Electrocatalytic oxidation of formic acid and formaldehyde on platinum nanoparticles decorated carbon-ceramic substrate

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**Abstract**

Electrochemical characteristics of formic acid (FM) and formaldehyde (FM) oxidation on a potent catalyst, platinum nanoparticles supported on carbon-ceramic substrate (CC/Pt), were investigated via cyclic voltammetric and chronoamperometric analysis in mixed 0.75 M FM (or 0.75 M FM) and 0.1 M H2SO4 solutions. The results were compared to those at a polycrystalline platinum electrode and platinum particles deposited on platinum and glassy carbon electrodes. It was found that CC/Pt was catalytically more active than smooth platinum and platinum particles supported on platinum and glassy carbon electrodes. On the other hand, such nanoparticles on CC substrate exhibit better catalytic behavior towards FA and FM than the corresponding platinum and glassy carbon electrodes, which is raised from high porosity of CC substrate for better distribution of platinum particles and to produce of platinum particles in nano size. The effect of some experimental factors was studied and optimum conditions were suggested. Finally, the long-term stability of the modified electrode has also been investigated. These results indicate that the system studied in the present work is the most promising system for use in fuel cells.

1. **Introduction**

As an attractive candidate to replace methanol and hydrogen, formic acid (FA), a non-toxic, non-explosive and non-flammable liquid at room temperature has considerable advantages in polymer electrolyte membrane (PEM) fuel cells for powering portable devices [1–6]. In addition, FA has several advantages as a fuel for PEM fuel cells: it is easily transported and stored, it has low fuel crossover through the PEM, it has high theoretical open circuit potential of 1.45 V, and it has less poisoning to platinum-based electrocatalysts than that of methanol. Therefore, development of anodic materials having high catalytic activity towards the oxidation of FA is an important aspect in the field of the PEM fuel cells. Platinum nanoparticles have important applications in electrocatalysis because of their large surface areas [7–11]. Some platinum nanocatalysts have been prepared and used as effective electrocatalysts for the oxidation of FA and formaldehyde (FM) [12–17].

In fact, the choice of a suitable supporting material is an imperative factor that may affect the recital of supported platinum electrocatalysts owing to their interactions and surface reactivities [18–22]. On the other hand, physico-chemical characteristics and surface chemistry of substrate influence properties of supported catalysts [23–25]. Carbon materials are of special interest due to their outstanding properties, such as their tuneable shape, size, porosity, chemical stability, corrosion resistance, low cost, good thermal resistance and electrical conductivity. The combination of all these characteristics has promoted the use of these
materials as electrode supports. Sol–gel technology has aroused great interest in designing and application of electrochemical sensors and electroanalysis due to its simplicity, stability, physical rigidity, transparency, porosity, permeability, versatility and flexibility in the preparation procedure [26–34]. Now, the sol–gel process conducted in the presence of graphite powder was proposed for fabrication of carbon-ceramic (CC) electrodes as a new kind of carbon substrates in electrochemical systems [35–37]. Considering the stability, permeability, simplicity, especially low cost, easy production and good porosity of CC substrate [28,38], it is one of the best materials that can be used as catalyst supporter in FA fuel cells.

In this work, we have prepared CC supported platinum nanoparticles by a two-step procedure: (I) the CC substrate was produced by using sol–gel technique and (II) platinum nanoparticles were precipitated electrochemically on the surface of CC substrate and the resulting electrode was referred as CC/Pt. The electroactivity of CC/Pt towards the FA surface of CC substrate and the resulting electrode was determined by cyclic voltammometric and chronoamperometric measurements and the obtained results were compared with those obtained on the smooth platinum and platinum particles on platinum and glassy carbon electrodes. It was found that CC/Pt was catalytically more active than smooth platinum and platinum particles supported on platinum and glassy carbon electrodes. The effect of some experimental factors was studied and optimum conditions were suggested. Finally, the long-term stability of modified electrode has also been studied.

### 2. Experimental

#### 2.1. Chemicals

Methyltrimethoxysilane (MTMOS) was from Fluka. Formic acid, formaldehyde, methanol, H₂PtCl₆·5H₂O, HCl, H₂SO₄ and graphite powder of high purity were obtained from Merck. All solutions were prepared with double distilled water.

