Anode catalysts for enhanced methanol oxidation: An in situ XANES study of PtRu/C and PtMo/C catalysts

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Abstract

Pt/C, PtRu/C and PtMo/C electro catalysts were prepared in different compositions by incipient wetness impregnation method. These catalysts were characterized by X-ray diffraction (XRD) and X-ray absorption near-edge structure (XANES) to understand the miscibility into solid solution and to calculate the d-orbital vacancy, respectively. Pt with Ru and Mo forms a single alloy which was confirmed by XRD date. XANES was measured at Pt L II and LIII edges and K edges of Ru and Mo to determine the oxidation states of these metals in different compositions. Further calculations of d-orbital vacancy of Pt revealed more information that increasing the Ru or Mo content increases d-orbital vacancy. As Mo oxidizes faster than Ru, magnitude of d-orbital vacancy is high in the case of Ru compared to Mo. In situ XENES study was also conducted in methanol fuel cell to understand the oxidation states and methanol oxidation mechanism.© 2005 Published by Elsevier B.V.

1. Introduction

Fossil fuels are exploited in large quantities as the number of vehicles increased sharply around the world resulted in increased fuel costs and also they imply severe damage to the environment. To overcome these problems there is an urgent need to develop alternative energy sources to run our machines and vehicles. Hydrogen is considered as one of the most important energy source which is available in abundant quantity in the universe. Even though its combustion heat per mass is considerably high compared to other fuels, the number of electrical charges per mass is very low. Also it has disadvantages like production of pure gas in larger quantities and storage in tanks or in suitable medium [1].

Proton exchange membrane fuel cells (PEMFC) are an excellent source of alternative energy and have enormous attention due to their easy construction and handling [2]. Some organic substances are considered as very promising fuels for electrochemical energy conversion. These substances are oxidized on the anode surface and reduced on cathode surface even in room temperature. Among organic sources as fuels for electrochemical energy conversion systems methanol and ethanol have received great attention because of their less polluting nature and more efficiency [3,4].

One of the important problems associated with these fuel cells (both oxidation of hydrogen and direct methanol fuel cell) is to overcome the oxidation of carbon monoxide which is deposited onto the metallic electrode surface during electrochemical reaction. So the development of anode electro catalyst which either absorbs minimum amount of CO while still able to oxidize hydrogen at an acceptable rate or that oxidizes CO at significantly
duced overpotential [5]. Most of the commercial fuel cells use platinum nanoparticles alloyed with second component especially Ru as electrocatalyst to enhance the catalytic activity with respect to platinum. In addition to Ru some other metals are used as second component to improve the performance of catalyst such as Mo, Sn, W, Rh, etc. [6–9]. Mechanism of enhanced electrochemical activity of Ru is under discussion by many authors. Two kinds of pathways have been proposed for the role of Ru in catalysis. The carbon monoxide oxidation is considered as bifunctional mechanism originally suggested by Watanabe and Motoo which states that Ru surface acts as absorption centers for oxygen containing surface species reacting with CO to produce CO2 [10]. Mean time some authors suggested other mechanism also in which they propose adsorption of CO is weakening on the surface of Pt–Ru alloy with respect to pure platinum which enhances the catalytic activity [11].

Under these circumstances some investigations tried to explain the mechanism of catalysis for metallic systems with the evidence of in situ X-ray absorption near-edge structure (XANES). Mansour et al. [12] reported the quantitative estimation of number of unoccupied d-electron states in Pt catalyst, supported on silica, using LIII X-ray absorption near edge spectra. They calculated d-band vacancy by considering the area under white line in the spectra. Then onwards many groups utilize the XANES techniques to explain electrochemical catalytic activity of Pt with different metals supported on carbon.

In the present study, we present a systematic analysis of XANES spectra of PtRu/C and PtMo/C catalysts. We have recorded XANES spectra for these catalysts in Pt L-edges (II and III) and K-edges of Ru and Mo for different compositions. Spectra were compared with pure metals and oxides of Ru and Mo to understand the oxidation states of the metals in catalysts. d-Orbital vacancy of Pt metal also been calculated and discussed in detail to ascertain the formation of oxides of Ru and Mo.

