

THE COMPARISON OF FUEL AND ELECTROLYTE TYPE IN FUEL CELL APPLICATIONS USING PtRuCe/MWNTs ELECTROCATALYSTS

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Introduction

The Direct Alcohol Fuel Cells (DAFC) is a promising technology for transportation and portable electronic devices [1]. Among the different possible alcohols, methanol is the most hope-giving organic fuel, because its use as a fuel has several advantages in aqueous electrolytes, liquid fuel available at low cost, easily handled, transported and stored, high theoretical density of energy comparable to that of gasoline. Other alcohol such as ethanol has also been considered for use in fuel cells. Ethanol is less toxic compared to methanol, and can be easily produced in great quantity.

It has been found that the catalytic activity of platinum and palladium-based for electrooxidation of ethanol or methanol can be enhanced with addition of certain metal oxides in a high pH environment [2]. It has been known that the oxides such as ceria are capable of adsorbing large quantities of OH species, which are involved in the oxidation/reduction mechanisms taking place between the different possible oxidation states of the metal oxides [3].

Taking into account to these subjects, the effect of electrolyte (H₂SO₄ and KOH) and fuel (methanol and ethanol) used in the present investigation for PtRuCe catalyst, was considered.

Experimental

One-step polyol process method was used to produce desired catalyst. Initially, MWNTs was dispersed in ethylene glycol (EG) using ultrasonication for 20 min. Then, metal precursors (H₂PtCl₆.6H₂O, RuCl₃.2H₂O and Ce(NO₃).6H₂O) was added to this reaction mixture under vigorous stirring, followed by adjustment of pH at 12. The solution was rapidly heated up to 160°C, while refluxing under argon gas. The reaction mixture was held in this temperature for 3 h, then was filtered and dried in vacuum oven at 90°C for 4 h. The molar ratio of Pt:RuCe was corresponded to 1:1:0.1 molar ratio. Here, Pt loading was considered 20 wt%.

Electrocatalytic activities of catalysts were measured by cyclic voltammetry with use of half-cell involving in three-electrode at room temperature. A thin film of dispersed electrocatalyst-nafion mixture was spread on a glassy carbon disk (2 mm in diameter) having a Teflon covering as the

working electrode. The Pt loading of catalysts on electrode was 0.4 mg/cm². A Pt wire used as the counter electrode and a saturated calomel electrode (SCE) was served as the reference electrode. At beginning of each test, the solution was purged with high-purity N₂ before scanning. In all experiments, the scan rate of CV analysis was set at 50 mVs⁻¹.

Results and Discussion

Fig. 1 shows CV curves of PtRuCe/MWNTs catalyst in 1 M methanol containing different electrolyte solution. Electrocatalytic current of methanol oxidation sharply increases in alkaline solution, as indicated in Fig. 1. The onset potential values of catalyst are 0.26 and 0.58 V, respectively, for basic and acidic solution. The maximum peak of methanol electrooxidation occurs at 0.76 V, for alkaline solution, while it was happened at values greater than 0.8 V in acidic electrolyte. The enhanced performance of electrocatalyst in alkaline medium is attributed to the presence of OH groups which aids to remove CO-like intermediate species on which the Pt sites there are. In alkaline medium, following reaction occurs, which confirms the better catalytic performance of PtRuCe [4]:

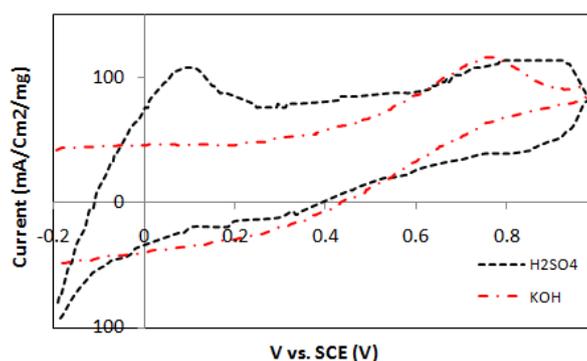
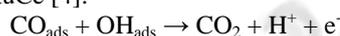


Fig. 1 Cyclic Voltammograms of PtRuCe catalyst in 1 M methanol containing 0.5 M H₂SO₄ or KOH solution.