#### 2.2. Procedure of CC/Pt preparation

The sol–gel processing method was used for fabricating CC substrate according to the following procedure: The amount of 0.9 ml MTMOS was mixed with 0.6 ml methanol. After addition of 0.6 ml HCl 0.1 M as catalyst, the mixture was magnetically stirred (for about 15 min) until it produced a clear and homogeneous solution. Then, 0.3 g graphite powder was added and the mixture was shaken for another 5 min. Subsequently, the homogenized mixture was firmly packed into a Teflon tube (with 3 mm inner diameter and 10 mm length) and dried for at least 24 h at room temperature. A copper wire was inserted through the other end to set up electric contact. The electrode surface was polished with 1500 emery paper and rinsed with water. The platinum nanoparticles were electrochemically deposited at the surface of CC substrate from 1 mM H₂PtCl₆ in aqueous 0.1 M H₂SO₄ solution as the supporting electrolyte.

### 2.3. Instrumentation

The electrochemical experiments were carried out using an AUTOLAB PGSTAT-30 (potentiostat/galvanostat) equipped with a USB electrochemical interface and a driven CEPS software was used for electrochemical experiments. A conventional three electrode cell was used at room temperature. A disc of CC/Pt (3 mm diameter) was used as a working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrodes, respectively. JULABO thermostat was used to control cell temperature at 25 °C. Scanning electron microscopy (SEM) was performed on a LEO 440i Oxford instrument.

### 3. Results and discussion

#### 3.1. Deposition of platinum on the CC substrate

Electrochemical deposition is an efficient method for the preparation of metal particles. It is widely used with different strategies/methodologies, such as potential step deposition [39], cyclic voltammetry [40], double-pulse [41] and galvanostatic methods [42]. Among these, potential step deposition (confirmed in 3.5.1 Section) provides a tool to fine-tune the amount of the metal deposited, the number of metallic sites and their size. Electrodeposition of platinum on CC substrate was performed potentiostatically at −0.2 V vs. SCE. The mass of platinum deposited was obtained by integration of the charge consumed during the deposition process $Q_{Pt}$ (C cm⁻²). It was assumed that the current efficiency was 100% and the following effects were negligible: partial reductions of Pt⁴⁺, hydrogen evolution at the electrodeposited platinum and double layer charging. On the other hand, it was also assumed that the only contributing reaction was the Faradaic process (1):

\[
PtCl₆^{2−} + 4e^{−} → Pt + 6Cl^{−}
\]  

(1)

So, the quantity of deposited platinum ($W_{Pt}$) is obtained from:

\[
W_{Pt} = \frac{Q_{dep} M}{zF}
\]  

(2)

where $M$ is the atomic weight of platinum (195.09 g mol⁻¹), and $F$ is the Faraday constant (96485.309 C mol⁻¹).

Fig. 1 (curve a) shows the cyclic voltammogram (CV) of the CC/Pt electrode in 0.1 M H₂SO₄. As seen in Fig. 1 (curve a) three pairs of peaks (I/I’, II/II’ and III/III’) are discernible. The oxidation and reduction peak couples (I/I’ and II/II’) at negative potential regions corresponding to the adsorption/desorption of hydrogen, while the other pair appeared in positive potential regions (III/III’) corresponding to the formation of platinum oxide and its reduction, respectively. The figure is similar to that represented by Breiter et al. [43]. Since the electrocatalytic properties are expected to depend on the number of available surface sites, activities referred to real platinum surface area, $A_s$, have a clear physical significance. Measurement of hydrogen adsorption is widely used in determining $A_s$ [44–46]. The $A_s$ of deposited platinum was estimated from hydrogen adsorption on the voltammogram.
Physical characteristics of the different platinum deposited electrodes.

