Preparation and physical/electrochemical characterization of Pt/poly(vinylferrocenium) electrocatalyst for methanol oxidation

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ABSTRACT

Preparation and characterization of a platinum (Pt)-based catalyst using a redox polymer, poly(vinylferrocenium)(PVF⁺), as the support material was described. Pt was obtained from aqueous solution of K_2PtCl_4 in the complex form. Pt particles were reduced by chemical and electrochemical means. Chemical reduction was performed using aqueous hydrazine solution and electrochemical reduction was carried out in H_2SO_4 solution. The Pt/PVF⁺ catalyst system showed catalytic activity towards methanol oxidation. Cyclic voltammetry was used for the electrochemical characterization of the catalyst system. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectrum (EDS) of the catalyst system were also recorded. The system was tested in a single fuel cell configuration at ambient temperature and atmospheric pressure. The open circuit voltage (OCV) was 680 mV for the system and the maximum power density was 0.31 mW cm⁻² at a current density of 0.63 mA cm⁻². Catalytic activity of Pt/PVF⁺ system towards methanol oxidation was comparable with the related catalysts in the literature.

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1. Introduction

Methanol is one of the most widely studied organic molecules owing to its use in direct methanol fuel cells (DMFC). Despite the fact that there are opposite views about methanol being an alternative fuel in the future [1–4], DMFCs are considered to be promising power sources for portable, stationary and vehicular applications. Having a complex reaction mechanism, the electrocatalysis of methanol oxidation is the most difficult task in the realization of a DMFC. The thermodynamic potential for methanol oxidation to CO_2, lies very close to the equilibrium potential of hydrogen (i.e. $E^0 = 0.02$ V for methanol oxidation); however, compared with hydrogen oxidation, this reaction is by several orders of magnitude slower and requires a suitable catalyst [5].

Recent studies show that platinum (Pt)-based catalysts are the most efficient ones for methanol oxidation. This nobel metal is known to activate the dissociative adsorption of methanol at an appreciable rate. However, it is well known that some intermediate products of the reaction are strongly adsorbed at the electrode surface, acting as poisons and leading to a loss of electrocatalytic activity of the electrode. To solve the problem, incorporation of

transition metal (e.g., Pt, Ru, Pd, etc.) particles into conducting polymer electrodes, which exhibits enhanced electrocatalytic activities as compared with the bulk-form metal electrodes in the oxidation of small organic molecules, has been studied [6–11].

There are many factors affecting the electrocatalytic activity of nobel metal particle-based catalysts, such as particle size and dispersion, preparation methods, supporting materials, etc. Generally, the small particle size and high dispersion of metal particles will result in high electrocatalytic activity. Studies dealing with the synthesis and catalytic applications of transition metal particles stabilized in various microenvironments [4,6–9,12–22] and their application to DMFC have been appeared in the literature [3,9,14,17,23–31].

As described by Kralik and Biffis, preparation of metal particles supported on functional polymers involves three steps, namely (1) synthesis of a suitably functionalized polymer; (2) loading of the polymer with convenient metal particle precursors and (3) generation of the metal particles within the polymer [32].

Poly(vinylferrocene) (PVF), is a redox polymer, which has long been used as a fundamental conducting polymer system, with the advantages of simple electrochemistry (a reversible one-electron process), high stability (allowing multiple measurements to be made over extended time scale), and the ease of deposition of thin films using a variety of methods [33]. PVF-coated electrodes can be easily prepared by the constant potential anodic electrolysis of methylene chloride solution of PVF. It has been stated that the electrodeposited polymer contains both ferrocene and ferrocenium

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(PVF$^+$) forms of the polymer [34]. PVF-modified electrodes have been extensively studied by our research group in various areas such as electrochemical oxidation and reduction [35,36], electro-analysis and electrocatalysis [37–41], and biosensors [42–49].

