

ELECTROCHEMICAL OXIDATION OF METHANOL ON MULTI-WALLED CARBON NANOTUBE SUPPORTED PtRuCe AS ANODE ELECTROCATALYST

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Introduction

The Direct Methanol Fuel Cells (DMFC) is a promising technology for transportation and portable electronic devices [1]. The excellent catalytic activity of platinum with respect to methanol oxidation at low temperatures brings about Pt to be in electrocatalytic ideal for use as an anode in DMFCs [2].

The formation of CO intermediate species on the Pt sites during the methanol oxidation reaction reduces the efficiency of the cell and this matter was converted as a challenge. According to the bifunctional mechanism, the CO intermediate species formed on the Pt sites can be oxidized by active oxygen atoms formed on the second metal of the bimetallic catalysts, especially PtRu. However, the use of the PtRu catalyst still cannot completely eliminate the CO species, which prevents complete oxidation of methanol to CO₂. Therefore, the improvement in the electrocatalytic activity of the PtRu catalyst is required to reduce or completely eliminate the CO intermediate species [3].

It has been suggested 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 [4]. In the present investigation, ceria-modified PtRu catalysts with different composition of Ce were synthesized via polyol method. These catalysts were compared in electrocatalytic activity with varying Ce content.

Experimental

Catalysts used in this study was prepared via polyol process method which reported in the literature [5]. In this study, MWNTs and ethylene glycol (EG) were sonicated for 20 min. Afterwards, metal precursors (H₂PtCl₆.6H₂O, RuCl₃.2H₂O and Ce(NO₃).6H₂O) was added to this mixture under vigorous stirring, followed by pH adjustment at 12. The solution was rapidly heated up to 140-160°C and refluxed 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:Ru was corresponded to 1:1, respectively, as Ce content was varied with molar ratios of 0.1, 0.5 and 0.7 which denoted as

PtRuCe1, PtRuCe5 and PtRuCe7, respectively. Also, Pt loading for all samples is 20 wt%.

X-ray diffraction (XRD) with Cu K α radiation (using Philips X'pert) was used to identify crystalline phase of Pt, PtRu alloy and Ce-modified PtRu. TEM (CM-FEG-Philips) image by an accelerating voltage of 200 kV was used to obtain the nanoparticles sizes.

Electroactivities of catalysts were measured by cyclic voltammetry with use of three-electrode test cell at room temperature. A thin film electrode technique was used to make the measurements. A glassy carbon disk (2 mm in diameter) held in a cylindrical Teflon cover as the working electrode, on which a thin layer of nafion-impregnated catalyst was placed. 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 acted as the reference electrode. At beginning of each test, the solution was purged with high-purity N₂ before scanning.

Results and Discussion

The XRD patterns of catalysts was shown in Fig. 2. The characteristic diffraction peaks of the FCC Pt in all catalysts, namely (111), (200) and (220) in the regions of 39.76°, 46.24° and 67.45° (2 θ), respectively demonstrate the presence of Pt in metallic form. Decreasing of 2 θ in PtRu catalyst confirms the formation of alloy between Pt and Ru. The formation of broad peaks in Ce-modified PtRu catalyst indicated the presence of smaller PtRu particles.

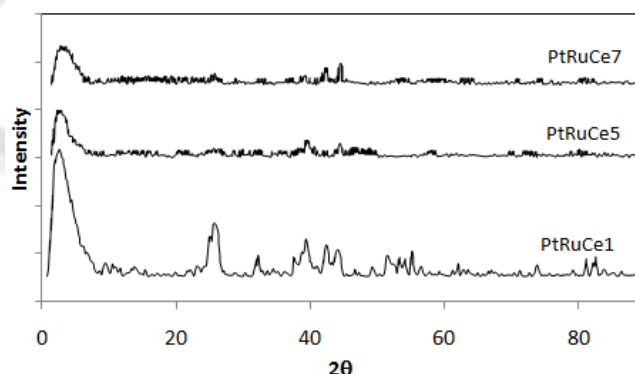


Fig. 1 XRD patterns of PtRuCe1, PtRuCe5 and PtRuCe7 catalysts.

Fig. 2 shows the CV curves of MWNTs supported PtRu with different molar ratio of Ce catalysts in 0.5 M H₂SO₄ solution. The hydrogen desorption peak of Pt/MWNTs catalyst is observed in the potential range of -0.2 to 0.25 V. Obviously, the electrochemical surface area (ESA) value is very high for PtRuCe5 electrode which may be attributed to the surface enrichment using Pt nanoparticles, on which hydrogen atoms can easily adsorb/desorb.

