Evaluation of Stability and Catalytic Activity Of direct Methanol Fuel Cell nano-catalysts by Cyclic Voltammetry

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Abstract

Cyclic voltammetry (CV)is a very useful technique for theevaluation of fuel cell catalysts.CV is commonly employed to determinenot only the electrocatalytic activity and durabilitybut also to investigate reaction kinetics on the catalyst surface. Nanoparticles of platinum, Pt–Ni alloy and Ni@Pt core-shell as catalysts supported on multi-walled carbon nanotubes (MWCNTs)have beeninvestigated in 0.5M $LiClO_4$(neutral medium) using the CV technique. This has been employed for the electro-oxidation of methanol on catalysts surfaces.In the anodic sweepwell-defined peaks have been obtained around 0.75Vversus saturated calomel electrode (SCE), while in cathodic sweep alsosharp reverse anodic peaksaround 0.45 V havebeenobserved for the methanol oxidation reaction. In evaluation of peak currents, specific activities and mass activities Ni@Pt/MWCNTs has shown the highest values and Pt is at the lowest.Anodic polarization curves have been plotted using Tafel equation for all the catalysts and exchange current densities (i^o)arecalculated from the curves for comparison yielding higher values off^{o}for better catalysts.Specific activity showed a linear increase with square root of scan rate($v^{1/2}$) suggeststhe reaction is diffusion controlled. Plots of peak potentials vs. lnv indicate that the electro-oxidation of methanol is an irreversible process. Heterogeneous rate constants for methanol oxidationhave been calculated and are described.Durability studies of the catalysts up to fifty cycles have also been estimated. All the above features suggest that Ni@Pt/MWCNTs can be a promising catalystfor the direct methanol fuel cells.

Keywords: Core-shell nanocatalyst, Multi-walled carbon nanotubes, Cyclic voltammetry, Methanol oxidation, Direct methanolfuel cells.

Introduction

Direct methanol fuel cells (DMFCs)have received significant attention due to their economically viable and environmentally friendly characteristics like high power density, rapid start-up, lightweight andlow operating temperature with leastpollutants emission; because only water and CO_2 are produced as a by-product [1-3].The main problems faced byDMFC arelow catalyticactivity and poisoning of Pt catalysts due to CO formation. Overall,the efficiency offuel cells is highly dependent uponcatalytic activity and durability of the catalyst. In this regard development of more efficient anode and cathode nanomaterial are required to be used as a catalyst.Cyclic voltammetry (CV) is a most versatile technique employed to investigatethe various parameters of electrochemical process such asreaction kinetics, efficiency and stability of catalyst[4,5].Methanol oxidation,oxygen reductionand hydrogen evolution reactions are commonly studied on the electrode surface to investigate the electrocatalytic activity of the catalysts using CV [6-7].

Carbon nanotubes (CNTs) have gained significant attention due to theirhigher surface area and electrical conductivity as compared to Vulcan carbon (XC-72). The catalytic activity have been improved significantly when CNTs were used as a catalyst support [8,9].Moreover, bimetallic Pt-M (M = Fe, Co, Ni and Cr) nano materials supported on CNTs exhibited better efficiency and durability for methanol oxidation reaction than the nano particles of Pt alone [10-14].Efficiency of bimetallic nanoparticles depends on numerous factors like constituent of metals, their composition, particle size and surface morphology [15,16].

The fabrication of core-shell nanostructures gives high catalytic activity, excellent selectivity and long-term stability due to their unique collective and synergetic properties as compared to single component materials [17].Synthesis method also plays significant role in enhancing catalytic activity of the catalyst. Chemical co-reduction [18],successive reduction [19]and micro-emulsion [20] methodsare significant for preparation of core-shell nanoparticles.The objective of the research work is to enhance efficiency and stability of fuel cell catalyst for methanol oxidation reaction. The catalytic activity can be enhanced by increasing surface area of Pt-catalyst.While durability can be increased by using a secondary metal like Ni, Co etc. which may help the regeneration of Pt-active sites through bi-functional mechanism[10,19].

The present study comprises the evaluation of catalytic activity and stability of Ni@Pt (core-shell), Pt–Ni nanoalloy and Pt nanoparticles supported on multi-walled carbon nanotubes (MWCNTs).CV technique has been employed to investigate the electro-oxidation of methanol on the catalysts surface in neutral medium. The different electrocatalytic activity parameters like peak currents, exchange currents and heterogeneous rate constants have been estimated from the cyclic voltammograms.The stability of the catalystsup to 50 cycles has also been studied here.

