Pt-Ru nanoparticles Supported on MWCNT as PEM fuel cell electrocatalysts

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ABSTRACT

Multi Wall Carbon Nanotubes (MWCNT) are used as catalyst support due to their properties such as thermal stability and electron conduction among others [1]. In the last few years, MWCNT have been synthesized using a wide variety of methods; one of them is spray pyrolysis [2]; it presents advantages over other methods, i.e. easiness to control operating conditions and scalability. It had been demonstrated that CNT are obtained using organometallic compounds as catalytic agents [3,4]. This work proposes nickelocene as catalytic agent to grow MWCNT and its use to support metallic nanoparticles. Pt-Ru precursors were deposited on MWCNT using an aqueous deposition method assisted by ultrasound. Electrocatalysts were characterized by SEM-EDS and TEM. MWCNT shows length of 30 microns and diameter between 50 and 70 nm. Pt, Ru and Ni particles obtained are in nanometric scale. Synthesized nanostructured material could be considered as a good candidate for catalyst in PEM or Methanol fuel cells [5].

Keywords: carbon nanotubes, nickelocene, Pt-Ru nanoparticles, electrocatalysts, fuel cells

1 INTRODUCTION

During the last time the structural, mechanical and electrical properties of Multi Wall Carbon Nanotubes (MWCNT) have allowed the development of wide study field. Several authors have been reported different synthesis methods to obtain MWCNT [6]. One of the most useful, due to its efficiency, low cost and capability to control the synthesis conditions, is the spray pyrolysis synthesis. The MWCNT structure are very functional to metals support; their properties have demonstrated to provide chemical and thermal stability and good particle dispersion. Synthesis method has a direct influence in the catalysts properties; consequently a variety of methods to deposit metal particles on MWCNT have been developed [7]. In this work, MWCNT obtained by spray pyrolysis using nickelocene are used as support for platinum and ruthenium nanoparticles.

2 EXPERIMENTAL METHODS

2.1 Multi wall carbon nanotubes synthesis

MWCNT synthesis was done by the spray pyrolisis method previously reported by Aguilar et al. [2]. Nickelocene (Aldrich) was used as catalytic agent and toluene (JT Baker) as carbon source. A nickelocene–toluene solution mist is produced with argon gas in pneumatic nebulizer. Manganese oxide thin film was deposited previously on a Vycor tubing (VT). VT was into a tubular furnace at 800°C. MWCNT structure and composition were analyzed by SEM (JEOL JSM-5800LV).

2.2 Electrocatalyst synthesis

Pt-Ru over MWCNT deposition has been carried out by aqueous deposition method assisted by ultrasound. MWCNT were ultrasonically dispersed in ethanol during 30 min, then precursor solution was added and remained in the ultrasound bath by one hour. $(NH_4)_2PtCl_6$ (Alpha Aesar) and $RuCl_3$, (Alpha Aesar) were used as Pt-Ru metallic particles precursors. In order to get the Pt-Ru particles in metallic form a chemical reduction was used. During the deposition process 10 mL of a 0.1M $NaBH_4$ solution was added drop by drop as reduction agent. The obtained material was filtered with vacuum system and rinsed with ultrapure water to remove the residual products of the reduction reaction. Finally the material was dried over night at 80°C. SEM (JEOL JSM-6390) and TEM (TEM - Philips CM200) analyzes were done in order to get particle size. Chemical elemental microanalysis was carried out by X-ray energy dispersive spectroscopy (EDS).

