

# Electrooxidation of methanol on Pt-Ru catalysts supported on different carbon materials

Zhaolin Liu<sup>\*,†</sup>, Leong Ming Gan<sup>†</sup>, Jim Yang Lee<sup>‡</sup>, Ming Han<sup>†</sup>

<sup>†</sup>Institute of Materials Research & Engineering, 3 Research Link, Singapore 117602

<sup>‡</sup>Department of Chemical and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

The preparation of highly dispersed Pt-Ru electrocatalysts with high metal loadings on carbonaceous supports is one of the current goals in DMFC research. In this regard it is of interest to determine what type of carbon materials is the most suitable as a support. Carbon is not only used to conduct electrons and serves as a catalyst carrier, it also stabilises the three-phase boundary and affects the morphology of the dispersed particles. Use of various carbon blacks [1-2], graphite [3], carbon nanofibers [4-5] and carbon nanotubes [6] as catalyst support has been reported. In this communication, we compare the electrochemical performance of similarly prepared Vulcan XC-72 carbon black and multi-walled carbon nanotube supported Pt-Ru catalysts for methanol electro-oxidation.

## Preparations

Multi-walled carbon nanotubes (CNT) were synthesized by catalytic chemical vapor deposition (CCVD). The surface of the CNTs was subsequently functionalised by chemical oxidation, and treated with an activator for metal deposition. The typical preparation of a Pt-Ru/CNT (40% Pt-Ru 1:1) catalyst therefore consists of three steps: (i) functionalization of CNT in a mixture of 98% H<sub>2</sub>SO<sub>4</sub> and 70% HNO<sub>3</sub> (3:2) for 6 h at 140°C; (ii) ultrasonic treatment of the functionalized CNTs in PdCl<sub>2</sub>(1g/L) / SnCl<sub>2</sub>(2.5g/L) / HCl(100ml/L) / H<sub>2</sub>O(100ml/L) solution for 5 min at room temperature; (iii) deposition of Pt-Ru on the CNT surface via N<sub>2</sub>H<sub>4</sub> reduction of the ammonical solution of H<sub>2</sub>PtCl<sub>6</sub> H<sub>2</sub>O and RuCl<sub>3</sub> (pH=10.5) which proceeded for 5 h at 70 °C. The Pt-Ru/Vulcan XC (40% Pt-Ru 1:1) catalyst was prepared by reducing the mixed Pt and Ru solution in the presence of the carbon black. Both the Pt-Ru/CNT and the Pt-Ru/Vulcan XC catalysts were then vacuum dried at 60 °C for 5 h, followed by calcination in N<sub>2</sub> at 450 °C for 2 h.

Catalyst morphology was examined by TEM using a Philips CM 300 FEG system. TEM samples were first ultrasonicated in acetone for 1 hr before they were deposited on 3 mm Cu grids covered with a continuous carbon film. XPS measurements were carried out on a VG ESCALAB MKII spectrometer using a Mg K $\alpha$  X-ray source at a constant analyser. The powder samples were affixed to standard holders by adhesive copper tapes. Narrow scan photoelectron spectra were recorded in the C<sub>1s</sub>, O<sub>1s</sub>, Ru<sub>3p</sub> and Pt<sub>4f</sub> regions. An EG&G 273 potentiostat and a conventional three-electrode cell were used for electrochemical characterizations by cyclic voltammetry. A vitreous carbon disk electrode coated with Nafion suspensions of the catalyst powders was used as the working electrode. A Pt gauze and a saturated calomel electrode (SCE) served as the counter and the reference electrodes respectively. The electrolyte was a 2 M CH<sub>3</sub>OH solution in 1 M H<sub>2</sub>SO<sub>4</sub>.

## Results

From the TEM images in Fig 1, the Pt-Ru dispersion on Vulcan XC was homogeneous with a narrow particle size distribution centring on 4nm. For the CNT supported catalyst, however, some isolated domains and Pt-Ru particle aggregates about 5 nm in size were detected. Among the various factors possibly affecting the catalytic activities of Pt-Ru alloy catalysts in methanol oxidation, the Pt-Ru particle size has long been recognized as the most important. Ultrafine catalyst metal particles are more active than larger particles because of a higher concentration of low-coordination surface metal atoms. Takasu et al. [7] have reported maximum mass activity for a Pt<sub>50</sub>-Ru<sub>50</sub> catalyst with 3nm particles. XPS spectra in the Pt<sub>4f</sub> and Ru<sub>3p</sub> regions for both catalysts showed that the Pt<sub>4f</sub> signal was a composite of three Pt doublets. The most intense doublet (at BE= 71.02 and 74.3 eV) was due to metallic Pt. The second doublet at 72.4 and 75.2 eV could be assigned to the Pt(II) chemical state in PtO and Pt(OH)<sub>2</sub>. The third Pt doublet, which was weakest in intensity, and occurred at the highest BEs (74.5 and 77.8 eV), was the result of a small amount of Pt(IV) species

on the surface. The Ru<sub>3p<sub>3/2</sub></sub> spectrum could be deconvoluted into two peaks with different intensities at BE of 461.1 and 462.7 eV, corresponding well with Ru(0) and RuO<sub>2</sub> respectively. The cyclic voltammograms of methanol oxidation on these catalysts are shown in Fig 2. It is obvious that the electrochemical activity of Pt-Ru/Vulcan XC was higher than that of Pt-Ru/CNT.

## References

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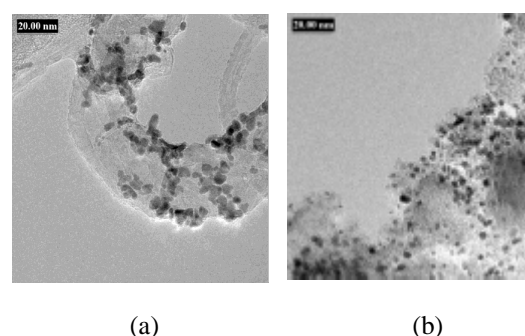


Fig.1 Transmission electron micrographs of Pt-Ru catalysts supported on different carbon materials. (a) Pt-Ru/CNT, (b) Pt-Ru/Vulcan XC.

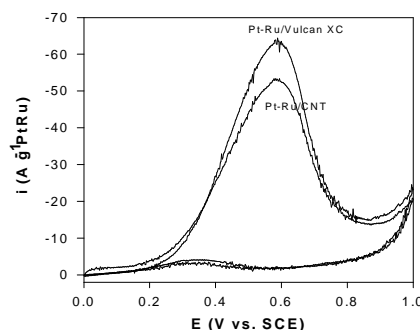


Fig.2 Cyclic voltammograms of Pt-Ru catalysts supported on different carbon materials in an electrolyte of 2M CH<sub>3</sub>OH+ 1M H<sub>2</sub>SO<sub>4</sub>, scan rate = 15 mV/s.