In the present paper, we prepared an electrocatalyst with PVF$^+$ as the supporting material and used tetrachloro-complex of Pt metal as the metal particle precursor, which has not been widely used in the literature [15,50,51]. Pt particles were immobilized in the polymer matrix via cyclic voltammetric scans from aqueous solution of PtCl$_4^{2-}$ complex. Finally, Pt particles were obtained by chemical/electrochemical reduction of the Pt-complex. The Pt/PVF$^+$ electrocatalyst system showed catalytic activity towards methanol oxidation.

2. Experimental

2.1. Reagents and instruments

Poly(vinylferrocene) was synthesized according to the procedure described by Aso et al. [52]. Vinylferrocene was purchased from Aldrich. 2,2′-Azo-bis(2-methyl-propionitrile) (AIBN) was obtained from Alfa. Tetra-n-butyl ammonium perchlorate (TBAP) was synthesized by the reaction of tetra-n-butyl ammonium hydroxide (40% aqueous solution, Merck) with perchloric acid (BDH) and recrystallized from the 1:9 mixture of water and ethyl alcohol (Merk), by volume, several times. It was then dried at 120 °C under vacuum for 12 h. This salt was always kept under nitrogen atmosphere.

Methylene chloride (HPLC grade, Riedel de Häen), methanol (Riedel de Häen) and H$_2$SO$_4$ (Merck) were used as-received. K$_2$PtCl$_4$ was obtained from Merck. Hydrazine solution was prepared using hydrazinium sulfate (NH$_2$·NH$_2$·H$_2$SO$_4$, BDH). 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 and electron dispersive spectrometer was used for images and analysis, respectively.

2.2. Electrodes

In electrochemical studies, a Pt disc electrode ($A = 7.85 \times 10^{-3}$ cm^2) was used as the working electrode. Before each experi-
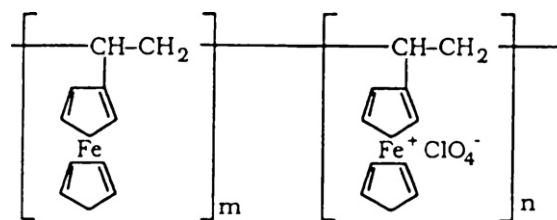

Fig. 1. Electrochemically doped PVF.

ment, the working electrode was polished with alumina (5.0 μm), then rinsed with triple distilled water, cleaned in ultrasonic bath and dried. In the methylene chloride medium, 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 the electrochemical experiments that were carried out 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 electrode with a surface area of 2 cm^2 in spiral form was used as the counter electrode.

2.3. Preparation of Pt/PVF$^+$ catalyst

The polymer was electrodeposited on 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) [53]. The resulting film is in a porous structure containing ClO$_4^-$ ions as the counter ion, ferrocene and ferrocenium groups (Fig. 1).

Pt particles were incorporated into the polymer matrix via cyclic voltammetric scans in aqueous 2 mM K$_2$PtCl$_4$ solution without supporting electrolyte. In this step, Pt is in complex form and does not show catalytic activity. Two separate methods were used for reduction of Pt particles. In the first method, polymer-coated electrode containing Pt complex was immersed in 0.1 M hydrazine solution stirred continuously at open circuit. In the second method, Pt particles were electrochemically reduced in 0.5 M H$_2$SO$_4$ solution. After
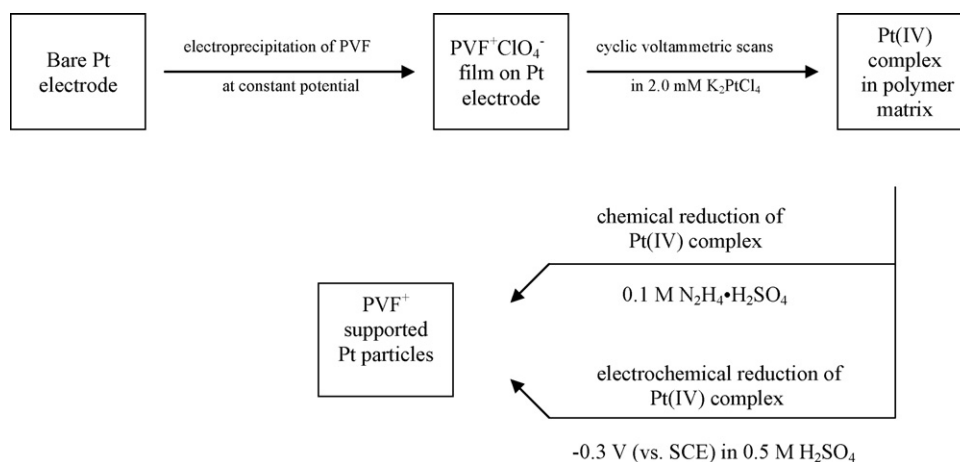
Scheme 1. Schematic procedure for the preparation of PVF$^+$-supported Pt particles.