2. Experiments

Cathodes were prepared by incipient wetness impregnation method. Aqueous solutions of H2PtCl6 and RuCl3 (or MoCl3) were mixed well in desired proportions. 0.3 g of carbon powder was added to the solution and mixed thoroughly to get carbon slurry. It was kept at 120 °C for 2 h for drying and taken out from the oven. Small amount of water has been added again and mixed well to slurry to get homogeneity. This slurry was dried for 12 h at 120°C in an air oven to completely remove the moisture from powder and ground well. Dried powder was reduced under hydrogen atmosphere at 250 °C for 4 h to get metal catalysts. Samples were characterized by X-ray diffraction (XRD) using SCITAG (X1) diffractometer with Cu Kα radiation. XRD data were collected from 10° to 80° (2θ) in a step size of 0.02 with a count time of 10 s per step. Appropriate quantity of electrode materials, PtRu/C and PtMo/C catalysts, were suspended in Nafion and water to form a catalyst ink. The ink was stirred for 15 min and then spread onto carbon paper. The sheet was pressed at 14 kg cm−2 at 120–130 °C for 20 s. Electrodes of area 2.5 cm2 were cut from the compressed sheet for EXAFS measurements. The carbon paper backed catalyst working electrode is placed against a gold foil current collector and soaked in electrolyte (20 vol.% methanol dissolved in 1.0 mol dm−3 H2SO4 prepared in 18 MΩ cm water). The Ag/AgCl electrode was used as a reference electrode. The in situ EXAFS measurements were carried out with an electrochemical cell. This cell designed by us was assembled by using Teflon frameworks and sealed with Kapton windows to allow X-rays to pass through. The in situ XAS data will be collected in a transmission mode. In situ Pt LIII- and LII-edges XANES were carried out at the Wiggler beamline BL17C1 and BL01C1 of National Synchrotron Radiation Research Center (Taiwan), and in situ Ru and Mo K-edge XANES were carried out at the beamline BL12B2 of Spring-8 (Japan). The spectra were normalized with respect to the edge jump using the code AUTOBK [13].

3. Results and discussion

X-ray diffraction (XRD) results (XRD pattern not shown) of PtRu catalysts show that different composition of PtRu/C catalysts such as 40%Pt–10%Ru/C, 30%Pt–10%Ru/C, 20%Pt–10%Ru/C forms single phase face-centered cubic (fcc) structure. The investigations of the relationship between the composition and the crystal structure of nano-sized PtRu particles on the surface of carbon support were performed. XRD patterns indicate the absence of Ru peak and the shift from original Pt(1 1 1) of 39.79° to the value of PtRu 40.30° and from the original Pt(2 2 0) of 67.45° to that of PtRu 68.10°. No diffraction peaks from either pure Ru or a Ru-rich hexagonal close packed (hcp) phase and the shift of Pt(1 1 1) to the high angle side are consistent with the catalysts being composed only of face-centered cubic (fcc) Pt–Ru alloy particles. However, in order to assess the particle size of the bimetallic clusters and to verify the high degree of alloy formation, we analyzed the (2 2 0) diffractions. The reason is that at a low 2θ range in the vicinity of the fcc (1 1 1) diffraction peak of the alloys, strong background peaks from carbon black and an overlapping peak with Pt (2 0 0) can be observed. Therefore, the average particle size of the PtRu

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catalyst by detailed measurement at the (2 2 0) diffraction was 3–7 nm, similar to the high-resolution transmission electron microscopy (HRTEM) results, by using the Scherrer equation \[14\]. The lattice parameters of these alloys from the (220) reflection were 0.391–0.388 nm, a value slightly decreased from that of pure Pt (0.392 nm). As the platinum content is higher in the compositions and Ru atomic radius is smaller than that of Pt, Ru atom very well fit into the crystal lattice of fcc and forms a single phase alloy. It is worth to note that Pt and Ru are mutually soluble in each other and forms solid solution in the above said compositions. As the percentage of Ru increases in catalysts that are in the case of 15%Pt–10%Ru/C to 10%Pt–40%Ru/C they tend to form hcp (hexagonal close packing) structure because of thermodynamic limitations. From the above discussion it is inferred that to enhance the activity of catalysis the distance between Pt and Ru should be limited by varying the experimental conditions to get effective catalysts. So we prepared five different PtRu catalysts incorporating Ru from 10% to 65% in different compositions inside the optimum composition to study their properties in detail by XRD and XANES. All compositions have good single phase fcc structure and good solid solutions.

