning electron microscope equipped with Leo 32 Supra 35VP field emission scanning system.

Electrodes

In electrochemical experiments, a Pt disc electrode (A=7.85 x 10^{-3} cm^2) was used as the working electrode. Before each experiment, the working electrode was polished with alumina (5.0 μm), then rinsed with triple distilled water, cleaned in ultrasonic bath and dried. During the electrodeposition of the polymer film onto

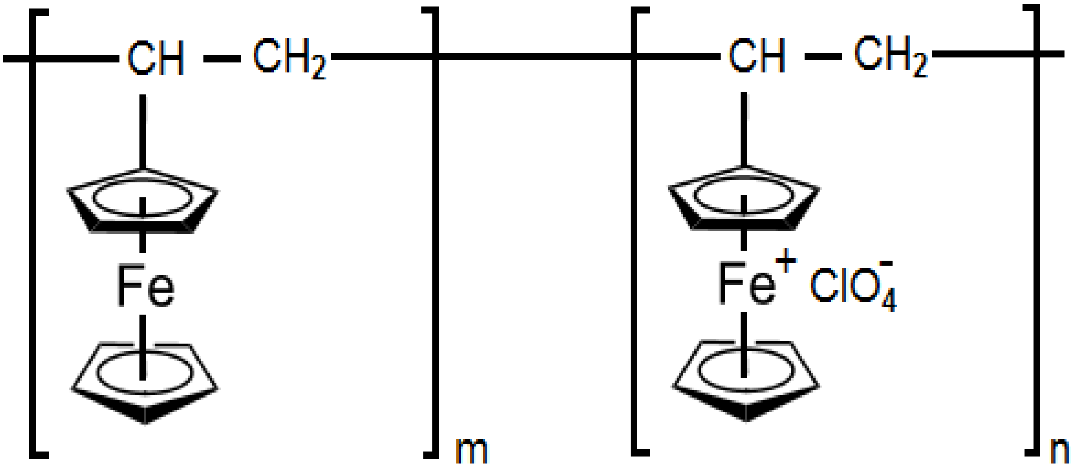

Figure 1. Electrochemically doped PVF.

the working electrode, a Ag/AgCl electrode was used as the reference electrode. This electrode was prepared by anodic electrolysis of a silver electrode in 0.1 M HCl solution for 3 h at +2.1 V with a current density of 2 mA cm^{-2}. The electrode was immersed in a separate compartment containing methylene chloride/0.1 M TBAP solution with a saturated amount of AgCl. In methylene chloride medium, a Pt wire in separate compartment containing methylene chloride/0.1 M TBAP solution was used as the counter electrode. In aqueous medium, a saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire with a surface area of 2 cm^2 in spiral form was used as the counter electrode.

Preparation of Pt/PVF Catalyst

Pt/PVF electrocatalyst was prepared according to the procedure described in our previous work [11]. The polymer was electrodeposited onto the electrode surface by the electrooxidation of 1.0 mg mL^{-1} PVF solution in methylene chloride containing 0.1 M TBAP at +0.7 V vs. Ag/AgCl. The thicknesses of PVF+ClO_4^- films were controlled by the charge passed during the electroprecipitation. A charge of 1×10^{-3} C corresponded to 1.32×10^{-6} mol of the oxidized PVF per cm^2 (dry thickness of ~300 μm, which corresponds to about 3×10^5 layers) [33]. The resulting film is in a porous structure containing ClO_4^- ions as the counter ion, ferrocene and ferrocenium groups (Figure 1).

Pt complex ($PtCl_4^{2-}$) anions were incorporated into the polymer matrix using cyclic voltammetric scans between potentials -0.85 and + 1.15 V vs SCE via counter ion exchange process in aqueous 2 mM K_2PtCl_4 solution without supporting electrolyte. Polymer-coated electrode containing Pt complex ($PtCl_4^{2-}$) as the counter ion was immersed in 0.1 M hydrazine solution stirred continuously at open circuit in order to reduce the Pt complexes completely to metallic Pt nanoparticles.