reduction of Pt particles, the Pt/PVF[+] system showed catalytic activity towards methanol oxidation. Steps for preparation of the catalyst are represented schematically in Scheme 1. Methanol solutions were daily prepared, the methanol concentration was 0.5 M and the solution included 0.5 M H_2SO_4 as supporting electrolyte.

2.4. Single cell test

Nafion® membrane (NE 450, Aldrich) was used in the DMFC construction. The anode was Pt/PVF[+] catalyst system prepared using Pt foil electrode (1 cm × 1 cm). Pt black-coated Pt electrode was used as the cathode material. 2 M CH_3OH 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.

3. Results and discussion

In order to evaluate the effect of PVF[+] support on the performance of the catalyst, oxidation of methanol was recorded with and without use of PVF[+] during the preparation of the catalyst (Fig. 2). As seen in the figure, oxidation of methanol was not observed with the bare Pt electrode (Fig. 2(a)). In the cyclic voltammogram (CV) shown in Fig. 2(b), Pt particles were deposited directly onto the uncoated Pt disc electrode by cyclic voltammetric scans in K_2PtCl_4 solution. The CV shown in Fig. 2(c) was recorded with the PVF[+]-supported electrocatalyst which was prepared according to the procedure described in Scheme 1. Two peaks of methanol oxidation were observed at the potentials 0.56 and 0.52 V vs. SCE, respectively from curve (c) in Fig. 2. The shape of the CV and the peak potential values are consistent with the data in the literature [6,7,19–22].
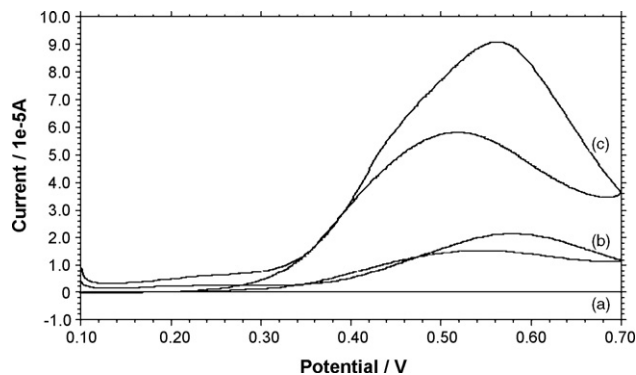

Fig. 2. CVs of 0.5 M methanol containing 0.5 M H_2SO_4 recorded with (a) bare Pt disc electrode, (b) Pt black on uncoated Pt disc electrode and (c) Pt/PVF[+] catalyst on Pt disc electrode. Scan rate: 5 mV s^{−1}.

The onset potential of methanol oxidation is observed at 0.30 V which is in agreement with other work cited. Presence of the polymer support in the catalyst greatly enhanced the oxidation peak current of methanol. This enhancement can be attributed to three effects: (1) as being a positively charged polymer matrix, the negatively charged Pt complexes can be more easily immobilized into the polymer, (2) as being a redox polymer, poly(vinylferrocene) acts as a mediator and increases the catalytic activity of the Pt/PVF[+] catalyst, and (3) as being in a porous structure, the polymer supplies an appropriate matrix for the Pt particles.

