Electrophoretic deposition an emerging technology to support fuel cell nanoelectrocatalysts

M. T. Oropeza Guzmán[*], Y. Gochi Ponce[*] and G. Moreno[*]

[*]National Institute of Technology of México/Technological Institute of Tijuana, Blvd. Alberto Limón Padilla S/N, Mesa de Otay, C.P. 22500 Tijuana, B.C., Mexico
oropeza1@yahoo.com

ABSTRACT

Electrophoretic Deposition, EPD, is a known method to prepare even advanced coatings, as well as advance functionally graded materials. EPD followed by thermal treatments, accomplish better adherence of thin layers. In this work the coating was composed by nanoelectrocatalytic materials expecting to improve fuel cells electrode's life time and the possibility to fabricate larger electrodes (10 cm^2). Using EPD to obtain thin film electrodes allow to test the nanoelectrocatalysts under flow conditions in real fuel cells. EPD was performed controlling voltage, deposition time and composition of for three different colloidal dispersions: single walled, multiwalled and funtionalized multiwalled carbon nanotubes, SWCNT, MWCNT, and FMWCNT respectivily. Later on CNTs modified with $Pt_xW_yS_z$ nanoparticles are going to be tested. Results are compared and evaluated taking into account the homogenity of the nanoelectrocatalytic layer as well as the electrocatalytic properties of fuel cells electrodes at medium scale. EPD is a cheaper method requiring minimal operating and maintenance costs, with the possibility to re-concentrate the colloidal dispersion just replenishing with nanoelectrocatalysts.

Keywords: electrophoretic deposition, fuel cell, nanoelectrocatalysts

1. INTRODUCTION

It can be said that the heart of a fuel cell is the electrocatalyst, since electrode reactions are the main concern of electricity generation. Several electrode materials have been investigated to asses anodic and cathodic reactions, assuming that the electrocatalyst of a fuel cell is the main drawback for its commercialization. Since platinum is known as the best electrocatalyst and carbon nanostructured materials are usually employed as metal's support [1], the interest in current fuel cells studies is to use metallic salts and alloys to emulate Pt properties. For example the oxygen reduction reaction, ORR has been studied using Pt, Ni, Pd, Fe and Co [2] and Pt/C [3]. Neverthless, the capability of the electrocataly depend on how to support the material on the electrode for extended lifetime and decreasing the metal loading.

On the other side, the direct methanol fuel cells (DMFCs) are known as the most popular type of DLFCS because of methanol has: low cost, good electrochemical activity and biodegradability [4]. Eventhough, one of the current challenges of the anodic electrode of DMFC (containing nanostructured electrocatalysts) is to optimize the surface area by having a better nanostructures dispersion, thus to reduce as much as possible the platinum loading to make more affordable fuel cells.

A flip side of the electrocatalyst is the carbon nanomaterial use as the support for the metal nanoparticles, whereas carbon nanotubes stand out for their mechanical and electrical properties. They possess higher mechanical resistance, electrochemical activity and surface area than carbon commonly used [5, 6, 7, 8]. Besides of the great performance that carbon nanotubes had over the electrocatalyst, in some cases it's necessary a previous treatment of this nanomaterial to increase their activity. In concern with the deposition of nanoparticles on carbonaceous materials, there are different methods that can be attained. However, the problem of the homogeneously dispersion it's crucial for the given application.

The electrophoretic deposition (EPD) has been increasingly applied in a wide range of studies because of its short formation time and simple use of apparatus. This technique provides a much better dispersion of nanoparticles as electrocatalysts for fuel cells. With EPD, one can control the metal loading on carbonaceous supports [9, 10] and the deposit thickness, microstructural homogeneity, and deposition on complex shaped substrates. Unlike the screen-printing and spraying method, EPD offers uniformity of deposits with process simplicity and a low cost. In this technical paper EPD was tested as a deposition technique of single walled carbon nanotubes SWCNT, multiwalled carbon nanotubes MWCNT, and functionalized multiwalled carbon nanotubes FMWCNT. Later on composite electrocatalysts are going to be prepared.

2. EXPERIMENTAL SETUP

2.1 CNTs dispersions

The preparation of a homogenous dispersion of CNT is essential for a successful EPD. The dispersions consist of

10 mg of CNT added to 20 ml of solvent and 1.2 ml of a water and Nafion mix that was introduced into an ultrasonic bath for 45 minutes.

