



## Electro Oxidation of Methanol on Copper Nanoparticles Supported Poly (*O*- Amino Phenol) Nanotubes

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**Abstract:** In this article, the electrochemical synthesis and the characterization of Cu nanoparticles dispersed poly (*o*-aminophenol) (POAP) nanotube electrode is reported. The morphology of the electrode was characterized by scanning electron microscopy (SEM). Catalytic activity and stability for the oxidation of methanol were studied by using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed. The results show that poly (*o*-aminophenol) nanotubes electrodes significantly enhance the catalytic activity of copper nanoparticles for oxidation of methanol. The results obtained affirm that the dispersion of the copper particles is connected with catalytic response to a higher activity. The nanotubular morphology of poly (*o*-aminophenol) helps in the effective dispersion of Cu particles facilitating the easier access of methanol to the catalytic sites. The poly (*o*-aminophenol) nanotubes modified with copper nanoparticles cause a great increase in electroactivity and the electro-catalytic oxidation of methanol.

**Key words:** Methanol oxidation; Conducting polymers; Nanostructured materials; Electro-catalyst

### INTRODUCTION

The generation of nanostructured materials on a surface is a new thrust in materials science due to the continuing miniaturization of electronic and mechanical devices. Nanostructure materials have attracted much recent attention due to their important roles in many technological areas such as heterogeneous catalysis, photonics and single electron and quantum devices [1]. Nano particles have been commonly grown in physical and electrochemical processes [1, 2]. Organic conducting polymers, particularly in the form of thin films, are attractive candidates for microelectronic applications [3, 4] due to their unique combination of electrical, mechanical and physical properties. Furthermore, self-assembly of metal nanostructures on diblock polymer substrate by making use of different wetting properties of the polymers has been demonstrated [5, 6]. Conducting polymers have been studied intensively in recent years because of their useful properties and possible utilization in many practical applications, such as charge storage

devices, electrochromic displays, modified electrodes, anticorrosion coating, molecular transistors and high surface area support for metal catalyst particles [7, 8]. Another typical property of some conductive polymers is perm selectivity or rather permeability towards some species [9, 10]. The conducting polymers used are mainly polyaniline, polypyrrole and polythiophene. These polymers offer great advantages due to their very good conducting and mechanical properties and good adhesion to the electrode substrate. However, it is of interest to extend such studies to other polymers and same polymers especially polyaniline on low price substrates, which might be suitable as host materials for the catalyst micro and nanoparticles [11, 12]. Recent developments in the preparation of micro- and nano-structured metal particles and their dispersion in porous materials have opened up the possibility of preparation of high performance electrocatalysts for technologically important reactions. A simple and efficient method of dispersing catalysts is the electro- crystallization of metals producing catalytic materials based on the properties of small clusters. Thus,