(Fig. 1 curve a). Integration in a potential range from −300 to +100 mV, allows estimation of the charge, \(Q_e\) (\(\mu\)C), due to the hydrogen adsorption. To obtain \(A_r\) from value of \(Q_e\), assumption must be made about the atoms on the surface which are accessible to hydrogen adsorption. Assuming one \(H_{ad}\) per platinum surface atom, a theoretical charge associated with a monolayer of hydrogen formed on the basis of: \(H^+ + e^- \rightarrow H_{ad}\). \(Q_h\) has been commonly taken as 210 \(\mu\)C/real cm\(^2\) estimated as follows:

\[
Q_h(\mu\text{C}/\text{real cm}^2) = F \times n/N
\]

where \(n\) is the number of platinum atoms \((1.3 \times 10^{15}/\text{cm}^2)\) and \(N\) is Avogadro constant \([47]\).

Accordingly, \(A_r\) (cm\(^2\)) can be obtained from charge for hydrogen adsorption as \(A_r = Q_h/Q_e\). The specific surface area \(S\) (in m\(^2\) g\(^{-1}\)) was also estimated as follows:

\[
S = 100 A_r/W_A\)
\]

with \(A_r\) the real surface area, \(A_g\) the geometric surface area \((A_g = 0.07 \text{ cm}^2)\) and \(W\) (in \(\mu\)g cm\(^{-2}\)) the platinum loading. Assuming spherical particles of similar radius, an average-sized particle of platinum, \(d\) (in nm) was calculated from the following equation using the procedure of Gloaguen et al. \([48]\):

\[
d = 6000/\rho S \quad (5)
\]

where \(\rho\) is the density of platinum \((\rho = 21.4 \text{ g cm}^{-3})\) and \(S\) is the specific surface area (in m\(^2\) g\(^{-1}\)).

The real surface areas of the different investigated electrodes together with other physical characteristics are given in Table 1.

In order to surface characterization of the CC/Pt catalyst, the micrograph of CC substrate and CC/Pt has been investigated by SEM and the corresponding results were shown in Fig. 2. Fig. 2A shows the structure of the bare CC surface immediately after polishing with emery paper grade 1500. As seen in this image the surface is dense, scaly and has a high porosity. The average pore size of CC substrate is 0.2 \(\mu\)m. The surface area of CC was also investigated by cyclic voltammetry using Fe(CN)\(_6\)^{3−/4−} as probe ion and the Randles–Sevcik equation \([49]\). The electrochemical area of CC (geometric area \(= 0.07 \text{ cm}^2\) was 0.162 cm\(^2\) \([50,51]\). Fig. 2B shows the SEM micrograph of the CC surface after platinum deposition. As seen, the platinum nanoparticles are spherical and separate and the surface coverage is almost uniform without any holes and deficiency. Most likely, the particulate structures of platinum in this image are not the individual platinum crystallites. They are, most probably, clews consisting of crystallite aggregates.

On the other hand, curve b in Fig. 1, shows the CV of bare CC substrate in 0.1 M H\(_2\)SO\(_4\) solution. No adsorption/desorption peaks of hydrogen appeared at the bare CC. Also, inset Fig. 1 shows the voltammetric properties of a pure platinum electrode under the same conditions. The current density of adsorption/desorption of hydrogen at this electrode is very low compared with the CC/Pt modified electrode (curve a), indicating that the catalytic activity of the pure platinum electrode is quite low.

### 3.2. The electrocatalytic oxidation of FA

Fig. 3 shows the cyclic voltammograms (CVs) of the CC/Pt and pure platinum (inset A) in a 0.75 M FA + 0.1 M H\(_2\)SO\(_4\) solution. During the forward scan of the CV of pure platinum, the first anodic peak results from FA oxidation, while the second peak at 1.06 V can be attributed to CO oxidation and FA oxidation on sites that were previously blocked by CO \([6]\). The CV of CC/Pt shows the usual characteristics of pure platinum except that both for forward and reverse scan directions the oxidation currents of FA on the CC/Pt are significantly higher than on the platinum. It can be seen from voltammogram of FA oxidation

