ETHANOL ELECTRO-OXIDATION ON Pt-BASED CATALYSTS DEPOSITED BY THERMAL DECOMPOSITION ON TITANIUM MESH

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ABSTRACT

Ethanol is an alternative choice as a fuel in a direct combustion fuel cell because of its non toxicity and availability from biomass resources. Electro-oxidation of ethanol is studied by modifying atomic ratios and type of catalysts. Platinum-based catalyst; Pt_3Ru_1, Pt_5Ru_1, Pt_4Ru_1, Pt_3Sn_1, and Pt_1Ni_1, are deposited on Ti mesh by thermal decomposition. It was shown that Pt_3Ru_1 catalyst had better activity than others when it was characterized by linear sweep voltammetry. However, the electro-oxidation in sulphuric acid indicated by increasing current densities began at higher potential than in perchloric acid. It is found that catalysts are more active in perchlorid acid than in sulphuric acid.

Keyword : direct ethanol fuel cell, ethanol electro-oxidation, thermal decomposition

INTRODUCTION

Since oil crisis of 3 decades ago, point of view of world energy has changed. Most nations reduce their dependency on oil and diversify domestic energy sources. In addition, interest in cleaner fuels has increased. The green house effect that cause atmospheric heating has encouraged people to improve environmental quality.

Fuel cells offer superiority to contribute significantly to energy and environmental challenges. Fuel cells convert primary energy into electricity at up to 70 % efficiency with very low pollutant emissions. An important fuel cell is the Polymer Electrolyte Membrane Fuel Cell (PEMFC) which depending upon the membrane can operate typically in the range 60°C-190°C and are suitable for transport and portable applications and for co-generation in buildings. There is a large interest in the application of the technology with liquid fuels, such as ethanol.

Ethanol offers certain characteristics superior to other liquid fuel; lower vapour pressure, non-toxic, established production from renewable feed-stocks and established infrastructure for use as a fuel. A major challenge to science and engineering is developing suitably effective electro-catalysts for ethanol oxidation and thereby Solid Polymer Electrolyte (SPE) fuel cells. Overall there appears to be significant potential in the use of ethanol as a fuel in SPE fuel cells but a major challenge to science and engineering is developing suitably effective electro-catalysts for ethanol

oxidation in conjunction with an appropriate fuel cell design to improve the performance of SPE fuel cells.

Ethanol electro-oxidation has been investigated for over two decades, nevertheless it is still difficult to exactly elucidate the reaction mechanism of anodic oxidation. The complete electro-oxidation of ethanol produces 12 electrons from one ethanol molecule and three water molecules:

Anode reaction:

$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 2H^+ + 12e^-$ (1)

Cathode reaction:

$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$ (2)

Overall reaction:

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ (3)

The oxidation reaction must be complete for recovering the maximum energy from the alcohol molecule, that is, it must lead to CO_2. Some papers shown that species such as, acetaldehyde, acetic acid and other byproduct can be identified by infrared spectroscopy [de Sauza et.al., 2002, Perez et.al., 1989] or by chromatographic techniques [Hitmi et.al., 1994] or by DEMS [Fujiwara et.al., 1999, de Sauza et.al., 2002]. Those by product proved that parallel and consecutive oxidation reaction were occurred as well, except primary reaction producing CO_2. The presence of by product decreases the useful energy density of the fuel.

Even though the direct ethanol fuel cell (DEFC) has been developed, there still remain problems in term of efficiency and ethanol crossover. At low temperature, (80°C), the poor performance of electro-catalysts in the anode region has been proved when using pure Pt because of the catalyst poisoning caused by the adsorbed CO. More over the breaking of C-C bond to form final product (CO_2) does not easily take place at low temperature.

Anode catalyst modification by adding a second and a third metal can improve the performance of electro-catalytic activity of Pt in order to overcome poisoning effect and reduce ethanol crossover. Some researchers have studied binary and ternary platinum-based electro-catalysts in order to improve the electro-catalytic activity of Pt to ethanol oxidation. In acidic system, carbon suported Pt modified with Sn, Ru, Pd and W showed the increasing of ethanol electro-oxidation activity [Zhou, 2003, Delime, 1999]. It was reported that PtSn/C electro-catalysts were more active than other for ethanol oxidation.

The purpose of this paper was to find out characteristic of anodes for ethanol oxidations. Some platinum anodes modified by ruthenium, tin, and nickel, were synthesized by thermal decomposition. The prepared electrodes were characterized by linear sweep voltammetry (LSV).