Experimental
Preparation of catalysts

The pretreatment of MWCNTs is described in detail elsewhere[21]. The oxidative treatment of the MWCNTsin presence of 4:1 v/v acid mixture of 8 M HNO_3(Merck, 65%) and H_2O_2 (Applied Chem, 35%) has been performed ultrasonically.Ni@Pt core-shell nanoparticles supported

onthe treated MWCNTs have been synthesized by chemical co-reduction method in the presence of sodium dodecyl sulfate (SDS) surfactant.While Pt–Ni (nanoalloy) and Pt nanoparticles supportedon the MWCNTs have been prepared by conventional chemical co-reduction method. Loading of Ni@Pt (1:1),Pt–Ni (1:1) and Ptnanoparticles on MWCNTs is 20%, 20% and 10% respectively. The synthesized Pt/MWCNTs was taken as a reference catalyst.

Electrochemical characterization

Electrochemical measurements of the catalysts were performed using Eco Chemie Autolab PGSTAT 12 (Netherlands) with software package GPES 4.9. Three-electrode system was employed throughout the electrochemical process.Graphite rod having exposed surface area of 0.785 cm^2 was taken as a working electrode. Saturated calomel electrode (SCE) of Fisher Scientific Company with a plastic tip was employed as a reference while Pt wire gauze served as a counter or auxiliary electrode. All the measurements were carried out under Argon atmosphere at ambient temperature. For electro-oxidation of methanol in neutral medium, cyclic voltammograms (CVs) were recorded in the aqueous solution containing 0.2 M CH_3OH (Sigma-Aldrich, 99.7%) and 0.5 M $LiClO_4$ (BDH, 99%).

Working electrode fabrication

Graphite rod was insulated from the sides using epoxy resin, then washed with ethanol and distilled deionized water ultrasonically to remove organic and inorganic impurities from the surface. The electrode was polished with 0.5 μm alumina powder (CHI Inc., USA). For uniform working electrode fabrication, 8 mg of the catalyst was ultrasonically dispersed in1 mL of 2-propanol for 30 minutes, 60 μL from the resulting catalyst slurrywas carefully spread on the polished surface. After the solvent evaporation, 10 μL Nafion solution (Sigma-Aldrich, 0.5%) was applied as a binder and finally dried in desiccator.

Results and discussion

The electrocatalytic activity and stability of various catalysts towards methanol oxidation have been investigated in neutral medium using 0.5M $LiClO_4$ solution. Before electrochemical oxidation of methanol, working electrode was immersed in the electrolyte solutionto remove any impurities from the catalyst surface. For this purpose, cyclic voltammograms (CVs) were recorded in aqueous solution of 0.5M $LiClO_4$ several times until a steady-state voltammogram was obtained (6~8 cycles).

Fig. 1 exhibited characteristic CVs of Ni@Pt, Pt–Ni and Pt supported on MWCNTstowards the methanol oxidation recorded in 0.5 M $LiClO_4$ having 0.2 M CH_3OH at scan rate 50 $mV^.s^{-1}$. It can be clearly seen that the CVs measured for various catalyst shave shown similar behavior. In anodic sweeps, a well-defined and broad peak has been observed around 0.70 V due to methanol oxidation[22]. While in cathodic sweeps, a very sharp peak has been obtained at 0.46 V; itmay be attributed to the removal of carbonaceous species which were notcompletely oxidized in the forward scan [23,24]. The presence of only oxidation peaks in both forward and reverse sweeps indicates that electro-oxidation of methanol is an irreversible process [25].
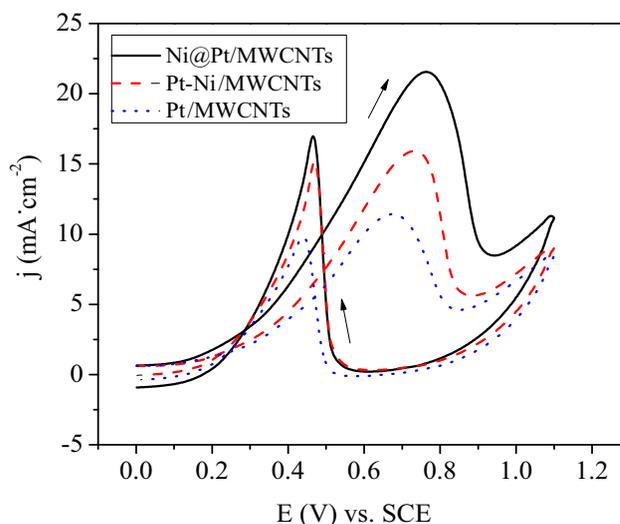
Fig. 1: Cyclic voltammograms represent methanol oxidation for various catalysts recorded in neutral medium having 0.5 M $LiClO_4$ and 0.2 M CH_3OH at scan rate 50 $mV^.s^{-1}$.