Single Fuel Cell Test

Nafion® membrane (NE 450, Aldrich) was used in the DFAFC construction. The anode was Pt/PVF catalyst system prepared using Pt foil electrode (1cm×1cm). Pt black-coated Pt electrode was used as the cathode material. 6 M HCOOH solution containing 0.5 M H_2SO_4 was used as the fuel and 0.5 M H_2SO_4 solution which was saturated by pure O_2 gas was used as the oxidant. The system was tested with a homemade single cell with a working area of 1 cm^2. The cell performance was tested at ambient temperature and atmospheric pressure.

RESULTS and DISCUSSION

In order to observe the physical structure of the catalyst system, Pt/PVF catalyst was prepared on a piece of Pt foil (3 mmx3 mm) and monitored by SEM. The obtained SEM images revealed well dispersion of Pt particles over highly porous

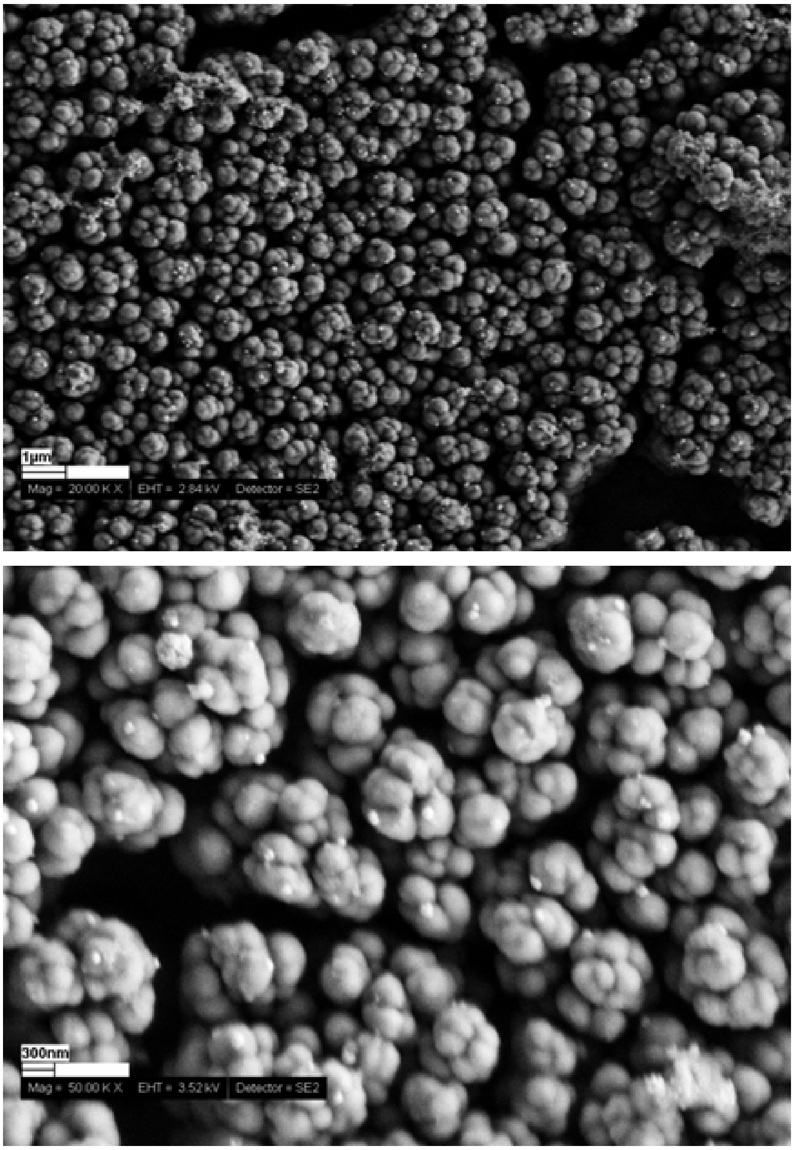

Figure 2. SEM images of Pt/PVF catalyst at two different magnifications.

polymer matrix with diameters at the nanoscale around 50-60 nm (Figure 2).

