

Methanol Electro-Oxidation on Pt-Ru-P/C and Pt-Ru-P/MWCNT in Acidic Medium

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Abstract

Pt-Ru-P was prepared by the chemical reduction method using sodium hypophosphite as a reducing agent on Vulcan XC 72 and multi-walled carbon nano-tubes (MWCNTs). Sodium citrate was added as the stabilizer during electro-catalyst preparation. The electro-catalytic activity towards methanol oxidation in acidic medium was studied by cyclic voltammetry and linear sweep voltammetry. Pt-Ru-P/MWCNT showed excellent activity than Pt-Ru-P/C. This may be attributed to the effectiveness of the MWCNTs acting as good catalyst support material. The particle size of both electro-catalysts obtained with the transmission scanning electron microscopy (TEM) ranged between 2-4nm desirable for the direct methanol fuel cells.

Keywords: Hypophosphite, Citrate, PtRuP nanoparticle, MWCNT, Methanol electro-oxidation

Introduction

Direct methanol fuel cells (DMFCs) are regarded as potential power sources for portable applications. In polymer electrolyte membrane fuel cell (PEMFC), platinum is recognized to be the most active metal for methanol oxidation. However, there is a strong CO adsorption tendency, which blocks the surface for further methanol adsorption and leads to very low power densities [1, 2]. It is well known that supported Pt-Ru alloys are the most promising binary catalysts for methanol oxidation due to the improved CO tolerance but its power density in DMFC is about a factor of 10 lower than that of the hydrogen PEMFC [1- 4]. Hence it is important to investigate ways of improving Pt-Ru performance. Methanol electro-oxidation activity on the PtRu/C catalyst can be enhanced by producing particles in a nanoscale range (2–4 nm) with good dispersion on the carbon support [5]. It has been reported that the addition of non-metallic elements such as nitrogen (N), phosphorus (P) and sulphur (S) reduced the Pt-Ru/C size, with improved catalyst activity and efficiency [6, 7]. Daimon et al [6] reported a power density of 59mW/cm² in passive DMFC using Pt₄₅Ru₄₄P₁₁/C. Xing et al [8] obtained a power density of 61.5mW/cm² at 30°C using Pt_{1.01}Ru_{0.98}P_{0.79}, pure oxygen and 2M methanol at 5ml/min. For low temperature fuel cell application, carbon nanocomposites decorated with precious metals or alloys as electrocatalysts were proposed to replace conventional activated carbon black due to their higher specific surface areas that are essential to disperse catalyst particles and reduce the catalyst loading [9, 10, 11]. MWCNT have excellent mechanical characteristics, nanometer size and high surface area.

1. Scientific Approach

The effect of using multi-walled carbon nanotubes (MWCNTs) as a support for Pt-Ru-P was investigated using cyclic voltammetry and linear scanning voltammetry. Pt-Ru-P/MWCNT activity for methanol electro-oxidation in acidic solution was compared to that of Pt-Ru-P/C. The electro-catalysts were prepared following the chemical reduction method using sodium hypophosphite as a reducing agent and sodium citrate as a stabilizer. The particle size of the two electro-catalysts was determined using TEM.

2. Experiments

2.1 Preparation of electro-catalysts

Firstly the multi-walled carbon nano-tubes (MWCNTs Sigma Aldrich, O.D. × I.D. × L 7-15 nm × 3-6 nm × 0.5-200 μm) were refluxed in a mixture of 8M HNO₃ and 2M H₂SO₄ at 80°C for 6 hours to remove impurities and introduce functional groups on the surface using the Lordi method [12]. The pretreated MWCNTs were washed with copious distilled water, air dried and heated at 80°C for overnight. 0.3g of Vulcan XC-72 (Cabot Corporation) was sonicated in distilled water for 10 minutes. Aqueous solutions of H₂PtCl₆.6H₂O (Sigma-Aldrich) and RuCl₃.xH₂O (Sigma-Aldrich) (Pt:Ru molar ratios of 1:1) were added to Vulcan XC-72 with stirring and then stirred on a magnetic stirrer for 30min. Sodium hypophosphite (NaH₂PO₂.H₂O, Sigma Aldrich), as the reducing agent and sodium citrate (KIMIX), as a stabilizer were added to the catalyst slurry. The amount of NaH₂PO₂.H₂O added was varied in order to optimize the P on Pt-Ru. The molar ratio of Pt: P was varied (1:20, 1:40, 1:60 and 1:80). 5% NaOH was added to adjust pH to 9. The catalytic solution was refluxed at 90°C for 10hrs while stirring. The catalysts were filtered, washed with copious distilled water and then dried at 80°C for overnight. The catalysts prepared were denoted as Pt-Ru-P (1:20), Pt-Ru-P (1:40), Pt-Ru-P (1:60) and Pt-Ru-P (1:80). The above procedure was

followed using the acid treated MWCNT instead of Vulcan XC-72. The catalyst is denoted as Pt-Ru-P/MWCNT.

2.2 Characterization of electro-catalysts

Transmission electron microscopy (TEM) JEOL JEM 2100F was used to observe the morphological structure and to determine the particle size. Particle composition was estimated using Energy dispersive X-Ray spectroscopy (EDX) with the accelerating voltage of 15keV. The catalyst particles were dispersed in methanol by ultrasonication for a few seconds and a drop of the suspension was placed on a Cu-grid covered with carbon film. The solvent was evaporated before measurements were taken. XRD diffractograms were acquired using a Cu-K α radiation (wavelength 0.15405nm) and XPERT-PRO diffractometer system.