The solvents used were isopropanol and ethanol 98%, respectively. Regarding the CNT, three types were used for each solvent: Sigma Aldrich FMWCNT, SWCNT and MWCNT pristine.

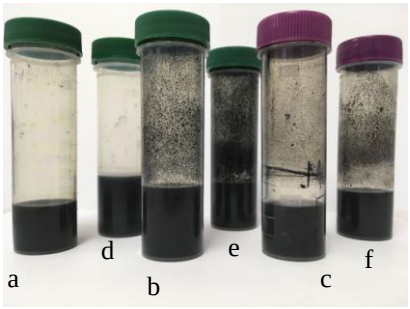


Figure 1: CNTs dispersions using ethanol a) MWCNT, b) SWCNT, c) FMWCNT and isopropanol d) MWCNT, e) SWCNT, f) FMWCNT

2.2 Electrochemical cell

Two graphite bars were used as working electrodes in a two electrode cell. The electrodes were connected to a positive and negative potential of a power supply using appropriate electronic cables, as shown in Figure 1. The well dispersed solutions were pour into a beaker and the electrodes had a distance of 1.5 cm.

a

b

Figure 2: a) Power supply and b) electrochemical cell used for EPD.

2.3 SEM images

A JEOL 7200F Field Emision Scanning Electron Microscope was used to obtain the different CNT's images.

3. EPD OF CNTs DISPERSIONS

In Table 1 are listed the general properties of CNTs used to prepare dispersions.

CNT	D	L
MWCNT	10-30 nm	1-10 µm
SWCNT	0.7-0.9 nm	≈100 nm
FMWCNT	9.5 nm	1.5 µm

Table 1: Diameter and length of CNTs used to prepare dispersions

Table 2 shows the EPD conditions used to prepare nanoelectrocatalysts layers on graphite substrate.

	CNT	EPD Time (min)	Volts
Isopropanol	MWCNT	10	60
		30	60
		10	20
		30	20
	FMWCNT	10	60
		30	60
		10	20
		30	20
	SWCNT	10	20
		30	20
Ethanol	MWCNT	10	60
		30	60
		10	20
		30	20
		30	35
	FMWCNT	10	20
		30	20
		30	35
	SWCNT	10	20
		30	20
		30	35

Table 2: EPD conditions used to prepare the CNTs deposits on graphite substrates.

For 60V, MWCNT and FMWCNT presented low mass loading on the deposit. The same result was observed for 10 and 30 min. Thus, the voltage was reduced to 20 V for the same period time (10 and 30 min). The formed deposits were better as shown on Figure 3. It is worth mentioned that this homogenous and uniform deposit was with the ethanol dispersions. Isopropanol dispersions did not enhance as much as ethanol with this voltage, but better depositions were observed than the ones at 60 V. However, for this technical paper we consider as important factor the homogeneity for the dispersions and depositions as shown in Figures 1 and 3.

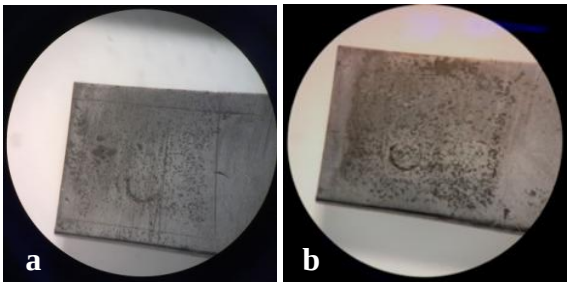


Figure 3: FMWCNT with isopropanol using a) 60 V and b) 20 V, per 30 min.

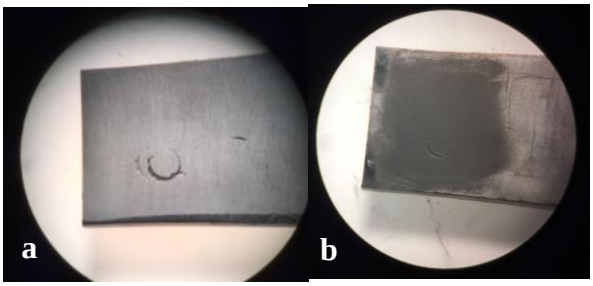


Figure 4: Graphite substrate a) raw and b) with MWCNT, electrophoretic deposition at 20 V per 30 min.

In Figure 4, the EPD at 30 min, 1.5 cm between electrodes and 20 V on graphite substrates was succesfull for all dispersions, however optic images show some inhomogeneous deposit in the lower part of the electrode. Since these results were better than the ones at 60 V, it was proposed to use 35 V giving a significant improvement (see Fig. 5).