Scanning electron microscopy (SEM) images of the PVF[+] film and Pt/PVF[+] catalyst were recorded using Pt foil electrode (3 mm × 3 mm) and are given in Fig. 3. As can be seen from the images, the Pt particles immobilized in PVF[+] matrix are well dispersed. Dimensions of the particles are variable with an average
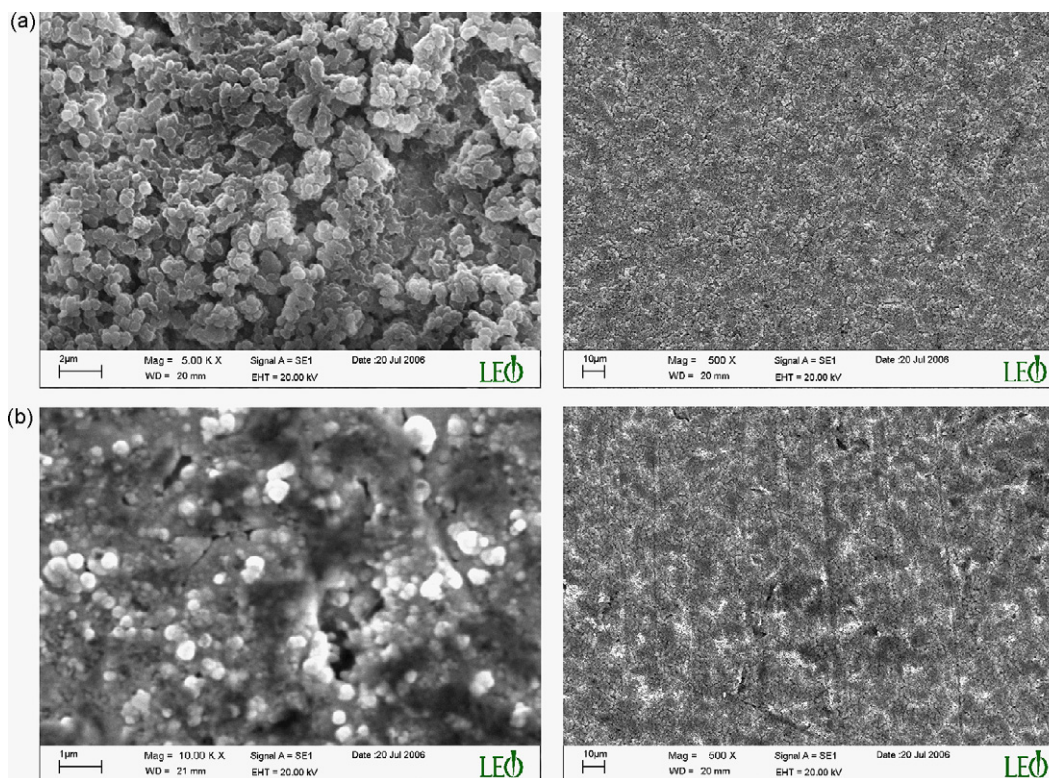

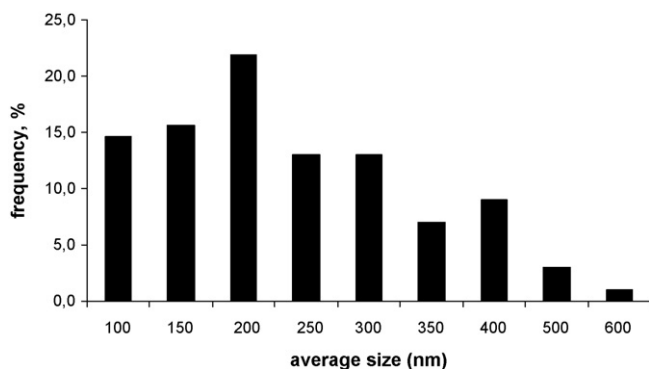**Fig. 3.** SEM images of (a) PVF[+] film and (b) Pt/PVF[+] catalyst.