Methanol oxidation activity was determined at room temperature using cyclic voltammetry, linear chronoamperometry and impedance spectroscopy in a three electrode cell using AutoLab PGSTAT302 potentiostat/galvanostat/FRA. A Pt rod and Ag/AgCl (3M KCl) were used as counter and reference electrodes respectively. Nitrogen gas (99.99%) was purged through the cell for 60 minutes before the experiments. 0.025g of the electro-catalyst powder, 2.5ml deionised water and 0.5ml 5wt% Nafion solution (Sigma Aldrich) were ultrasonicated for 20 minutes to prepare a catalytic ink. 1 μ l of the ink was pipetted onto a polished glassy carbon disk electrode with area of 0.0314 cm², air dried for 30 minutes and then at 95°C for 15 minutes. The Pt metal loading in Pt-Ru-P/C and Pt-Ru-P/MWCNT was 0.080mg/cm².

3. Results

A highly concentrated nitric acid and sulphuric acid were used to generate carbonyl and hydroxyl groups on the surface of MWCNTs. These functional groups will help in the formation of better electro-catalysts as reported by Han et al [13] favourable for use in DMFCs. Acid treatment time of 6 hrs was used in order to avoid over-treatment which might result in low conductivity and chemical stability of the carbon nano-tubes [14].

60wt% Pt-Ru-P was successfully deposited on carbon black and MWCNTs using sodium hypophosphite and sodium citrate.

The onset potential for methanol electro-oxidation as shown in Table 1 was used in determining the optimum amount of P to be added on Pt-Ru catalyst. Pt-Ru-P/C (1:40) showed a better onset potential for methanol electro-oxidation, hence the Pt: P molar ratio of 1:40 was selected as the best molar ratio.

Table1: Onset potential for methanol electro-oxidation

Electro-catalyst	Onset Potential (V vs Ag/AgCl)
Pt-Ru-P/C 1:20	0.108
Pt-Ru-P/C 1:40	0.105
Pt-Ru-P/C 1:60	0.120
Pt-Ru-P/C 1:80	0.166

The molar ratio of Pt:P (1:40) was used in the preparation and characterization of Pt-Ru-P/C and Pt-Ru-P/MWCNT.

Figure 1 shows the cyclic voltammograms of Pt/C (E-TEK Inc.), Pt-Ru-P/C and Pt-Ru-P/MWCNT in 0.5M H₂SO₄. Platinum electrode exhibited a typical behaviour of a polycrystalline Pt as observed in figure 1 below. Peaks for the hydrogen redox reaction, in the lower potential region (-0.2V to 0.15V), and the redox reactions of oxygen-like species on Pt surface (Pt-O and Pt-OH) at high potentials and the double layer region (0.18 to 0.55V) can be clearly seen [15]. The anodic current in the double layer region increases, suggesting that the adsorption of oxygen-like species on Pt-Ru-P/C and Pt-Ru-P/MWCNT immediately follow desorption of hydrogen. The presence of oxygen-like species on the electrode surface could help oxidizing the adsorbed intermediates during methanol oxidation [16, 17].