Table 1 shows various electro catalytic activity parameters like peak current (i_p), specific activity (SA) and mass activity (MA) for different catalysts evaluated from the corresponding CVs. Amount of methanol oxidized and the peak height (current)attained in forward scan is proportional to the catalyst activity[26].The MA of Ni@Pt/MWCNTs (242.29 $mA^.mg^{-1}Pt$) and Pt–Ni/MWCNTs (183.5 $mA^.mg^{-1}Pt$) is 97% and 49% higher than that of Pt/MWCNTs (122.92$mA^.mg^{-1}Pt$), respectively. Among the catalyst, Ni@Pt/MWCNTs has shown the highest value of electro catalytic activity towards methanol oxidation. It may be attributed to its higher surface area with unique collective and synergetic properties in core-shell nanostructures[17]. The comparison exhibited that the bimetallic nanoparticles has a great influence on the catalyst efficiency due to diversesurface structure, morphology of the nanoparticles and presence of the secondary metal like Ni, Co etc.

Table 1: Various activity parameters for the different catalysts determined from cyclic voltammograms measured in 0.2 M CH_3OH having 0.5 M $LiClO_4$ solution: peak current (i_p), specific activity (SA) and mass activity (MA) and heterogeneous rate constant (k_{het}) at 298 K.

The catalytic activities may be assessed by comparing value of exchange current density(i^o) that can be evaluated from the analysis of Tafel equation:$E = E^o - b^.\log i^o + b^.\log i$ [27]. Where, E is the electrode potential (V), E^o is standard potential (V), i is apparent current density ($mA^.cm^{-2}$) and b is the Tafel slope. Usually, value of potential (E^o) is taken at 0.85 i_p for irreversible system[22].Polarization curves can be drawn by plotting E vs. log i called Tafel plot. Fig. 2 depicts the anodic polarization curves for various catalysts from the corresponding CVs measured in 0.2 M CH_3OH having 0.5 M $LiClO_4$ at scan rate 50 $mV^.s^{-1}$.Values of i^o areevaluated from intercept of the Tafelplots and presented in the Table 2. The highest value of i^o for Ni@Pt/MWCNTs (16.69$mA^.cm^{-2}$) further supports the above result about its catalytic activity.

Table 1: Various activity parameters for the different catalysts determined from cyclic voltammograms measured in 0.2 M CH₃OH having 0.5 M LiClO₄ solution: peak current (i_p), specific activity (SA) and mass activity (MA) and heterogeneous rate constant (k_{het}) at 298 K.

Catalyst	i_p (mA)	SA (mA·cm^{-2})	MA (mA·mg^{-1}Pt)	$k_{het}/10^{-4}$ (cm·s^{-1})
Ni@Pt/MWCNTs	11.63	14.82	242.3	2.84
. . . ―	8.81	11.22	183.5	2.07
Pt/MWCNTs	5.90	7.52	122.9	1.44
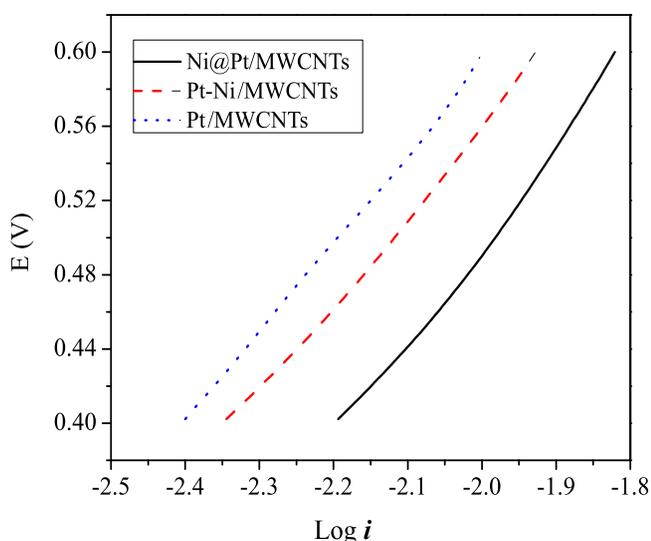
Fig. 2: Anodic polarization curves (Tafel plots) for different catalysts measured in neutral medium having 0.2 M CH₃OH and 0.5 M LiClO₄ at scan rate 50 mV·s⁻¹.

