Study of electrocatalytic properties of platinum-loaded poly-ortho-aminophenol film towards methanol oxidation and hydrogen evolution

N Bahrami Panah*, M G Mahjani*, M Jafarian* & F Gobalb

*Kajeh Nasir-AL-Deen Toosi University of Technology, Chemistry Department, P. O. Box. 15875 - 416, Tehran, Iran
Email: mahjani@kntu.ac.ir

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Platinum microparticles electrodeposited at a glassy carbon surface (Pt/GC) and within a poly-ortho-aminophenol film formed on a GC substrate (Pt/PoAP/GC) have been used for investigating their catalytic activity towards hydrogen evolution reaction and methanol oxidation by cyclic voltammetry, impedance spectroscopy and chronoamperometry. The effect of the deposition time (t_{dep}) of the Pt particles dispersed into GC and PoAP electrodes and of the acid anions (SO\textsuperscript{2-}, ClO\textsubscript{4}\textsuperscript{-}) on the hydrogen adsorption/desorption peaks and hydrogen evolution reaction has been studied. It has been shown that the main cause of immediate blocking of the PoAP-SO\textsuperscript{2-} pores with platinum microparticles is its smaller scaling yardstick. The higher electrocatalytic activity of the PoAP as compared to that of GC due to its higher surface area for the methanol oxidation has been proved by a substantial improvement in transition current in chronoamperometric and in the maximum anodic current of the methanol in cyclic voltammetric measurements.

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Electrochemical reactions involved in energy conversion processes, such as fuel cells are catalyzed by electrode surfaces. In order to increase the overall catalytic activity, electrode materials are dispersed into a convenient electron-conducting substrate (e.g. carbon powders). However, for most of these electrode materials, the electrochemical reaction is limited to the catalytic surfaces and the bulk material is not involved in the catalytic process. One way to avoid this limitation is to disperse the electrocatalyst material into a convenient electron-conducting matrix (such as a conducting polymer) in a way that each catalytic site will be accessible to the reactive molecules.

Conducting polymers usually have no catalytic activities by themselves, but their porous structures are suitable for dispersion of metals (catalysts) because of their large surface area and high conductivity. Hence, polymer films with metal particles incorporated into the film either by electrodeposition onto the films or during film formation are good catalysts for electrochemical reactions such as methanol oxidation. Conjugated polymers provide higher surface areas of metallic aggregates and are conductive in the potential range where the Cl molecules (oxygenated molecules containing one carbon atom) are oxidized. In fact, the aim of inclusion of metal microparticles into these porous films is to increase the specific surface area of the films and develop their catalytic efficiency. Most of these investigations are performed in acidic electrolyte and conducting polymers are found to be suitable for preparing the catalytic electrodes due to their high stability in this medium. Amongst the active electrode materials, PoAP (as a cation-exchanger) has been used in this work because of its stability against electrochemical degradation. Also, the simultaneous presence of lone pair electrons available from nitrogen and oxygen atoms to coordinate with most transition metal cations makes this polymer modifiable. The conducting ability of PoAP films is high in the potential range of 0-0.7 V without causing extensive degradation of the polymer. Utilization of this polymer in this potential range should permit facile charge transport to occur through the polymer structure. Therefore, the electrooxidation of methanol was studied on PoAP films containing Pt particles (as catalysts).

Methanol is one of the well-known fuels used in fuel cells because of its high energy density, simple
structure and easy storage. Its oxidation is an interesting example of a typical electrocatalytic reaction in fuel cells. Although this reaction proceeds faster in alkaline than in acidic media, usually an acidic electrolyte is preferably used in practical applications because carbonate residues are not formed. The main problem during the electro-oxidation of methanol is the poisoning of the platinum surface by chemisorbed particles such as carboxylic acid, aldehyde, and especially CO. These poisoning species cause a decrease in electrode activity. So, one way of minimizing the poisoning effects is incorporation the platinum microparticles in a matrix with large surface area such as a conducting polymer.