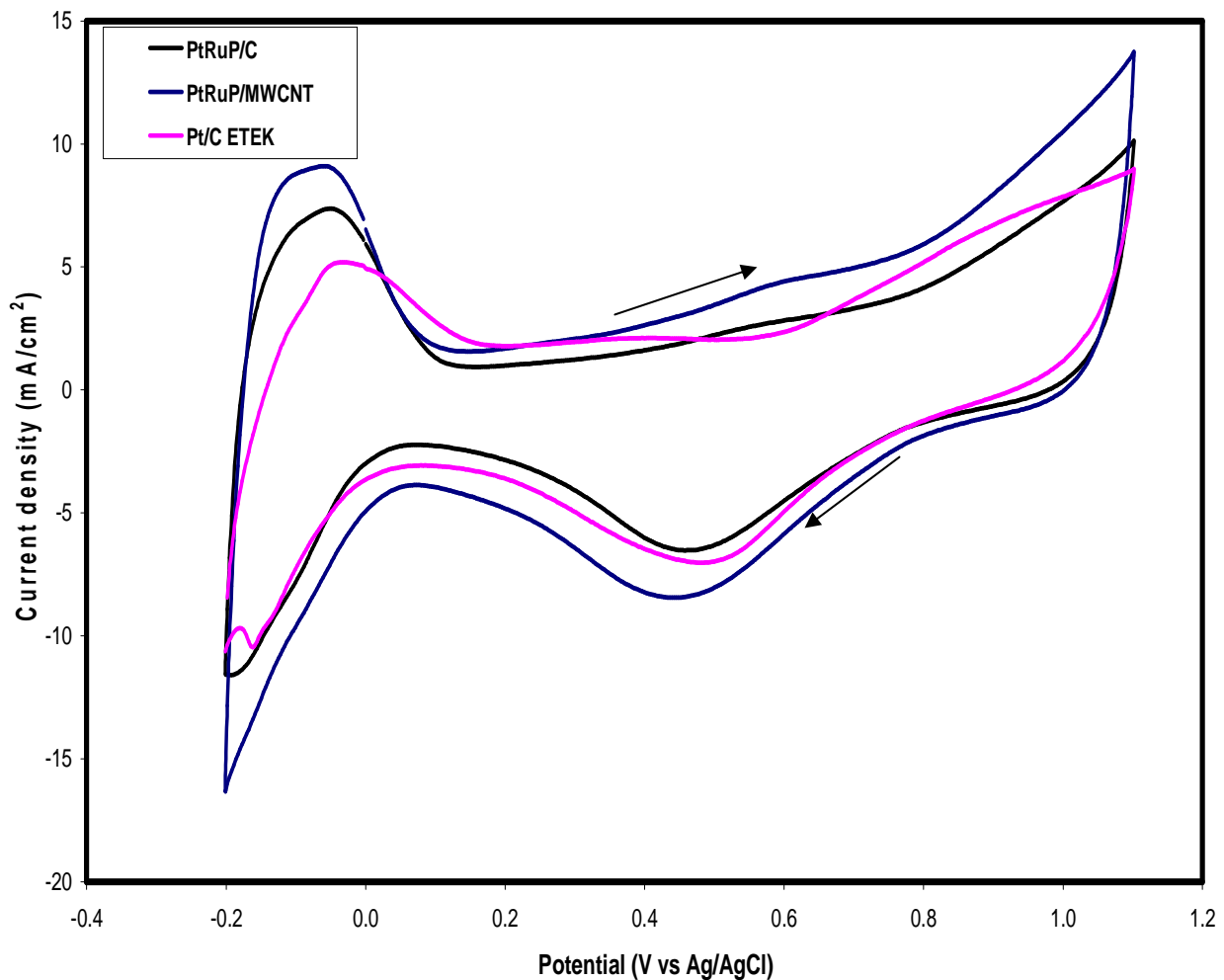


Figure 1: Cyclic voltammograms of Pt-Ru-P/C, Pt-Ru-P/MWCNT and Pt/C (E-TEK) in 0.5M H₂SO₄ at room temperature. Scan rate 50mV/s

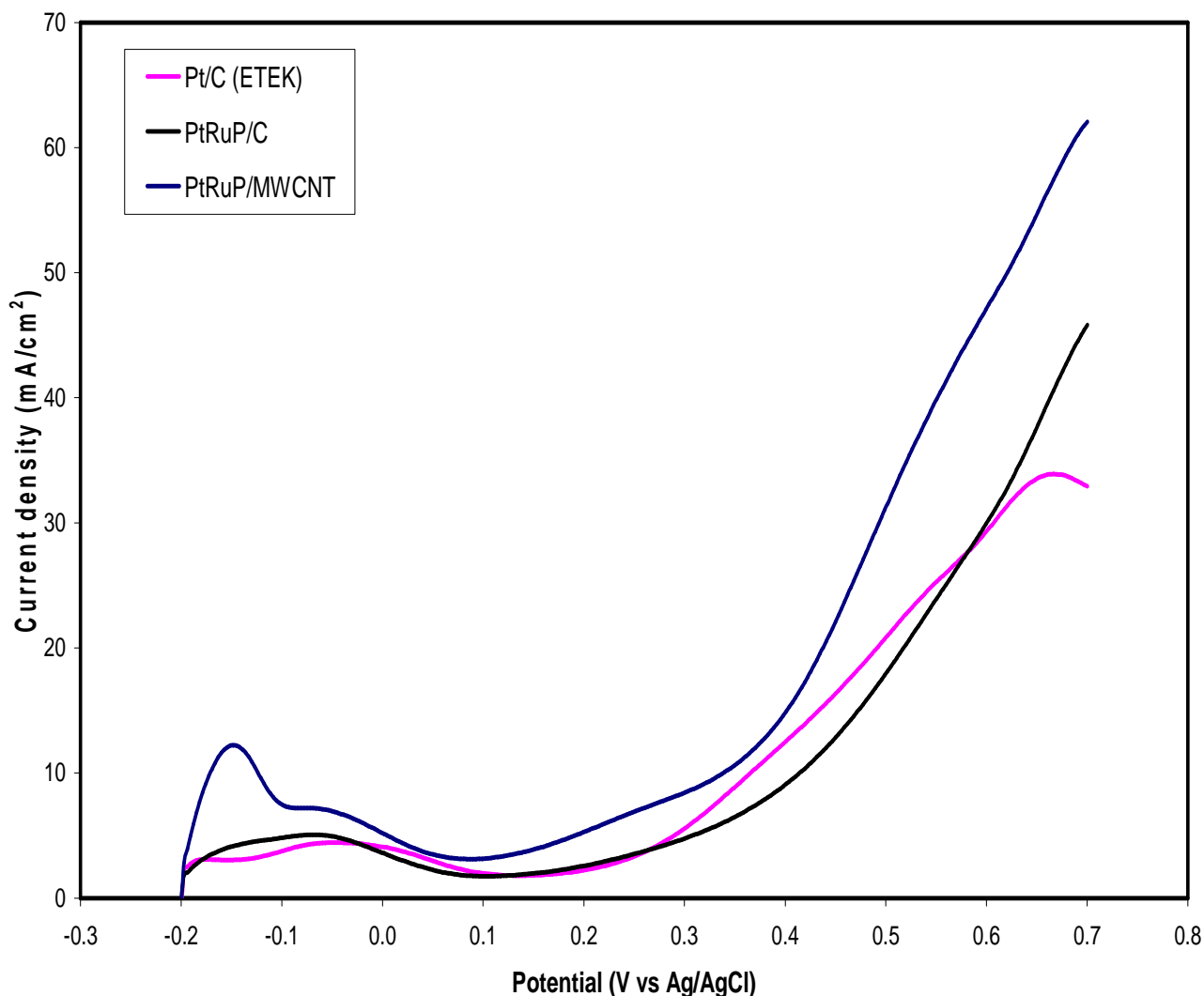


Figure 2: Linear scanning voltammograms of Pt-Ru-P/C, Pt-Ru-P/MWCNT and Pt/C (E-TEK) in 0.5M H₂SO₄ + 0.5M CH₃OH at room temperature. Scan rate 50mV/s