effective electrocatalysts are now routinely prepared by the electrodeposition and dispersion of metal crystals or crystal aggregates in conducting polymer films, previously electrodeposited on an inert electrode [13, 14]. It has been shown that such modified electrodes with Pt and Pt-based multimetallic assemblies are better catalysts than smooth platinum for the oxidation of organic fuels, that is,  $\text{CH}_3\text{OH}$ ,  $\text{HCHO}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{OHCH}_2\text{OH}$  and glucose [15]. Direct methanol fuel cells (DMFCs), an important electrochemical energy conversion system suitable for a variety of applications, have attracted extensive attention during the past two decades due to its simplicity, low pollution, low operating temperatures and high theoretical efficiency of energy conversion [16]. Recently, carbon nano-tubes (CNTs), which could be classified as single-wall carbon nano-tubes (SWNTs) and multiwall carbon nano-tubes (MWNTs) [17], were more and more investigated as advanced catalyst supporting materials owing to their outstanding mechanical characteristics such as high surface area, high electric conductivity, thermal stability and good corrosion resistance [18, 19]. Fuel cells are efficient and environmentally acceptable conversion devices. Electric current is generated in the fuel cell by the direct electrochemical oxidation of either hydrogen (proton exchange membrane fuel cell, PEM) or methanol (Direct Methanol Fuel Cell, DMFC). The electrochemical processes that yield energy are essentially pollution free. Water formed during the operation of the device is beneficial in space travel and submarines. Applications of fuel cells are diverse ranging from stationary (individual homes or district schemes) or mobile (transportation as cars, buses, etc.), mobile phones and lap top computers [20]. The methanol fuel has a superior specific energy density (6000 Wh/kg) in comparison with the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. This means longer conservation times using mobile phones, longer times for use of laptop computers and more power available on these devices to support consumer demand. Another significant advantage of the direct methanol fuel cells over the rechargeable battery is their potential for instantaneous refueling [21, 22]. The methanol fuel cells in alkaline solutions have many advantages such as increasing their efficiency, a wider selection of possible electrode materials, a better efficiency of oxygen cathode and the oxidation reactions of organic fuels exhibit almost no sensitivity to the surface structure [23]. Moreover, the use of the methanol fuel cells is limited by the poor anode performance and counteract the poisoning effects at the cathode due to the methanol cross-over.

## MATERIALS AND METHODS

**Materials:** The *o*-aminophenol (Fluka, purity >99%),  $\text{NaH}_2\text{PO}_4$  (Fluka, purity >98%),  $\text{NaHPO}_4$  (Merrk, purity >97%),  $\text{HCl}$  (Fluka, purity >98%) and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Merrk, purity >98%) was used. Bidistilled water was used for the preparation of solutions.

**Electrode Preparation and Electro Polymerization:** The used working electrode was a glassy carbon (GC) electrode. A platinum wire was also used as a counter electrode (CE). All potentials are reported versus the reference electrode  $\text{Ag}/\text{AgCl}$  (saturated  $\text{KCl}$ ). We cleaned the GC electrode surface by successively polishing it with a 0.05-1 m alumina slurry. After each polishing, the electrode was carefully washed with distilled water. POAP (Poly Ortho Amino Phenol) film was generated by electrochemical oxidation on the GC electrodes at 0.9 V versus ( $\text{Ag}/\text{AgCl}$ ) by using of monomer OAP in buffer solution of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  in  $\text{pH}=7$  and then after generation, the film was washed with water. After generating of POAP film on GC electrode, nanoparticle copper was deposited electrochemically on the POAP in a solution of 0.01 M  $\text{CuSO}_4$  and 0.1M  $\text{HCl}$  at  $\text{pH}=2$  under potentiostatic at -0.2 V at 10 min. All solutions were purged with argon gas for 15 min before the electrochemical tests.

**Instrumentation and Procedure Used:** Electrochemical measurements were performed in a one-compartment cell with a three-electrode configuration. CV study was conducted with a potentiostat/galvanostat (EG&G model 263 A, Oak Ridge, TN) with an electrochemical set up that controlled by M270 software. Electrochemical impedance spectroscopy (EIS) was performed with a frequency response detector (EG&G model 1025) with electrochemical set ups and under the control of M 398 software. An alternating-current voltage of 5 mV in amplitude with a frequency range from 50 mHz to 65 kHz was applied for the EIS measurements. The POAMP deposited with nanoparticle Cu ( $\text{Cu}/\text{POAP}/\text{GC}$ ) and  $\text{Cu}/\text{GC}$  were tested at direct-current (dc) potential of 0.5 V in 0.1M  $\text{Fe}/\text{Fe}(\text{CN})_6^{2-}$  for comparing of  $R_{ct}$  (charging transfer resistant) process assessment in the same frequency range. Scanning electron microscopy (SEM) images of the film poly ortho amino phenol deposited with Cu, ( $\text{Cu}/\text{POAMP}/\text{GC}$ ) were taken with Vega 5135 (Tescan, Brno, Czech Republic) and HV (high potential) 1500-V instrument at various magnifications. Sample films for imaging were grown on the GC electrode.

