The effect of P on the electrochemical activity of carbon supported Pt-Ru alloy catalyst for methanol oxidation

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INTRODUCTION

In polymer electrolyte membrane fuel cell (PEMFC), platinum is recognized as the most active metal for alcohol oxidation, however there is a strong CO adsorption tendency, which blocks the surface from further methanol adsorption and leads to very low power densities [1, 2]. Pt-Ru is the most promising of the binary catalysts for methanol oxidation due to the improved CO tolerance. The following mechanism shows the effect of adding Ru on methanol oxidation:

$$Pt + CO \longrightarrow Pt\text{-}CO_{ad}$$

$$Ru + H_2O \longrightarrow Ru\text{-}OH_{ad} + H^+ + e^-$$

$$Pt\text{-}CO_{ad} + Ru\text{-}OH_{ad} \longrightarrow CO_2 + H^+ + e^-$$

On the other hand, the power density of Pt-Ru anode catalyst for direct methanol fuel cell is about a factor of 10 lower than that of the hydrogen PEMFC [3,4]. It is important to investigate other ways of improving Pt-Ru performance. The presence of P in Pt-Ru decreases the particle size, which in turn decreases the amount of noble metal required.

EXPERIMENTAL WORK

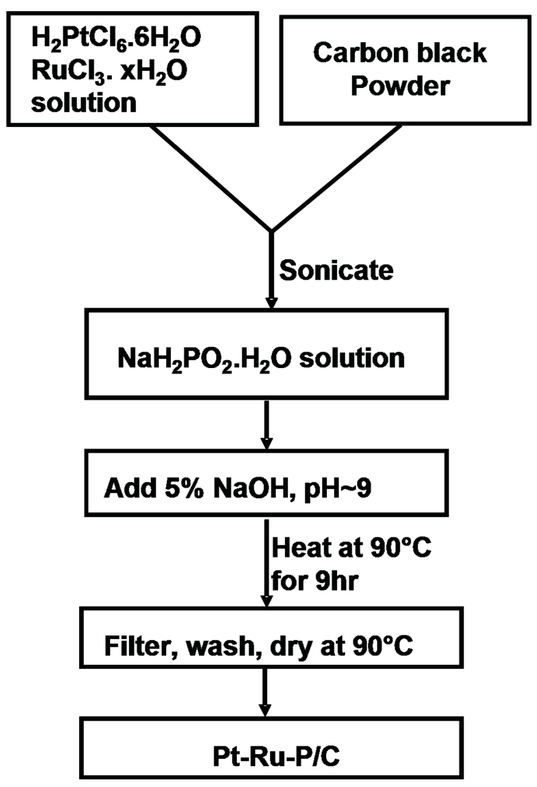


Figure 1: Schematic representation of the preparation of electro-catalyst

RESULTS

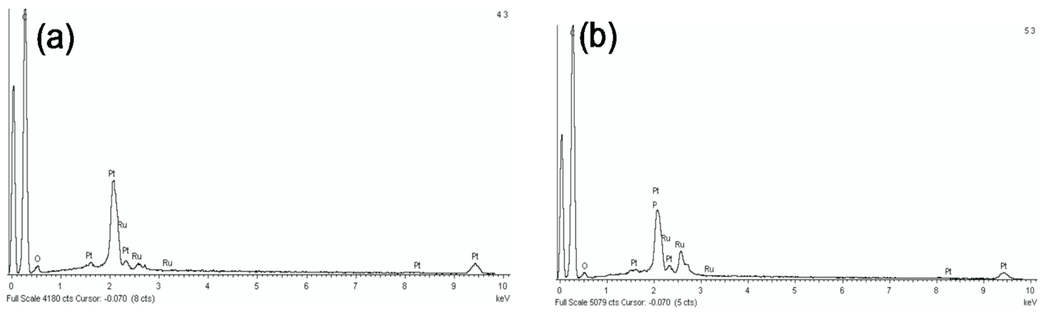


Figure 2: EDX profiles of prepared electro-catalysts. 20wt% Pt-RU (1:1)/C

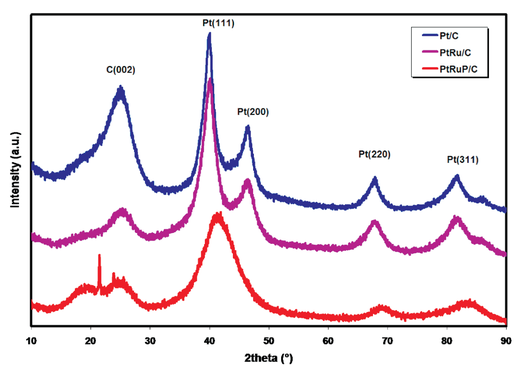
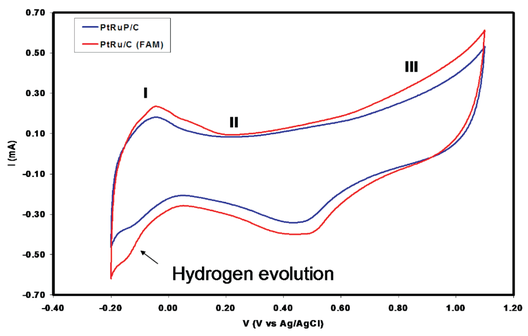


Figure 3: XRD spectra, Cu-Kα source

Table1: Crystallite size

Electro-catalyst	D (nm) (111)	D (nm) (200)	D (nm) (220)	D (nm) (311)
Pt/C	4.6	6.2	5.0	3.9
Pt-Ru/C	3.4	5.8	3.6	3.0
Pt-Ru-P/C	1.4	-	3.3	2.8