We calculated the maximum theoretical amount of Pt loaded to the catalyst system taking into account the precipitated PVF per cm^2 as 104 μg cm^{-2} [33]. This amount of Pt loading itself is better than similar Pt nanoparticles-based catalysts for formic acid oxidation [9,34]. In fact, considering the actual ratio of Fe:Pt (hence PVF:Pt) as 10:1 based on our previous work [11], we obtained a Pt loading as low as 10 μg cm^{-2}. This Pt loading can be regarded as a comparable catalyst loading indicating a reasonable noble metal consumption [35-37].

According to the most-accepted mechanism of formic acid oxidation, the reaction occurs via dual pathway mechanism [1,38-40]. In pathway 1, direct oxidation of formic acid occurs via a dehydrogenation step without any intermediate. However, in the second pathway, formation of adsorbed carbon monoxide as a reaction intermediate occurs by dehydration followed by formation of carbon dioxide as the end product. For formic acid fuel cell applications, dehydrogenation is the preferable reaction pathway in order to avoid poisoning of the catalyst. CVs of uncoated Pt disc electrode and Pt/PVF catalyst in 0.5 M HCOOH solution containing 0.5 M H_2SO_4 are

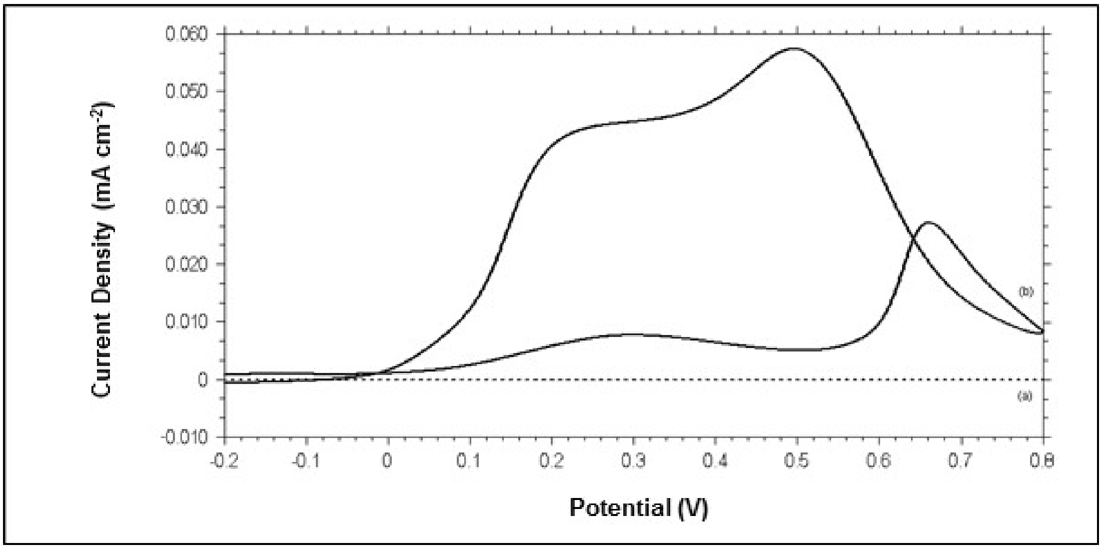

Figure 3. CVs recorded with (a) uncoated Pt disc electrode and (b) Pt/PVF coated Pt disc electrode in 0.5 M HCOOH + 0.5 M H_2SO_4 solution, scan rate = 50 mV s^{-1}.