## RESULTS AND DISCUSSION

**Electron Microscopy Study:** The SEM image of the conventionally synthesized conducting poly (*o*-aminophenol) is shown in Fig. 1a. The image shows ladder morphology revealing a dense coverage of poly (*o*-aminophenol) on GC electrode, which is not uniform in nature. Fig. 1b shows the SEM image of the Cu deposited conventionally synthesized poly (*o*-aminophenol) on GC electrode. Though, the Cu crystallites are clearly seen from the image, the cluster size and the geometry of the Cu particles are not uniform and the cluster size was found to be high with agglomerates as seen over the scanned region. It is further evident from the image that the large Cu crystallites are randomly distributed on poly (*o*-aminophenol) and the ladder morphology of the poly (*o*-aminophenol) is also seen in the SEM image.

**Cyclic Voltammetry Measurements:** Figs. 2a and 2b show voltammograms of bare GC electrode and GC electrode coated with nanoparticle Cu (Cu/GC) from 0.0 to 1.5 V in a 0.1M NaOH solution at a scan speed of 0.2 V/s respectively. In the Fig. 2a, we did not see an anodic peak, but in the Fig. 2b, we see a broad peak at 1.23 V with anodic current  $5.24 \times 10^{-4}$ , that related to oxidation of methanol at Cu/GC surface.

The cyclic voltammetry of the bare GC electrode at a 0.1M NaOH and GC electrode in 0.1M NaOH/CH<sub>3</sub>OH are shown in Fig. 3a. and Fig. 3b. Clearly, no peak current seen that shown no oxidation happen, another hand methanol did not oxidate.

The cyclic voltammogram of the GC electrode modified by copper (Cu/GC) is shown at Fig. 3a. The anodic current was seen at 1.23 V with anodic current  $4.66 \times 10^{-4} \mu\text{A}\cdot\text{cm}^{-2}$  in the potential range 0.0 to 1.5 V Ag/AgCl<sub>(3M)</sub> in 0.1M NaOH/CH<sub>3</sub>OH solution that related to methanol oxidation on the Cu/GC electrode surface.

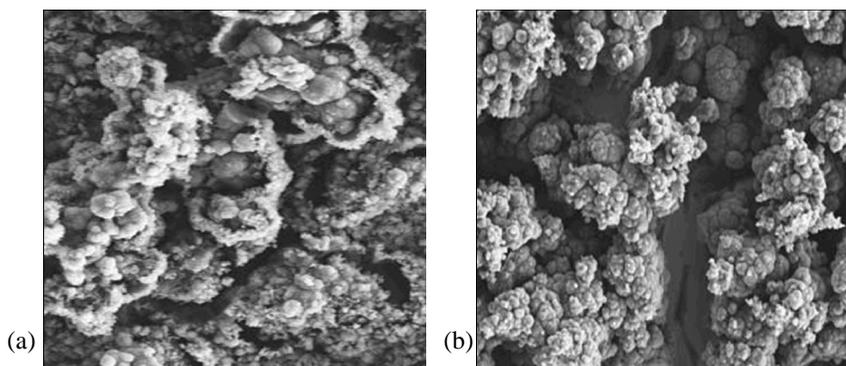


Fig. 1: SEM images of (a) poly (*o*-aminophenol) and (b) Cu deposited conventionally synthesized poly (*o*-aminophenol) on GC electrode coated on glassy carbon

Fig. 4. shows the cyclic voltammogram for the Cu/POAP/GC electrode in 0.1M NaOH/CH<sub>3</sub>OH solution. The methanol oxidation is clearly evident from the CV with a maximum current density of  $1.93 \times 10^{-3} \mu\text{A}\cdot\text{cm}^{-2}$  at 0.67 V in the potential range 0.0 to 1.5 V versus Ag/AgCl<sub>(3M)</sub>.