The purpose of this paper is to study adsorption and desorption of hydrogen on Pt/GC electrode and Pt/PoAP/GC film in H₂SO₄ and HClO₄ electrolytes by cyclic voltammetry (CV) and impedance spectroscopy (IS). The effect of the deposition time (tdep) of Pt deposits onto polymer films and GC electrodes on the hydrogen evolution reaction is studied. Chronoamperometry (CA) and CV methods have been used to obtain the dependence of the rate of methanol oxidation on GC and PoAP modified by platinum upon various methanol concentrations in 1 M H₂SO₄.

Materials and Methods

All chemicals were of reagent grade and used without further purification. All the electrolyte solutions were prepared with doubly distilled water. Electrochemical studies were carried out in a conventional three-electrode cell powered by an electrochemical system comprising of EG&G (model 273) potentiostat/galvanostat and Solartron (model 1255) frequency response. The system was run by a PC through M270 and M398 softwares via a GPIB interface. The frequency range of 100 KHz to 10 mHz and modulation amplitude of 5 mV rms was employed for impedance studies. A glassy carbon rod of area 0.471 cm² was used as working electrode for hydrogen evolution reaction (her) experiments and a glassy carbon disk with a geometric area of 0.0707 cm² for methanol oxidation. Counter and reference electrodes were platinum wire and Ag/AgCl (sat. KCl). The poly-ortho-aminophenol modified electrodes were prepared by cycling between -0.2 and 0.9 V vs. Ag/AgCl in 1 M HClO₄ and 0.3 M and 1 M H₂SO₄ containing 0.1 M monomer, at a scan rate of 50 mV s⁻¹. The film was cleaned of low-molecular organic impurities by cycling in a background solution (changing the solution four times). The thickness of the deposited films on GC rod and disk was estimated as 0.12 and 0.5 μm respectively, from the charge consumed in reducing the polymer and the molar concentration of electroactive sites in the film, obtained by Faraday law, considering n=2 and assuming that the PoAP density is 1.328 g cm⁻³ at 25°C (ref. 13).

For hydrogen evolution reaction experiments, platinum was electrodeposited on GC rod and into PoAP by electroreduction of 0.001 M K₂PtCl₆ solution in 1 M HClO₄ and in some other experiments in 0.005 M H₂PtCl₆.6H₂O in 0.3 M H₂SO₄ at a constant potential of Edep=0 V vs. Ag/AgCl at varying times (10-160 s). The deposition potential of 0 V vs. Ag/AgCl was chosen because Pt (IV) is reduced at this value, while hydrogen adsorption does not appreciably occur. The presence of Pt particles on the electrode surface was proved by proton induced X-ray emission (PIXE) technique (Fig. 1). Using this technique, the sample kept in a vacuum chamber was bombarded with 9.434 KeV proton beam (with a current of 10 nA from AEOI's Van de Graaff accelerator). The characteristic X-ray spectrum was registered with a Canberra Si (Li) semiconductor detector with an energy resolution of 170 eV coupled to standard electronics and a PC based multichannel analyzer. The analysis of spectrum was performed using the AXIL software. The PIXE spectrum of the polymer containing dispersed platinum showed several emission lines of L₁ (Pt), L₂ (Pt), L₃ (Pt) and L₇ (Pt). There is a good agreement between experimental spectrum and the simulated one. The PIXE result was combined with Williams Backscattering...
Spectrometry (RBS), a surface analytical technique that is useful in thin-film and diffusion studies. The analysis of a modified poly-ortho-aminophenol surface with fine-grained platinum particles was done by means of RBS with energy of 2 MeV and by a Canberra particle detector using resolution of 60 KeV at an interaction angle of 165°. The RBS peak was simulated by PRA (Particle Reaction Analysis) software. The computer simulation showed that while the platinum sharp peak was in agreement with the observed results, in the region related to the C, O, and N atoms of the polymer film, the accordance was poor. This is due to the fact that for these low atomic number (Z) elements present in the PoAP film, beam scattering cross-section is very different from the Rutherford cross-section. So, the fitting is poor for this part of the spectrum, which is attributed to the presence of carbon atoms. The amount of platinum, \( m_{Pt} \), dispersed into PoAP modified GC disk (doped with \( SO_4^- \) anions) in 0.001 \( M \) \( K_2PtCl_6+1 \ M \) \( H_2SO_4 \) during electrolysis at \( E_{dep}=0 \) V vs. Ag/AgCl and \( t_{dep}=640 \) s per unit area was estimated as 113.43 \( \mu g \) \( cm^{-2} \) by RBS technique and as 110.69 \( \mu g \) \( cm^{-2} \) from the integral of the cathodic charge passed during the deposition process assuming that the reduction of \( Pt^{IV} \) to \( Pt^0 \) is achieved with 100% efficiency during electrolysis. This value of platinum deposits can produce optimal response for methanol oxidation. The oxidation of methanol on the modified GC and PoAP electrodes was performed using different concentrations of \( CH_3OH \) in 1 \( M \) \( H_2SO_4 \) at \( v=20 \) mV s\(^{-1} \). Furthermore, attempts were made to correct for the effect of internal resistance (IR) drops. All the experiments were done at a controlled temperature of 25°C.