Fig. 3: Cyclic voltammograms for Ni@Pt/MWCNTs catalyst recorded at different sweep rates in 0.2 M CH₃OH having 0.5 M LiClO₄.

Table 2: Anodic polarization data evaluated from the corresponding Tafel plots: Standard potential (E^o) and exchange current density (i^o).

Catalyst	Slope "b" (V)	Intercept "a" (V)	i^o (mA·cm^{-2})
Ni@Pt/MWCNTs	0.535	1.566	16.69
Pt–Ni/MWCNTs	0.477	1.514	11.50
Pt/MWCNTs	0.480	1.555	7.68

Fig. 3 represent the CVs for Ni@Pt/MWCNTs catalyst measured in 0.2 M CH₃OH having 0.5 M LiClO₄ at different sweep rates from 20-100 mV·s⁻¹. It can be seen that the forward peak potential and current density for methanol oxidation increases when scan rate increase from 20 to 100mV·s⁻¹.

Randles-Sevcik equation [28] has been employed in order to acquire the information about the dynamic parameters of this process.A linear relationship achieved(R^2 = 0.99) between the peak current density (j) from the plot of forward CV scans and square root of the scan rate ($\upsilon^{1/2}$) is demonstrated in the Fig. 4(a). It suggests that the electrocatalytic oxidation of methanol on the catalyst surface may be controlled by diffusion process in neutral medium.Similar results have been obtained for the other two catalysts. Moreover, a linear relationship can be attained between the forward peak potential (E_p) and natural logarithm of scan rate ln(υ), as revealed in Fig. 4(b) which indicates that the electro-oxidation of methanol is an irreversible process[25, 29].Comparable results have been attained for the remaining catalysts.

The electro-oxidation of methanol on platinum catalyst is a multi-step process in which all the intermediate steps are assumed to be fast (except for the removal of CO), overall rate of the electrochemical reaction may be controlled by the oxidation of adsorbed CO[30]. The approximate values of heterogeneous rate constants (k_{het}) for the methanol oxidation on catalyst surface have been estimated from peak
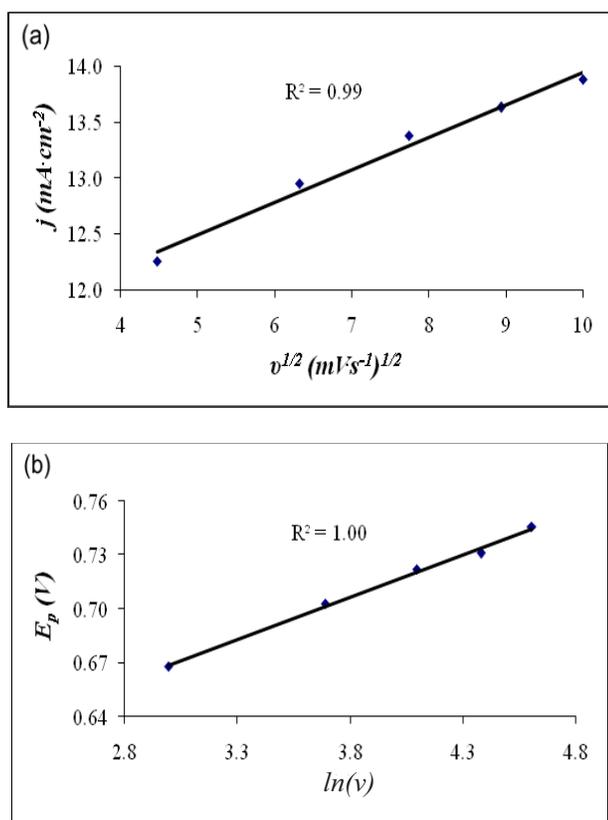
Fig. 4: (a) Plot of peak current density (j) vs. square root of sweep rate ($\upsilon^{1/2}$), (b) irreversibility plot showing peak potential (E_p) vs. ln of the sweep rate (all other details in Fig.

height using a well-known Nicholson and Shainequation for totally irreversible system[22,31]:

$$i_p^{a} = 0.227\ nFA\ Co^*\ k_{het}\ exp\ [(\alpha n_{\alpha}F/RT)(E_p - E^o)] \quad (1)$$

