ELECTRO-CATALYSTS USED FOR CO TOLERANCE IN PROTON EXCHANGE MEMBRANE (PEM) FUEL CELL

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ABSTRACT:

The fuel cells are efficient source of electrical energy from the fuel energy. Proton Exchange Membrane (PEM) fuel cell due to its high power density, quick starts up, rapid response to varying loads and low operating temperature preferred in automobile applications. The hydrogen fuel used in PEM fuel cell is mostly obtained by partial oxidation or stream reforming of methanol and contains impurities like CO and CO_2. CO present in the hydrogen fuel is a poison for the catalyst and reduces the rate of reaction. Catalyst is used to increase rate of electrode reaction. Hence, CO tolerance is an important factor in the catalyst operation and selection in PEM fuel cell. The binary and ternary catalysts are used to increase CO tolerance. The catalyst used for in PEM fuel cell are studied and analyzed for CO tolerance. Modeling and experimental studies by various groups show that Pt-Ru/C and Pt-Sn/C are more CO tolerance than pure Pt/C catalyst.

Key words: PEM fuel cell, electro catalysis and CO tolerance.

1. INTRODUCTION

Proton Exchange Membrane (PEM) fuel cell is also referred as solid polymer fuel cell is likely to achieve commercial application in a wide variety of areas including the automotive industry, because of having the inherent properties of high current density, being lightweight, operating at low temperatures, and containing no corrosive materials [1]. A single PEM cell has three main components: A membrane electrode assembly (MEA), two bipolar plates and two seals [2, 3]. The simple diagram of PEM fuel cell is shown in following Fig.1.
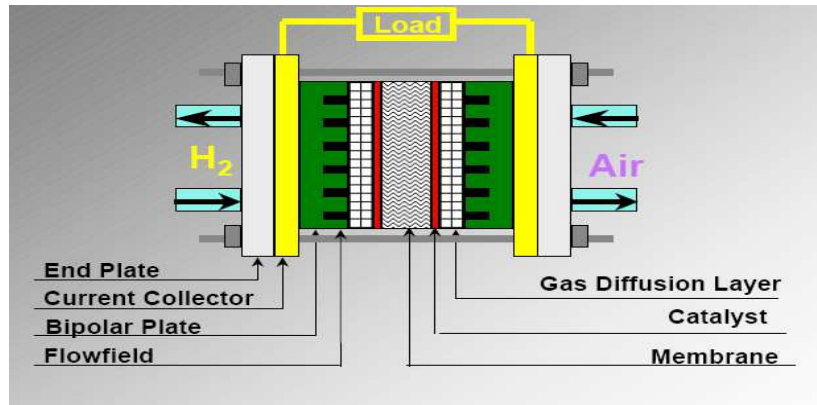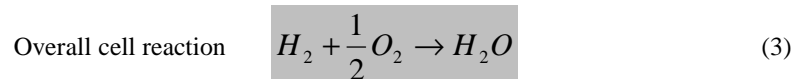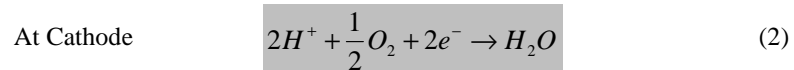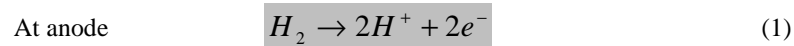
Fig.1. PEM Fuel cell [3]

In the simplest form MEA consists of a membrane, two dispersed catalyst layers and two-gas diffusion layers (GDL). The membrane separates the half reactions allowing the proton to pass through to complete overall cell reaction. The electron created on anode side is forced to flow through external circuit generating current. GDL allows direct and uniform fuel and oxidant supply to catalyst layer. In fuel cell stack, each bipolar plate supports two adjacent cells. The bipolar plates have different functions like distribution of fuel and oxidant in cell, water management within the cell, carry current away from cell and separate two cells [3].Reactions taking place in PEM fuel cell [3] are as follows:

At anode
$$H_2 \rightarrow 2H^+ + 2e^-$$
(1)

At Cathode
$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$$
(2)

Overall cell reaction
$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$
(3)

The catalyst used in PEM fuel cell is depends on the type of the fuel used. CO tolerance is the most important issue particularly when the hydrogen is formed from the methanol by steam reforming or partial oxidation process. PEM fuel cell performance drops with the few ppm of CO concentration in feed. This is due to the strong adsorption of CO on the catalyst [4]. The electro-catalyst serves two purposes in PEM fuel cell: 1) it increases the rate of reaction and 2) increases CO tolerance. Platinum is the catalyst of choice due to the high current densities obtained [1]. Platinum–ruthenium catalysts have attracted considerable interest in recent years as highly active and more CO tolerant anode catalysts [1].