The electro-catalytic activity of Pt-Ru-P on MWCNTs was significantly improved and higher than that of Vulcan XC 72. This demonstrates that MWCNTs can act as efficient support material for effective dispersion of electro-catalysts. Linear scanning voltammograms for methanol electro-oxidation on Pt/C (E-TEK Inc.), Pt-Ru-P/C and Pt-Ru-P/MWCNT are illustrated in Figure 2. Hydrogen desorption peaks were observed between -0.2 and 0.1V for Pt/C (E-TEK Inc.) and Pt-Ru-P/C, while for Pt-Ru-P/MWCNT were between -0.2 and 0.07V due to the adsorption of methanol on the surface. Methanol electro-oxidation starts at approximately 0.16V, 0.11V and 0.105V for Pt/C (E-TEK Inc.), Pt-Ru-P/C and Pt-Ru-P/MWCNT respectively and the current increases due to this reaction. Pt-Ru-P/MWCNT showed a higher current density than Pt-Ru-P/C. The lower onset potential of methanol electro-oxidation (0.105V) indicates better electro-catalytic activity of Pt-Ru-P/MWCNT than other electro-catalysts.

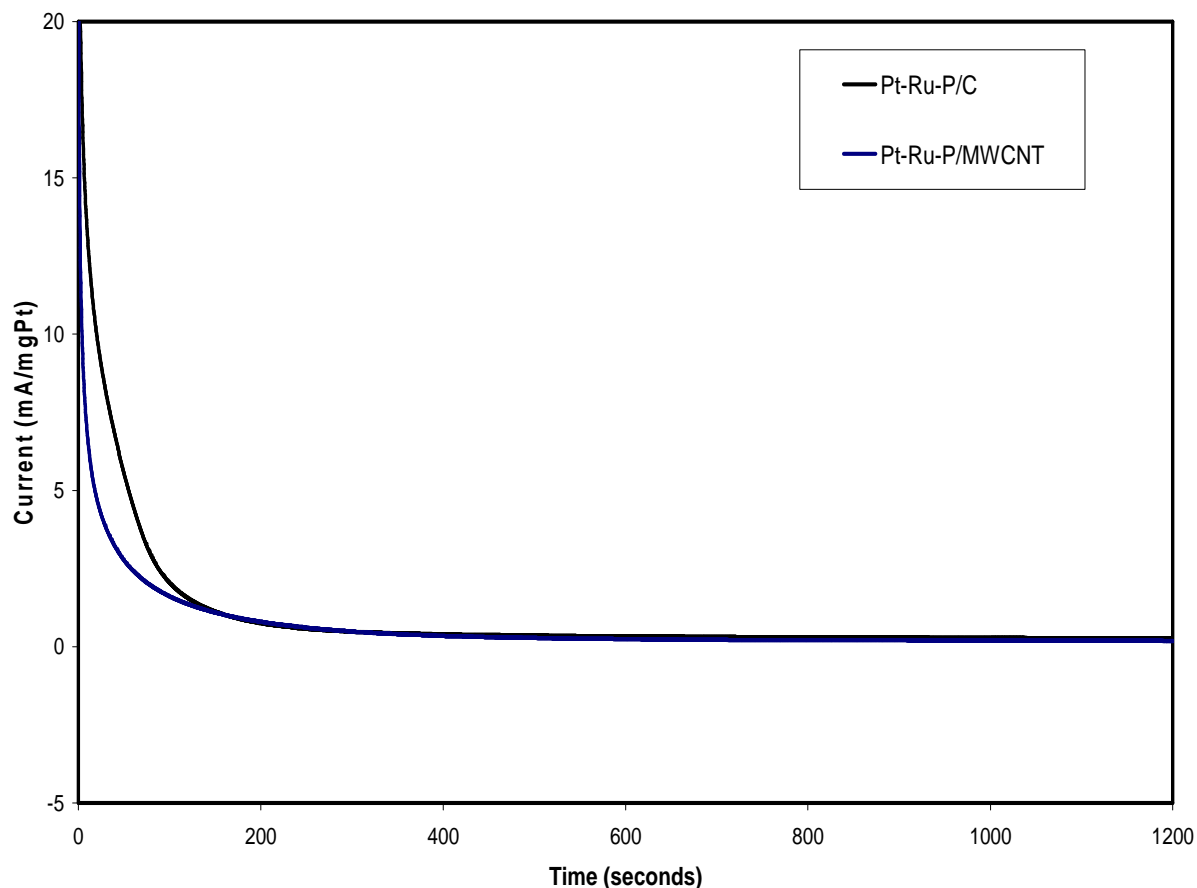


Figure 3: Chronoamperometric curves at (a) 0.75V (vs. Ag/AgCl) of Pt-Ru-P/C and Pt-Ru-P/MWCNT in 0.5M H_2SO_4 + 0.5M CH_3OH at room temperature. Scan rate 50mV/s

Figure 3 illustrates the stability of methanol on Pt-Ru-P/C, and Pt-Ru-P/MWCNT. The initial high currents were due to the double layer charging. The current decay with time followed a parabolic behaviour and then reached a steady state within 450 seconds for Pt-Ru-P/C and Pt-Ru-P/MWCNT. Methanol oxidation currents were almost equal for both electro-catalysts indicating that both electro-catalysts show the same stability and poisoning-tolerance [18].