Fig. 4. Average size distribution histogram for Pt particles-supported on PVF⁺ film.

size of 220 nm with a standard deviation of 107 nm. A representative size distribution histogram of Pt particles on PVF⁺ support is given in Fig. 4.

Energy dispersive X-ray spectrum (EDS) of the Pt/PVF⁺ system is shown in Fig. 5. The electrocatalyst was prepared on glassy carbon electrode (GCE) ($r = 0.3$ cm) to avoid Pt peaks coming from the electrode material. The spectrum indicated that C, Fe and Pt were the major elements. While the C atoms come both from the electrode material and the polymer support, Fe atoms come from the ferrocenium groups of PVF⁺ support and Pt atoms come from the Pt particles obtained by reduction of the $PtCl_4^{2-}$ complex. Quantitative analysis indicated that the ratio of Fe atoms to Pt atoms was 10:1.

Effect of polymer film thickness on methanol oxidation was studied. Polymer films were electrodeposited onto the Pt disc electrode controlling film thicknesses with the amount of charge passing during electrolysis. Then, Pt particles were incorporated from 2 mM K_2PtCl_4 solution and the Pt particles were chemically reduced using hydrazine as the reducing agent. Maximum oxidation peak current was obtained with the film thickness cor-
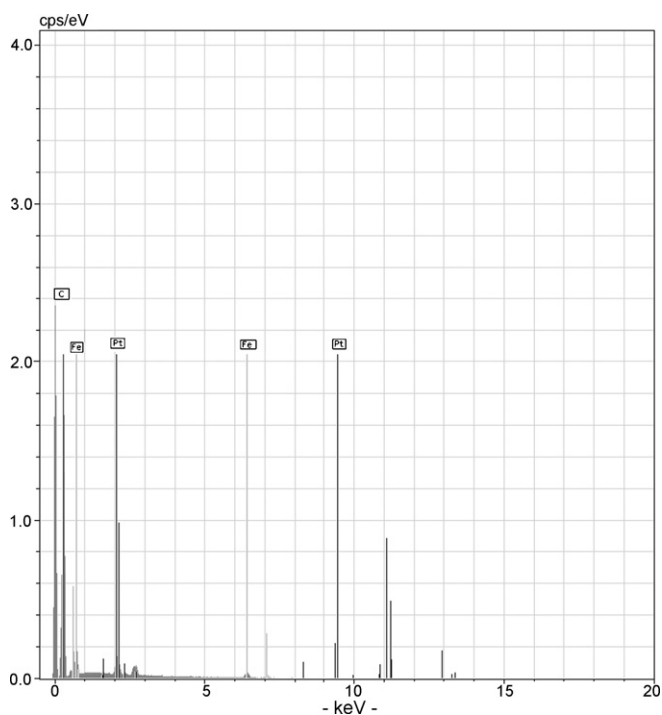

Fig. 5. Energy dispersive X-ray spectrum (EDS) of Pt/PVF⁺ catalyst system prepared on GCE.
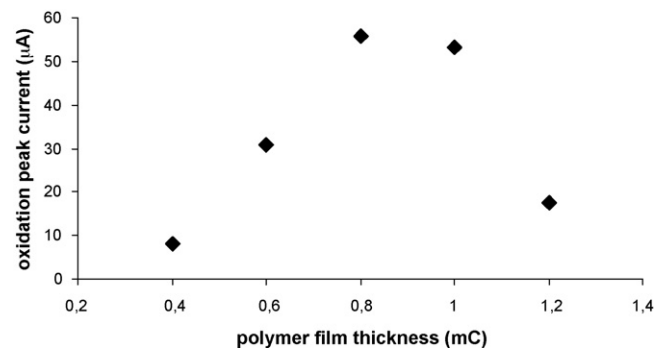