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2. ELECTRO CATALYSIS IN PEM FUEL CELL

Electro-catalysis may be defined as the acceleration of an electrodic reaction by substance, which is not consumed in the overall reaction. It is analogous to heterogeneous catalysis since at least one step of electrochemical reaction occurs at the electrode solution interface and it is the property of electrode surface that affect the overall reaction rates.

The rate of the acceleration of the reaction at electrode is depends on the catalyst used. The commonly used catalysts are Pt, Rh, Ir, Pd and Au as pure metal or as alloy. The electro catalyst also functions as chemical catalyst. The surface plays a dual role in the fuel cell electrode reactions. It can enhance the rate of reaction if chemical kinetics is rate controlling like chemical catalyst. It can influence the potential of the cell by minimizing the free energy loss due to chemisorptions.

2.1. Anodic Electro catalyst

The catalyst at anode must serve two purposes. One it must rapidly adsorb (chemisorb) the fuel gas to make it oxidize and minimize free energy due to chemisorptions. When alloying the catalyst to counter the problem of CO, binary catalyst or ternary catalysts are used. Binary and ternary anode catalysts are typically, but not always, Pt-based and supported on carbon. It can be summarized that for hydrogen contaminated with CO there are at least seven Pt-based catalysts that give performance equal or similar to that given by Pt/C with pure hydrogen cell: Pt-Ru/C, Pt-Mo/C, Pt-W/C, Pt-Ru-Mo/C, Pt-Ru-W/C, Pt-Ru-Al4, and Pt-Re- (MgH_2).

Iwase and Kawatsu (1995) investigated catalysts: Pt-Ru/C, Pt-Ir/C, Pt-V/C, Pt-Rh/C, Pt-Cr/C, Pt-Co/C, Pt-Ni/C, Pt-Fe/C, Pt-Mn/C, and Pt-Pd/C [4]. Each catalyst was made of a 20-wt.% alloy on carbon with a Pt loading rate of 0.4 mg/cm^2 in a 5-wt.% PFSA solution. They found that only the Pt-Ru catalyst showed cell performance equivalent to that of pure hydrogen cell with a single metal Pt/C catalyst when exposed to reformate gas with 100 ppm of CO. Also, they found that Ru in the binary catalyst absorbs water and facilitates the oxidation of CO. Although adequate CO tolerance can be obtained over a Ru-range of 15–85%, the optimum ratio of Pt/Ru was determined by Iwase and Kawatsu to be 50:50.

Bauman et al. (1998) found Pt-Mo/C to achieve high tolerance to low levels (10–20 ppm) of CO in reformate without the need of an air bleed [5]. However, at CO levels above 20 ppm, the benefit of this catalyst is lessened. Although Pinheiro et al. (2000) also found Pt-Ru/C to outperform Pt-Mo/C [6]; Bauman et al. (1998) found better performance with Pt-Mo/C as compared to Pt-Ru/C catalyst [5].

Tertiary catalysts are typically based on a Pt-Ru alloy. Scientists at ECI Laboratories have investigated the largest number of tertiary catalysts along with some binary catalyst and performances were compared to pure Pt/C catalyst performance. They investigated Pt-Ru alloys with Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Zr, and Nb. They found that out of all the catalyst investigated, in the presence of CO, the binary catalysts $Pt_{0.53}$-$Ru_{0.47}$ and $Pt_{0.82}$-$W_{0.18}$ were far superior to pure platinum. Of the two, Pt-Ru was better in the low potential region while Pt-W proved superior in the plateau region except at very high current densities. But the performance of ternary $Pt_{0.53}$-$Ru_{0.32}$-$W_{0.15}$ alloy exceeded both binaries in the low potential and potential plateau regions. Similarly, Pinheiro et al. (2000) analyzed the performance of Pt-Ru, Pt-Mo, and Pt-Ru-Mo/C and found the tertiary catalyst to have the best performance [6].

