

# Synthesis and Characterization of PtPd and PtRuPd Anode Catalysts for Direct Methanol Fuel Cells

G. Horvath, K. W. Park, Y. E. Sung

Department of Materials Science and Engineering  
Kwangju Institute of Science and Technology

## Abstract

In this study, Pt/Pd (1:1), PtPd (2:1) and PtPd (3:1) binary catalysts and Pt/Ru/Pd (5:4:1) ternary catalyst were designed. The catalysts were synthesized by impregnation method using  $\text{NaBH}_4$  as a reducing agent. A good catalyst for methanol oxidation requires low on-set potential, stable durability and low activation energy. In order to investigate the catalytic activity for the methanol oxidation, electrochemical measurements such as cyclic voltammetry and chronoamperometry were performed in sulfuric acid with/without methanol solution. In order to calculate the activation energy of the reaction, electrochemical measurements were also tested at different temperatures. For investigation of the structural analysis such as particle size and alloying, X-ray diffraction and transmission electron microscopy analysis were used. In order to identify the role of the Pd and to determine the composition of the surface of the Pt/Pd nanoparticles, X-ray photoelectron spectroscopy (XPS) analysis was investigated. The XPS spectra of Pd showed that Pd appears only as a metallic state in the binary catalysts. The chemical states of Pt in PtPd catalysts are both metallic and oxidative. Polarization curves and power density data were obtained by testing the DMFC unit cell performance of PtPd and PtRuPd catalysts. These data showed that Pt/Pd (2:1) and Pt/Ru/Pd (5:4:1) have better performance than Pt and Pt/Ru, respectively.

## 1. Introduction

The direct methanol fuel cell (DMFC) is one of the promising candidates as energy storage applications, mainly for electric vehicle and portable electronic devices. DMFC has the advantage of running at low temperatures (around 100 °C) and using methanol as a liquid fuel which can be easily stored, handled and produced. The main drawback of the DMFC is the poor performance of anode catalyst. Pure Pt is a relatively poor catalyst for methanol oxidation reaction, being poisoned by CO adsorbed on the surface. Pd is a noble metal and has same face centered cubic (fcc) structure as Pt. By adding

a 2<sup>nd</sup> metal the catalytic activity can be increased by means of two mechanism : bifunctional mechanism and electronic effect. Although PtRu is considered the most widely used anode catalyst, better design is pursued by the addition of a 3<sup>rd</sup> metal such as Pd.

## 2. Experimental

All the catalysts were synthesized by impregnation method using NaBH<sub>4</sub> in hydrous solution as a reducing agent. H<sub>2</sub>PtCl<sub>6</sub>, PdCl<sub>2</sub> and RuCl<sub>3</sub> were mixed in Millipore water (18.2 MΩ · cm) until they dissolved completely. In order to identify the structural characteristics, average particle size and the alloy formation of nanoparticles, XRD and TEM analysis were carried out at room temperature. XPS measurements were performed in order to characterize the surface composition of catalysts.

Electrochemical measurements were performed in a three-electrode cell at room temperature using solutions of 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub>. A Pt wire and a Ag/AgCl electrode were used as a counter and a reference electrode. The working electrode consists of a carbon electrode brushed with the catalyst ink. Cyclic voltammetry and chronoamperometry curves were recorded with an Autolab of Eco Chemie.

Polarization curves and power density data were obtained by testing the direct methanol fuel cell performance of catalysts. 2 M methanol solution was supplied by a liquid micropump at anode and dry O<sub>2</sub> at cathode.

The performance of catalysts is affected by temperature. For this reason, to compare the catalytic activity of the catalysts, methanol oxidation was tested using cyclic voltammetry and chronoamperometry measurements at different temperatures. The temperature of the electrochemical cell was controlled by immersing the cell in a constant temperature bath (Fisher Scientific Isotemp).