There is a clear different between electrochemically behavior of the Cu/GC and Cu/POAP/GC electrode, because methanol oxidated on the Cu/GC electrode at 1.23 V versus Ag/AgCl<sub>(3M)</sub> with anodic current density  $4.66 \times 10^{-4} \mu\text{A}\cdot\text{cm}^{-2}$  but as Cu/POAP/GC electrode applied, oxidation of methanol occurred at 0.67 V versus Ag/AgCl<sub>(3M)</sub> with anodic current density  $1.92 \mu\text{A}\cdot\text{cm}^{-2}$ . This different is due to the nanotubular morphology of the polymer surface which can load nanoparticle copper to a higher extent and at maximum loading that increase the catalytic activity of electrode for oxidation of methanol.

**Effect of Increasing the Methanol Concentration:** Fig. 5 shows the effect of methanol concentration on the anodic current of methanol oxidation for Cu/GC and Cu/POAP/GC electrodes. It is clearly observed that the anodic current increases with increasing methanol concentration and levels off at concentrations higher than 0.3M at both electrodes. We assume that this effect may be due to the saturation of active sites on the surface of the electrode. In accordance with this result, the optimum concentration of methanol to obtain a higher current density may be considered about 0.1-0.3 M. As seen in Fig. 5 the largest current for a given concentration of methanol was observed on the Cu/POAP/GC electrode in same experimental conditions.

**EIS Measurements:** EIS experiments were conducted to characterize the oxidation of methanol on the Cu/GC and Cu/ POAP/ GC electrodes. Fig. 6 displays the typical impedance spectra of the Cu/GC and Cu/POAP/GC

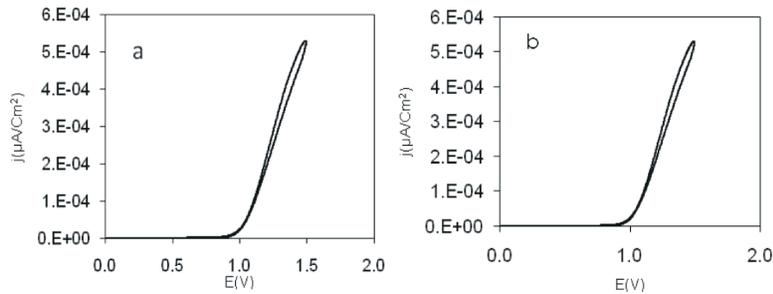


Fig. 2: Cyclic voltammograms of bear (a) GC electrode and (b) Cu/GC electrode from 0.0 to 1.5 V in a 0.1M NaOH solution at a scan speed of 0.2 V/s respectively

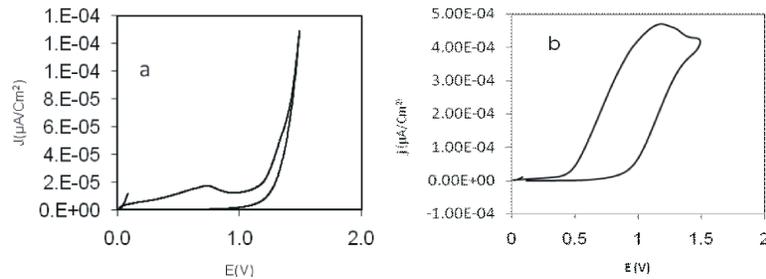


Fig. 3: Cyclic voltammograms of bear (a) GC electrode and (b) Cu/GC electrode from 0.0 to 1.5 V in a 0.1M NaOH solution at a scan speed of 0.2 V/s respectively