Impedance patterns for Pt-Ru-P/C and Pt-Ru-P/MWCNT in methanol are illustrated in Figure 4. The diameter of the arc obtained from impedance studies for Pt-Ru-P/C and Pt-Ru-P/MWCNT was the same, indicating that the charge transfer resistance for the methanol electro-oxidation was equal.

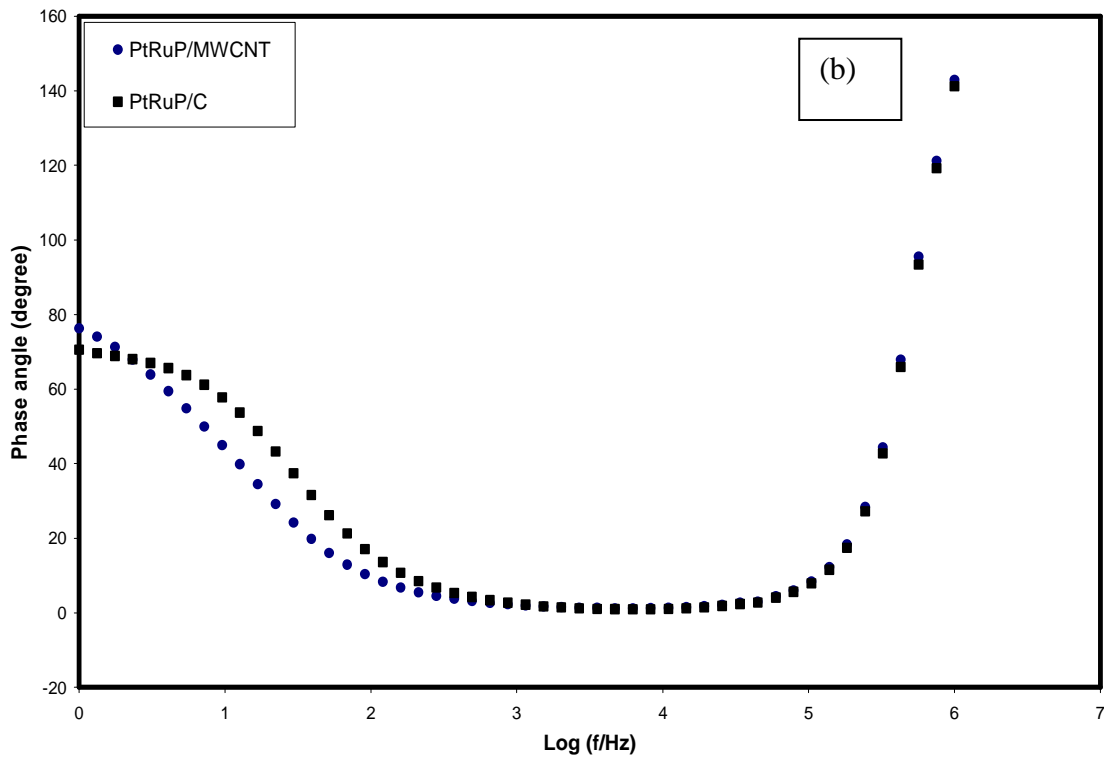
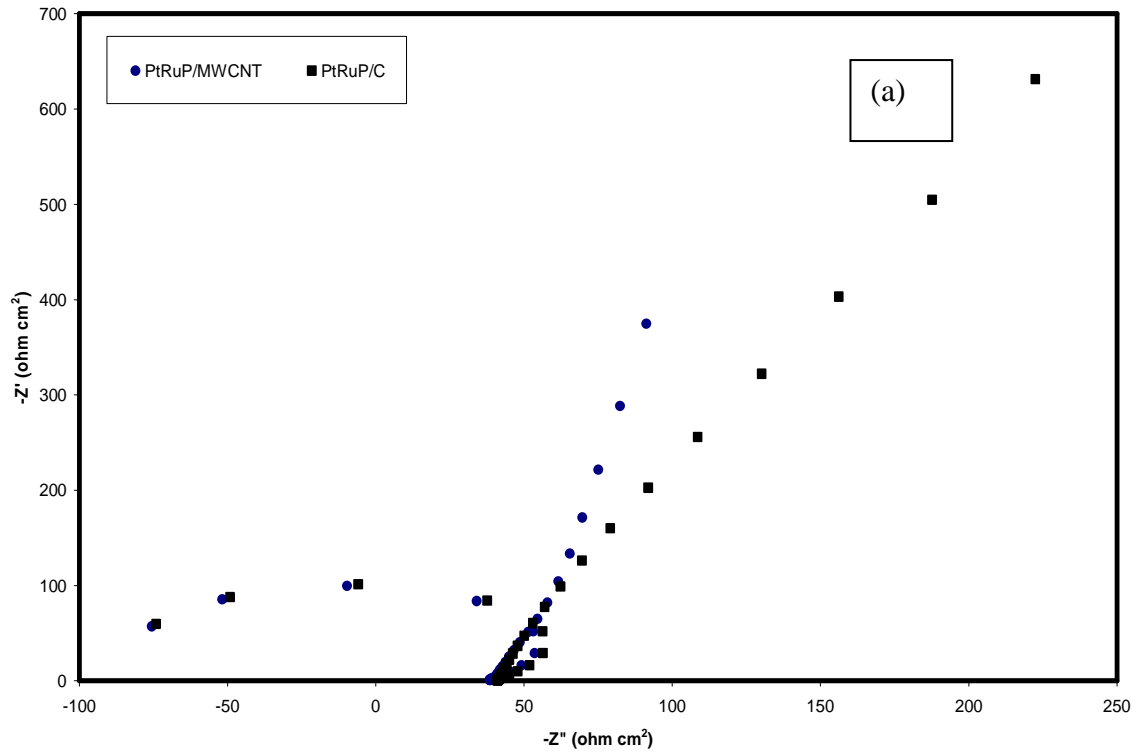


