

# INFLUENCE OF CERIA-DOPED PtRu/MWNTs NANOALLOY AS ANODE CATALYST FOR DIRECT METHANOL FUEL CELLS

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## Introduction

Direct methanol fuel cells (DMFCs) are one of the potential power sources for portable electronic devices [1]. The excellent catalytic activity of platinum with respect to methanol oxidation at low temperatures makes ideal it for use as an anode in DMFCs [2]. It is well known that the formation of CO intermediate species on the Pt sites during the methanol oxidation reaction creates an overpotential, which reduces the efficiency of the cell. According to the bi-functional 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, such as PtRu. However, the use of the PtRu catalyst still cannot completely eliminate the CO species, which prevents complete oxidation of methanol to CO<sub>2</sub>. Therefore, the improvement in the electro-catalytic activity of the PtRu catalyst is required to reduce or completely eliminate the CO intermediate species [3]. It has been suggested that the oxides 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, we employed CeO<sub>2</sub> as a cocatalytic material along with the PtRu bimetallic catalyst.

## Experimental

Catalysts used in this study was prepared via polyol process method which reported in the literature [5]. In this way, MWNTs dispersed in ethylene glycol (EG) was sonicated for 20 min. After this, metal precursors (H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O, RuCl<sub>3</sub>.2H<sub>2</sub>O and Ce(NO<sub>3</sub>).6H<sub>2</sub>O) was added to this solution under vigorous stirring, followed by pH adjustment at 12. The solution was rapidly heated up to 140-160°C under reflux and argon gas and held in this temperature for 3 h. Products were filtered and dried in vacuum oven at 90°C for 4 h. The molar ratio of Pt:Ru:Ce is corresponding to 1:1:0.5, respectively, and Pt loading for all samples is 20 wt%.

X-ray diffraction (XRD) with Cu K $\alpha$  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 Teflon cylinder was used as the working electrode, on which a thin layer of nafion-impregnated catalyst was cast. The Pt loading of catalysts on electrode was 0.4 mg/cm<sup>2</sup>. A Pt wire served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The solution was purged with high-purity N<sub>2</sub> before scanning.

## Results and Discussion

It is indicated highly-dispersed nanoparticles of MWNTs supported Pt and PtRu. PtRu alloys shows smaller particle sizes and better particle size distribution than Pt catalyst which is consistent with Fig. 1.

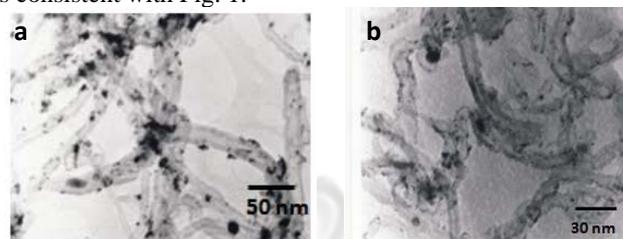


Fig. 1 TEM images of a) Pt/MWNTs and b) PtRu/MWNTs.

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 $\theta$ ), respectively demonstrate the presence of Pt in metallic form. Decreasing of 2 $\theta$  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.

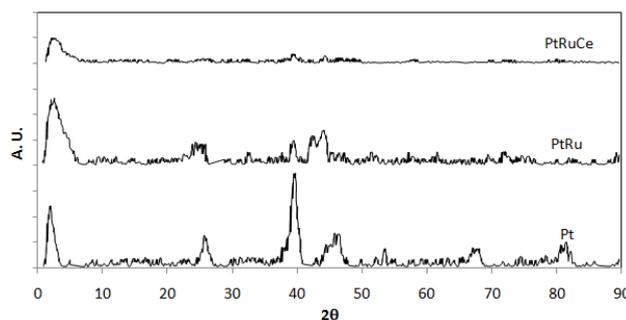
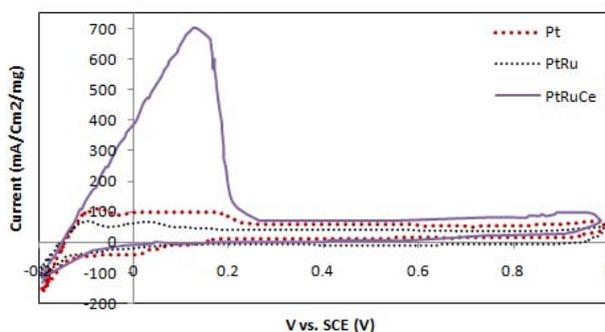


Fig. 2 XRD patterns of Pt/MWNTs, PtRu/MWNTs and PtRuCe/MWNTs.