### Results and Discussion

#### Hydrogen evolution reaction on Pt/GC

Figure 2A shows the cyclic voltammograms for the platinum microparticles catalytic electrodeposition on the GC electrode at a constant potential of 0 V vs. Ag/AgCl at varying time periods (10-160 s) in 1 \( M \) \( HClO_4 \) solution free of \( K_2PtCl_6 \) (0.001 \( M \)). Higher currents of hydrogen evolution were obtained by increasing deposition times. The cathodic peak at 0.5 V vs. Ag/AgCl reflects reduction of Pt-OH species to metallic Pt while the reverse reaction at 0.53 V vs. Ag/AgCl shows oxidation of Pt to Pt-OH.

The amount of platinum catalysts, \( m_{Pt} \), deposited at GC electrode by the same procedure described above in \( HClO_4 \) (1 \( M \)) containing anionic hexachloro-platinate was estimated to be 4.93-5.02 \( \mu g \) \( cm^{-2} \) from the integral of the cathodic charge (reduction of \( Pt^{IV} \) to \( Pt^0 \) ) passed during the deposition process. The same experiments were also done on Pt/GC in 0.3 \( M \) \( H_2SO_4 \) +0.005 \( M \) \( H_2PtCl_6.6H_2O \). In this case, in 0.3 \( M \) \( H_2SO_4 \) (Fig. 2B), the first negative potential CV scans showed only one adsorption/desorption hydrogen peak and another characteristic feature for Pt, i.e., oxide formation/reduction. As the catalyst-loading surface was increased, these current peaks grew due to formation of more electroactive platinum sites and an increase in surface coverage by chemisorbed oxo radicals (\( OH_{ads} \), \( O_{ads} \) or \( \{H_2O\}_{ads} \)) produced by electrochemical discharge of water. The voltammetric curves of this catalyst represent the well-known hydrogen adsorption/desorption characteristic for Pt after remaining at \( E_{dep}=0 \) V vs. Ag/AgCl for some
time; two cathodic adsorption peaks and three anodic desorption peaks, belong to weakly, strongly and molecular bonded hydrogen, respectively. At higher platinum loadings, the hydrogen desorption peaks shift towards more positive potentials. Platinum deposits were also characterized by their mass specific surface area, \( S_{sp} \), in \( m^2 \cdot g^{-1} \) \( (S_{sp}=S_{true}/m_{Pt}) \), the true surface area of platinum catalyst, \( S_{true} \), was determined using the hydrogen desorption charge, considering that the oxidation of one monolayer of \( H_{ads} \) on polycrystalline Pt surface\(^9\) is associated with a charge of \( 210 \mu C \cdot cm^{-2} \) and by the average diameter of platinum particles, \( d \), calculated by the equation: \( d=6 m_{Pt}/\pi S_{true} \), assuming homogeneously dispersed spherical particles\(^2\), where \( \rho \) is the specific density of platinum \( (21.4 \, g \cdot cm^{-3}) \). These parameters of platinum deposits on GC electrode in H\(_2\)SO\(_4\) \((0.3 \, M)\) solution are given in Table 1. It can be seen that with increasing platinum loading level the particle size increases and the mass specific surface decreases. This means that although the platinum contents increase, but portions of platinum are not electrochemically available.