## 3. Results and Discussion

XRD analysis show that the diffraction peaks in PtPd catalyst are slightly shifted to higher angle values with respect to the same reflections of Pt. Such evidence accounts for the presence of alloy in the catalyst. The TEM image shows that no agglomerations of particles were found in PtRuPd (5:4:1) but both agglomerations and individual particles were found in the PtPd nanoparticles. The average particle sizes obtained from TEM image is approximately 4 nm which is in a good agreement with XRD measurements. In XPS spectra of Pt 4f peak shows that this is slightly shifted to lower

binding energy compared to pure Pt peak. The spectra of Pd 3d and Pt 4f indicate that Pd is present in the alloy only as a metallic state and Pt appears in both metallic and oxidative state. The most acceptable mechanism for methanol oxidation is based on electronic effect. According to this effect, Pd atoms in PtPd donate electrons to Pt atoms. This is in agreement with the electronegativity values for Pd and Pt which are 2.20 and 2.28, respectively. A charge transfer from Pd to Pt has also been found by XPS analysis, as reflected in a negative shift in the Pt 4f binding energy of PtPd (2:1) catalyst. It can be concluded that the addition of Pd to Pt slightly increased the catalytic activity due to the modification of the electronic environment around Pt.

The on-set potential of pure Pt catalyst is relatively high because of CO poisoning. All of the PtPd binary catalysts except PtPd (2:1), which is almost similar to Pt, have higher on-set potentials than pure Pt. Among PtPd catalysts, PtPd (2:1) has the lowest on-set potential of 0.35 V. In order to investigate the durability of methanol oxidation, chronoamperometry measurements were conducted for 30 minutes at an applied constant potential of 0.35 V (vs. Ag/AgCl). From these measurements can be concluded that the decay ratio in PtPd (1:1) and PtPd (3:1) is larger than that of pure Pt and PtPd (2:1). As the decay ratio increases the catalytic activity of nanoparticles is worse.

In case of the ternary system, PtRuPd (5:4:1) have lower on-set potential, which is 0.26 V, compare with that of PtRu (1:1), which is 0.27 V. Chronoamperometry data show that the decay ratio after 30 minutes of PtRuPd (5:4:1) is lower than that of PtRu (1:1). By comparing voltammetry and chronoamperometry data, it can be concluded that PtPd (2:1) and PtRuPd (5:4:1) has a better catalytic activity than pure Pt and PtRu (1:1), respectively.

DMFC performance curves were obtained using as anode materials, pure Pt, PtPd (2:1), PtRu (1:1) and PtRuPd (5:4:1) catalysts. Pt black (Johnson Matthey) was used as a cathode material. The catalyst loadings were 5–6 mg / cm<sup>2</sup> at both electrodes. Comparison of the cell polarization curves shows that the catalytic activity for methanol oxidation of PtPd (2:1) and PtRuPd (5:4:1) is higher than that of pure Pt and PtRu (1:1), respectively. Also the OCVs of PtPd (2:1) and PtRuPd (5:4:1) are higher than those of Pt and PtRu (1:1). Power densities data indicate that the maximum power density of PtPd (2:1) and PtRuPd (5:4:1) is higher than that of pure Pt and PtRu (1:1), respectively. From cell polarization curves and power density data one can conclude that the catalytic activity for methanol oxidation of PtPd (2:1) is higher than that of Pt and that of PtRuPd (5:4:1) is higher than that of PtRu (1:1).

In order to calculate the turnover number and the activation energy, voltammetry and chronoamperometry measurements for PtRu (1:1) and PtRuPd (5:4:1) were used at 25, 40 and 60 °C. At 60 °C the double layer is much thicker due to increasing of OH

adsorption peak. As temperature increased the OH adsorption reaction and oxidation current were increased. The voltammograms in 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> show that on-set potential depends on the temperature. As the temperature increased the on-set potential was lower. This means that higher catalytic activity for methanol oxidation can be obtained at higher temperatures. In order to test the durability for methanol oxidation, chronoamperometric measurements were conducted for 30 minutes in methanol solution at 25, 40 and 60 °C for PtRu (1:1) and PtRuPd (5:4:1). For both catalysts after 30 minutes the current density is higher as the temperature is increased. Using these data turnover number and activation energy can be calculated. The current density after 30 minutes was considered as a steady state current density at different temperatures. In Table 1 are shown the turnover numbers of PtRu (1:1) and PtRuPd (5:4:1) catalysts at 25, 40 and 60 °C. From this table can be concluded that the turnover number is a function of temperature and is higher for both catalysts at higher temperatures. Table 2 shows the activation energy values at 0.3 V for PtRu (1:1) and PtRuPd (5:4:1). Activation energy can be calculated from the effective surface area using H desorption peak in each voltammogram. To calculate activation energy, Arrhenius plots of log*i* vs. 1/T were used for both catalysts. From these plots can be concluded that PtRuPd (5:4:1) has lower activation energy compare to PtRu (1:1). This means that PtRuPd (5:4:1) has higher catalytic activity for methanol oxidation than PtRu (1:1).