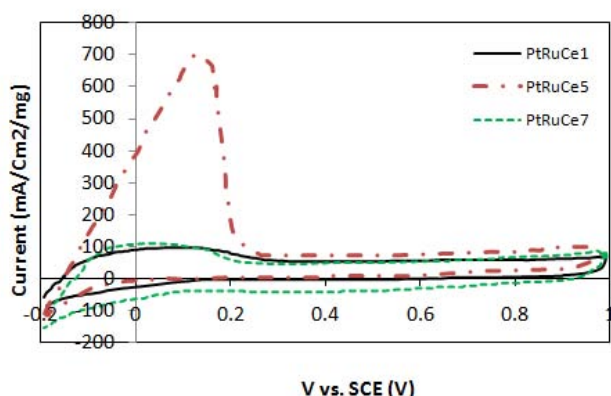


Fig. 2 Cyclic Voltammograms of PtRuCe1, PtRuCe5 and PtRuCe7 in 0.5 M H₂SO₄ solution.

The results of methanol electrooxidation on different electrocatalysts in 0.5 M H₂SO₄ containing 1 M methanol was shown in Fig. 3. Methanol oxidation current of PtRuCe7 is higher at maximum peak, having smaller onset potentials than those of PtRuCe1 and PtRuCe5. The onset potential values of PtRuCe1, PtRuCe5 and PtRuCe7 are 0.58, 0.39 and 0.28 V, respectively. In the other word, the onset potential value diminishes, and, the maximum current density increases up to about 350 mA/Cm²/mg, with addition of Ce amounts. Additionally, thickness of double layer was lowered, as Ce quantity was increased. It is not clear what kind of resistance is there, and the performance drops after the optimum level of Ce.

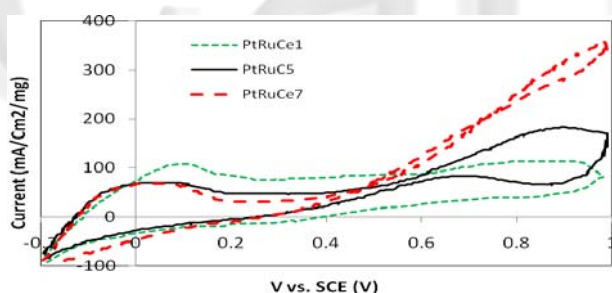


Fig. 3 Cyclic voltammetric curves of PtRuCe1, PtRuCe5 and PtRuCe7 in 0.5 M H₂SO₄ containing 1 M methanol.

Chronoamperometry results of PtRu catalysts with various molar ratio of Ce, can be seen in Fig. 4. Total current density of PtRuCe catalysts was sharply increased with addition of Ce value, showing the modification of PtRu catalyst using Ce, which is due to the ability of Ce in activation of OH groups and enhancement of bifunctional mechanism effect of Ru. At initial times, in spite of higher total current densities at high contents of Ce, severe decrease of current was observed in Fig. 4, however, this phenomena was not well known.

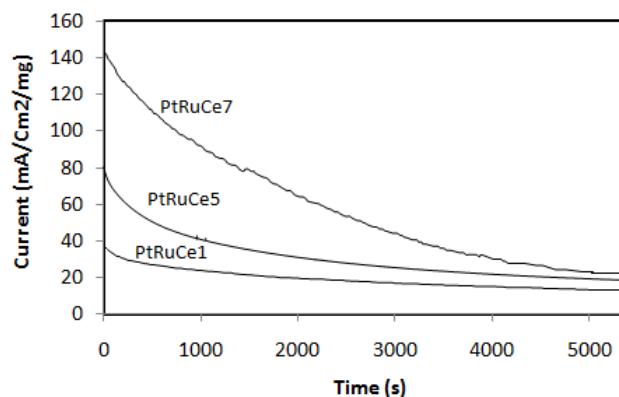


Fig. 4 Chronoamperometry curves for PtRuCe1, PtRuCe5 and PtRuCe7 in 0.5 M H₂SO₄+ 1 M methanol at 0.6 V for 5400 s.

Conclusions

Electrooxidation of methanol is significantly affected based on added Ce contents. Onset potential of catalysts is decreased, as Ce content is increased which is attributed to the activation of OH groups in solution.

In this study, the optimum molar ratio of Ce is obtained at 0.5 with respect to Pt. PtRuCe5 catalyst showed very high electrochemical surface area which can be attributed to surface enrichment by Pt. It seems that at higher ratios (such as 0.7), unknown resistance prohibits enhanced electrocatalytic activity, as PtRuCe7 electrode showed very high poisoning rate, inspite of high total current densities in chronoamperometry curve.

References

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