In similar manner we prepared PtMo catalysts in different compositions like 29%Pt–1%Mo/C, 28%Pt–2%Mo/C, 25%Pt–5%Mo/C. All these catalysts form single phase fcc alloy solid solutions. As in the case of PtRu in this system also the radius of Mo is smaller than Pt and the Mo content is higher than Pt in all compositions. Therefore, Mo atoms are very well fit into the fcc structure which is a favorable condition for catalysis.

In the present study, XANES has been applied to investigate the metal oxidation states of different compositions of catalysts and under different voltages in methanol fuel cell. We have calculated Pt d-orbital vacancy also to understand fully the activity of Ru and Mo along with Pt. Fig. 1a, b shows the \(\text{L}_{\text{III}}\) and \(\text{L}_{\text{II}}\)-edge XANES spectra of PtRu/C catalysts. From edge jump at 0.5 of normalized absorption intensity, it is observed that there is no change in oxidation state of Pt for different combinations of Pt and Ru as compared to the standard Pt foil. The most interesting observation in this figure is the white line characteristic (shown inside dotted rectangle). All the white lines of catalysts are present well above the Pt foil indicating the Pt 5d-orbital vacancy. Comparing the absorption edge of the normalized spectra of different catalysts shows increasing Ru content increases the white line area indicating the higher 5d-orbital vacancy of Pt. If we compare the \(\text{L}_{\text{III}}\) and \(\text{L}_{\text{II}}\)-edges, \(\text{L}_{\text{II}}\)-edge shows clear and larger increase of d-orbital vacancy. This is because in the case of \(\text{L}_{\text{III}}\)-edge electrons are migrated from 2p_{1/2} to 5d_{3/2} and 5d_{5/2} orbitals in which 5d_{5/2} is half filled up to Fermi level and empty above Fermi level thereby showing higher vacancy. But as for as \(\text{L}_{\text{II}}\)-edge is concerned electrons are migrated from 2p_{1/2} to 5d_{3/2}, in which the target orbital 5d_{3/2} is fully filled up, obviously shows lesser d-orbital vacancy when compared to \(\text{L}_{\text{III}}\)-edge. Pt d-orbital vacancy has been calculated quantitatively and plotted with respect to Ru content in PtRu/C catalyst in Fig. 2a \[12,15,16\]. From the figure it is obvious that Pt d-orbital vacancy is directly proportional to Ru content. This increase of vacancy with increasing Ru content is due to the redistribution of Pt 5d-electrons to the low energy 4d orbital of Ru in PtRu/C catalyst.

Fig. 3 shows the Ru K-edge spectrum of different PtRu/C catalysts along with Ru powder and RuO2 standards. Edge position, near 0.5 of normalized absorption intensity, has been considered to understand the oxidation states. From the figure it is observed that except 28%Pt–2%Ru which is same as Ru powder (metallic state) all other compositions 25%Pt–5%Ru/C, 20%Pt–10%Ru/C and 15%Pt–15%Ru/C show the valence state in between Ru powder and RuO2 that is between zero and four. Increasing Ru content increases the surface distribution of Ru over the catalyst surface. So Ru forms oxides even at room temperature on the surface of the catalyst in all proportions. It is evident from
the XANES spectra of different catalysts that is higher the Ru content higher is the oxidation state.