### Electro Catalytic behavior of Platinized poly-ortho-aminophenol film

The poly-ortho-aminophenol film was deposited on a GC electrode in the acidic media as described in the experimental section. The resultant film, which was subsequently washed and transferred to a monomer free solution, contained a redox couple ascribed to the existence of a self-exchange process of electrons between oxidized and reduced sites\(^3\).

The cyclic voltammetric responses of PoAP film in the absence of platinum and also after holding at 0 V vs. Ag/AgCl during different deposition times \((10-160 \, s)\) in \(1 \, M\) H\(_2\)SO\(_4\) free of \(K_2PtCl_6\) \((0.001 \, M)\) solution are presented in Fig. 3. Platinum microdeposits parameters at PoAP/GC electrode are given in Table 1. The deposit content was within the range of \(11.64-15.08 \, \mu g \cdot cm^{-2}\). The same dependence of \(S_{sp}\) and \(d\) upon \(m_{Pt}\) as described for Pt/GC \((0.3 \, M\) H\(_2\)SO\(_4\)) was observed for Pt/PoAP/GC in \(1 \, M\) H\(_2\)SO\(_4\). According to Golabi’s report\(^3\), the S shape of the plot of consumed charges as a function of potential cycle’s number suggests that the growth of PoAP film at GC surface is not a straightforward process. On the other hand, it seems that a slow and two-dimensional growth of PoAP film occurs in the beginning (up to \(50 \, \) cycles of potential sweep corresponding to the charges of \(15.9 \, mC \cdot cm^{-2}\)) until the entire electrode surface is covered \( (dQ/dt \, \) is low). So in the present work, it is reasonable to compare reactivity of the polymer \( (\) thickness of \(0.12 \, \mu m \) corresponding to the charge of \(13.4 \, mC \cdot cm^{-2}\) \) distributed Pt particles to the two-dimensional platinum deposits on glassy carbon. It can be concluded from the data obtained that the platinum loading level on PoAP/GC is higher than that on GC, although platinum catalyst was deposited on these two electrodes by the same condition. The peak currents of the polymeric film gradually decrease after electrolysis at constant potential \((0 \, V \, vs. \, Ag/AgCl)\) using an acidic solution of the platinum salt. This indicates the closure of the polymer network. In all of the voltammetric curves of PoAP

### Table 1—Platinum microdeposits on GC electrode

<table>
<thead>
<tr>
<th>Pt deposition time (s)</th>
<th>Platinum loading level (\mu g \cdot cm^{-2})</th>
<th>Specific surface area (m^2 \cdot g^{-1})</th>
<th>Av. dia. of platinum particles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.3 , M) H(_2)SO(_4) solution</td>
<td>(10)</td>
<td>13.95</td>
<td>214.41</td>
</tr>
<tr>
<td></td>
<td>(20)</td>
<td>16.40</td>
<td>186.83</td>
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<td>(40)</td>
<td>18.65</td>
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<td></td>
<td>(80)</td>
<td>22.26</td>
<td>161.37</td>
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<td></td>
<td>(160)</td>
<td>29.38</td>
<td>138.39</td>
</tr>
<tr>
<td>(1 , M) H(_2)SO(_4) solution</td>
<td>(10)</td>
<td>11.64</td>
<td>84.11</td>
</tr>
<tr>
<td></td>
<td>(20)</td>
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<td>81.78</td>
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<td>13.16</td>
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<td></td>
<td>(160)</td>
<td>15.08</td>
<td>68.77</td>
</tr>
</tbody>
</table>
film (doped with \( \text{ClO}_4^- \) anions) modified by platinum microdeposits (Pt/PoAP-\( \text{ClO}_4^- \)), we can see only the molecular hydrogen desorption peak and hydrogen evolution wave which are representative of platinum on the surface and the redox peaks of the Pt-OH formation/reduction.

The electrocatalytic activity of Pt/PoAP-\( \text{ClO}_4^- \)/GC electrode was investigated in a 1 M \( \text{HClO}_4 \) solution by measuring the hydrogen evolution current. The exchange current densities of this electrode based upon the GC geometric area, modified with platinum particles during different time deposition in 1 M \( \text{HClO}_4 \), were determined from quasi-steady state Tafel plots in the overpotential range of \(-0.14 \) to \(-0.24 \) V vs. Ag/AgCl, \( v = 2 \) mV s\(^{-1} \) (Fig. 4). As shown in Table 2, the exchange current densities increase as the Pt loading levels go up. Exchange current densities of 0.3-5.5 mA cm\(^{-2} \) were obtained in a potential range of diminished polymer conductivity.