EXPERIMENTAL

In this study, the catalysts; platinum, ruthenium, tin, and nickel were deposited onto a titanium mesh support. For a half cell study, the titanium mesh was cut into 1.5 cm x 1.5 cm pieces. Firstly, the mesh was washed in acetone to degrease and then boiled, individually to prevent adhesion, in 37% HCl until bubbles were produced on the surface, to etch. The mesh was rinsed by deionised water and left to dry in air. To apply a catalyst layer, the substrate was dipped in the coating medium. When removing, the substrate was touched to the inside of the container to remove excess liquid, and was dried evenly under a lamp. When dry, it was placed onto a titanium grid and cured in an oven at 200°C for 10 minutes. The

procedure was repeated until the required weight of catalyst was achieved; approximately 1 mg cm^{-2} of platinum on the mesh. Calcinations were then performed in an oven at 430°C for 1 hour.

Ethanol oxidation tests carried out using LSV in a solution of 1M Ethanol-0.5M H_2SO_4/1M $HClO_4$. The LSVs were recorded using a potensiostat (Model 362 EG&G). Each solution was purged with nitrogen during measurement. The scan rate was 2 mVs^{-1}, and as the reference electrode was standard calomel electrode (SCE).

RESULT AND DISCUSSION

Figure 1. compares five voltammograms obtained in the ethanol-sulphuric acid electrolyte at room temperature from 0-450 mV for electrodes prepared by thermal decomposition. On the positive scan, it is noted that ethanol electro-oxidation on Pt_3Ru_1 starts at around 100 mV. On the Pt_4Ru_1, Pt_5Ru_1, Pt_3Sn_1, and Pt_1Ni_1 catalysts, it is started at 300-330 mV. It is clear that the presence of second metal gives a different effect to the electro-oxidation of ethanol. The increase in the current density of ethanol electro-oxidation on Pt_3Ru_1 at lower potential indicates that a lower energy is necessary for oxidation of ethanol.

At the same potential, for example 450 mV, the current density of ethanol electro-oxidation on Pt_3Ru_1, Pt_5Ru_1, Pt_4Ru_1, Pt_3Sn_1, and Pt_1Ni_1 are respectively 35, 22, 18, 7, and 3 mA cm^{-2}. These appear that Pt_3Ru_1 is thought to be more active than others catalyst, and the Pt_1Ni_1 catalyst has the lowest activity. Also, it can be observed in Figure 1 that atomic ratio of Pt to Ru influences the activity of the catalyst. A Pt:Ru ratio of 3:1 seems to present the best activity. It was reported that ethanol oxidation indicated an optimum Pt:Ru composition of 1.5:1 (60:40), and electrodes with low Ru content exhibited a very low activity because there were not enough Ru sites to effectively assist the oxidation of adsorbed residues [Camara et.al., 2004].

The results of LSV in the ethanol-perchloric acid solution at room temperature on the five catalysts are reported in Figure 2. The Electro-oxidation of ethanol in perchloric acid has same tendency as in sulfuric acid. On the Pt_3Ru_1 catalyst, the electro-oxidation starts at a lower potential, 100 mV, than other catalysts; Pt_5Ru_1, Pt_4Ru_1, Pt_3Sn_1, and Pt_1Ni_1. However, the electro-oxidation in sulfuric acid indicated by increasing current densities begins at a higher potential than in perchloric acid. It is found that those catalysts are more active in perchlorid acid than in sulfuric acid. It is possibly because SO_4^- anion can adsorb onto surface of the catalyst, whereas there are no anion effects with percloric acid. Comparison of catalyst activity in the different acid is given in Figure 3.

As mentioned above, the Pt-Ru catalyst exhibited a good activity, especially compared with Pt-Sn. However, according to the literature [Delime et.al, 1999, Lamy et.al., 2001, Zhou et.al., 2003, Zhou et.al., 2004a, Zhou et.al., 2004b, Zhou et.al., 2005], the addition of Sn to Pt was more enhancing to ethanol oxidation than Ru on Pt. It was reported that ethanol oxidation on carbon supported Pt_1Sn_1 and Pt_1Ru_1 catalyst began at 90 and 60 mV (vs SCE) [Zhou et.al, 2004a]. A Pt:Sn ratio of 2:1 on carbon at 90°C was found as a more suitable anode catalyst for direct ethanol fuel cells in term of the fuel cell maximum power density [Zhou, 2005].

CONCLUSIONS

It was found that by the thermal decomposition method, PtRu catalyst showed more active for electro-oxidation of ethanol than PtSn, or PtNi. The catalytic activity of PtRu toward the etanol oxidation reaction was strongly dependent on the Ru content. A better Pt:RU composition is 3:1 in atomic ratio. It was also exhibited catalyst activity in perchloric acid had better performance than in sulphuric acid.