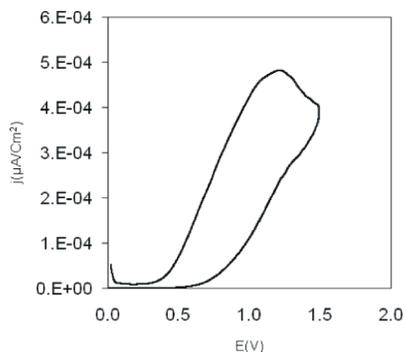


Fig. 4: Cyclic voltammograms of Cu/POAP/GC electrode from 0.0 to 1.5 V in 0.1M NaOH/CH<sub>3</sub>OH solution at a scan speed of 0.2 V/s respectively

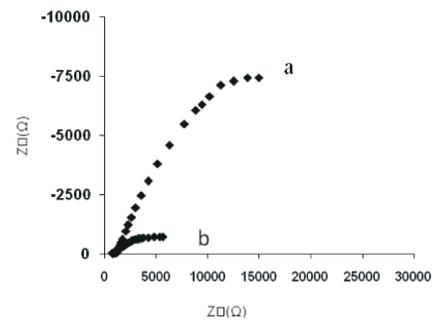


Fig. 6: Displays the typical impedance spectra of the (a) Cu/GC and (b) Cu/POAP/GC electrodes in 0.1M Fe/Fe(CN)<sub>6</sub><sup>-</sup> recorded at the dc potential 0.5V at frequency range of 50 mHz to 65 kHz

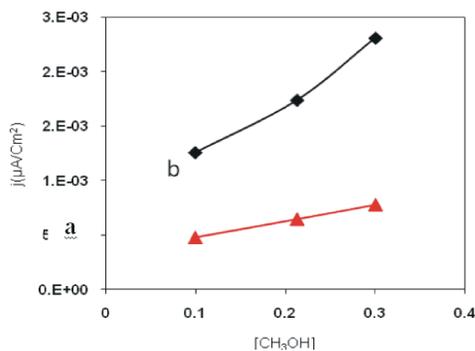


Fig. 5: Shows the effect of methanol concentration on the anodic current of methanol oxidation for Cu/GC (a) and Cu/POAP/GC (b) electrodes

electrodes in 0.1M Fe/Fe(CN)<sub>6</sub><sup>-</sup> recorded at the dc potential 0.5V at frequency range of 50 mHz to 65 kHz. The semicircle obtained from the high-frequency region was ascribed to the blocking properties of a single electrode, which rendered the faradic process of the ion exchange extremely slow at the polymer/electrolyte interface. The electrode modified with Cu/POAP at the dc potential 0.5 V had a higher electronic conductivity, that is, a low impedance and vice versa. The charge-transfer resistance ( $R_{ct}$ ) calculated by using of boukamp soafwar for the Cu/POAP/GC is lower than Cu/GC which shows the electrode modified with Cu/POAP had a higher electronic conductivity (see Table 1).

Table 1: Impedance parameters values extracted from the fit to the equivalent circuit for the impedance spectra recorded of the Cu/GC and Cu/POAP/GC electrodes in 0.1 M Fe/Fe(CN)<sub>6</sub><sup>-</sup> recorded at the dc potential 0.5V at frequency range of 50 mHz to 65 kHz

Type	$R_{ct}$ ( $\Omega/\text{cm}^2$ )	$R_s$ ( $\Omega/\text{cm}^2$ )	$R_{sol}$ ( $\Omega/\text{cm}^2$ )
Cu/GC	124.25	575.10	78.30
Cu/POAP/GC	59.348	374.41	74.92

Table 2: The effect of the scan rate on the oxidation of methanol was investigated in a 0.1M NaOH/CH<sub>3</sub>OH solution for comparing catalyst property of electrode modified with Cu/POAP/GC

$v$ (mv.s <sup>-1</sup> )	I ( $\mu\text{A}$ )	E (V)
20	$1.91 \times 10^{-3}$	0.53
40	$2.04 \times 10^{-3}$	0.64
60	$2.43 \times 10^{-3}$	0.74
[CH <sub>3</sub> OH]	I ( $\mu\text{A}$ )	E (V)
0.1	$1.26 \times 10^{-3}$	0.53
0.2	$1.39 \times 10^{-3}$	0.57
0.3	$1.31 \times 10^{-3}$	0.63