<table>
<thead>
<tr>
<th>Type of electrodes</th>
<th>Pt loading W (mg cm(^{-2}))</th>
<th>True surface area (A_r) (cm(^2))</th>
<th>Relative surface area ((A_r/A_g))</th>
<th>Specific surface area (S) (m(^2) g(^{-1}))</th>
<th>Particle size (d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC/Pt</td>
<td>0.40</td>
<td>2.82(^{b})</td>
<td>40.36</td>
<td>10.09</td>
<td>27</td>
</tr>
<tr>
<td>CC/Pt</td>
<td>0.70</td>
<td>7.31(^{b})</td>
<td>104.48</td>
<td>14.92</td>
<td>18.78</td>
</tr>
<tr>
<td>GC/Pt</td>
<td>//</td>
<td>3.6(^{b})</td>
<td>51.38</td>
<td>7.34</td>
<td>38.19</td>
</tr>
<tr>
<td>Pt/Pt</td>
<td>//</td>
<td>2.50(^{b})</td>
<td>35.71</td>
<td>5.1</td>
<td>54.95</td>
</tr>
<tr>
<td>Bulk Pt</td>
<td>Bulk Pt</td>
<td>0.1(^{b})</td>
<td>1.43</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{a}\) Real surface area \((A_r)/\text{geometric surface area (A}_g\).  
\(^{b}\) As determined from hydrogen adsorption.  

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**Fig. 1** – Cyclic voltammograms of CC/Pt (a) and CC (b) electrodes in 0.1 M H\(_2\)SO\(_4\) at a scan rate of 50 mV s\(^{-1}\). The inset is CV of smooth Pt in the same conditions.
on the CC/Pt that the reaction commences in the hydrogen region and proceeds slowly in the positive direction, and then reaches a plateau at ca. 0.21 V. At potentials with more than ca. 0.5 V, the reaction becomes accelerated and maximum rate at ca. 0.81 V occurs. A rapid increase in current at potentials more than ca. 0.95 V is assigned to oxygen evolution. Upon reversing the potential sweep, a very steep increase of the reaction rate at ca. 0.59 V develops and a maximum current is observed at ca. 0.54 V. After that, the current gradually decreases but the reaction rate is still faster than in the forward scan. This large anodic peak in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan [52]. It has been widely accepted in the literature that FA is oxidized to CO₂ via a dual path mechanism [53–59], which involves a reactive intermediate (main path, dehydrogenation) and adsorbed CO as a poisoning species (parallel path, dehydrogenation). In one pathway, direct oxidation of FA is said to occur (Scheme 1, pathway 2) whereas in the other pathway, FA is oxidized to CO (Scheme 1, pathway 1), which in turns must be removed by activating water (Scheme 1, water dissociation). While the net reaction is the same in both of the pathways, the water dissociation reaction is rather difficult. The OH_ads formed by the dissociation of water molecules on platinum surface [60] aids in removing the adsorbed surface poison CO_ads by oxidizing it (Scheme 1, water dissociation reaction). But indeed this process is very intricate, as a higher potential is required for water activation (>0.5 V) on platinum surfaces. Consequently, the electrode surface will be blocked by large amounts of CO species thereby hindering further adsorption of other FA molecules on the electrode surface. This drawback will make only a few number of FA molecules to be oxidized as the electrode poison CO remains on the electrode surface for a long time occupying active catalyst sites thereby reducing the overall activity of FA oxidation. Hence, the rate of FA oxidation primarily depends on the amount of CO removed from the electrode surface [59,61].