The effect of the acid anions on the rate of hydrogen evolution on platinum particles dispersed into PoAP matrix was studied. Figure 5 illustrates the cyclic voltammogram of PoAP film doped with \( \text{SO}_4^{2-} \) anions in 0.3 M \( \text{H}_2\text{SO}_4 \) free of \( (0.005 \) M) \( \text{H}_2\text{PtCl}_6.6\text{H}_2\text{O} \) solution. However, there is only one adsorption/desorption peak related to weakly bonded hydrogen at lower time periods \( (t_{\text{dep}} < 160 \) s), but two cathodic (adsorption) and three anodic (desorption) peaks (weakly, strongly and molecular bonded hydrogen) are observed at higher time periods \( (t_{\text{dep}} \geq 160 \) s).

The platinum amount deposited at PoAP/GC in \( \text{H}_2\text{SO}_4 \) (0.3 M) solution was between 6-25.74 \( \mu \)g cm\(^{-2} \). A comparison between CVs of Pt/PoAP-\( \text{ClO}_4^- \) and Pt/PoAP-\( \text{SO}_4^{2-} \) (Figs 3 & 5) shows that the film characteristic in \( \text{H}_2\text{SO}_4 \) disappears at low deposition times but it is apparent in \( \text{HClO}_4 \) even at high deposition times. It can, thus, be concluded that the hydrogen adsorption/desorption character is influenced by the platinum particle loading level and the platinum-loaded polymer films prepared in the presence of different anions.

In our previous work\(^{23} \) we have shown that the electrodeposited PoAP film is a fractal object. We concluded that polymeric surface is sensed as bumpy in plane as perpendicular to the surface in presence of \( \text{SO}_4^{2-} \) and \( \text{ClO}_4^- \) anions and so we have self-similar fractals in both cases. Distinction between outer and inner cutoffs in the polymer sensed in the presence of \( \text{ClO}_4^- \) (3.02-10.70\( \AA \)) and \( \text{SO}_4^{2-} \) (2.98-3.18\( \AA \)) shows that since the inner cutoff for \( \text{ClO}_4^- \) is higher than that.
for SO$_4^{2-}$, and hence the scaling yardstick in the presence of ClO$_4^-$ is larger than that in the presence of SO$_4^{2-}$ anions. Thus, the main cause of disappearance of the polymer (doped with SO$_4^{2-}$) redox peak at the elementary step of Pt dispersion and observing only the platinum character, i.e., immediate blocking of the PoAP-SO$_4^{2-}$ pores with platinum microparticles, is its smaller scaling yardstick. However, this phenomenon does not occur for PoAP-ClO$_4^-$ film even at high catalyst loadings.

For further insight, the Nyquist diagrams of PoAP films doped with ClO$_4^-$ and SO$_4^{2-}$ anions before and after depositing platinum particles were studied in the frequency range of 100 KHz-10 mHz with the de-offset potential 0.34 V vs. Ag/AgCl (for PoAP-ClO$_4^-$) and 0.25 V vs. Ag/AgCl (for PoAP-SO$_4^{2-}$) corresponding to the anodic peak potential of PoAP film (Fig. 6). In both the cases, platinum ions were reduced to metallic particles at 0 V vs. Ag/AgCl in 160 s. The polymer Nyquist plots consist of a small semicircle at high frequencies (above 6.31 Hz) terminated to a large one at low frequency side of the spectrum. The former is due to a parallel combination of charge transfer resistance, $R_\text{ct}$, and constant phase element, CPE$_\text{i}$, which is attributed to the electron injection at the polymer/back contact interface and the latter represents the charge transport resistance, $R_2$, in parallel with the CPE$_2$, which accounts for the anions insertion into the polymer matrix to maintain charge neutrality within the polymer phase$^{23}$. The equivalent circuit for data fitting has been proposed previously$^{24}$. The equivalent circuit is shown as an inset in Fig. 6. Table 3 shows the results of the fitting of impedance data given in Fig. 6(A & B) using Boukamp equivalent circuit software$^{25}$. Quality of fitting can be judged by the estimated relative errors as given in the parentheses. The bulk solution resistance, $R_\infty$, is low and irrelevant to the presence of platinum particles and the type of anions in the solution. The data show that after platinum deposition there is a decrease of 65% and 82% in charge transport, $R_2$, of PoAP-ClO$_4^-$ and PoAP-SO$_4^{2-}$, respectively. The constant phase element behaviour of interface has also ascribed to a fractal nature of the interface$^{26}$. For rough surfaces, impedance, $Z$, vs. frequency, $w$, often behaves like a CPE, So that$^{27}$:

\[ Z(w) = 1/[C(\omega)^n] \]  

... (1)

Fig. 6—Presentation of the Nyquist diagrams of: (A) freshly prepared PoAP-ClO$_4^-$ film (a) and the same film into which Pt particles were incorporated during 160 s at $E_{de} = 0$ V at de-offset potential ($E_0$) of 0.34 V vs. Ag/AgCl (b$_1$). (B) freshly prepared PoAP-SO$_4^{2-}$ film (a) and the same film into which Pt particles were deposited during 160 s at $E_{de} = 0$ V at $E_0$ = 0.25 V vs. Ag/AgCl (b$_2$). Inset shows equivalent circuit used to analyze the impedance data.

| Equivalent circuit elements of the impedance diagram fitted to Fig. 6(A&B). The applied de-offset potentials are 0.34 V and 0.25 V vs. Ag/AgCl for PoAP-ClO$_4^-$ and PoAP-SO$_4^{2-}$, respectively. |
|------------------|------------------|------------------|------------------|------------------|
| Equivalent circuit elements | PoAP-ClO$_4^-$/GC | Pt/PoAP-ClO$_4^-$/GC | PoAP-SO$_4^{2-}$/GC | Pt/PoAP-SO$_4^{2-}$/GC |
| $R_\infty$ (Ω) | 10.04 (4.02%) | 10.12 (9.58%) | 11.07 (2.49%) | 11.39 (3.84%) |
| $R_1 \times 10^3$ (Ω) | 4.35 (16.67%) | 45.93 (13.94%) | 1.74 (3.37%) | 0.06 (3.11%) |
| CPE$_1 \times 10^6$ (Ω$^{-1}$ s$^{n_1}$) | 0.68 (2.62%) | 2.60 (1.62%) | 0.96 (2.41%) | 1.10 (53.81%) |
| $n_1$ | 0.69 (2.19%) | 0.85 (2.02%) | 0.56 (0.56%) | 0.87 (11.64%) |
| $R_2 \times 10^3$ (Ω) | 3.26 (16.80%) | 1.11 (7.67%) | 528.32 (7.41%) | 93.52 (18.29%) |
| CPE$_2 \times 10^6$ (Ω$^{-1}$ s$^{n_2}$) | 0.86 (6.89%) | 1.68 (4.39%) | 1.53 (0.92%) | 0.99 (1.16%) |
| $n_2$ | 0.56 (0.80%) | 0.51 (1.14%) | 0.84 (0.54%) | 0.56 (0.45%) |
where \( C \) is a capacitance parameter with dimension \( \text{Fe}^{-1} \) and \( n \) is a positive frequency dispersion parameter (named CPE exponent) between 0 and 1. It was found that\(^{28} \) surface roughness causes interfacial impedances to be modified with respect to those of smooth electrodes by an exponent, \( n \). The exponent \( n \) and, through it, the fractal dimension, \( D_f \), clearly serves as a measure of the interfacial roughness.

\[
N = \frac{1}{(D_f - 1)} \quad \ldots (2)
\]