In another ternary catalyst development, Denis et al. (1998) investigated the ternary electro catalyst of Pt-Ru-Al$_4$ with no carbon support [7]. Their results show that an unsupported Pt-Ru-Al$_4$ catalyst produced by high-energy ball

milling gives equal performance to Pt-Ru/C when exposed to reformate gas with 100 ppm of CO. Using similar kind of ball milling technique, Dodelet et al. (2002) produced a ternary catalyst Pt-Re-(MgH$_2$) without carbon support that performed better than Pt-Ru/C when exposed to reformate gas with 100 ppm of CO [8].

### 2.2. Cathodic electro catalyst

Cathode catalysts for PEM fuel cells need not to be CO tolerant. Addition to the use of Pt/C, Ross et al. (2002) at Lawrence Berkeley National Laboratory reports the use of Pt-Ni/C and Pt-Co/C as cathode catalyst [3].Flaubert et al. (1998) produced a special, non-platinum based cathode catalyst. The catalyst is produced by pyrolysis of iron acetate adsorbed on perylenetetracarboxylic dianhydride in Ar:H$_2$:NH$_3$ under ambient conditions [9].

3. CO TOLERANCE IN PEM FUEL CELL

CO tolerance is defined as the ability to electro oxidizes H$_2$ in presence of an acceptable polarization loss. CO tolerance generally given as concentration (ppm), which can be tolerated at some current density and polarization loss (20-100mV). The fuel feed to anode is reformed fuel which consists of H$_2$, CO$_2$, CO and H$_2$O. The reaction of H$_2$ oxidation on Pt is a two step reaction [10]. In the following reactions S represents Pt catalyst site.

$$H_2 + 2S \rightarrow 2SH \qquad (4)$$

$$SH \rightarrow S + H^+ + e^- \qquad (5)$$

First step requires two sites of Pt for the dissociation. They assumed that this is rate-limiting step. The second step is discharge and it is rapid on the Pt. CO present in the fuel can adsorb on directly on bare Pt site or S-H sites as follow.

$$CO + S \rightarrow S = CO \qquad (6)$$

$$2CO + 2SH \rightarrow 2S = CO + H_2 \qquad (7)$$
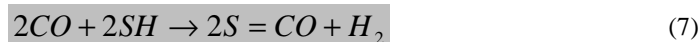
Due to blockage, sites are not available for the dissociation and hence the rate of dissociation decreases. The S=CO is formed by reducing CO2 polarizes H$_2$ electro oxidation in the same manner as CO adsorbed.

$$CO_2 + 2SH \rightarrow C = O + H_2O + S \qquad (8)$$
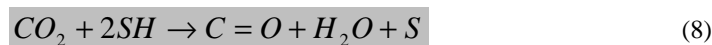
This reaction can be considered as surface equivalent of the well-known water gas shift reaction. Adsorbed CO can be electrooxidised at higher electrode potential and it can be followed electrochemically from the current given off formation of fresh Pt oxides.

$$S = CO + S = O \rightarrow CO_2 + 2S \qquad (9)$$

Bellows et al (1996) described a COx inventory model for the accumulation of the CO on the polycrystalline Pt. They combined three major reactions that add or remove the CO to electrocatalyst surface. The reactions are direct adsorption of CO, electrooxidation of CO$_2$ and electro oxidation of CO. They assumed that all CO on electrode are equivalent and CO adsorption on Pt is kinetically very fast. CO fluxes are given by following equation [10].

$$\frac{d\theta_{CO}}{dt} = \sum \left(CO\ adsorption + CO\ reduction \right) - CO\ oxidation \quad (10)$$

CO in the anode feed will be strongly adsorbed onto Pt sites because of the access of the gaseous reactant to electro catalyst in gas diffusion electrode will be rapid. The model assumes that CO approaches complete monolayer coverage even for CO as low as 1ppm such high equilibrium coverage would preclude any CO tolerance.

Non-equilibrium coverage is possible whenever flux of CO removal exceeds the flux of CO accumulation. The non-equilibrium condition is defined as

$$CO\ elctro - oxidation \geq \left(CO\ adsorption + CO\ reduction \right) \quad (11)$$

If accumulation terms are larger, the CO will continue to build up on the Pt surface Co coverage will approach complete monolayer, and polarization losses will become unacceptably large. CO coverage will gradually decrease when CO electro-oxidation term is larger coverage that will provide additional sites for hydrogen activation and lowering electrode polarization. Electrode polarization and CO coverage will gradually adjust until the fluxes are in balance.