Figure 4: Impedance patterns at 0.2V of Pt-Ru-P/C and Pt-Ru-P/MWCNT in 0.5M H₂SO₄ + 0.5M CH₃OH at room temperature. (a) Nyquist plots (b) phase shift plots

The micrographs of the acid treated MWCNT and Pt-Ru-P/MWCNT electro-catalysts have been investigated by SEM as shown in Figure 5.

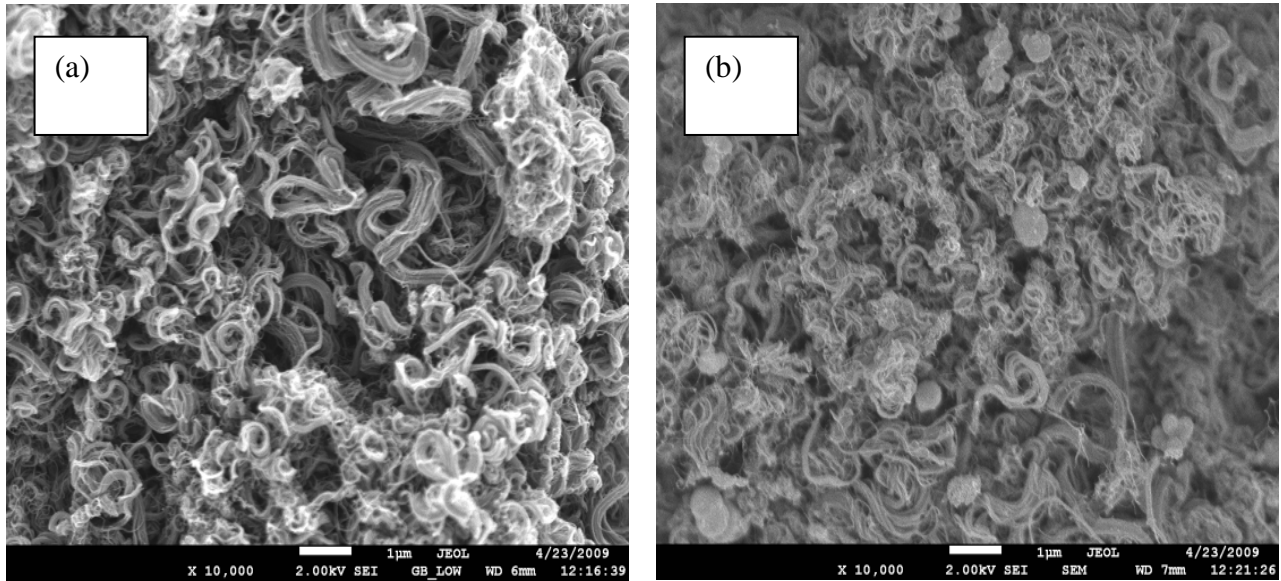


Figure 5: SEM profiles of (a) acid treated MWCNT and (b) Pt-Ru-P/MWCNT

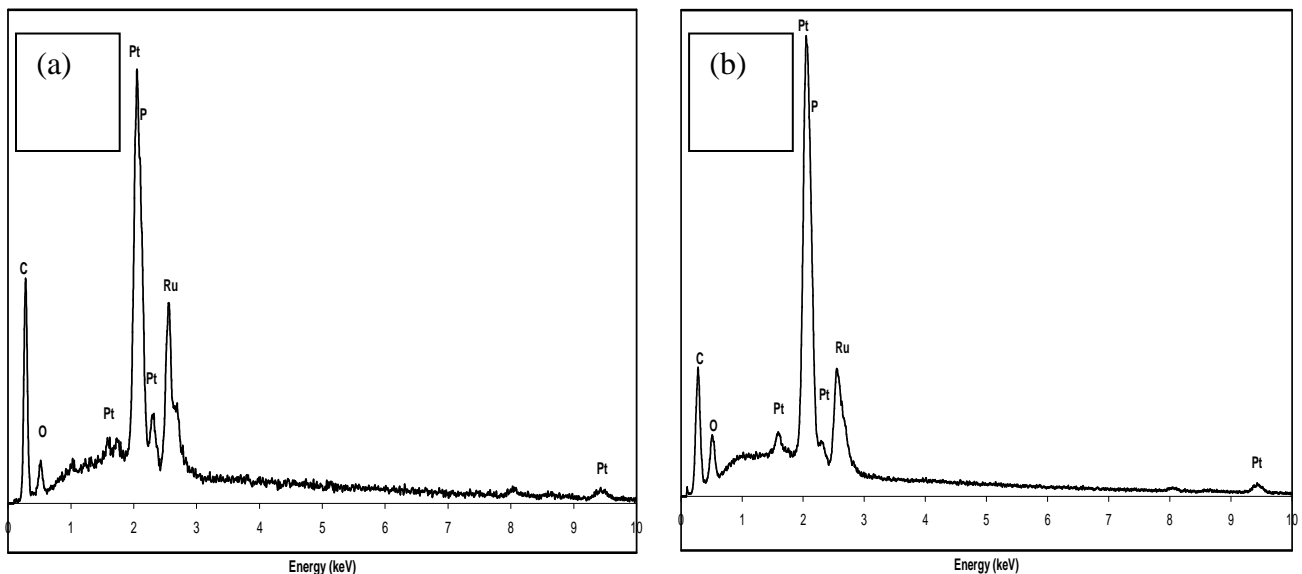


Figure 6: EDX spectra of (a) Pt-Ru-P/C and (b) Pt-Ru-P/MWCNT electro-catalysts

The presence of Pt, Ru and P on the surface of Vulcan XC 72 and MWCNT were confirmed by EDX as shown in Figure 6. The phosphorous peak overlaps with that of Pt. Since Pt has a higher energy than P it was difficult to quantify the