A closer examination of the onset potential in Fig. 3 compared to the FA free electrolyte shows that the magnitudes of the hydrogen adsorption/desorption peaks were reduced by the presence of FA (inset B Fig. 3), implying that FA is adsorbed preferentially on the electrode surface at those potentials [12,62–64]. It should be noted that, for low concentration of FA in the first sweep (not shown), the formation of platinum oxides and their reduction peaks were observed (peaks III and III') and the hydrogen adsorption/desorption peaks are still visible showing that FA does not prevent completely the hydrogen adsorption. On the other hand, in order to reveal the correlation between FA oxidation and platinum oxide species, we have studied the effect of upper limit potentials (EU) in cyclic potential scanning on the FA oxidation. Fig. 4 shows the CVs of FA oxidation on the CC/Pt electrode for EU of 1.0–1.5 V. As seen in Fig. 4, by increasing the final positive potential limit, the anodic current of FA oxidation in the positive going potential sweep (PGPS) remains unchanged, but oxidation current in the negative going
potential sweep (NGPS) decreased. In lower limit potential, the platinum oxides with high valence haven’t developed greatly, so the effect of the platinum oxides with high valence on FA oxidation in the NGPS is relatively small. It can be seen that the potential of FA oxidation peak remains invariable in the PGPS, while the potential of FA oxidation peak shifts positively in the NGPS. On the other hand, the peak current in the NGPS decreased as the EU increased. Indeed by increasing final positive potentials the conversion of platinum to PtO is accelerated and it caused a decrease of oxidation current in the NGPS, which further demonstrates that FA can only be oxidized on clean metallic platinum nanoparticles surface. Finally, in view of investigating the role of CC substrate on the electrocatalytic activity of platinum nanoparticles towards FA oxidation via having high porosity [65] leads to the production of fine size of platinum particles, CVs were run for platinum particles deposited on platinum and glassy carbon (GC) electrodes (0.70 mg Pt/cm² in each case). It can be seen from the results that the electrocatalytic activity of platinum nanoparticles decorated CC substrate towards FA oxidation \([i_{p}(PGPS) = 49.43 \text{ mA/cm}^2(A)]\) was greatly improved than those with platinum \([i_{p}(PGPS) = 8.57 \text{ mA/cm}^2(A)]\) and GC \([i_{p}(PGPS) = 12.28 \text{ mA/cm}^2(A)]\). This is rising from high porosity surface of CC than that of smooth platinum and GC, thereby proving to be an efficient catalyst support, which appears as a promising field of research.

### 3.3. The electrocatalytic oxidation of FM

Fig. 5 shows the CVs of 0.75 M FM in 0.1 M H₂SO₄ on platinum nanoparticles decorated on CC substrate. As can be seen from Fig. 5, the electrochemical behavior of FM on CC/Pt is similar to FA. As in the case of FA, the electrooxidation of FM on platinum also results in the formation of poisonous CO_ads species as the overwhelmingly predominant stable intermediate on the electrode surface, which leads to electrode poisoning. At higher potentials, a quick increase in current is observed during the PGPS, which aids in transforming the poisonous intermediates to carbon dioxide resulted from FM (Scheme 2, water dissociation). The surface poison shown in pathway 1 in Scheme 2 can be removed by reacting with OH_ads formed by the dissociation of water molecules on platinum surface (Scheme 2, water dissociation).

Also, in view of investigating the role of CC substrate in the electrocatalytic activity of deposited platinum particles, the electrocatalytic activity of platinum particles on various substrates was evaluated towards FM oxidation. The obtained results show that the electrocatalytic activity of platinum supported on CC substrate towards FM oxidation \([i_{p}(PGPS) = 65.57 \text{ mA/cm}^2(A)]\) was significantly improved and higher than that of smooth platinum \([i_{p}(PGPS) = 0.70 \text{ mA/cm}^2(A)]\), Pt/Pt \([i_{p}(PGPS) = 10.30 \text{ mA/cm}^2(A)]\) and GC/Pt...
$I_{[\text{PCPS}]} = 18.28 \text{ mA/cm}^2(A_0)$. This proves that platinum nanoparticles promote the electrooxidation of FM and CC substrate acted as an efficient supporting material to effective dispersion of catalyst.

A further investigation was done to find out the transport characteristics of FA and FM in nanoparticles-modified electrode. The influence of the scan rate ($\gamma$) on the electrooxidation of FA and FM at the CC/Pt electrode was investigated and shown in Fig. 6. From the figure it can be observed that a straight relationship exists thereby showing that the process of FA (Fig. 6A) and FM (Fig. 6B) oxidation may be controlled by diffusion. The anodic peak currents are linearly proportional to $\gamma^{1/2}$ as shown in the insets of Fig. 6A and B suggest that the electrocatalytic oxidation of FA and FM on nanoparticles-modified electrode is diffusion-controlled processes.