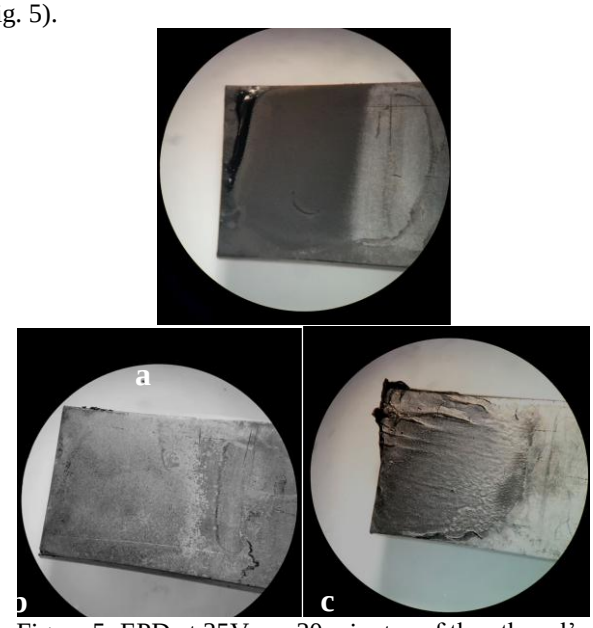


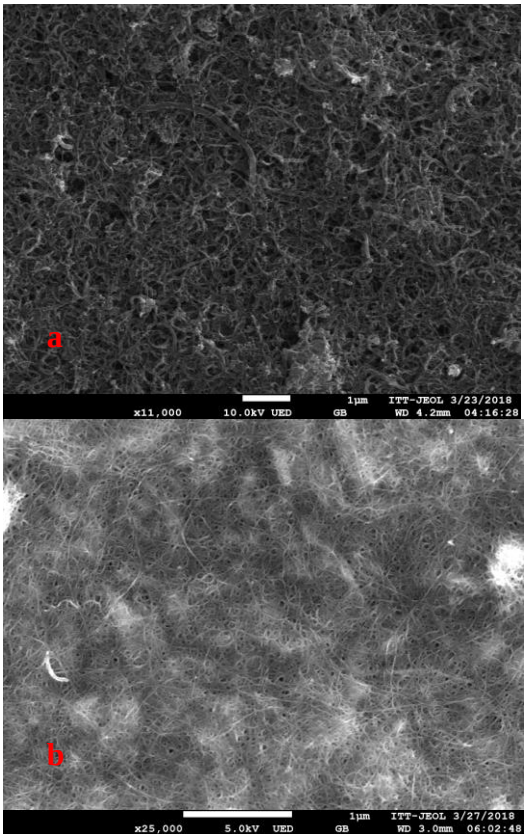
Figure 5: EPD at 35V per 30 minutes of the ethanol's dispersions with a) MWCNT, b) SWCNT, and c) FMWCNT.

As shown in Figure 5, the MWCNT are susceptible to reach a better deposition than the other samples of CNT, as showed above, an homogenous dispersion is necessary for an optimum deposition.

4. RESULTS AND DISCUSSION

To analyze the deposit microstructures, in Figure 6 are showed the SEM images of MWCNT, SWCNT, and FMWCNT using 35 V per 30 minutes.

Figure 6a shows a better deposition to the substrate, there are no agglomerates nor significant spaces between the nanotubes. This can be attributed to the bigger diameter size of the MWCNT, and as shown in Figure 1a, it shows the best dispersion. Unlike, the SWCNT (see Fig. 6b) exhibit small holes indicating an inhomogenous surface because of their smallness. Moreover, for seeing this nanotubes it was necessary to apply a higher voltage because of their diameter size and the poor deposition. Although the FMWCNT differ on length and diameter with the MWCNT, the SEM images are very similar to each other, the FMWCNT have aglomerates which are represented by the luminous sections.



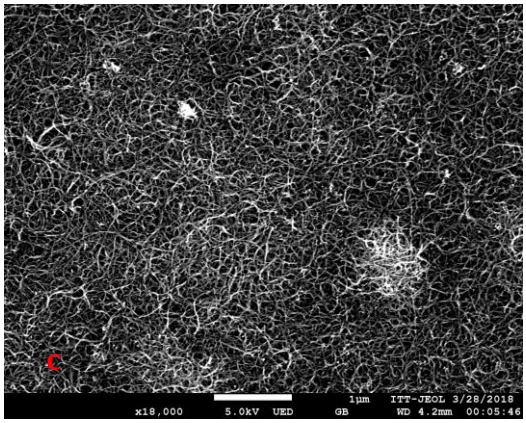


Figure 6: FE-SEM images of a) MWCNT, b) SWCNT, and c) FMWCNT electrophoretic depositions.