Springer et al (1999) based on their simple kinetic model showed that the polarization of the hydrogen electrode at low current density is limited essentially by the maximum rate of the hydrogen dissociative chemisorption on a small fraction of the CO free catalyst surface [11]. They also found that the rate of CO oxidation as low as 10nA/ cm (Pt) could have a significant effect in lowering the CO steady state coverage. This increases the magnitude of hydrogen electro oxidation current.

4. COMPARISON OF ELECTROCATALYSTS FOR CO TOLERANCE

The small amount of CO presence in hydrogen fuel reduces PEM fuel cell performance due to unacceptable polarization losses. The presence of the second element with Pt such as Ru, Sn, Os, Mo etc. yield significant improvement in the CO tolerance relative to the pure Pt.

Lee et al (1999) studied polarization characteristics of CO tolerance of the Pt-Ru/C and Pt-Sn/C relative to Pt/C in hydrogen oxidation reaction in PEM fuel cell at various temperatures and CO partial pressures [12].
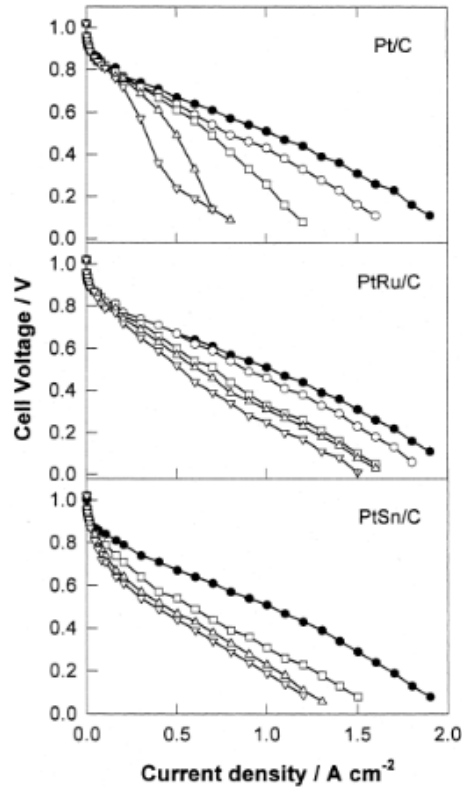
Fig. 2. Single Cell Performance for three different catalysts at 85 °C at several CO concentrations. (($\bullet$) 0 ppm, ($\circ$) 5 ppm, ($\square$) 20 ppm, (Δ) 50

ppm & (∇) 100 ppm) [12]

   They observed the effect of CO partial pressure on PEM fuel cell performance for the Pt Ru/ C and Pt Sn/ C and Pt / C at constant temperature 85 °C.The Pt/C catalyst polarization losses are strongly depends on the CO partial pressure, the other two alloy catalyst Pt Ru/ C and Pt Sn/ C show higher CO tolerance than Pt/C at higher CO partial pressure but shows much larger performance degradation at low partial pressure of CO of 5 ppm as shown in Fig.2.The reaction order are found out with respect to CO concentration by the plotting log-log plots of limiting current obtained at 0.1 V as function of CO concentration for three catalysts. They found that reaction order approximately -0.5 with respect to CO concentration for Pt/C and Pt Ru/C and -1.0 for Pt Sn /C. But they cannot able to assign a specific physical meaning for these reaction orders.

4.1. The effect of temperature [12]

Lee et al (1999) also assumed that hydrogen adsorption on the Pt is the rate-limiting step for the hydrogen oxidation in presence of the CO. The value of the limiting current density will be proportional to the fraction of the surface free of the CO or Hydrogen.

$$i_L = k\theta_C^2 \qquad (12)$$

Where, k is the constant related to the hydrogen pressure, the diffusion coefficient and faraday law. According to this equation the value of the current density increases with temperature because both k or/ and increases with temperature. Based on the Arrhenius approach the current density is related to the temperature by following equation.