3.4. Chronoamperometric study of oxidation of FA and FM

Fig. 7 shows the typical chronoamperometric response curves of FA (A) and FM (B) in 0.1 M H$_2$SO$_4$ on CC/Pt and platinum as the working electrodes. It was found that the current observed from chronoamperograms was in good agreement with the current observed from cyclic voltammetry. A further investigation was done to find out the effect of applied potential in chronoamperometric response of oxidation of FA at the CC/Pt electrode. Chronoamperometric data of the CC/Pt were recorded by potential steps from 0 mV for 60 s to the various potentials for 500 s. The current–time transient for the FA oxidation at different anodic potentials shows that the steady-state current at the ending time ($t = 500$ s) increases with an increase in applied potential. Phenomenologically, the oxidation current increases slowly with time at 200 and 300 mV, while at higher potentials the current increases sharply during short times and then decreases slowly at longer times. This may be caused by the CO-poisoning effect which results in deactivation of the catalyst surface and blocks further oxidation of FA. Similar behaviors were obtained for FM oxidation.

3.5. Parameters affecting the anodic peak currents of FA and FM oxidation

3.5.1. Influence of electrodeposition method of platinum particles

As mentioned above, the electrocatalytic activity of deposited platinum is dependent on the method employed for platinum particles electrodeposition. A change in the electrodeposition

![Scheme 2 — Schematic representation of FM oxidation.](image)

![Fig. 6 — Effect of scan rate on 0.75 M FA (A) and 0.75 M FM (B) electrooxidation obtained in 0.1 M H$_2$SO$_4$ using CC/Pt electrode. Scan rates are shown on CVs. The insets show the dependence of the anodic peak currents on the square root of scan rates in each case.](image)
methods may offer a control over the properties of the crystalline structure and the platinum particles morphology on the surface [66,67]. We performed the electrodeposition of platinum particles through the application of three electrochemical methods including potentiostatic (one and two steps), potentiodynamic, and galvanostatic methods. The charge of each method was controlled and kept constant. The deposition steps (if needed) were repeated until the applied charge reached the value corresponding to the desired mass of platinum. After deposition of desired mass of platinum, a cyclic voltammetry experiment was carried out and the measured anodic peak current in PGPS of FA or FM together with other electrode characteristics were presented in Table 2.

As can be seen in Table 2, the maximum current is obtained for one step potentiostatic method. Hence all the experiments were performed using this method for platinum deposition.

3.5.2. Effect of platinum mass

As reported in literature [12,46,48,68–71], the electrochemical catalytic activity of platinum particles strongly depends on the deposited mass of platinum. In this work, the effect of different platinum nanoparticles deposited mass ranging from 0.1 to 2.5 mg cm$^{-2}$ at the CC surface on the oxidation of FA and FM was studied. The CVs obtained in 0.1 M H$_2$SO$_4$ + 0.75 M FA or FM at scan rate of 50 mV s$^{-1}$ were driven (figures not shown) and the variation of anodic peak currents for FA in PGPS vs. the amount of deposited platinum were plotted in Fig. 8A. As can be seen, the anodic peak currents of FA increases with an increase in the platinum loading from 0.1 to 0.7 mg cm$^{-2}$ and then remains constant for the optimum platinum amount of 0.7–1.0 mg cm$^{-2}$. The anodic peak currents obtained for FA oxidation decrease with an increase in the platinum loading to 1.0 mg cm$^{-2}$. For platinum loadings above 1.0 mg cm$^{-2}$, the accumulation of platinum occurs and results in a saturation of active sites of CC/Pt surface. On the other hand, at the lower platinum depositions, metal particles are almost uniformly deposited on the surface of the CC substrate and the real area of platinum particles increases that causes an enhancement in the electrocatalytic activity of the modified electrode. When the platinum loading further increased, the metal particles agglomerate during the reduction process and result in the decrease of the electrochemical active area. Nearly the same results were obtained for FM oxidation. Therefore, the amount of 0.7 mg cm$^{-2}$ was used as minimum and optimized mass of platinum particles on CC substrate.

