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DEVELOPMENT OF AN ELECTRODE FOR DIRECT METHANOL FUEL CELL

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Abstract

This paper presents the efficient use of platinum catalyst ruthenium with in the anode of a Direct Methanol Fuel Cell (DMFC). This is achieved by depositing platinum and ruthenium nano-particles on the pre-refluxed multi-walled carbon nano-tubes (MWCNT). MWCNTs were synthesized using the Chemical Vapor Deposition (CVD) with floating catalyst technique. The synthesized carbon nanotubes (CNT) were refluxed in 12M nitric acid to produce anchoring sites on the surface of the CNT. The platinum and ruthenium nano-particles were in a ratio of (3:1). These particles are deposited on the surface of the CNT at 60 wt % by reduction in ethylene glycol. Transmission micrograph (TEM) and scanning electron micrograph (SEM) images show the success of the deposition method.

Keywords: DMFC, floating catalyst CVD, multi-walled carbon nano-tubes, platinum-ruthenium nano-particles.

INTRODUCTION

A fuel cell is like an ordinary battery, provides DC electricity from two electrochemical reactions. These reactions occur at electrodes where the reactants are continuously fed. The anode is maintained by supplying a fuel (e.g. methanol) whereas the positive cathode is maintained by the supply of oxygen or air. There are various types of fuel cells. Types of fuel cells vary by the different materials used to make the electrolyte. Every type of fuel cell is specific on its own in terms of electrolyte used, operating temperature and application. Direct methanol fuel cell (DMFC), methanol is used as the electrolyte. DMFC is a low temperature fuel cell hence has a potential to be used for portable and mobile purposes similar to daily used batteries. The principle of DMFC is to oxidize methanol to carbon dioxide at the anode and reduce oxygen and water at the cathode. This electrochemical reaction produces 6 electrons. A sectional diagram is shown below:

Fig. 1 shows the operating principles of a fuel cell utilizing methanol as fuel. Methanol is electrochemically oxidized at the anode electro-catalyst to produce the six electrons which travel through the external to the cathode electro-catalyst. They are then consumed together with oxygen in a reduction reaction. Hydrogen ions pass through the membrane which is an ionic

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conducting membrane. The oxygen from air is reduced to water at the cathode. At the anode for methanol and water to change into carbon dioxide, proton ions and electrons we need a catalyst. In this experiment we used platinum as a catalyst. The most efficient anode catalyst for the electrochemical oxidation reaction is the platinum nano-particles (2 – 4 nm) supported on a high surface area carbon (Pt/C) [Pazio *et al*. 2000]. However, it has been reported that carbon monoxide (CO) formed during the reaction as a byproduct. This CO reacts with Pt and hence poisoning the surface of the anode which in turn causes a dramatic decrease in anode performance. A possible solution for that was to use a CO – tolerant electro-catalyst by alloying Pt with another transition metal. It was reported that the best CO-tolerant electro-catalyst is Pt-Ru alloy [Adzic *et al*. 2003]. CO_2 is the only product opposed to formic acid and formaldehyde when Pt catalyst alone is used [Pazio *et al.* 2000]. So far the state of the art bi-catalyst is the Pt-Ru alloy. However, the optimum ratio of the alloy composition is still under investigation. Different papers presented different ratios. Gasteiger *et al*. [1994] reported that 30% Ru was optimal for Pt-Ru alloys. However, 50% Pt – 50% Ru was also reported as the most active catalytic ratio [Gurau *et al*. 1998]. Meanwhile, considering the CO tolerance, Camara *et al*. [2002] reported the best results achieved at Pt:Ru 3:1 alloy real proportion. In addition to the ratio of Pt to Ru, another area has to be explored to promote the commercialization of the DMFC. Since the Pt-Ru are extremely expensive, a reduction in loading of these precious metals is one of the target. It was found that if the metal alloy is dispersed on a conductible support, such as carbon, then the cost will decrease.