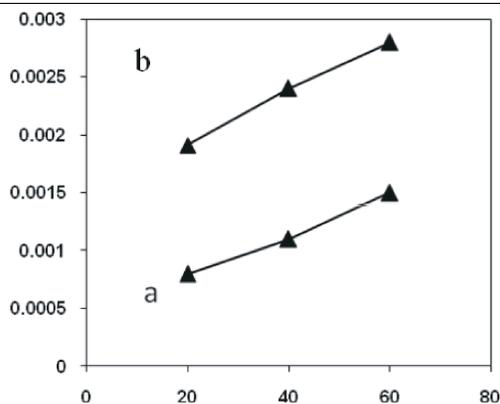


Fig. 7: The effect of the scan rate on the oxidation of methanol was investigated in a 0.1M NaOH/CH<sub>3</sub>OH solution for comparison catalical property of electrode modified with Cu/ GC (a) and Cu/ POAP/GC (b)

**Effect of the Scan Rate:** The effect of the scan rate on the oxidation of methanol was investigated in a 0.1M NaOH/CH<sub>3</sub>OH solution for comparison catalical property of electrode modified with Cu/POAP/GC and Cu/GC. The results are shown in Fig. 7. The oxidation current increased with increasing scan rate. An increase in the scan rate was likely to enhance the electron flow. It appeared that the increased collision of electrons resulted in a reduction in the velocity of electrons and led to saturation in the current which for electrode modified with Cu/POAP/GC is higher than Cu/GC electrode (See Table 2).

## CONCLUSIONS

The electrochemical synthesis and characterization of electrode modified with nanoparticle copper which deposited onto the poly (*o*-aminophenol) nanotube and copper deposited on the GC electrode have been achieved. We observed different voltammograms for electrode modified with nanoparticle copper which deposited onto the poly (*o*-aminophenol) nanotube and copper deposited on the GC electrode in a 0.1M NaOH/CH<sub>3</sub>OH solution. With increasing of concentration methanol and scan rate, oxidation of methanol increased as electrode modified with nanoparticle copper which deposited onto the poly (*o*-aminophenol) nanotube (Cu/POAP/GC) is used in comparison with copper deposited on the GC electrode. The Cu/POAP/GC shown excellent electro-catalytic activity and stability for electro-oxidation of methanol which the EIS measurements confirmed it.

## REFERENCES

- Sarkar, D.K., X.J. Zhou, A. Tannous, M. Louie and K.T. Leung, 2003. Growth of self assembled copper nanostructure on conducting polymer by electro deposition. Solid State Communications, 125: 365-368.
- Ji, C., G. Oskam and P.C. Searson, 2001. Electrochemical nucleation and growth of copper on Si (111). Surface Science, 492: 115-124.
- Vermeir, I.E., N.Y. Kim and P.E. Laibinis, 1999. Electrical properties of covalently linked silicon/polypyrrole junctions. Applied Physics Letters, 74: 3860-3863.
- Lonergan, M.C., 1997. A tunable diode based on an inorganic semiconductor conjugated polymer interface. Sci., 278: 2103-2106.
- Lopes, W.L. and H.M. Jaeger, 2001. Hierarchical self-assembly of metal nanostructures on diblock copolymer scaffolds. Nature, 414: 735-738.
- Higgins, A.M. and R.A.L. Jones, 2000. Anisotropic spinodal dewetting as a route of self-assembly of patterned surfaces. Nature, 404: 476-478.
- Habibi, B. and M.H. Pournaghi-Azar, 2010. Methanol oxidation on the polymer coated and polymer-stabilized Pt nano-particles: A comparative study of permeability and catalyst particle distribution ability of the PANI and its derivatives. International J. Hydrogen Energy, 35: 9318-9328.