I: Hydrogen region

II: Double layer region

III: Oxygen region

Figure 4: Cyclic voltammograms of electro-catalysts in 0.5M H_2SO_4 at 50mV/s and 25°C

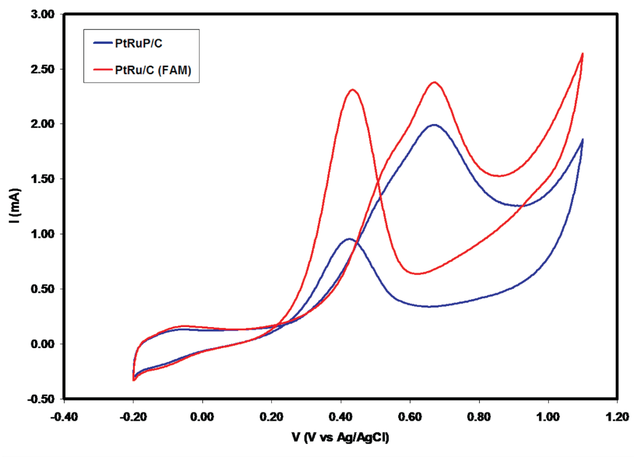


Table 2: Electrochemical data

Electro-catalyst	Onset potential (V)	Forward peak potential (V)	Forward peak current density (mA/cm^2)*	i_f/i_b ratio
Pt-Ru/C	0.300	0.676	33.38	1.04
Pt-Ru-P/C	0.248	0.673	28.03	2.10

Figure 5: Cyclic voltammograms of electro-catalysts in 0.5M H_2SO_4 +0.5M CH_3OH at 50mV/s and 25°C

CONCLUSIONS AND FUTURE WORK

- The preliminary results shows that the prepared electro-catalyst, Pt-Ru/C and Pt-Ru-P/C, are active towards methanol oxidation.
- Introduction of P decreased the re-oxidation peak. Suggesting that the effects of poisoning in methanol oxidation might be reduced.
- EDX and XRD results suggest that P was deposited in smaller amounts or co-exist with Pt.
- Future work will include optimization of P amount added in the Pt-Ru/C.
- Various P precursor salts will be used during the preparation of Pt-Ru-P/C.
- Fabrication of the Membrane Electrode Assemblies using prepared electro-catalysts and their performance in direct methanol fuel cell will be investigated.

REFERENCES

1. D.C. Papageorgopoulos, M.P. de Heer, M. Keijzer, J.A.Z. Pieterse, F.A. de Bruijn, J. Electrochem. Soc. 151 (2004) A763
2. G.T. Burstein, C.J. Barnett, A.R. Kucernak, K.R. Williams, Catal. Today 38 (1997) 425
3. M. Watanabe, M. Uchida and S. Motoo, J. Electroanal. Chem. 229 (1987) 395
4. C.G. Lee, M. Umeda, I. Uchida, J. Power Sources 160 (2006) 78
5. Xinzhong Xue, Junjie Ge, Changpeng Liu, Wei Xing, Tianhong Lu, Electrochem Comm. 8 (2006) 1280–1286

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