#### 4. Conclusion

PtPd (2:1) has lower on-set potential and higher stability for methanol oxidation than pure Pt, PtPd (1:1) and PtPd (3:1). Power density data show also that PtPd (2:1) has better catalytic activity than pure Pt. PtRuPd (5:4:1) has higher stability for methanol oxidation, lower on-set potential, larger turnover number and smaller activation energy than PtRu (1:1). This means that PtPd (2:1) and PtRuPd (5:4:1) have a higher catalytic activity for methanol oxidation than pure Pt and PtRu (1:1), respectively. The role of Pd in the enhancement of catalytic activity can be explain by electronic effect by modification of electronic properties of Pt. No oxidative states of Pd were found on the surface. That means Pd is not involved in bifunctional mechanism.

#### 5. References

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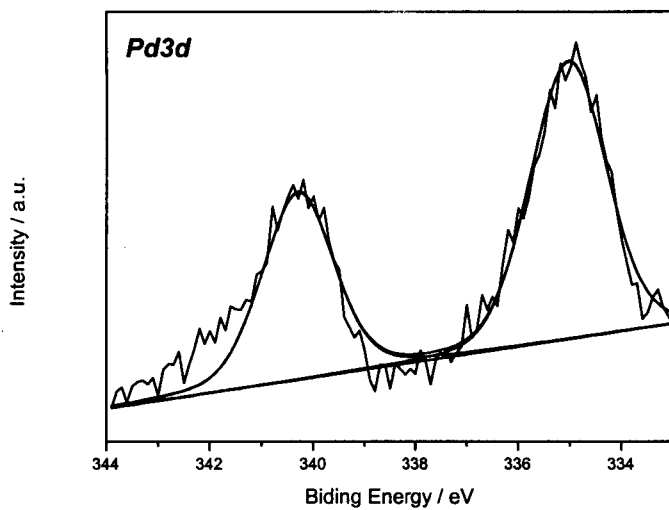