In situ Ru K-edge spectra for 20%Pt–10%Ru/C catalyst recorded in different voltages from 0.1 to 1.0 V (vs. RHE) in methanol half cell and relevant references (Ru powder and RuO₂) were shown in Fig. 4. The XANES of ruthenium oxide (RuO₂) is significantly different from that of the Ru metal powder with a 6 eV positive edge shift for the oxides as compared to Ru powder. The oxide reference sample has two closely spaced peaks separated by a saddle point at 22.14 keV. The K-edge XANES spectra of PtRu/C catalyst operating at lower potentials (0.1 and 0.5 V vs. Ag/AgCl reference electrode) are similar to that of Ru powder, except that there is a minor increase in peak intensity (at 22.14 keV) of the catalyst compared to the Ru powder. This suggests that Ru is metallic and alloyed with Pt. The shift of Ru K-edge toward higher energy is found at higher potentials (0.8 and 1.0 V). This implies that a ruthenium oxide layer or oxygen-containing adsorbed species on the surface is formed. Moreover, the extent of oxidation of Ru increases with higher potential. The results support the mechanism of bimetallic catalyst in which Ru sites play the role for providing oxidant to react with CO adsorbed on Pt sites. The reaction formula is shown as follows: Pt–CO + Ru–OH → Pt + Ru + CO₂ + H⁺ + e⁻. Considering the 0.1 V spectrum it is very close to Ru metal that is originally Ru is reduced from higher oxidation state at this potential, as it is supported by Fig. 2 that 20%Pt–10%Ru/C is present in between 0 and 4+. When the voltage slowly increased to 1.0 V it moves towards RuO₂ that is oxidation state of Ru in the catalyst at this potential is approximately 2+. So during the oxidation process, Ru surface is maintained between 0 and 2+ and the Pt surface is not disturbed in this potential range (XANES not shown). Oxidation of Ru at lower potential may result in the formation of adsorbed species on the surface of Ru. At the same time methanol oxidized on Pt surface by breaking C–H bond results in the formation adsorbed CO on Pt surface. Higher potential is necessary to desorb CO from Pt surface. But the adsorbed species on Ru surface

Fig. 2. (a) Ru atomic percentage vs. the electron vacancy of Pt 5d electron energy band and (b) Ru atomic percentage vs. the electron vacancy of Pt 5d electron energy band.

Fig. 3. K-edge XENES of different Pt/Ru ratio with Ru powder and RuO₂ standards.

Fig. 4. Ru K-edge in situ XANES of 20%Pt–10%Ru/C in different voltages.
oxidizes CO to CO₂ [9]. So in multistep process fresh Pt surface is maintained for methanol oxidation as well as oxidized Ru surface is available for CO oxidation.

Pt L_{III} and L_{II}-edge XENES spectra for different compositions of PtMo/C catalysts (spectra not shown) show increased white line area as in PtRu/C (Fig. 1) which obviously indicates Pt 5d-orbital vacancy. But there is no change in oxidation state observed as there is no edge movement at 0.5 position with respect Pt foil. d-orbital vacancy has been calculated quantitatively and plotted against Mo content, shown in Fig. 2b [12,15,16]. The Mo K-edge XANES spectra of PtMo/C catalyst and relevant references (MoO₂ and MoO₃) are shown in Fig. 5. Increasing Mo content in the PtMo catalyst increases Pt d-orbital vacancy but not to the extent of PtRu catalysts. This phenomenon is explained as, compared to Ru, Mo oxidation rate is higher at atmospheric temperature causes only less no of 5d electrons available for redistribution with Mo 4d orbital results in low d-orbital vacancy.

In methanol oxidation due to the easy oxidation of Mo it produces more number of oxygen species than Ru which helps easy oxidation of CO deposited on Pt surface which was formed during the oxidation of methanol. As Mo is having more species it removes more CO species at a given time results in enhanced catalytic activity of Pt than Ru.

4. Conclusion

PtRu/C and PtMo/C anode catalysts were prepared in different compositions on carbon support to investi- gate their performance in methanol oxidation fuel cells. XRD and XENES techniques were utilized to study their homogeneity and oxidation states respectively. Systematic study of XENES in Pt L-edges (L_{III} and L_{II}) and K-edges of Ru and Mo for all compositions and in situ XANES measurement of methanol oxidation in Ru K-edge revealed the following results. Calculation of Pt d-orbital vacancy for both PtRu and PtMo indicates that Mo is easily oxidizable than Ru which in turn is a favourable situation for oxidation of CO adsorbed on Pt surface which is produced by methanol oxidation. So it is concluded from the above results, among these two catalyst systems, PtMo is superior in methanol oxidation than PtRu.

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