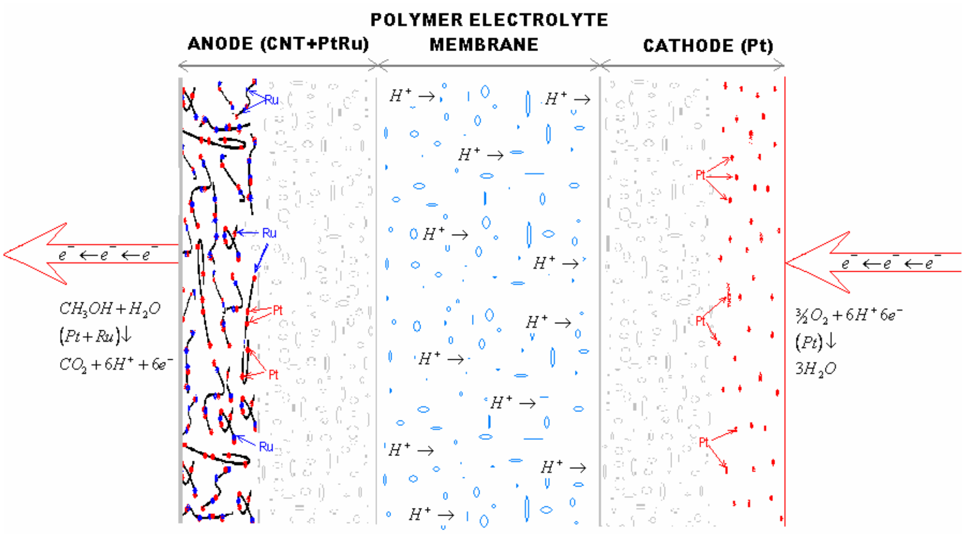

Fig. 1: A sectional diagram of Direct Methanol Fuel Cell.

Carbon is in general the wining candidate due to its attractive and essential properties. Ideally, a perfect support material should have the following properties such as: high surface area, high level of dispersion of nanosized catalysts, excellent crystallinity or low electrical resistance to facilitate the electron transport during the electrochemical reaction, a pore size suitable for maximum fuel contact and byproduct release and good interactions between catalyst nanoparticles and the support [Park *et al*. 2004]. It is extremely difficult to synthesize carbon materials possessing all the above properties especially the high surface area and good crystallinity. In addition, the conventional catalyst supported on a porous carbon, 90% of platinum atoms may be inactive. The platinum particles deposited within the porous carbon nanostructure may be inaccessible to the polymer electrolyte [Thompson *et al*. 2001]. Traditionally, carbon black has been extensively used as a support for the catalyst. For the past decade, another form of carbon, carbon nanotubes, have attracted great interest due to their unique structure and excellent electrical properties [Li et al. 2002]. Oxidations of methanol by PtRu or Pt loaded on multi-walled carbon nanotubes with different catalyst metal loadings were reported [Carmo *et al*. 2004, Han *et al*. 2004, Matsumoto *et al*. 2004, Liu *et al*. 2005]. In this paper, Multi-walled carbon nano-tubes were synthesized using the floating catalyst chemical vapor deposition method, oxidized and deposited with the precious metals Pt-Ru.

EXPERIMENTAL

The synthesis of Multi-Walled Carbon Nanotubes (MWCNT) is carried in the Chemical engineering laboratory, UPM, as per the design and set parameters [Rajalakshmi *et al*. 2005] [reference- Muutaz Ali PhD thesis]. The production of CNT at present is carried out via the floating catalyst chemical vapor deposition method. In brief, MWCNTs are grown in a horizontal tubular reactor using ferrocene as the catalyst and benzene as the source of hydrocarbons. The gases used in this system are Hydrogen, as the reactant gas, and Argon, for flushing out air. The MWCNTs are of high purity as confirmed by TEM. The MWCNTs were then refluxed in 12 M nitric acid to introduce acid / anchoring sites on the CNTs surface. These acid sites are composed of COOH, CHO, OH functional groups which act as nucleation center for metal ions [Han *et al*. 2005]. The metal precursors used are Potassium tetrachloroplatinate (11) $K_2Pt_{11}C_{l4}$ (Kanto Chemicals) and Ruthenium (111) Chloride $RuIIICl_3$ (Merck). A calculated amount of the metal precursors and CNTs were added together in ethylene glycol under refluxing atmosphere for 8 hours. The metals are attached to the surface-oxidized CNTs by the chemical reduction of the metal precursors in the presence of a reducing agent. The amounts mixed were to achieve metal to CNT loading of 60 wt% and a catalytic ratio of 3:1 Pt:Ru. The wet solids were then washed using deionized water, filtered and dried overnight.

The synthesized MWCNT were examined by the scanning electron microscope SEM (SEM JEOL 6400) and TEM (TEM Hitachi H-7100) at Microscopy & Microanalysis Unit in the Institute of Bioscience, Universiti Putra Malaysia (UPM). The composition of the prepared catalysts was determined by the energy-dispersive X-ray analysis (EDX) in a scanning electron microscope (LEO, 1455VP SEM-EDX) system.