relative amount of P to Pt. TEM images of Pt-Ru-P/C and Pt-Ru-P/MWCNT at various magnifications are presented in Figure 7.

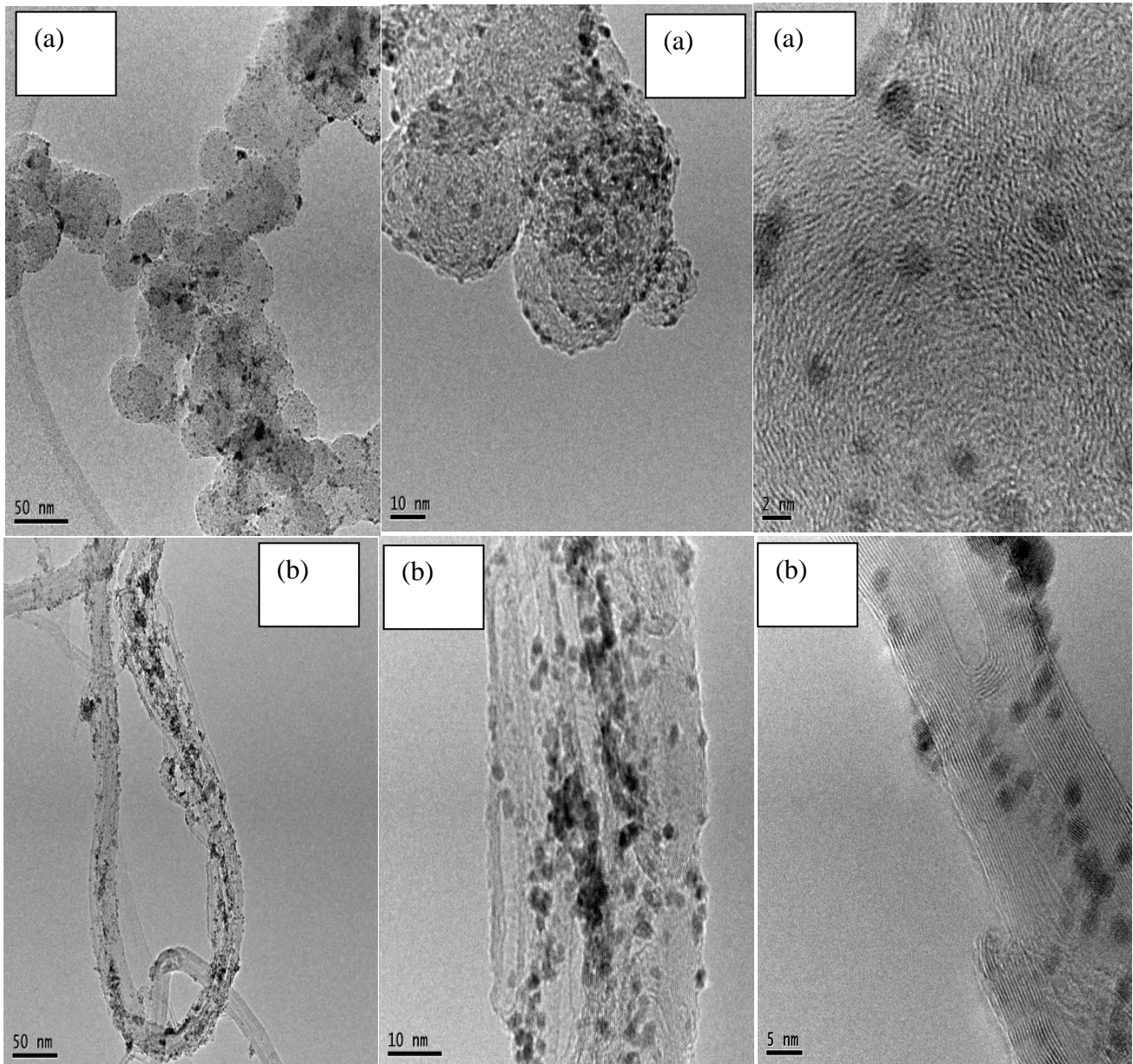


Figure 7: TEM images of (a) Pt-Ru-P/C and (b) Pt-Ru-P/MWCNT at low and high magnifications

The micrographs suggest that Pt-Ru-P was well dispersed on Vulcan XC 72 and on the external walls of MWCNTs. The larger (~40nm) and grey particles are Vulcan XC-72 carbon support. The smaller and black particles are the catalyst particles (Pt-Ru-P). The average particle size obtained on Vulcan and MWCNTs was 2-4nm. The lattice structure can be observed at 2nm scale. The average particle size of the prepared electro-catalysts was within the acceptable range for direct methanol fuel cells [19].