The fractal dimensions of the PoAP films were calculated from the CPE exponent of the first semicircle of the Nyquist plots, \( n_1 \) (in Table 3), and Eq. 2. In the absence and presence of the platinum particles, the \( D_f \) values are 2.45 and 2.17 for PoAP-CIO\(_4^-\) and 2.78 and 2.15 for PoAP-SO\(_4^2-\) films, respectively. The decrease of the fractal dimension of the films after platinum deposition indicates a decrease in the films’ porosity with the coverage of the surface by platinum particles. The two cathodic adsorption peaks and three anodic desorption peaks in the CV of platinum particles electrodeposited (\( t_{dep} = 160 \) s) on PoAP/GC in 0.3 M H\(_2\)SO\(_4\) solution, which exhibit the characteristic platinum surface reactions as observed on single crystal\(^{28} \) and polycrystalline\(^{30} \) platinum electrodes, also confirm the complete surface coverage with platinum particles. It may, thus, be concluded that the PoAP-SO\(_4^2-\) surface has more regular platinum particles and despite the higher resistance and smaller specific surface area of Pt/PoAP-SO\(_4^2-\) relative to the platinum-loaded PoAP-CIO\(_4^-\) film, its catalytic activity towards hydrogen evolution reaction is higher due to nearly complete surface coverage with platinum particles. (This can be demonstrated by the disappearance of the characteristic polymer peak even at shorter time of platinum deposition).

Electrooxidation of methanol on Pt-loaded PoAP film

The PoAP film has conductivity in the potential range of 0-0.7 V vs. Ag/AgCl without being degraded. Thus, utilizing this polymer in this potential range causes easy charge transport through polymer structure. For this reason, the electrocatalytic oxidation of methanol was studied on the PoAP films modified GC disk containing dispersed platinum particles. The cyclic voltammetric curves of methanol electrooxidation on platinum modified PoAP with different Pt loadings were obtained in 1 M H\(_2\)SO\(_4\) + 1 M CH\(_3\)OH solution at a scan rate of 20 mV s\(^{-1}\) (not shown). The film was preconditioned at a potential of 0.5 V vs. Ag/AgCl (where the reaction kinetics is controlled by the interaction rate of adsorbed organic species and OH particles\(^{31} \)) for 600 s before the cyclic voltammograms were recorded for obtaining steady state oxidation currents of methanol. This pretreatment does not cause an increase in poisoning of the catalyst sites by CO species produced during methanol oxidation since in the course of multicyclic oxidation of methanol at PoAP modified electrode, the poisoning of catalytic sites is not a progressive process\(^{32} \). These curves show that the catalytic current of methanol oxidation has an increase in its maximum value (3.50 mA cm\(^{-2}\)) when the platinum amount is 110.69 \( \mu \)g cm\(^{-2}\). Thereafter, any extra platinum loading does not increase the electrode activity, probably because of a decrease in platinum active surface area. Thus, for investigating the dependence of oxidation rate on methanol concentration in 1 M H\(_2\)SO\(_4\), the voltammograms have been recorded for platinum deposits onto PoAP film and at GC disk with an optimum deposit mass of 110.69 \( \mu \)g cm\(^{-2}\). Methanol could not be oxidized on GC and PoAP film in the absence of platinum particles. However, the presence of platinum microparticles on their structures leads to electrocatalytic property of these electrodes against methanol oxidation.

The effect of the methanol concentration on the oxidation of methanol was tested by recording the corresponding cyclic voltammogram of Pt/GC and Pt/PoAP/GC in a solution of methanol with different concentrations (10\(^{-2}\)-10 \( M \)) in 1 M H\(_2\)SO\(_4\) at a scan rate of 20 mV s\(^{-1}\). The electrodes surface was cleared of organic residues by piranha solution (mixture of concentrated sulfuric acid with hydrogen peroxide in volume ratios of 3:1) after each experiment. The general shape of these two curves is the same. This points to similar reaction mechanisms of methanol oxidation in the systems investigated. The curves show that the onset of methanol oxidation on platinum modified PoAP (0.5 \( \mu \)m) starts from 0.13 V vs. Ag/AgCl (exactly after hydrogen desorption) and from 0.17 V vs. Ag/AgCl in the case of Pt/GC. This indicates that the polymer causes an improvement in methanol adsorption on platinum particles surface. The oxidation rate increases at more positive potentials, reaching a maximum. Then, the anodic current decreases due to high platinum surface coverage by the strongly chemisorbed OH species formed from electrochemical discharge of water molecules in acidic solution at lower potentials. During the
negative scan of potential, platinum sites are nearly blocked by the surface oxide layer. The presence of another oxidative peak during the positive-going scan demonstrates that the intermediates produced in the anodic sweep (CO and OH species) have not had enough time to undergo full oxidation and their oxidation continues even after reverse scans. Oxidative methanol peaks are located in the potential region that coincides with OH formation peak in a solution free of methanol. Chemisorbed methanol species suppresses the hydrogen adsorption on the platinum particle surface. Hydrogen adsorption on the polycrystalline platinum is also inhibited. In fact, the electrode surface coverage by chemisorbed organic species (in solutions containing methanol) can be demonstrated from the decrease of hydrogen adsorption after cathodic-anodic electrode activation.