RESULTS AND DISCUSSION

Fig. 2 shows SEM image of the synthesized and purified MWCNTs. Purification process involved the refluxing of CNTs in 12M nitric acid. This is also called surface oxidation of the surface of CNTs. As can be confirmed from the SEM images, the MWCNTs are of high purity and with diameters ranging from 10-40 nm. The significance of highly pure CNTs is that the impurities present in some samples poison the Pt metal during the oxygen reduction reaction.

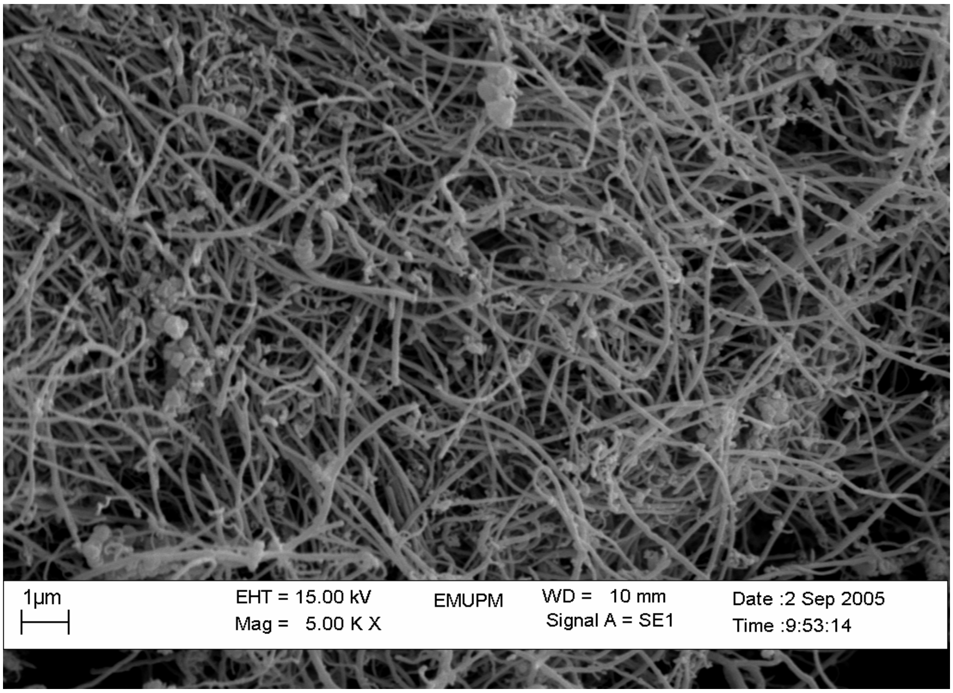

Fig. 2: Scanning electron micrograph of synthesized and purified MWCNTs

In Fig. 3 single MWCNT having a diameter approximately 30 nm is sufficiently decorated by the bi-metallic catalyst Pt – Ru as with more or less a uniform distribution. The composition on the CNTs is further confirmed by the scanning probe microscopy - The particle sizes of the Pt and Ru are in the range of 10-15 nm. The particle size of the Pt may be correlated with the oxidation of CNTs, which indicates that the efficient deposition of Pt nanoparticles is due to a strong interaction between the metal salt precursor and the graphene edges of the CNTs [Rajalakshmi *et al.* 2005]. It was observed by Rajalakshmi *et al*. [2005] that for the oxidized CNTs, the diameter of the metal particles deposited is less than that of the non-oxidised CNTs.

The morphology and composition of the PtRu /CNT has been investigated by SEM and energy dispersive x-ray spectroscopy (EDS) for the elemental analysis of the surface composition. The results are summarized in Table 1.

As can be seen from Table 1, the composition of the catalyst is relatively close to the target in terms of the ratio of Pt to Ru. However, for the Pt-Ru to CNT, the real ratio differs from the target ratio. This can be due to some losses of the CNTs during the surface oxidation process as at least 30wt. % is reduced due to the removal of the catalyst Fe particles that were present in during the CNT synthesis.