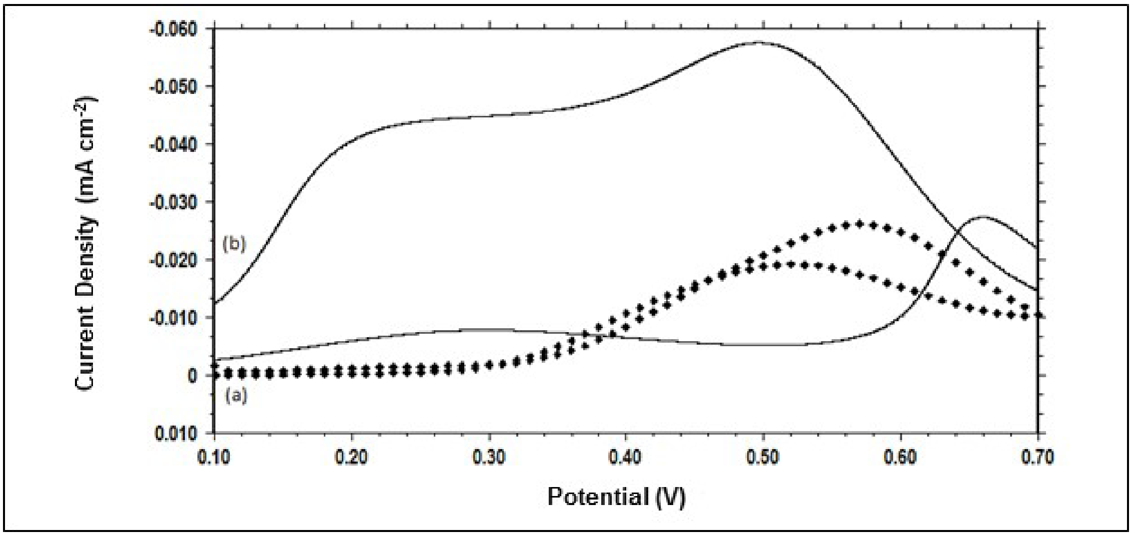

Figure 4. CCVs recorded with Pt/PVF coated Pt disc electrode in (a) 0.5 M CH_3OH + 0.5 M H_2SO_4 (scan rate: 50 mV s^{-1}) and (b) 0.5 M HCOOH + 0.5 M H_2SO_4 (scan rate: 5 mV s^{-1}).

given in Figure 3 (vs. SCE). The shape of the CV of HCOOH on Pt nanoparticles is consistent with similar studies [9,41,42]. As shown, bulk Pt has negligible catalytic activity towards formic acid oxidation. For Pt/PVF catalyst, two peaks were observed in the forward scan. The first peak around 0.30 V results from direct oxidation of formic acid while the second peak at 0.66 V refers to the indirect path. According to these observations, oxidation of formic acid occurs via both pathways with Pt/PVF catalyst.

We also compared the intensity of formic acid oxidation peak with methanol oxidation peak at the same concentration (Figure 4). It was observed that formic acid oxidation peak current was superior to that of methanol oxidation when recorded with identical Pt/PVF catalyst, which indicates advantage of formic acid over methanol for fuel cell applications.

In order to test the fuel cell performance of the Pt/PVF catalyst, we constructed a home-made DFAFC with a working area of 1 cm^2 in batch mode. When the anode was fed with 6 M HCOOH containing 0.5 M H_2SO_4, an OCV of 724 mV was obtained with a maximum power density of 1.32 mW cm^{-2} at 4.4 mA cm^{-2}. Graphs of current

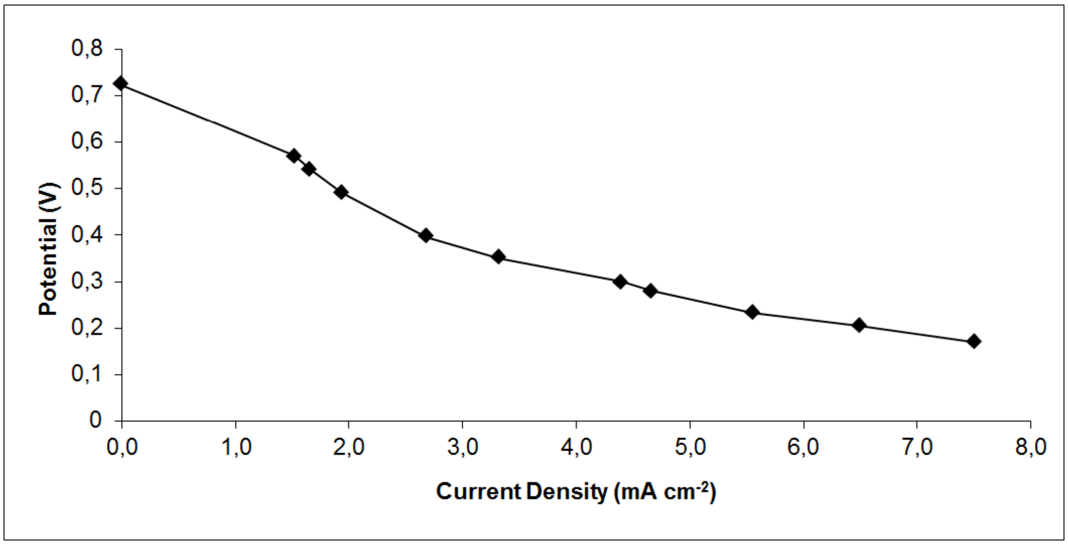

Figure 5. Current density/potential diagram for single DFAFC using Pt/PVF catalyst as anode and Pt black as cathode at ambient temperature and atmospheric pressure in 6 M HCOOH.