Therefore, SEM images indicate that SWCNTs were not as homogeneous as expected, due to the agglomeration formed in the initial dispersion and wide sizes distribution of nanotubes. The use of graphite as working electrode hinders to determine with precision the weight of depositions. The high porosity of this carbon substrate does not favor the reproducibility in therms of mass; however the mass increment lower than 1 mg clearly indicated the formation of thin layers on graphite substrates.

5. ACKNOWLEDGEMENTS

This work was supported by the National Council and Science and Technology of Mexico (CONACYT) and Graduated Center in Chemical Sciencies Research at the Tijuana Institute of Technology of the TECNM. And the authors would like to thank to Ph. D. Ignacio A. Rivero for the technical support with the FE-SEM images.

6. REFERENCES

[1] Ana M. Valenzuela-Muñiza, Gabriel Alonso-Nuñez, Mario Miki-Yoshida, Gerardine G. Botte, Ysmael Verde-Gómez, «High electroactivity performance in Pt/MWCNT and PtNi/MWCNT electrocatalysts,» *International Journal of Hydrogen Energy,* vol. 38, nº 28, pp. 12640-12647, 2013.

[2] Y. Gochi-Ponce, G. Alonso-Núñez, N. Alonso-Vante, «Synthesis and electrochemical characterization of a novel platinum chalcogenide elec trocatalyst with an enhanced tolerance to methanol in the oxygen reduction reaction,» *electrochemistry communications,* vol. 8, pp. 1487-1491, 2006.

[3] Y. Gochi-Ponce, R. Barbosa, L.G. Arriaga, G. Alonso-Núñez, N. Alonso-Vante, «Oxygen Reduction Reaction and PEM Fuel Cell Perfomrance of a Chalcogenide Platinum Material,» *ECS Transactions,* vol. 3, nº 1, pp. 189-197, 2006.

[4] B.C. Ong, S.K. Kamarudin, S. Basari, «Direct liquid fuel cells: A review,» *Hydrogen Energy,* vol. 42, pp. 10142-10157, 2017.

[5] Wenzhen Li, Changhai Liang, Weijiang Zhou, Jieshan Qiu, Zhenhua Zhou, Gongquan Sun, Qin Xin, «Preparation and Characterization of Multiwalled Carbon Nanotube-Supported Platinum for Carhode CAtalysts of Direct Methanol Fuel Cells,» *J. Phys. Chem. ,* vol. B, nº 107, pp. 6292-6299, 2003.

[6] Yongyan Mu, Hanpu Liang, Jinsong Hu, Li Jiang,‡ and Lijun Wan, «Controllable Pt Nanoparticle Deposition on Carbon Nanotubes as an Anode Catalyst for Direct Mehtanol Fuel Cells,» *J. Phys. Chem,* vol. B, nº 109, pp. 22212-22216, 2005.

[7] Wenjiao Huang, John M. Ahlfield, Xinsheng Zhang, Paul A. Kohl, «Platinum Supported on Functionalized Carbon Nanotubes for Oxygen Reduction Reaction in PEM/AEM Hybrid Fuel Cells,» *Journal of The Electrochemical Society,* vol. 4, nº 164, pp. F217-F223, 2017.

[8] Neetu Jhaa, A. Leela Mohana Reddya, M.M. Shaijumona, N. Rajalakshmib, S. Ramaprabhua, «Pt–Ru/multi-walled carbon nanotubes as electrocatalysts for direct methanol fuel cell,» *Hydrogen Energy,* nº 33, pp. 427-433, 2008.

[9] M. L. Laxmidhar Bersa, «A review on fundamentals and applications of electrophoretic deposition (EPD),» *Progress in Materials Science,* vol. 52, pp. 1-61, 2007.

[10] H. Tang, J. H. Chen, Z.P. Huang, D.Z Wuang, Z.F. Ren, L.H. Nie, Y.F. Kuang, S.Z. Yao, «High dispersion and electrocatalytic properties of platinum on well-aligned carbon nanotube arrays,» *Carbon,* nº 42, pp. 191-197, 2004.