On the nature of noble metal electrodes prepared using formaldehyde as reducing agent

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The noble metal electrodes used in fuel cells have many active sites in addition to the zero valent states. The other metals added like Ru have other roles to play in addition to removing the poisoning effects due to intermediate CO in the oxidation of methanol. The advantages of using formaldehyde for reduction of noble metal ions in relation to hydrogen reduction method are also given.

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The noble metal electrodes for fuel cell applications are usually prepared by reducing the metal ions with formic acid, a method that has the advantage of reducing the metal ions without introducing impurities. This reduction method has also been extended to bimetallic systems especially Pt-Ru electrode preparation (up to a certain atomic percentage of Ru) by Lazcano-Valbuena et al. and for Pt/Au-C and other binary systems like Pt/Ru, Pt/Pd. The main reason for using this method is that the reduction potentials of the various metal ions (namely Ru²⁺ to Ru is 0.455V, Rh²⁺ to Rh is 0.6V, Pd²⁺ to Pd is 0.951 V and Pt²⁺ to Pt is 1.188V) are appropriate for reduction by formaldehyde. Since the formaldehyde oxidation can give rise to various species, it is capable of reducing different metal ions of same valence state or metal ions of different oxidation states. However, there are some aspects of this reduction process which requires careful examination in the light of preparation of supported electrode preparation for fuel electrodes. This method has been advocated as the possible and suitable method for the preparation of carbon supported metal electrodes for fuel cells. The purpose of this study is to examine the merits of using formaldehyde instead of hydrogen for obtaining Pt/C electrodes.

Materials and Methods

The electrodes (Pt/C and Pt-Ru/C) used in this study were prepared by two different methods, namely, hydrogen reduction and formaldehyde reduction method.

Formaldehyde reduction method

Carbon (6.3 g) was dispersed in distilled water and 35 ml of 5% H₂PtCl₆ was added to it. The pH of the mixture was adjusted to 10-11 using 0.1M NaOH and 80 ml of 20% formaldehyde solution was added. The above mixture was heated at 343K for one hour under constant stirring. It was then washed thoroughly with distilled water, filtered and dried in hot air oven at 393K for four hours.

Hydrogen reduction method

H₂PtCl₆ was added dropwise to the carbon suspension in water and evaporated gently to dryness. The material was dried overnight in an air oven at 393K and reduced in hydrogen atmosphere at 823K for 4 hours. The Pt-Ru (1:1)/C was prepared by adopting similar procedure using H₂PtCl₆ and RuCl₃ as salt precursors. X-ray diffraction patterns of the materials were recorded with a Philips diffractometer using CuKα radiation. The methanol oxidation activities of the materials were measured at the scan rate 25 mV/sec using BAS cyclic voltammetry.

Results and Discussion

The cyclic voltammograms recorded with 10%Pt on carbon electrode in 1M methanol solution in sulphuric acid are shown in Fig. 1. The electrodes were prepared by using either hydrogen (a) or formaldehyde (b) for the reduction of Pt ions on the carbon support. There are certain features of the cyclic voltammograms which require careful examination. The peaks in the cyclic voltammograms have been properly de-convoluted and the data
generated are given in Table 1. The results show that there are two distinct peaks for Pt/C obtained by hydrogen reduction while three peaks are observed for the system generated using formaldehyde for reduction. The relative proportions of the two peaks for the electrode obtained using hydrogen reduction method correspond to peak II ~78% and peak I ~22%.