Where,i_p^{a} is the anodic peak current in amperes, n is number of electronsinvolved in methanol oxidation (n=6)[32], F is Faraday constant in $C \cdot mol^{-1}$, A is surface area of electrode in cm^2, C_o is concentration in $mol \cdot cm^{-3}$.The $k_{het}$is evaluated from the anodic peak currents (i_p^{a}) for various catalysts in 0.2 M CH_3OH at scan rate 50 $mV \cdot s^{-1}$ and listed in Table 1. The comparison indicates that Ni@Pt/MWCNTs nanocatalyst exhibited value of k_{het}equal to $2.84*10^{-4}$ $cm \cdot s^{-1}$ at 298 K which is almostdouble than that of Pt/MWCNTs.

Durability of the catalysts depends upon the mechanism of methanol oxidation occurring at the catalytically active sites. Fig. 5 depictsthe durability plots of the catalysts in term of current densities obtained for 0.2M CH_3OH having 0.5M $LiClO_4$at scan rate 50 $mV \cdot s^{-1}$ for fifty numbers of cycles (in a single run). After each cycle, value of current density for all catalysts decreased in neutral medium which may be due to the oxide formation of Ni (in bimetallic nanoparticles) and/or CO formation at the catalyst surface during methanol oxidation which decreased the catalytically active sitesof Pt[19]. The comparison revealed that in Pt-bimetallic nanoparticles the active sites are more effectively re-
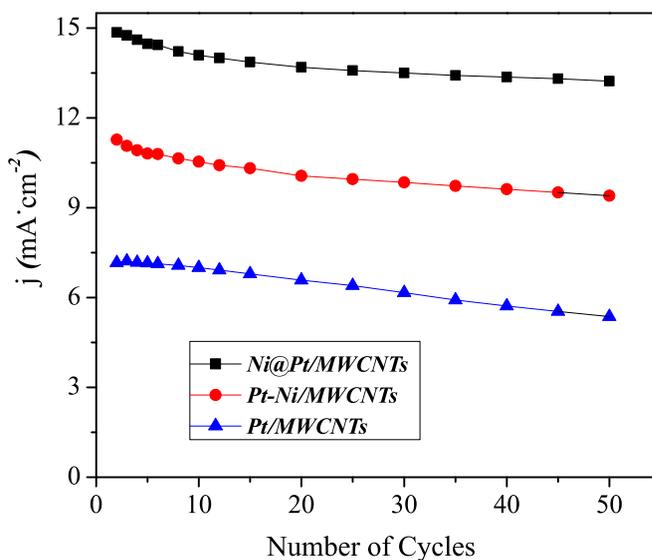
Fig. 5: Catalyst durability plots showing current density (j) vs. number of cycles in a neutral medium containing 0.5 $LiClO_4$ and 0.2 M CH_3OH (scan rate 50 $mV \cdot s^{-1}$).

generated may be due to presence of the secondary metal such as Ni through bi-functional mechanism[19], while in Pt-monometallic nanoparticles peak current density was continuously decreasing after each cycle which is due tocatalyst poisoning(CO-formation) during the methanol oxidation reaction.

Conclusion

Electrocatalytic activity and stability ofNi@Pt, Pt–Ni and Ptnanoparticles supported on MWCNTs have been evaluated for methanol oxidation reaction in neutral medium. The mass activity of Ni@Pt/MWCNTs and Pt–Ni/MWCNTs is 97% and 49% higher than that of Pt/MWCNTs, respectively. Moreover, similar trends have been observed for exchange current densities and heterogeneous rate constants for all the catalysts. The Ni@Pt/MWCNTs exhibited better efficiency and stabilitybecausethe catalytically active sites of Ptin the bimetallic nanoparticlesare more effectively re-generated through bi-functional mechanism. The present study suggests that Ni@Pt/MWCNTs can be a promising catalyst for direct methanol fuel cells.

References

1. M. Kheirmand, H. Gharibi, R. A. Mirzaie, M. Faraji and M. Zhiani, "Study of the synergism effect of a binary carbon system in the nanostructure of the gas diffusion electrode (GDE) of a proton exchange membrane fuel cell", Journal of Power Sources, Vol. 169, 2007, pp. 327-333.

2. H. Tawfik, Y. Hung and D. Mahajan, "Metal bipolar plates for PEM fuel cell-A review", Journal of Power Sources, Vol. 163, 2007, pp. 755-767.