Fig. 6. Effect of polymer film thickness (in means of charge passed during electrooxidation of PVF) on oxidation peak current of methanol (30 cycles in 2 mM K_2PtCl_4 during cyclic voltammetric scans, 60 min reduction time in hydrazine, 0.5 M methanol solution containing 0.5 M H_2SO_4).
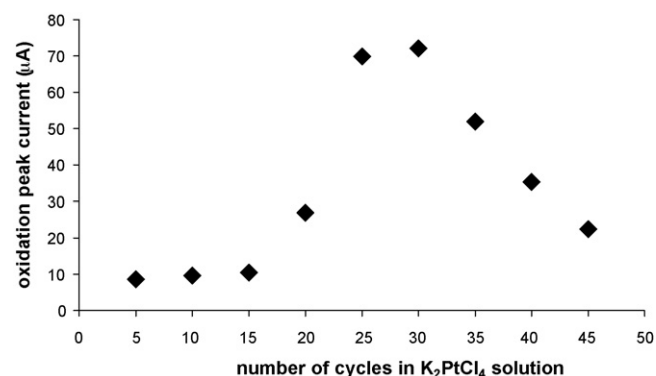

Fig. 7. Effect of number of cyclic voltammetric scans in K_2PtCl_4 solution on oxidation peak current of methanol (0.8 mC polymeric film thickness, 60 min reduction time in hydrazine, 0.5 M methanol solution containing 0.5 M H_2SO_4).

responding to a charge of 0.8 mC during the electroprecipitation of PVF⁺ film onto the electrode surface (Fig. 6).

During incorporation of Pt particles into the polymer matrix via cyclic voltammetric scans, number of cycles was quite important because it directly determined the amount of Pt particles immobilized in the polymer. Between cycle numbers from 5 to 45, oxidation peak current of methanol showed a maximum at 30 cycles and decreased afterwards. Number of cycles vs. oxidation peak current is given in Fig. 7.

After incorporation of Pt complexes into the polymer matrix, chemical reduction time of Pt particles vs. oxidation peak current of methanol was studied using 0.1 M hydrazine. As seen in Fig. 8, the oxidation peak current values increased and remained constant
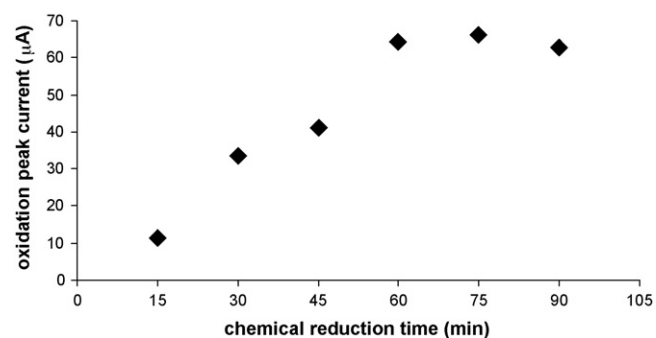

Fig. 8. Effect of reduction time in 0.1 M hydrazine solution on oxidation peak current of methanol (0.8 mC polymeric film thickness, 30 cycles in 2 mM K_2PtCl_4 during cyclic voltammetric scans, 0.5 M methanol solution containing 0.5 M H_2SO_4).
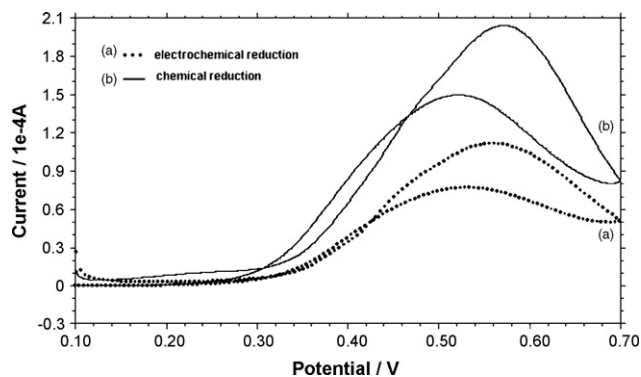
Fig. 9. CVs of 0.5 M methanol containing 0.5 M H_2SO_4 recorded with the Pt/PVF$^+$ system prepared by: (a) electrochemical reduction and (b) chemical reduction. Scan rate: 5 mV s^{-1}.