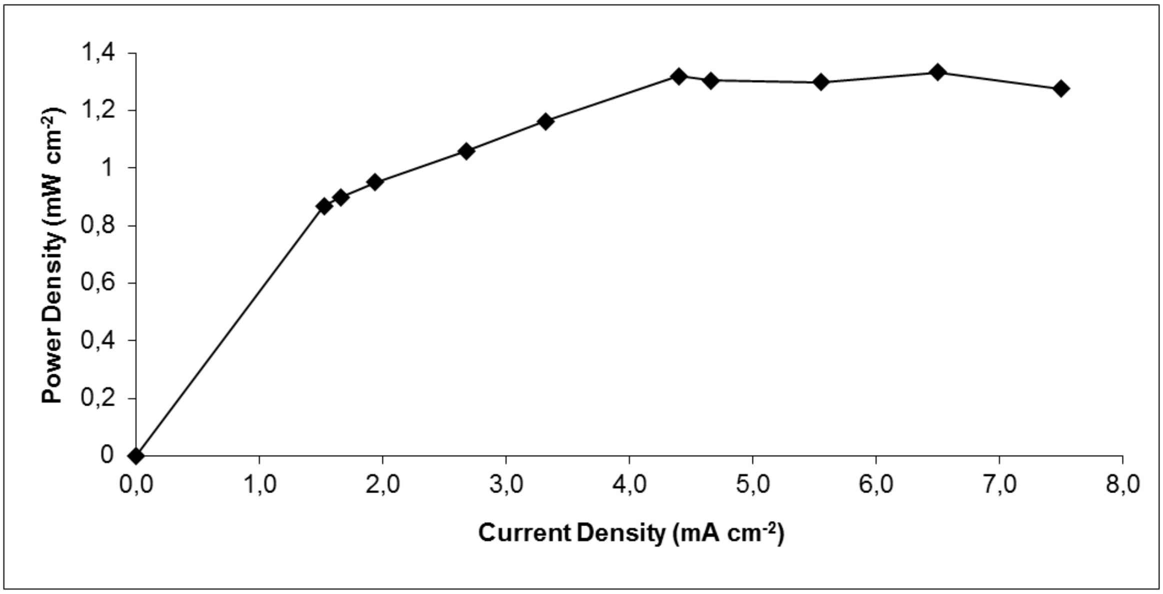

Figure 6. Current density/power density diagram for single DFAFC using Pt/PVF catalyst as anode and Pt black as cathode at ambient temperature and atmospheric pressure in 6 M HCOOH.

density versus potential and power density values are given in Figures 5 and 6 respectively.

Finally we compared fuel cell performances in DMFC [11] and DFAFC modes at identical conditions. According to the results presented in Table 1, using formic acid instead of methanol as fuel resulted with higher OCV and power density values at the same conditions.

CONCLUSIONS

Pt/PVF catalyst system was used for electrooxidation of formic acid in acidic medium. It was observed that the catalyst system with a low Pt loading showed enhanced catalytic activity towards formic acid oxidation. In order to reveal the advantage of formic acid over methanol as a fuel, CVs and fuel cell test results were compared

Table 1. Comparison of DMFC and DFAFC at the same conditions (2M fuel) with Pt/PVF anode.

	DMFC11	DFAFC
Open Circuit Voltage	680 mV	715 mV
Max. Power Density	0.31 mW cm^{-2} at 0.63 mA cm^{-2}	0.435 mW cm^{-2} at 1.5 mA cm^{-2}

at identical conditions. As expected, higher oxidation peak current values were obtained for formic acid with respect to methanol. Consistent with this result, a higher OCV was also obtained for DFAFC than that of DMFC.

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