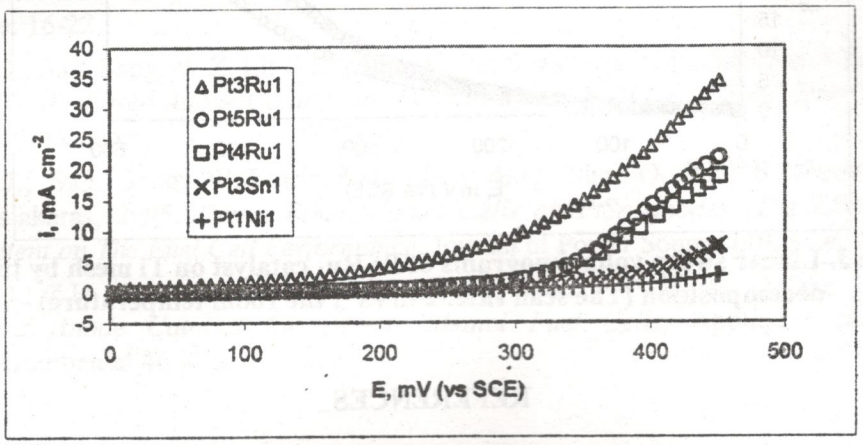

Figure 1. Linear Sweep voltammograms of bimetallic catalyst on Ti mesh by thermal decomposition (The scan rate: 2 mVs^{-1}; the electrolyte: 1M ethanol-0.5M H_2SO_4; the room temperature)

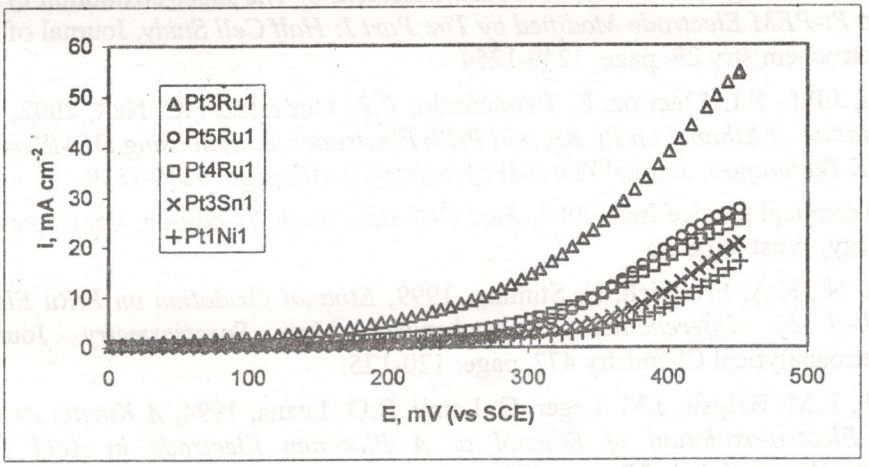

Figure 2. Linear sweep voltammograms of bimetallic catalyst on Ti mesh by thermal decomposition (The scan rate: 2 mVs^{-1}; the electrolyte: 1M ethanol-1M $HClO_4$; the room temperature)

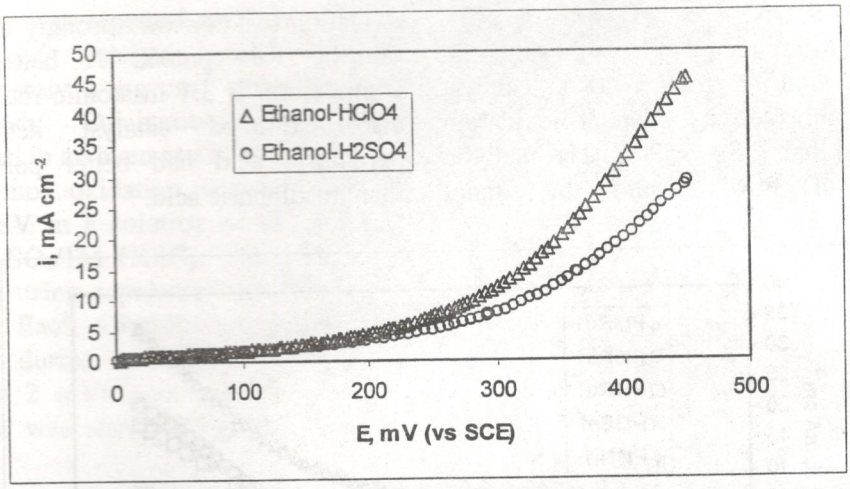

Figure 3. Linear sweep voltammograms of Pt_3Ru_1 catalyst on Ti mesh by thermal decomposition (The scan rate: 2 mVs^{-1}; the room temperature)

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