3.5.3. Effect of FA and FM concentrations

In order to evaluate the capacity of CC/Pt for electrooxidation of FA and FM, the effect of these compound concentrations on the corresponding anodic peaks currents (in PGPS) was investigated by CV. According to experimental data, the peak current of FA and FM were increased by these compound concentrations, and reached a nearly constant value for concentrations higher than 1.5 M for FA and FM. We assume this effect caused by saturation of active sites at the surface of electrode.

3.5.4. Effect of electrolyte concentration

The effect of H$_2$SO$_4$ concentration on the peak current related to the electrooxidation of FA and FM at CC/Pt has been investigated by cyclic voltammetry. The variation of peak current obtained for FA oxidation (peak current in PGPS) was plotted against H$_2$SO$_4$ concentration in Fig. 8B. The peak
current of FA oxidation increases with the increase of H$_2$SO$_4$ concentration to 0.1 M, and then it remains constant for the optimum H$_2$SO$_4$ concentration range 0.10–0.18 M. Further increase in H$_2$SO$_4$ concentration depressed the anodic peak current. A similar behavior was found for electrooxidation of FM. In high concentrations of H$_2$SO$_4$, the dissociation of acid decreases and causes the solution conductivity to be reduced. Also, the reducing effect of high level H$_2$SO$_4$ concentration on peak currents may be addressed according to the Le Chatelier’s principle, i.e. the thermodynamic tendency for oxidation of FA and FM was reduced by H$_2$SO$_4$ concentration [65]. Because, as can been seen in both ways of Schemes 1 and 2 (pathway oxidation of FA and FM, respectively), hydrogen ion was produced in the right sides. Therefore, as the concentration of hydrogen ion increases via increasing H$_2$SO$_4$ concentration, the reaction’s progress will be reduced. On the other hand, according to the Le Chatelier’s principle, if we are to add a species to the overall reaction, the reaction will favor the side opposing the addition of the species.

3.6. Long-term stability of the platinum nanoparticles decorated CC substrate

In practical view, long-term stability of the electrode is important. The long-term stability of CC/Pt electrode was examined in 0.1 M H$_2$SO$_4$ solution containing 0.75 M FA or FM (Fig. 9). It can be observed that the anodic current remains constant with an increase in the scan number at the initial stage. In the case of FA oxidation (curve A) using CC/Pt, the anodic current starts to decrease after 30 numbers of scans. The peak current of the 300th scan is about 92.5% than that of the first scan. In general, the loss of the catalytic activity after successive number of scans may result from the consumption of FA during the CV scan. It may also be due to poisoning and the structure change of the platinum nanoparticles as a result of the perturbation of the potentials during the scanning in aqueous solutions, especially in presence of the organic compound. Another factor might be due to the diffusion process occurring between the surface of the electrode and the bulk solution. With an increase in scan number, FA diffuses gradually from the bulk solution to the surface of the electrode. Similar results were obtained for CC/Pt towards FM oxidation (curve B). The peak current of the 300th scan is about 93.0% than that of the first scan. After the long-term CV experiments, the CC/Pt electrode was stored in water for a week; then FA and FM oxidation was carried out again by CV, and excellent catalytic activity towards both oxidations was still observed. This indicates that the CC/Pt composites prepared in our experiment have good long-term stability and storage properties.

4. Conclusion

The catalytic performance of CC/Pt catalyst against the electrooxidation of FA and FM was investigated by the cyclic voltammetric and the chronoamperometric method. The cyclic voltammetric response reveals that the FA and FM oxidation current on the surface CC/Pt catalyst is higher than that of smooth platinum, GC/Pt and Pt/Pt electrodes. This is attributed to the unique structural, good porosity and high electrical properties of CC substrate, uniform dispersion of platinum nanoparticles on CC substrate.

Factors such as platinum deposition method, mass of platinum on the CC substrate, concentration of catalyzed compounds, and electrolyte concentration all influence the anodic current of electrooxidation of FA and FM on the CC/Pt electrode significantly.
The prepared electrode exhibits satisfactory stability and reproducibility when stored in ambient conditions or continues cycling, which makes it attractive as anode in Direct-Formic Acid Fuel Cells (DFAFCs) and applications.

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