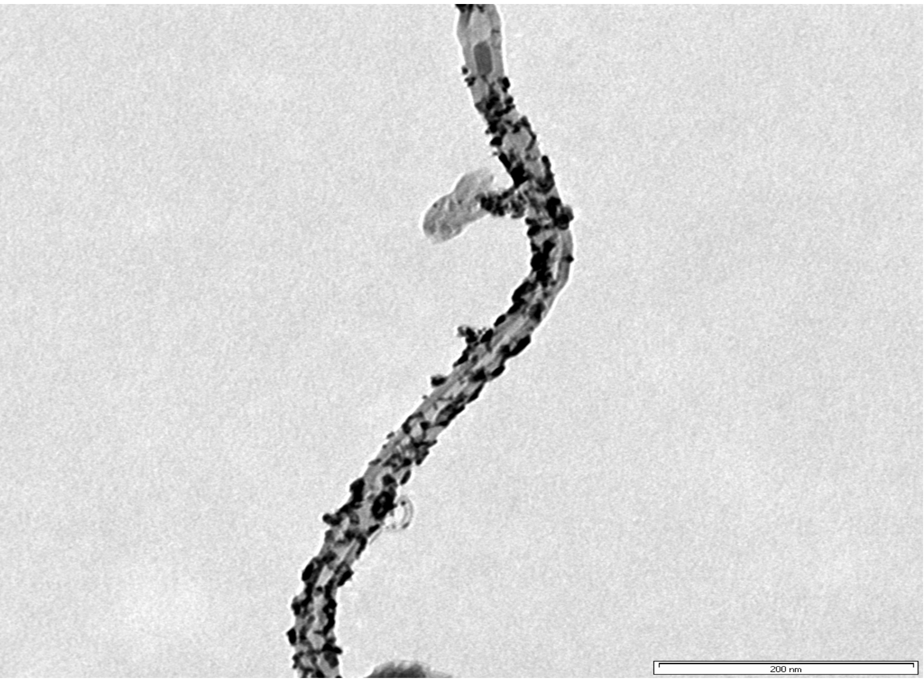

Fig. 3: Transmission electron micrograph of a single oxidized CNT supported platinum and ruthenium catalyst.

Table 1: Elemental surface composition of the prepared PtRu/CNT catalysts.

	Sample
Target ratio of PtRu to CNT	60 wt % - 40 wt %
Surface composition by EDS	75 wt % - 25 wt %
Target Composition Pt : Ru	Pt3 :Ru1
Surface Composition by EDS	Pt2.6 :Ru1

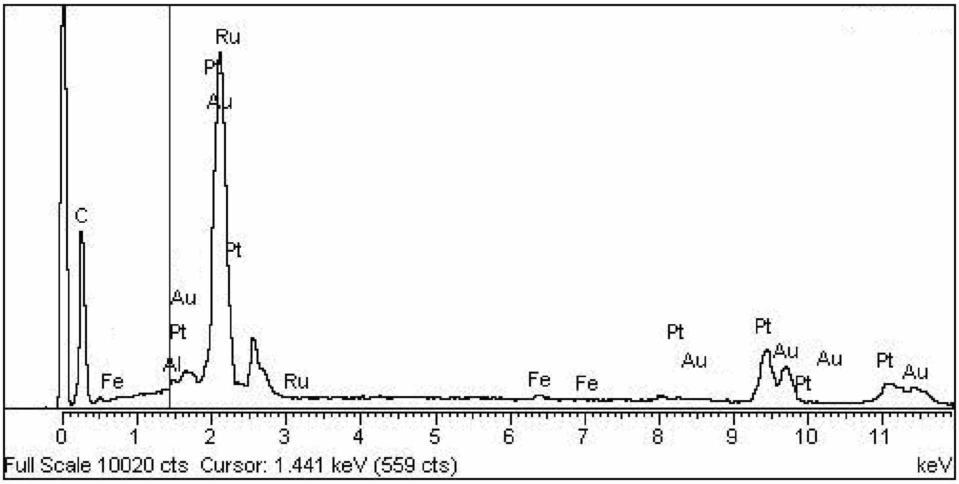

Fig. 4: Energy dispersive X-ray analysis of PtRu/CNT

In Fig. 4 EDX confirms the presence of the Pt-Ru catalyst on the surface of oxidized CNTs. It is noticed that other elements are also present. The Au and Al are present from the sample preparation for the SEM. The stub used in the SEM is made of aluminum and Au is from gold sputtering the stub before testing. A very small ratio (0.39 wt. %) is present. The reason is that not all the CNTs' caps / closed ends were opened during the oxidation process. Some Fe particles still existed, however, in very small quantities.

CONCLUSIONS

A chemical reduction method was used to deposit the Pt-Ru nanoparticles from there salt precursors using a reducing agent (ethylene glycol). This method proved to be a successful method in terms of simplicity and efficiency. The PtRu nanoparticles were uniformly dispersed on the surface of the oxidized CNTs. The nanoparticles synthesized were in the range of 10-15 nm in diameter. The floating catalyst chemical vapor deposition method produced high purity mulit-walled carbon nanotubes with diameters ranging from 6-40 nm.

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