

# Effect of NaBH<sub>4</sub> concentration on the activity of PtRu/C catalyst for DMFC prepared by the impregnation method

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## Introduction

PtRu alloy is generally regarded as the most appropriate catalyst for methanol electro-oxidation. It is known that Ru easily removes CO on Pt atom and enhances the catalytic activity of methanol electro-oxidation by bifunction mechanism or ligand effect. However, the commercialization of direct methanol fuel cell (DMFC) is still not easy because of its low power density caused by the low catalytic activity for methanol oxidation and the methanol crossover through the membrane. Many researchers have been trying to improve the activity of PtRu catalyst by various approaches. One is to increase the active surface area using the carbon support which has large surface area and high electron conductivity. Another is to add one or more elements into PtRu alloy to make ternary or quaternary catalyst.

In this work, the effect of NaBH<sub>4</sub> concentration in the aqueous co-impregnation method was investigated when NaBH<sub>4</sub> was used as the reducing agent for Pt and Ru metal precursors.

## Materials and Methods

Carbon black, Vulcan-P (about 150m<sup>2</sup>g<sup>-1</sup> BET surface area) from Cabot Corp. was suspended in distilled water and sonicated in ultrasonic bath. H<sub>2</sub>PtCl<sub>6</sub> and RuCl<sub>3</sub> were dissolved in diluted water and stirred. These solutions were mixed together and stirred sufficiently. Amount of metal precursor was adjusted that Pt and Ru had the molar ratio of 1:1 and total metal content in the catalyst was 60wt%. NaBH<sub>4</sub> solutions of different concentrations were prepared in which the molar ratio of NaBH<sub>4</sub> to Pt and Ru metals were 1, 2, 5, 15, 50 and 250. The mixed solutions of carbon blacks and metal ions were poured into each NaBH<sub>4</sub> solution rapidly. After 20 minutes the prepared catalysts were filtered and washed with boiling water for 3 hours. And the catalysts were dried in vacuum oven at 80 °C for 12 hours. The catalysts prepared under 1, 2, 5, 15, 50 and 250 times of NaBH<sub>4</sub> molar content to metal precursors were designated as 'x1', 'x2', 'x5', 'x15', 'x50' and 'x250' respectively.

## Results and Discussion

XRD patterns of the PtRu catalysts with different Ru content were reported in which the (200) peak broadening was observed [1-4]. The broadening of fcc (200) peak was found at the XRD patterns of x5, x15, x50, and x250 and particularly x15 showed the broadest peak and the biggest peak shift to higher angle. The broadest fcc (200) peak and the biggest decrease of d-spacing of x15 supports that x15 includes the highest amount of Ru in PtRu solid solution and Ru in the solid solution distorts the fcc structure although all samples have the same bulk composition of Pt and Ru (1:1). On the other hand, x1 and x2 showed narrow peaks and distinguished fcc (200) peaks, which were attributed to big particle and small amount of Ru in PtRu solid solution. Particle size is generally small under low concentration of reducing agent because the nuclei growth is faster than the nucleation. The critical point that the particle size dramatically decreases was observed at x5 in this experimental. Over the critical point, the particle size was not changed significantly.

In the cyclic voltammetry of the prepared catalysts, x1 and x2 showed the thicker pseudo-double layer capacitance, the smaller hydrogen desorption region and the lower oxide reduction peak potential around 0.2V than the commercial PtRu/C and than the other prepared catalysts. From the above result x1 and x2 have high surface Ru coverage than the others. Small amount of Ru in PtRu solid solution was observed for the x1 and x2 at the XRD experiment. It is reliable that the high Ru surface composition of x1 and x2 is derived from the Ru atoms which can not be incorporated into the PtRu solid solution. Furthermore, most of the isolated Ru particles lead to Ru dissolution in H<sub>2</sub>SO<sub>4</sub>. On the other hand, the change of curve shape with cycle number was not observed for x15 which means Ru dissolution did not occur and the surface state was maintained stable. XRD result that x15 contains the highest amount of Ru in PtRu solid solution supports that x15 contains smaller amount of the isolated Ru particles. Therefore the degree of PtRu solid solution determines the amount of Ru dissolution.

Linear sweep voltammetry were conducted in order to measure the catalytic activity of methanol oxidation (Fig. 1). x5 and x15 showed the highest activities but x1 and x2 showed the lowest. The excess Ru atoms on the catalyst surface of x1 and x2 block the active sites of Pt and reduced the activity of metal alloy. Also big particle size of x1 and x2 reduce the active area of the catalysts. Although Ru dissolution was observed at x5, x50 and x250, x5 showed a good performance. Therefore Ru dissolution is not considered to critically reduce the catalytic activity of methanol oxidation.

The surface compositions of Pt and Ru calculated from XPS results were represented at Table 1. x1 and x2 had high Ru surface composition which could be expected in the cyclic voltammetry result. Pt ions are reduced prior to Ru ions in low reducing agent because Pt metal has higher standard potential. Comparing the commercial Pt/C and PtRu/C, PtRu/C had more shifted peaks from Pt<sup>0</sup> state. x5 and x15 showed the most shifted peaks and the next was x50 and x250. This tendency coincides with the linear sweep voltammetry results that x5 and x15 show higher activity than other catalysts. The prepared catalysts which have high chemical shift in XPS results are more active for methanol electro-oxidation.

DMFC unit cell performances were tested with the prepared catalysts as the anode catalyst. The results correlated with the linear sweep voltammetry (Fig. 1). x15 showed the highest performance of DMFC. The low performance of x1 and x2 might be due to the high Ru surface coverage.

Table 1. The surface compositions obtained from XPS results.

	x1	x2	x5	x15	x50	x250	commercial
Pt:Ru	12:88	25:75	52:48	59:41	59:41	63:37	46:54

The surface compositions of the catalyst were converted to the ratio of only Pt and Ru.

## Significance

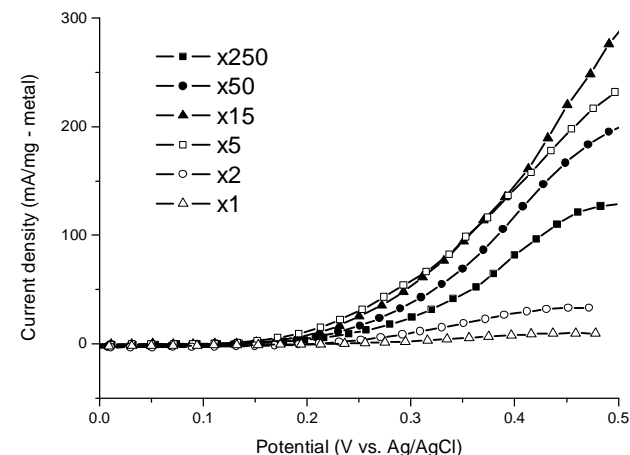


Figure 1. Linear sweep voltammetry curves of the prepared PtRu/C catalysts under 0.5M H<sub>2</sub>SO<sub>4</sub> + 1M methanol solution at 1mV/sec scan rate.

## References

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