8. Ohsaka, T., S. Kunimura and N. Oyama, 1988. Electrode kinetics of poly (*o*-aminophenol) film prepared by electro-oxidative polymerization of *o*-aminophenol and its electrochromic properties. *Electrochimica Acta*, 33(5): 639-645.
9. Golabi, S.M. and A. Nozad, 2002. Electrocatalytic oxidation of methanol on electrodes modified by platinum microparticles dispersed into poly (*o*-phenylenediamine) film. *J. Electroanalytical Chemistry*, 521(2): 161-167.
10. Tourillon, G. and F. Garnier, 1984. Thin polymer films on semiconductors: From their protection to the realization of molecular electronic devices. *The J. Physical Chemistry*, 88: 5281-5285.
11. Kelaidopoulou, A., A. Papoutsis, G. Kokkinidis, W.T. Napporn, J.M. LeÅger and C. Lamy, 1999. Chemical deposition of palladium on leucoemeraldine from solutions: state and distribution of palladium species. *The J. Appl. Electrochemistry*, 29: 101-106.
12. Kelaidopoulou, A., E. Abelidou and G. Kokkinidis, 1999. Electrocatalytic oxidation of methanol and formic acid on dispersed electrodes: Pt, Pt-Sn and Pt/M(upd) in poly(2-hydroxy-3-aminophenazine). *J. Appl. Electrochemistry*, 29: 1255-1261.
13. Wang, Z., G. Gao, Zhu, H. Sun ZD, H. Liu and S. Zhao, 2009. The operation energy consumption and energy-saving technologies of three green buildings in China. *International J. Hydrogen Energy*, 34: 9334-9340.
14. Wang, G., J. Ahn, J. Yao, M. Lindsay, H. Liu and S. Dou, 2003. Nanoparticle-dispersed PEO polymer electrolytes for Li batteries. *J. Power Sources*, 119: 16-23.
15. Shen, J., Y. Hua, C. Li, C. Qin and M. Ye, 2008. Pt-Co supported on single-walled carbon nanotubes as an anode catalyst for direct methanol fuel cells. *J. Electroanalytical Chemistry*, 53: 7276-7280.
16. Hsu, N., C. Chien and K. Jeng, 2008. Characterization and enhancement of carbon nanotube-supported PtRu electrocatalyst for direct methanol fuel cell applications. *Applied Catalysis B.*, 84: 196-203.
17. Dehbi, S., H. Aarouna Massai and A. Bdelilah Chtaini, 2010. Phosphate Modified Copper Electrodes for Methanol Fuel Cell Port. *Electrochimica Acta*, 28: 241-252.
18. Baglio, V., A. Di Blasi, E. Modica, P. Creti, V. Antonucci and A.S. Arico, 2006. Nanocatalysts Prepared by Microwave and Impregnation Method. *International J. Electrochemical Sci.*, 1: 71-79.
19. Ren, S., P. Zelenay, S. Thomas, J. Davey and S. Gottesfeld, 2000. Preparation of ultra high loading supported Pt catalyst for direct methanol fuel cell. *J. Power Sources*, 86: 111-116.
20. Shah, K. and R.S. Besser, 2008. Novel microfabrication approaches for directly patterning PEM fuel cell membranes. *J. Power Sources*, 123: 172-181.
21. Tripkolvi, A., S.L.J. Gojkovi, K.D.J. Popovi and J.D. Lovi, 2006. Methanol oxidation at platinum electrodes in acid solution: comparison between model and real catalysts. *J. the Serbian Chemical Society*, 71(12): 1333-1343.
22. Shukla, A.K., P.A. Christensen, A. Hamnett and M.P. Hogarth, 1995. A vapour-feed direct-methanol fuel cell with proton-exchange membrane electrolyte. *J. Power Sources*, 55: 87-91.
23. Antolini, E. and B. Mater, 2003. Performance of highly dispersed Pt/C catalysts for low temperature fuel cells. *Chemical Physics*, 78: 563-574.