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# High Performance PtRuIr Catalysts Supported on Carbon Nanotubes for the Anodic Oxidation of Methanol

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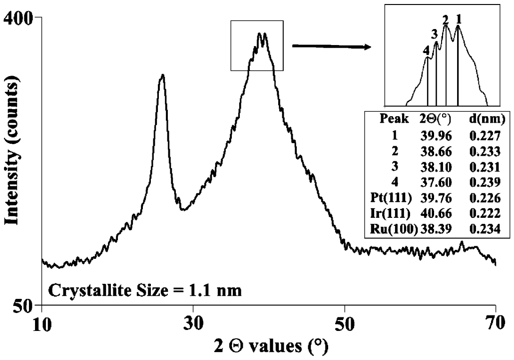
PtRu/C catalysts are viewed as very effective anode catalysts for direct methanol fuel cells (DMFC), and their preparation, characterization, and the mechanism of alcohol oxidation have been extensively investigated.[1−6] Also, several other binary and ternary catalysts, such as PtW, PtSn, PtRuMo, etc., have been reported to show good activity.[3,6] The most common methods used to prepare these types of catalysts include impregnation−reduction and colloidal approaches, both generally carried out in aqueous media and using relatively strong reducing agents, such as formaldehyde.[1,3]

The high cost, together with the still comparatively poor performance, of PtRu catalysts remains one of the impediments to DMFC commercialization. Therefore, the development of catalysts with smaller particle sizes (and hence higher active area) will decrease the amount of noble metal required and lower the fuel cell cost. Also, the discovery of new catalysts with high alcohol oxidation activity and good CO tolerance has been a key research objective for some time in the DMFC area.

There have been a few reports[7−9] in which PtRu/C catalysts have been prepared in organic media, including the work of Bock et al, who prepared PtRu/C catalysts using ethylene glycol as both the solvent and reducing agent. The fact that their catalyst has a very small particle size and showed very good activity toward the anodic oxidation of methanol suggested that the organic colloid method has important advantages. However, the high boiling point and viscosity of ethylene glycol cause some difficulties in the experimental steps, such as during filtering and rinsing of the mixtures. On the other hand, low boiling point organics evaporate very quickly, and no reports have been found in which PtRu/C catalysts were prepared in these types of solvents.

In the present work, we have used acetone as the solvent, ethylene glycol as the reducing agent, citrate as a complexing agent and stabilizer, multiwall carbon nanotubes (CNT, diameter 8−10 nm, Tsinghua University) as the support, and Ir as the promoter, to form highly active PtRuIr/CNT catalysts. The particle size has been found to be ∼1 nm, and the catalyst has shown excellent activity toward methanol oxidation.

The typical procedure used for the synthesis of our catalysts involved the following steps. Specific ratios of hexachloroplatinic acid, dihydrogen hexachloroiridate, ruthenium(III) chloride hydrate, and sodium citrate were dissolved in a mixture of acetone and ethylene glycol and then stirred for 30 min to entirely dissolve the citrate. Carbon powder (XC-72R) or carbon nanotubes were then added to the mixture, followed by pH adjustment to >10 by the dropwise addition of a KOH/ethylene glycol solution with vigorous stirring. The solution was then transferred into an autoclave with a Teflon liner and left to react at 160 °C for 8 h, followed by filtering, washing, and then drying in air at 90 °C.



| Peak | 2Θ(°) | d(nm) |
|---|---|---|
| 1 | 39.96 | 0.227 |
| 2 | 38.66 | 0.233 |
| 3 | 38.10 | 0.231 |
| 4 | 37.60 | 0.239 |
| Pt(111) | 39.76 | 0.226 |
| Ir(111) | 40.66 | 0.222 |
| Ru(100) | 38.39 | 0.234 |

***Figure 1.*** XRD pattern of PtRuIr/CNT catalyst. The average crystallite size is 1.1 nm, as determined from the software.

Figure 1 shows the XRD pattern of the PtRuIr/C catalyst, showing a significantly broadened Pt(111) peak, consistent with an average particle size of ∼1.1 nm, significantly smaller than seen for conventional commercial catalysts, which are on the order of ca. 2−4 nm in size. Also, the Pt(200) and Pt(222) peaks are not seen by XRD, and the Pt(111) peak is split into four peaks, which are shifted toward lower angles (higher *d* spacing). These results, taken together, show that the active components are highly dispersed on the surface of the CNT. Although Ru and Ir are clearly present in these catalysts, as seen from XPS analysis, we do not see their diffraction peaks, perhaps indicative of dispersion at the atomic level. Indeed, the XPS results revealed shifts in the $Pt_{4f}$, $Ru_{3p}$, and $Ir_{4f}$ binding energies of 0.45, 1.65, and 0.65 eV, respectively. This shows that there are strong interactions between the three components within the catalyst.

For comparison, we prepared a Pt/CNT catalyst using the same approach, giving an average particle size of ∼2 nm. In this case, the Pt(111) peak was not split or shifted, indicating that these characteristics in Figure 1 result from the presence of Ru and Ir in the catalyst.

Figure 2 shows the cyclic voltammograms seen during methanol oxidation at the PtRuIr/CNT, PtRu/CNT, PtRuIr/XC-72R, and a commercial PtRu/XC-72R catalyst supplied by Johnson Matthey Catalyst and Chemical Division, all in a room temperature 0.5 M MeOH + 0.5 M $H_2SO_4$ solution. The peak current densities at 50 mV/s are 81.7, 61.2, 33.4, and 17.4 mA/cm$^2$, respectively, showing that the activity of the PtRuIr/CNT catalyst is a factor of ∼4 higher than that of the commercial catalyst and ∼2 times higher than that of our PtRuIr/XC-72R catalyst. Almost no activity variation was observed, even after 16 h of uninterrupted cycling of the potential between 0 and 0.8 V, indicating the facile removal of adsorbed CO intermediates.