Figure 1. X-ray photoelectron spectroscopy spectra of Pt/Pd (2:1) catalyst

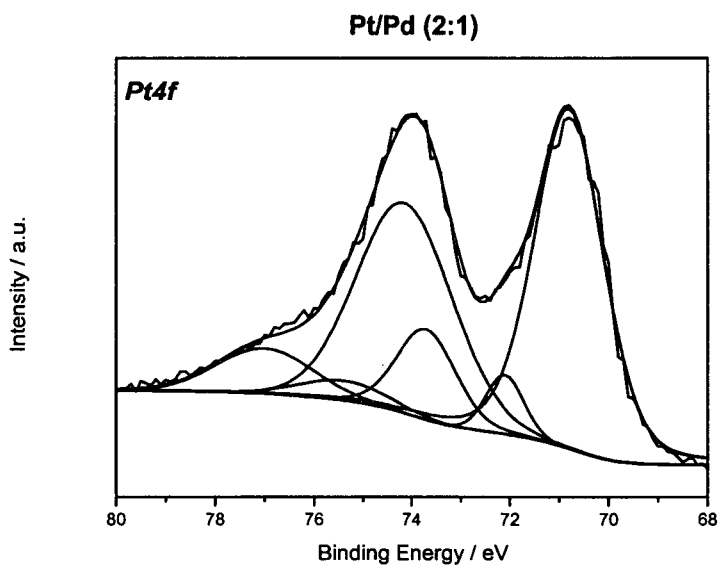


Figure 2. Pt4f spectra in Pt/Pd (2:1) catalyst

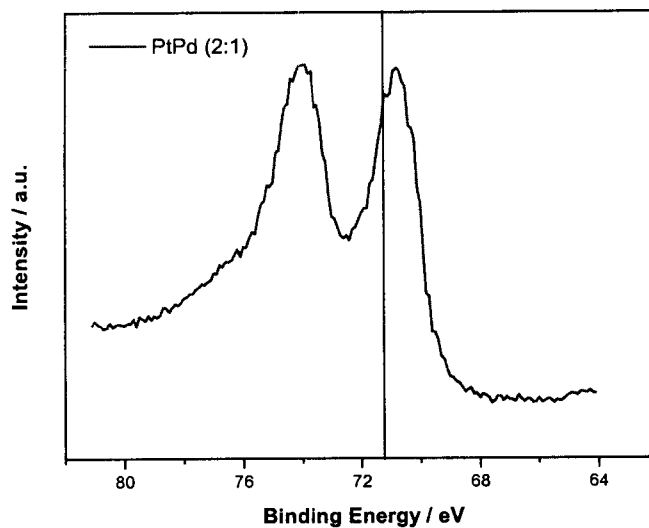


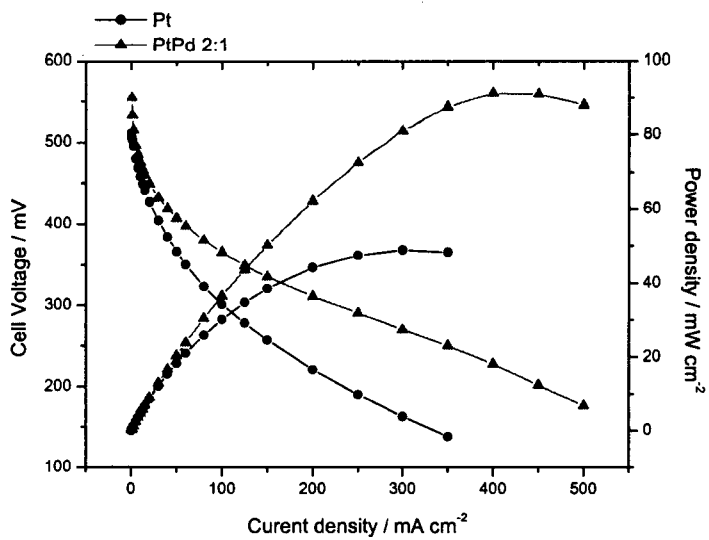
Figure 3. X-ray photoelectron spectra of Pt 4f in PtPd (2:1) catalyst

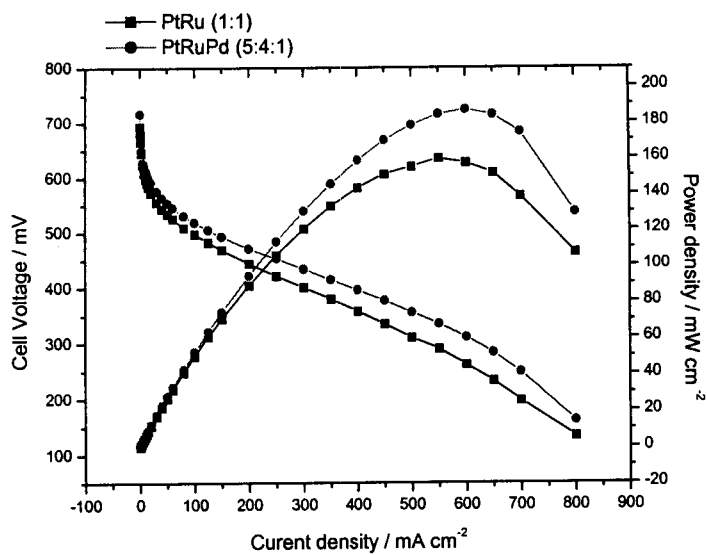
Table 1. Activation energy of PtRu (1:1) and PtRuPd (5:4:1) at 0.3 V.

Catalyst	Activation Energy ( kJ mol <sup>-1</sup> )
Pt/Ru (1:1)	16.41
Pt/Ru/Pd (5:4:1)	12.84

**Table 2.** Turnover numbers of PtRu (1:1) and PtRuPd (5:4:1) at 25, 40 and 60 °C.

Catalyst	Temperature (°C)	Turnover number at 0.3 V
PtRu (1:1)	25	$3.09 \times 10^{-2}$
	40	$3.46 \times 10^{-2}$
	60	$5.53 \times 10^{-2}$
PtRuPd (5:4:1)	25	$3.58 \times 10^{-2}$
	40	$4.15 \times 10^{-2}$
	60	$5.67 \times 10^{-2}$





**Figure 4.** DMFC unit cell performance : polarization curve and power density data. The cell operating temperature was 70 °C.