$$\log i = \log C - \frac{2E_S}{2.303RT} - \frac{E_H}{2.303RT} \qquad (13)$$

Where C is constant containing terms related with pre expontial factor of Arrhenius equation E_H is the activation energy of the reaction and E_s is the activation energy of the process involved in the formation of the free catalyst sites which can be related with desorption of the CO. They found out activation energy (E_H+2E_S) by plotting the log i vs 1/T. The value of this is found to be closer to 51KJ/mol for the Pt/C and 18 KJ/mol for the Pt-Sn/C. In the case of Pt-Ru/C slope changed with the temperature. Below 70 °C it corresponds to that of the Pt Sn/C while above this temperature it is close to that for Pt/C. The current decay at constant cell potential as a function of time at various temperatures was studied using hydrogen containing 20 ppm CO in the feed to the anode as shown in Fig.3. Fig. 3also shows that magnitude of the steady state current ratios for the Pt/C and Pt-Ru/C are more affected by the temperature than Pt-Sn /C. This is consistent with the polarization curves. For the Pt/C and Pt-Ru/C a lowering of the CO concentration result in an increase of time required reaching at steady state.

4.2. Linear Bonded and Bridge Bonded CO [11]

Camara et al (2002) has done the analysis of CO tolerance effect on highly dispersed nanocrystalline Pt/C, Pt Ru/C and Pt Sn/C catalyst. They developed a kinetic model taking in to account the formation of linear and bridge bonded adsorbed CO and linear bonded COOH and CHO derivatives. The Pt Ru/C and Pt Sn /C are CO oxidation is faster than in case of Pt/C. The CO oxidation starts mainly at bridge bonded sites for all catalyst. The linear adsorbed CO start oxidizing at higher anode potential. Due to these holes on the CO layer increases and thus the rate of oxidation process increases.

4.3. Effect of anode flow rate and cathode oxygen pressure [13]

Zhang et al (2002) reported that anode inlet flow and cathode oxygen partial pressure are found to be dramatically influence the anode over potential and overall cell performance in PEM fuel cell. They gave a quantitative inventory of CO in anode to account the effect of the anode flow rate as well as cathode oxygen partial pressure on the PEM fuel cell performance. They performed experiments and reported results for the cell with H_2/ 108 ppm CO, Pt loading 0.4 mg/cm^2 (20 % Pt/C), 80 °C and Nafion 115 membrane.
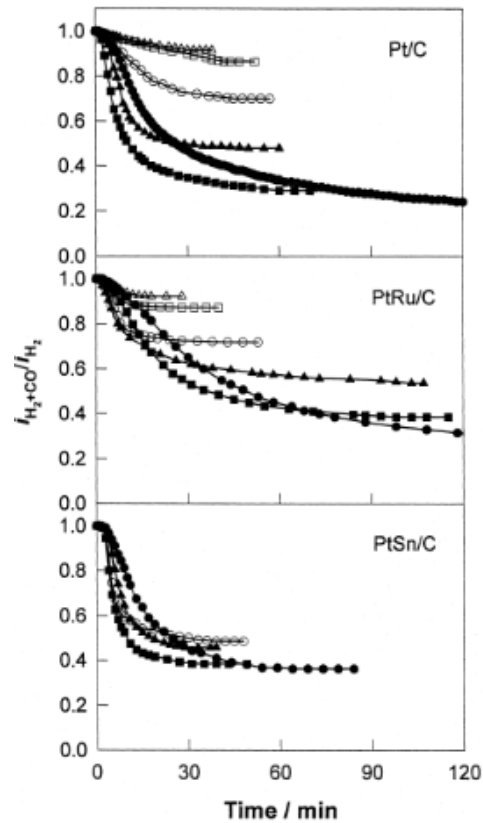
Fig. 3. i_{H_2+CO}/i_{H_2} vs time at 0.6 V for three different catalysts at 20 ppm CO at different temperatures.

((●) 40˚C, (■) 55 ˚C, (▲) 70 ˚C, (○) 85 ˚C, (□)100˚C, and (∆) 115˚C) [12]

The cell voltage is not influenced by anode flow rate for pure H_2, however it is dramatically influenced by anode flow rate when operating with H_2/ CO (108 ppm) mixture. At low anode flow rate, cell voltage deviation from that of pure is small. They conducted experiments under different cathode pressure using pure oxygen feed. The anode over-potential is plotted against anode flow rate at different cathode oxygen pressure. The anode over-potential is decreases as the cathode oxygen pressure increases.

5. CONCLUSION

The PEM fuel cell technology is attractive because of its low operating temperature and ease of start-up. Reformed methanol and liquid hydrocarbons are expected to be major fuel source in PEM fuel cells for terrestrial transportation application. The present state-of-art PEM fuel cell technology is based on platinum as a catalyst for both anode and cathode electrodes. This catalyst is highly active but susceptible to poisoning by fuel impurities like CO, which may be present in the H_2-fuel used or may be introduced during the fuel processing. These impurities poison the anode irreversibly and decrease the performance of the PEM fuel cells.