Comparison of CVs of Pt/GC and Pt/PoAP/GC electrodes in solution containing 1 M H2SO4 and methanol shows that the platinum particles with loading of 110.69 µg cm², which are deposited on the GC and onto PoAP film under similar condition, have different specific activities. The anodic current of methanol (10 M) oxidation at 0.5 V vs. Ag/AgCl is six times higher on Pt/PoAP/GC than on Pt/GC electrode. This may be explained by the higher surface area provided by the PoAP film (The platinum specific surface areas on GC and PoAP electrodes are calculated 11.38 and 16.87 m² g⁻¹, respectively.). The higher porosity of the polymeric film than that of the GC electrode probably allows the platinum particles to be deposited in a manner giving higher surface area for methanol oxidation. This was also confirmed by chronocamperometric measurements by an enhancement in transition current of the methanol oxidation on Pt/PoAP/GC with respect to Pt/GC. So, a polymer of ion exchange like PoAP can increase the utilization of platinum particles. The important role of polymer matrix during the methanol oxidation is its ability to provide high overall oxidation currents.

Golabi and Nozad have reported the same study on PoAP with almost the same thickness (0.52 µm) loaded with Pt particles (100 µg cm⁻²) in 0.1 M CH3OH and 0.1 M HClO4. The onset potential of methanol oxidation was at shortly before 0.17 V (vs. SCE). According to this report, there is a leveling off in anodic current peak of methanol oxidation at methanol concentrations higher than 0.7 M. We repeated these experiments in a wide range of methanol concentration (10⁻²-10 M) by CV and CA measurements. Results show that there is a substantial improvement in transition current in CA curves and in the anodic current peak of methanol oxidation in CV curves upon increasing the concentration of methanol up to 10 M. Subsequently, a constant level is obtained due to saturation of platinum active sites. The main cause of this difference between these two results is that probably the electrode surface had not been cleaned of the poisoning species thoroughly in the study reported by Golabi and Nozad. Also, they obtained the real surface area of platinum microparticles at Pt/PoAP/GC and Pt/GC from chronocamperometric experiments (step potential of 1 V vs. SCE) by assuming that the measured current is diffusion controlled, whereas the methanol oxidation on the surface of these electrodes that are not capable of mediating fast electron transfer from methanol electrooxidation is governed by a surface phenomena.

In order to show that Pt/PoAP/GC electrode still has catalytic activity at longer time scale, the methanol (10 M) anodic current changes during controlled potential electrolysis at 0.5 V vs. Ag/AgCl was measured. Results show that the anodic current due to methanol oxidation did not change up to 5 days, although a weak decrease was seen in peak current after 5 days.

Conclusions
The present study shows that the hydrogen adsorption/desorption characteristic is influenced not only by the platinum loading level but also by the platinum-loaded polymer films prepared in the presence of different anions. The PoAP-SO4²⁻ surface has more regular platinum particles than PoAP-ClO4⁻ because of its smaller scaling yardstick. The Pt-loaded PoAP film is more capable of providing higher overall methanol oxidation currents than the Pt/GC electrode because of its higher porosity and larger surface area. Investigation of methanol concentration effect on the rate of the methanol oxidation reaction shows that the rate of oxidation is increased as the methanol concentration is raised up to 10 M and a constant level is obtained due to saturation of Pt active sites. Pt/PoAP/GC electrode's catalytic activity is stable up to 5 days.

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References