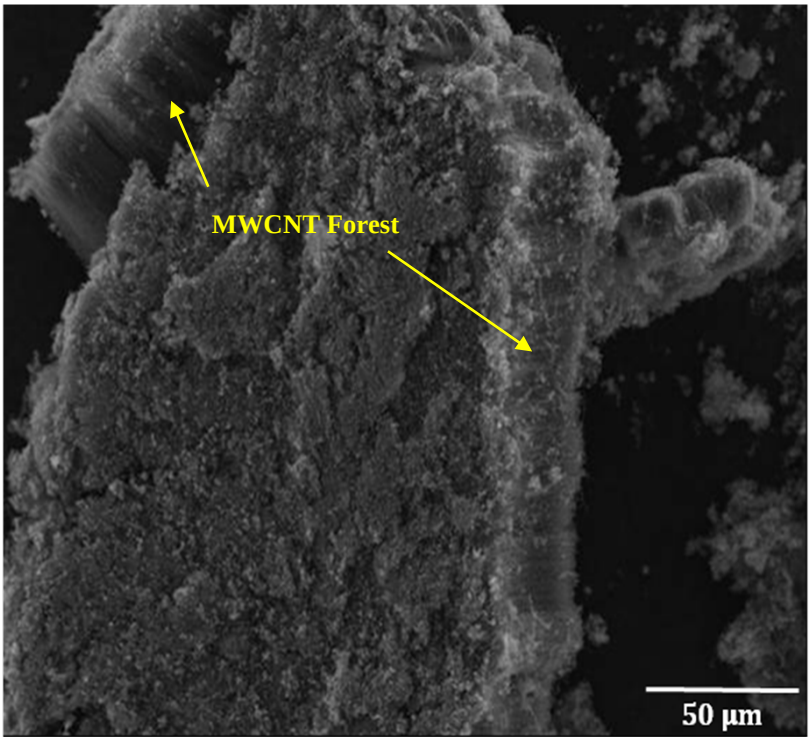

Figure 1. Scanning electron microscopy micrograph of MWCNT forest.

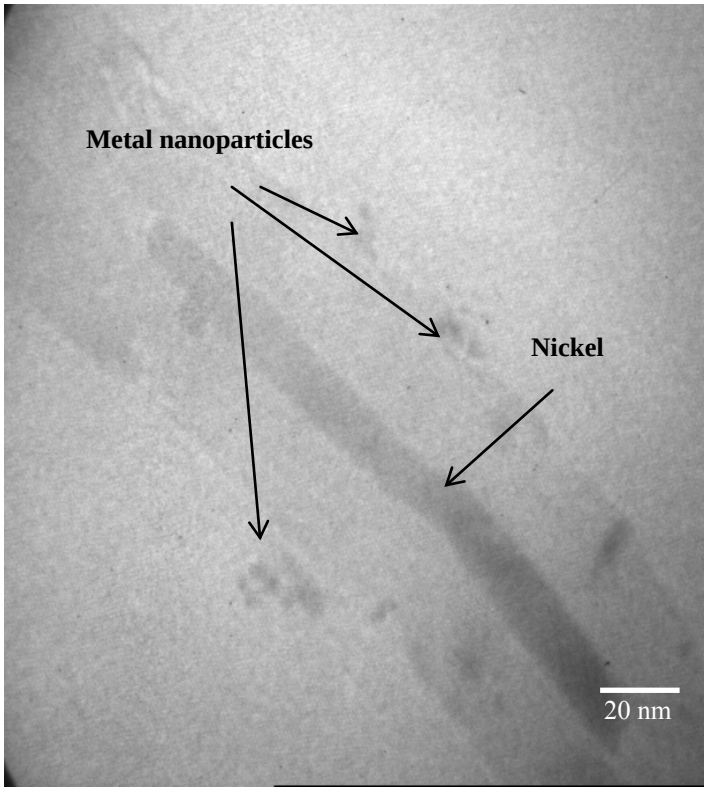

Figure 2. Transmission electron microscopy micrograph of Pt-Ru nanoparticles over a MWCNT with encapsulated nickel.

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3 RESULTS AND DISCUSSION

3.1 Multi wall carbon nanotubes

MWCNT were successfully synthesized using a manganese oxide substrate and nickelocene as catalytic agent. Figure 1 shows the forest of well aligned MWCNT. Obtained lengths are around 30 microns. Amorphous carbon and nickel particles remain on the MWCNT surfaces due to the growth mechanism. However nickel particles will help in the electrochemical fuel cells reaction [8].

3.2 Electrocatalyst

Support materials play an important role in catalyst activity. Small particle size in catalysts provides a high contact area between active phase and the reagents, having as consequence a better activity. Figure 2 reveal that MWCNT structures are not modified due to the ultrasound treatment. Pt, Ru and Ni nanoparticles were well dispersed on the external walls of the MWCNT with particles sizes under 10 nm. The obtained metal loading (weight percentage) over the MWCNT surfaces is 14, 8 and 6 for Pt, Ru and Ni respectively.

4 CONCLUSIONS

Well aligned MWCNT were obtained with spray pyrolysis technique, using nickelocene as catalytic agent and manganese oxide thin films as substrate. Carbon nanotubes diameters are between the 50 and 70 nm and its length around 30 microns. Platinum and ruthenium particles were deposited over the MWCNT using aqueous deposition method assisted by ultrasound. Particles under 10 nm can be observed by TEM. Pt-Ru-Ni on MWCNT material could be considered as a good candidate for catalyst in PEM or Methanol fuel cells.

5 ACKNOWLEGMENTS

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