The XRD diffractograms of the prepared electro-catalysts are presented in Figure 8. The first peak at 2θ about 25° was assigned to carbon. The diffraction peaks for Pt (200), (220) and (311) [20] disappears after modifying Pt-Ru/C with P. Diffraction peaks for Pt-Ru-P/MWCNT are shifted to the high 2θ value and were well pronounced compared to that of Pt-Ru-P/C. The Pt-Ru-P/C electro-catalyst showed a highly amorphous structure than Pt-Ru-P/MWCNT. However, the amorphous structure for Pt-Ru-P/MWCNT was expected due to the presence of P [21]. Xue et al [8] also observed an amorphous structure of Pt-

Ru-P/C and found that the amorphous Pt-Ru-P/C was more active towards methanol electro-oxidation than the crystalline Pt-Ru/C. In this study the crystalline Pt-Ru-P/MWCNT showed higher activity than the amorphous Pt-Ru-P/C.

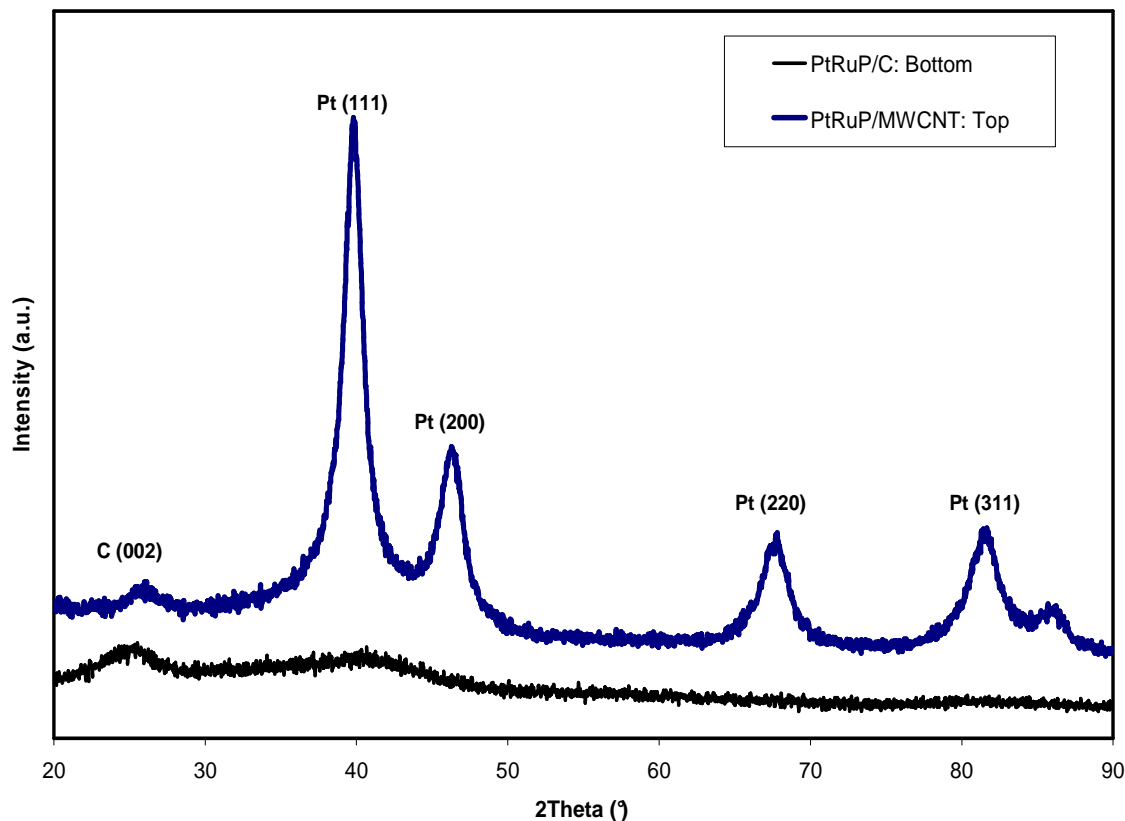


Figure 8: XRD patterns of Pt-Ru-P/C and Pt-Ru-P/MWCNT electro-catalysts

Conclusions

Pt-Ru-P/C and Pt-Ru-P/MWCNT were successfully prepared using sodium hypophosphite as reducing agent and sodium citrate as stabilizer. The average particle size of the prepared electro-catalysts obtained from TEM results were 2-4nm. Cyclic voltammetry results showed that these prepared electro-catalysts were active towards methanol oxidation in acidic solution. The electro-catalytic activity of Pt-Ru-P on MWCNTs was significantly improved and higher than that of Vulcan XC 72, thus demonstrating that MWCNTs can act as efficient support material for effective dispersion of electro-catalysts.

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