Usually it is considered that irrespective of the other metal present except Ru the extent of reduction of Pt ions is around ~80% and hence it can be deduced that the peak II in Fig. 1(a) is due to Pt in the zero valent state while peak I is methanol oxidation on the oxidized Pt ion sites. This result can be taken to mean that in addition to Pt(0) sites, Pt ion sites are also active for methanol oxidation. Stoyanova et al. have prepared Pt/C electrodes using different reduction conditions like electrochemical, chemical using NaBH4 thermal heating in air, argon or hydrogen and have shown that the catalysts prepared in air exhibit greatest activity. Chi Chang Hu and KweunYo Liu have shown that the coexistence of PtOH ads and Pt atoms on the electrode surface was responsible for the catalytic oxidation of methanol in the less positive potential region. The formation of Pt(IV) species which were active to methanol oxidation was found to depend strongly on the history of the Pt deposits. Burke and Hurley examined the data reported in literature and found that most of the solid metal surfaces are heterogeneous at the atomic level and the degree of heterogeneity or the variation of the surface atom activity is a function of the electrode pretreatment and history. This study thus established various reduction conditions can generate various types of surface species and each of these surface species can be active to different extents. The role of the oxidation state of Pt in the electro-catalytic oxidation of primary alcohols has been examined by Li et al. and they have shown that the reaction process depends on the formation of surface oxides on the Pt electrode at different potentials. These results reported in literature have so far not identified the actual species responsible in the electro-catalytic oxidation of methanol on Pt metal surfaces though various species are invoked to explain the results obtained. In this study it has been shown that not only two types of Pt sites (metallic and oxidized) are

<table>
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<th>Method of preparation</th>
<th>10% Pt/C</th>
<th>20% Pt-Ru/C</th>
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</thead>
<tbody>
<tr>
<td>Formaldehyde reduction</td>
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<tr>
<td>Hydrogen reduction</td>
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Table I—Cyclic voltammograms for 10% Pt/C and 20% Pt-Ru/C in 1 M methanol in sulphuric acid medium

<table>
<thead>
<tr>
<th>Method of preparation</th>
<th>Peak I</th>
<th>Peak II</th>
<th>Peak III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential (mV)</td>
<td>Current (mA)</td>
<td>Potential (mV)</td>
</tr>
<tr>
<td>10% Pt/C</td>
<td>597.9</td>
<td>3.0</td>
<td>774.7</td>
</tr>
<tr>
<td>Formaldehyde reduction</td>
<td>570.3</td>
<td>1.23</td>
<td>717.6</td>
</tr>
<tr>
<td>Hydrogen reduction</td>
<td>721</td>
<td>8.27</td>
<td>919</td>
</tr>
<tr>
<td>20% Pt-Ru/C</td>
<td>639</td>
<td>7.85</td>
<td>776</td>
</tr>
</tbody>
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generated during reduction by formaldehyde, both these sites are active for the observed electro-catalytic activity of methanol.

Extending this logic, the peak II in the cyclic voltammogram shown in Fig. 1(b) can be ascribed to the Pt in the zero valent state and peak I for methanol oxidation on Pt ions unreduced while peak III could be due to some complex Pt ion sites formed with the oxidized species of formaldehyde. The relative percentage of these species is 25:65:10. The complex species could have arisen from the species generated from formaldehyde which is used for the reduction.

Similar cyclic voltammograms were obtained with 20% Pt-Ru/C electrode prepared by using two different reduction methods (Table 1). Data show that the positions of the peaks are shifted to more positive values though essentially the same features as observed with Pt/C electrodes are obtainable with Pt-Ru/C electrode. In the case of Pt-Ru system, the extent of reduction of Pt to zero valent state appears to be less which is in agreement with the results reported in literature. The reason for this could be that Pt ions may be difficult to reduce in presence of Ru ions or the redox properties of this combined species might be different from that of the Pt ions alone. These differences in redox behaviour could have arisen from various factors. The morphology and distribution of the Ru in relation to Pt depend on the nature of the precursors used as well as the conditions employed to generate the Ru species on the single crystal planes of Pt. However, when formaldehyde is used as the reducing agent for Pt, the extent of reduction of Pt to the zero valent state is more which could be due to particle size effect. It is known that the hydrogen reduction method always results in Pt particles in the size range 8-10 nm while for the formaldehyde reduction method the particle size of Pt on carbon is 2-5 nm.

Secondly, the intrinsic activity of zero valent Pt sites generated from formaldehyde reduction method, is higher than that in the hydrogen reduction. This could be due to simple particle size effect (refer to the X-ray data below) or due to preferential exposure of Pt (111) planes or due to the particle sizes of the metallic components (the particle size decreasing with increase in Ru content) which are normally expected to show higher activity as compared to the other planes.