after 60 min. Effect of reduction temperature was also studied and maximum peak current was observed at the reduction temperature of 40 °C.

Electrochemical reduction of Pt particles was also studied in 0.5 M H_2SO_4 solution between potentials −0.20 and −0.40 V vs. SCE and for reduction time 5–25 min. When the electroreduction of Pt particles were performed at −0.30 V vs. SCE, oxidation peak current of methanol was maximum. On the other hand, 15 min was optimum for electrochemical reduction of Pt particles. In Fig. 9, a comparison of two reduction methods is given. It is known that Pt adsorbs a monoatomic H layer and this allows for the evaluation of the electrochemically active surface area of electrodes. However, Pt is also known to absorb molecular hydrogen which is one of the products in the electrochemical reduction of Pt particles. This property of Pt metal is a disadvantage in electrodeposition processes leading to high internal stress in the deposits [54]. Consistent with this property, the electrocatalyst system prepared by reduction in hydrazine solution gives higher oxidation peak current and chemical reduction is more convenient for obtaining Pt particles on PVF$^+$.

Cyclic voltammetric behavior of 0.5 M H_2SO_4 solution was recorded using (a) uncoated Pt disc electrode, (b) PVF$^+$-coated Pt disc electrode, (c) electrochemically reduced Pt particles on PVF$^+$ and (d) chemically reduced Pt particles on PVF$^+$. The CVs are presented in Fig. 10. In the voltammograms, oxidation of Pt was observed in the region 0.00–1.00 V vs. SCE. The oxidation and reduction peaks observed at 0.48 and 0.32 V are related to electrochemical oxidation and reduction of PVF, respectively. Between
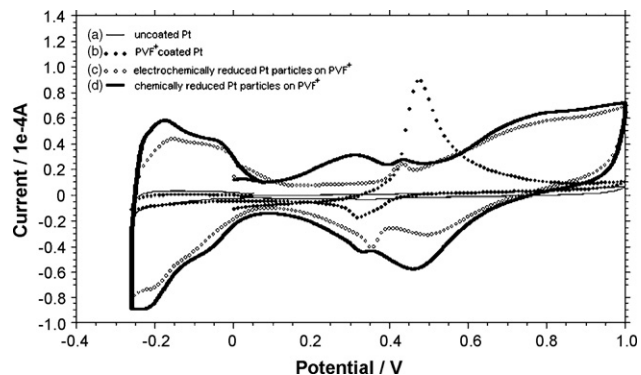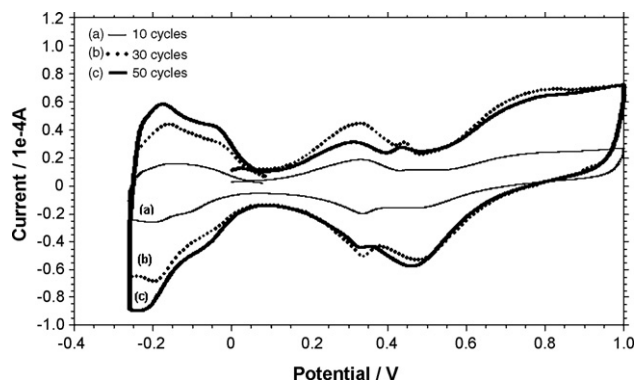

Fig. 11. CVs of 0.5 M H_2SO_4 recorded with Pt/PVF$^+$ catalysts with Pt loadings corresponding to (a) 10, (b) 30 and (c) 50 cycles in K_2PtCl_4 solution (0.8 mC polymeric film thickness, 60 min reduction time in hydrazine). Scan rate: 100 mV s^{-1}.