The real surface area and roughness factor of the PtRuIr/CNT catalysts are ∼880 m$^2$/g Pt and ∼560, respectively, based on the magnitude of the hydrogen underpotential deposition/removal

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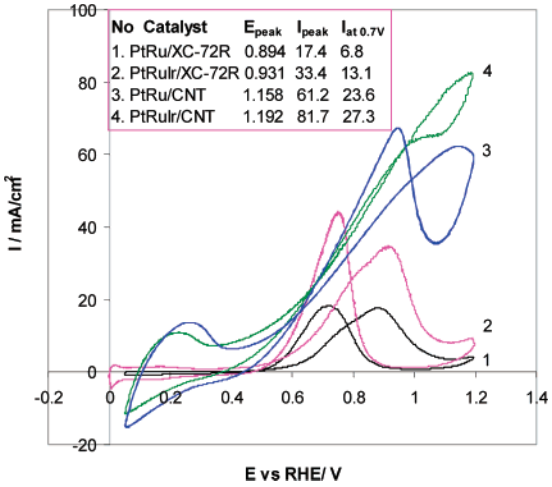

***Figure 2.*** Cyclic voltammogram (50 mV/s) of methanol oxidation at PtRuIr/CNT (4), PtRu/CNT (3), PtRuIr/XC-72R (2), and Johnson Matthey PtRu/XC-72R (1) in 0.5 mol/L $CH_3OH$ + 0.5 mol/L $H_2SO_4$ solution at room temperature. A glassy carbon RDE (6.8 mm diameter) was used. The catalyst loadings are 11.6, 11.5, 11.9, and 10.5 $\mu$g Pt, for catalysts 1−4, respectively.

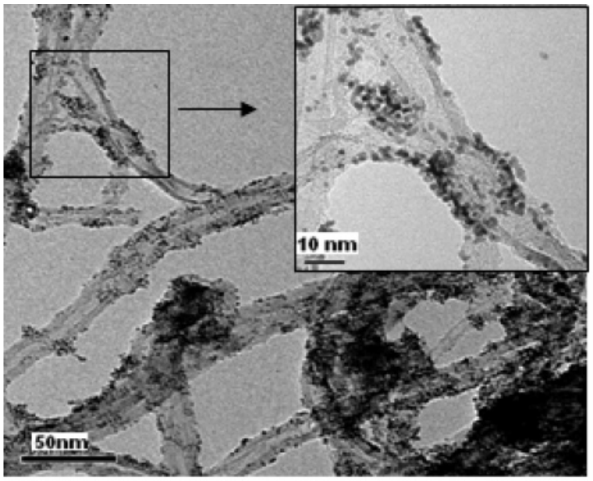

***Figure 3.*** TEM images of PtRuIr/CNT catalyst (higher magnification image shown in inset).

peaks.[10] These data indicate that the PtRuIr particles are highly dispersed on the CNT surface.

Figure 3 shows some TEM images of the PtRuIr/CNT catalyst. It can be seen that the metal nanoparticles are uniformly coated on the CNT surface and have sizes which range from 1 to 1.5 nm. This excellent dispersion of the metal nanoparticles is one of the reasons for the very high activity of these catalysts toward methanol oxidation.

To investigate the effect of Ir on the activity of the catalyst, we also synthesized a PtRu/CNT catalyst for comparison. It was found that the addition of Ir significantly improved the dispersion of the metallic components, thus enhancing the activity of the catalyst, as shown in Figure 2 and Table 1.

***Table 1.*** Properties of PtRuIr/CNT, PtRu/CNT, and PtRu/XC-72R Catalysts

| catalyst | real surface area ($m^2$/g Pt) | roughness factor | activity ($A/cm^2$/mg Pt)[a] |
|---|---|---|---|
| PtRuIr/CNT | 889 | 568 | 2.54 |
| PtRu/CNT | 395 | 261 | 1.89 |
| PtRu/XC-72R[b] | 146 | 42 | 0.65 |

[a] Per geometric area. [b] Johnson Matthey catalyst.

The effect of Ir and Ir oxide on the performance of Pt-based anodes for the oxidation of alcohol and as a cathode catalyst for the reduction of oxygen has been investigated previously. Yim et al. reported[11] recently that Ir and $IrO_X$ show a negative effect on the rate of oxygen reduction, while Zhang et al. reported[12] the reverse. Birss et al.,[13] Chen,[14] and Reetz[15] all reported a positive effect of Ir on methanol, carbon monoxide, and hydrogen oxidation. Similar to the role of Ru, it is likely that OH groups can be stabilized at the metallic Ir surface, thus assisting in the oxidation of CO or other adsorbed intermediates.

In conclusion, CNT-supported ternary PtRuIr catalysts, having very small particle sizes and excellent activity for the oxidation of methanol, have been successfully prepared using an organic colloid method. It has been found that the addition of Ir improves the performance of the catalyst significantly. The splitting and shifting of the Pt(111) XRD peak, together with the TEM results, shows that the metallic components are highly dispersed on the CNT support. The very high activities observed also attest to the very high surface area of the CNTs and their excellent potential as support materials for electrocatalytic applications.

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**Supporting Information Available:** Experimental details and preparation procedures are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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