Fig. 3 shows the cyclic voltammograms of MWNTs supported Pt, PtRu and ce-modified PtRu catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The hydrogen desorption peak of Pt/MWNTs catalyst is observed in the potential range of -0.2 to 0.25 V, which is consistent with the data reported in the literature [ ]. It is clear that the electrochemical surface area (ESA) value is very high for PtRuCe/MWNTs catalyst because of the

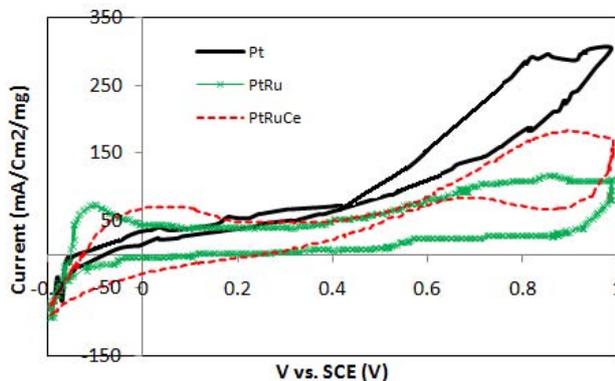
presence of relatively smaller size of Pt and Ru particles, in which hydrogen atoms can easily adsorb/desorb especially, on the surface of the Pt particles.



**Fig. 3** Cyclic Voltammograms of Pt/MWNTs, PtRu/MWNTs and PtRuCe/MWNTs in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

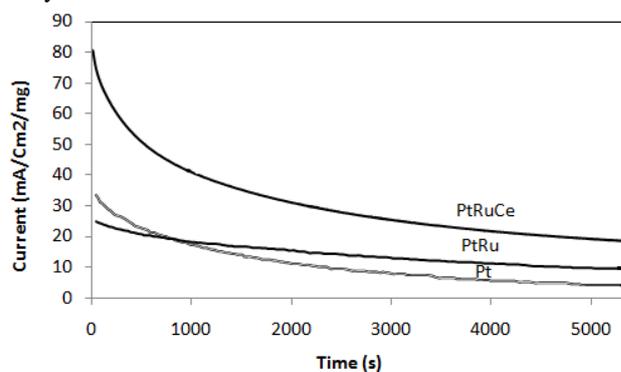
Fig. 4 shows the cyclic voltammetric curves of methanol electrooxidation on various electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1 M methanol. It is obvious that the current densities are higher at corresponding potentials on Pt/MWNTs than those of PtRu/MWNTs and PtRuCe/MWNTs. Decreasing of the current density of PtRu/MWNTs than that of Pt/MWNTs is attributed to blocking of Pt sites in presence of Ru, resulting in low electrochemical surface area. It can be seen from Fig. 4 that the electrooxidation of methanol with addition of Ce is increased than PtRu/MWNTs catalyst which is due to the synergism role of Ce in the formation of OH-containing groups, but it is lower than that of Pt/MWNTs which is attributed to particle size effect.

The onset potential values of Pt/MWNTs, PtRu/MWNTs and PtRuCe/MWNTs are 0.44, 0.41 and 0.39 V, respectively. The high value of onset potential of Pt/MWNTs is because of poisoning by CO-like species. The addition of Ru and Ce is brought about modification of surface properties of catalyst to produce OH-containing groups against CO-like species.



**Fig. 4** Cyclic voltammetric curves of Pt/MWNTs, PtRu/MWNTs and PtRuCe/MWNTs in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1 M methanol.

The enhanced stability of PtRu/MWNTs against poisoning in the presence of Ru confirmed using chronoamperometry analysis as observed in Fig. 5. The severe decrease of current density for Ce-modified catalyst is due to relative poisoning effect of Ce, but, generally, total current density is higher than those of Pt/MWNTs and PtRu/MWNTs catalysts.



**Fig. 5** Chronoamperometry curves for Pt/MWNTs, PtRu/MWNTs and PtRuCe/MWNTs in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M methanol at 0.6 V for 5400 s.

## Conclusions

In this study, the used catalysts were synthesized using polyol process. TEM images showed highly-dispersed Pt and PtRu electrocatalysts supported on MWNTs. Particle sizes of Pt and Ru are severely reduced with addition of cerium. The small particles of Pt and Ru is confirmed using XRD and CV curves, because CV results of PtRuCe showed significant increase of electrochemical surface area than those of Ce non-containing catalysts.

In addition to, the onset potential values of catalysts demonstrated lower values, by increase of Ce. However, the current densities of Pt/MWNTs was higher than that of PtRuCe which is attributed to particle size effect.

## References

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