The effect of fuel type used in anode section of fuel cell was depicted in Fig. 2. Taking into account to literature, ethanol has higher energy density than methanol [1], hence, higher current densities of ethanol in Fig. 4 may be attributed to this reality. The maximum peak of electrooxidation current of ethanol was taken place at higher voltage than that of methanol, which is probably due to the production of more intermediate species such as acetic acid, acetaldehyde and CO on the catalyst surface.

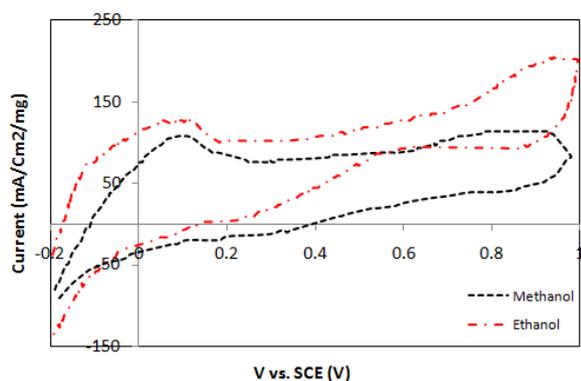


Fig. 2 CV curves of PtRuCe catalyst in 0.5 M H₂SO₄ containing 1 M methanol or ethanol as the fuel.

Chronoamperometry results of PtRuCe catalyst was implied in Fig. 3. Total current density of catalyst in acidic medium is relatively higher than one of the alkaline solution, however, sharper reduction in electrocatalytic current takes place. The proper stability of electrocatalytic activity in alkaline solution is because of accessibility of OH groups and prevention of CO poisoning of Pt sites on catalyst surface.

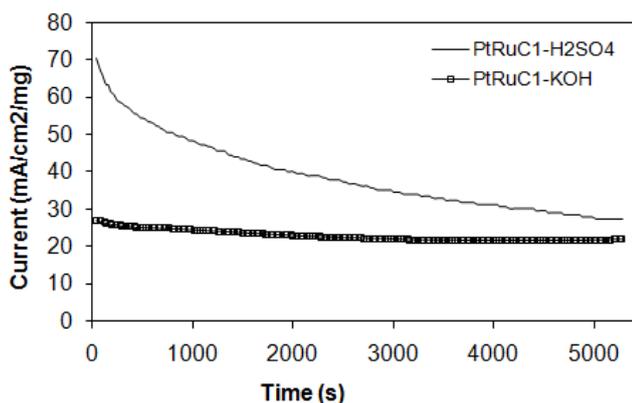


Fig. 3 Chronoamperometry curves for PtRuCe catalyst in 1 M methanol containing 0.5 M H₂SO₄ or KOH at 0.6 V for 5400 s.

Fig. 4 shows chronoamperometry curves of PtRuCe catalyst in solutions with different fuels. Total current density of catalyst using methanol is slightly greater than one of ethanol containing solution, but, generally, the poisoning rate of catalysts in both cases is similar. However, stability of catalyst in ethanol containing solution is a few low than that of methanol containing solution which is probably due to more intermediate species resulting in dehydrogenation of alcohol.

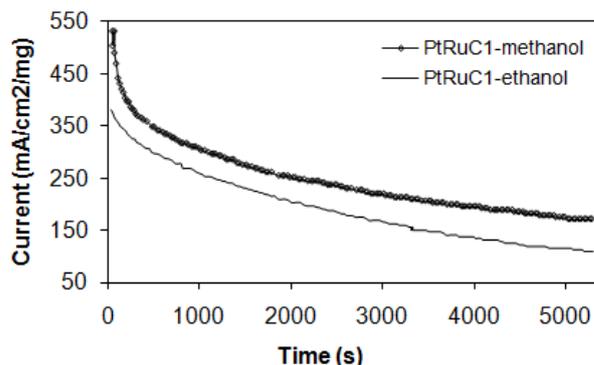


Fig. 4 Chronoamperometry curves for PtRuCe catalyst in 0.5 M H₂SO₄ containing 1 M methanol or ethanol at 0.6 V for 5400 s.

Conclusions

Ce-modified PtRu catalyst supported on MWNTs was synthesized via one-step polyol process method. Alkaline mediums are desired in stability, due to the elimination ability of CO-like intermediate using OH groups which are present in the solution. Current densities of ethanol electrochemical is shown higher values than one of the methanol. Using both fuels, the poisoning rate is relatively similar, which makes feasible the replacement of ethanol instead of methanol in DAFCs as the fuel.

References

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