0.00 and −0.25 V, oxidation and reduction behavior of weakly and strongly adsorbed hydrogen on Pt/PVF$^+$ catalyst was observed. This redox behavior in H_2SO_4 solution is typical for Pt particles [50,55–57].

Fig. 11 shows CVs of 0.5 M H_2SO_4 solution recorded with Pt/PVF$^+$ catalysts having different amounts of Pt. The amount of Pt was controlled by the number of cyclic voltammetric scans in K_2PtCl_4 solution during catalyst preparation. As we expected, the oxidation and reduction peak current values of hydrogen recorded with the catalyst having optimum amount of Pt (corresponding to 30 cycles in K_2PtCl_4 in Fig. 7) were considerably high with respect to the others.

Finally, the Pt/PVF$^+$ catalyst was tested in a single fuel cell configuration in a DMFC mode at ambient temperature and atmospheric pressure. 2 M CH_3OH solution containing 0.5 M H_2SO_4 was used as the fuel and 0.5 M H_2SO_4 solution saturated with pure O_2 was used as the oxidant. The open circuit voltage (OCV) was 680 mV for the system and the maximum power density was 0.31 mW cm^{-2} at 0.63 mA cm^{-2}. Current/voltage diagram for the fuel cell is given in Fig. 12. Additionally, PVF$^+$ support was compared with carbon support using the single fuel cell configuration. For this purpose, C-supported Pt particles were prepared with the same method using GCE as the support material. Despite the fact that C support is more conductive than the PVF$^+$ support, the OCV of the fuel cell using the carbon-supported Pt particles as the anode catalyst was lower (540 mV). This result also indicated the contribution of PVF$^+$ support to the catalyst system due to its characteristic properties described in Fig. 2 for Pt electrode.
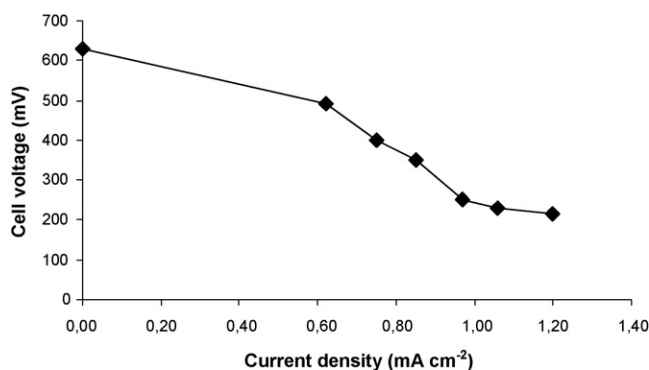

Fig. 10. CVs of 0.5 M H_2SO_4 recorded with (a) uncoated Pt disc electrode, (b) PVF$^+$-coated Pt disc electrode, (c) electrochemically reduced Pt particles on PVF$^+$, and (d) chemically reduced Pt particles on PVF$^+$. Scan rate: 100 mV s^{-1}.

Fig. 12. Current/voltage diagram for single fuel cell using Pt/PVF$^+$ catalyst as anode and Pt black as cathode at ambient temperature and atmospheric pressure.

4. Conclusions

A simple method of preparing Pt-based catalyst for methanol oxidation was described using PVF$^+$ as the support material. Preparation of the catalyst involved three steps: electrodeposition of the polymer 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 particles. Optimization of the catalyst system was carried out for many parameters and the Pt/PVF$^+$ catalyst was characterized by electrochemical and surface analysis techniques. The catalyst system was tested in a single fuel cell configuration in a DMFC. The catalyst had the innovation and advantage of using a redox polymer and the oxidation peak current values were comparable with the catalyst systems in the literature.

Acknowledgement

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