The X-ray diffractograms together with the indexing of Pt lattice for the four electrodes are given in Fig. 2. It is observed that the Pt (111) plane is predominant in the electrode generated using formaldehyde for the reduction either for pure Pt or Pt-Ru electrodes. This provides evidence for our deduction mentioned previously that the intrinsic activity of Pt sites generated by formaldehyde reduction is higher then that of the corresponding Pt sites generated by hydrogen reduction. The particle size of Pt is smaller in the case of formaldehyde reduction method as compared to the hydrogen method due to the high temperature employed for the reduction.

The results obtained in this study have to be examined in the light of reports available in the literature. Detailed XPS, K-absorption edge spectra and ESR studies on the Pt-Ru/C electrode obtained using sodium formate as the reducing agent have shown that multiple Ru species are present in addition to active Pt metal species and the oxidized Pt species. They have implied that only metallic Pt species are active for the observed electrochemical activity. However, our contention based on the deconvolution of the cyclic voltammograms is that all the Pt species, either in the metallic state or in the oxidized or complexed form, are active for the methanol oxidation though the intrinsic activity may be higher for the metallic species. Secondly, there is a claim in the literature that reduction with formic acid has the advantage of reducing the metals without introducing impurities. Though this may be true, it should be noted that on using reducing agents like formaldehyde
and formic acid, the partially oxidized products of these organic reducing agents can complex with Pt ions and thus inhibit the reduction of the Pt ionic species to the metallic state. This will not only limit the number active metallic sites but also these complexed Pt species on the carbon support may be less active than metallic Pt sites on carbon.

Another observation recorded in literature that the presence of Ru suppresses the formation of any oxide of Pt and that all the Pt is present in the active state has not been substantiated by the results of the present study. It is not clear why the presence of Ru alone should suppress the presence of oxidized form of Pt. However there are indications that in the presence of Ru, hydrous ruthenium oxides may be formed which could facilitate the reduction of Pt. Secondly, in the case of Pt-Ru, a solid solution is formed and hence exhibits a synergistic effect. But at the same time, a number of oxidized (2 or even 3) species of Ru has been reported. How these species affect the solid solution formation and also contribute to the synergistic effect is not clear. However, Hammett and Kenndy have examined a variety of Pt-M/C electrodes with a second metal like Au, Pd, Ir, Os, and Ru using formaldehyde as the reducing agent. There are two results of this study which are relevant for the present discussion:

(i) Within experimental error, the relative amounts of Pt(0) and Pt(II) appear to be the same for all the metals (Au,Pd,Ir and Os) except for Ru.
(ii) There is no obvious relationship between the amount of Pt oxides present and the observed catalytic activity. It is normally presumed that Pt in the zero valent state is active and oriented Pt(111) surfaces showed enhanced activity.

In the present study, deconvolution of the cyclic voltammograms show that the oxidized forms of Pt are also active, though intrinsic activity may be lower as compared to metallic Pt sites.

Another aspect on which comments may be appropriate in this context is the observation of Gonzalez et al. that the Pt-Ru/C electrodes obtained using formic acid as reducing agent showed that the alloy formation may not be predominant. This is a deduction based on their X-ray data and also on the values of the lattice parameters. Though they tend to recognize the role of formaldehyde reduction method to preferentially exposing Pt(111) planes they have not stated why Pt-Ru catalyst system is more active than the Pt system. The reason identified for this observation is the tolerance of methanol and the intermediates of the reaction. It is possible that both the reducing agent as well as the presence of Ru ions may be responsible for the preferential formation of Pt particles with predominant (111) faces being exposed. However, it has to be substantiated how or why Ru ions alone are promoting this particular crystallization process. Secondly, as reported elsewhere, the possibility of various oxidized species of Ru may promote this process while the same may not be true with other metals like Pd, Au and Ir.

In summary, it is concluded that the noble metal electrodes used in fuel cell applications have many active sites in addition to the metallic sites and the added metal like Ru has other roles to play in addition to removing the poisoning effect due to the intermediate CO generated in the oxidation of methanol.

Acknowledgements
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References