CO oxidation depends on the various factors like CO bonding linear or bridge, temperature, Anode feed flow rate and cathode oxygen pressure. The various other binary and ternary anode catalysts are developed for

encountering CO problem. Pt-Ru/C and Pt-Sn/C are most promising than pure Pt/C catalyst. Study of the different catalyst shows that Pt-Ru/C and Pt-Sn/C are more CO tolerance than pure Pt/C catalyst.

References

[1] Pitois, A.; Davies, J. C.;Pilenga, A.;Pfrang, A.;Tsotridis, G. (2009):Kinetic study of CO desorption from PtRu/C PEM fuel cell anodes: Temperature dependence and associated microstructural trasnformations, Journal of Catalysis, **265**,pp. 199-208.

[2] Datta, B.K.; Velayutham, G.; Groud ,A. P. (2002): Fuel cell power source for a cold region, J. Power Sources, **106**,pp. 370-376.

[3] Mehta, V.; Copper, J.S.(2003): Review and analysis of PEM fuel cell design and manufacturing, J. Power Sources,**144**, pp.32-53

[4] Iwase, M.; Kawatsu, S.(1995): Optimised Carbon monoxide tolerant electrocatalyst for proton exchange membrane (PEM) cells,Proceedings of the First International Symposium on Proton Conducting Membrane Fuel Cells, **Vol. 1**, pp.12-18.

[5] Bauman, J.; Zawodzinski, T.; Rockward, T.; Haridoss, P.; Uribe, F.; Gottesfeld, S. (1998): Enhanced CO tolerance in polymer electrolyte fuel cells with Pt-Mo anodes, In: Proceedings of the Second International Symposium on the Proton Conducting Membrane Fuel Cells, **vol. 2**, pp. 200–204.

[6] Pinheiro, A.L.N.; Neto, A.O.; De Souza, E.C.;,Perez, J.; Paganin, V.A.; Ticialli, E.A.; Gonzalez, E.R.(2000): Program and Abstracts on the Electrocatalysis of PEM fuel cell Reaction On Noble metal and Noble metal alloys,Proceedings of the fuel cells, pp.63-66.

[7] Densis, M.C.; Lalande, G.; Guay, D.; Dodelet, J.P.; Schulz R. (1998): Performing CO tolerant anodes for proton exchange membrane (PEM) cells, Proceedings of the second International Symposium on Proton Conducting Membrane Fuel Cells,**Vol.2**,pp.209-271.

[8] Dodelet, J.P.; Denis, M.C.; Gouerec, P.; Guay, D.; Schulz R. (2000), in: Proceedings of the Fuel Cell Program and Abstracts on the CO Tolerant Anode Catalysts for Fuel Cells Made by High Energy Ball-Milling, pp. 51–54.

[9] Faubert, G.; Cote, R.; Dodelet, J.P.(1998): A new method to prepare non-noble metal based catalysts for the reduction of oxygen in polymer electrolyte fuel cells, in: Proceedings of the Second International Symposium on the Proton Conducting Membrane Fuel Cells, **vol. 2**, pp. 31–38.

[10] Bellows, R. J.; Marucchi-Soos, E.P.; Buckley, D. (1996): Analysis of Reaction kinetics for the carbon monoxide and carbon dioxide on polycrystaloine platinum relative to the fuel cell operation, J. Electrochemical Soc.,**35**,pp. 1235-1242.

[11] Camara, G.A.; Ticianelli E.a.; Mukerjee, S.; Lee, S.J.; McBreen J. (2002): The CO poisoning mechanism of the hydrogen oxidation reaction in Proton Exchange membrane fuel cells,J. Electrochemical Soc.,**149(6)**, pp. A748-A753

[12] Lee, S.J.; Mukerjee, S.; Ticianelli, E.A.; McBreen, J.(1999): Electrocatalysis of CO tolerance in hydrogen oxidation reaction in PEM fuel cells, Electrochemica Acta , **44**,pp. 3283-3293.

[13] Zang, J.; Thampan, T.; Datta, R. (2002): Influence of the anode flow rate and cathode oxygen pressure on CO poisioning of proton exchange membrane fuel cells, J. Electrochemical Soc., **149(6)**, A765-A772.