3. A. Hayashi, T. Kosugi and H. Yoshida, "Evaluation of polymer electrolyte fuel cell application technology

R&Ds by GERT analysis", International Journal of Hydrogen Energy, Vol. 30, 2005, pp. 931-941.

4. A. J. Bard and L. R. Faulkner, "Electrochemical methods, fundamentals and applications", 2nd ed., New York: John Wiley & Sons, INC, 2001, pp. 92-105.

5. R. J. Klingler and J. K. Kochi, "Electron-transfer kinetics from cyclic voltammetry. Quantitative description of electrochemical reversibility," Journal of Physical Chemistry, Vol. 85, No. 12, 1981, pp. 1731-1741.

6. Z. D. Wei, S. H. Chan, L. L. Li, H. F. Cai, Z. T. Xia and C. X. Sun, "Electrodepositing Pt on a Nafion-bonded carbon electrode as a catalyzed electrode for oxygen reduction reaction", ElectrochimicaActa, Vol. 50, 2005, pp. 2279-2287.

7. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Markovic, "Improved oxygen reduction activity on Pt3Ni(111) via increased surface site availability", Science, Vol. 315, 2007, pp. 493-497.

8. E. Antolini, "Carbon supports for low-temperature fuel cell catalysts", Applied Catalysis B: Environment, Vol. 88, 2009, pp. 1-24.

9. Q.-Q. Fan, Z.-Y. Qin, X. Liang, L. Li, W.-H. Wu and M.-F. Zhu, "Reducing defects on multi-walled carbon nanotube surfaces induced by low-power ultrasonic-assisted hydrochloric acid treatment", Journal of Experimental Nanoscience, Vol. 5, No. 4, 2010, pp. 337–347.

10. C. -T. Hsieh and J.-Y. Lin, "Fabrication of bimetallic Pt–M (M=Fe, Co, and Ni) nanoparticle/carbon nanotube electrocatalysts for direct methanol fuel cells",Journal of Power Sources, Vol. 188, 2009, pp. 347-352.

11. N. Travitsky, T. Ripenbein, D. Golodnitsky, Y. Rosenberg, L. Burshtein and E. Peled, "Pt-, PtNi- and PtCo-supported catalysts for oxygen reduction in PEM fuel cells",Journal of Power Sources, Vol. 161, 2006, pp. 782-789.

12. E. Antolini, J.R. C. Salgado and E.R. Gonzalez, "The methanol oxidation reaction on platinum alloys with the first row transition metals. The case of Pt–Co and –Ni alloy electrocatalysts for DMFCs: A short review",Applied Catalysis B: Environment,Vol. 63, 2006, pp. 137-149.

13. J.-S. Choi, W.S. Chung, H.Y. Ha, T.-H. Lim, I.-H. Oh, S. -A. Hong and H.-I. Lee,"Nano-structured Pt–Cr anode catalyst over carbon support, for direct methanol fuel cell"Journal of Power Sources, Vol. 156, 2006, 466-471.

14. J.R. Croy, S. Mostafa, L. Hickman, H. Heinrich and B.R. Cuenya, "Bimetallic Pt-Metal catalysts for the decomposition of methanol: Effect of secondary metal on the oxidation state, activity and selectivity of Pt", Applied Catalysis A: General,Vol. 350, 2008, pp. 207-216.

15. R. Ferrando, J. Jellinek and R.L. Johnston, "Nanoalloys: From theory to applications of alloy clusters and nanoparticles", Chemical Reviews, Vol. 108, No. 3, 2008, pp. 845-910.

16. Z. Peng and H. Yang, "Designer platinum nanoparticles: Control of shape, composition in alloy, nanostructure and electrocatalytic property", Nano Today, Vol. 4, 2009, pp. 143-164.

17. G. Li and Z. Tang, "Noble metal nanoparticle@metal oxide core/yolk–shell nanostructures as catalysts: recent progress and perspective", Nanoscale, Vol. 6, 2014, pp. 3995-4011.

18. Y. Zhao, X. Yang, J. Tian, F. Wang and L. Zhan, "Methanol electro-oxidation on Ni@Pd core-shell nanoparticles supported on multi-walled carbon nanotubes in alkaline media", International Journal of Hydrogen Energy, Vol. 35, 2010, pp. 3249-3257.

19. X.-Z. Fu, Y. Liang, S.-P. Chen, J. -D. Lin and D.-W. Liao, "Pt-rich shell coated Ni nanoparticles as catalysts for methanol electro-oxidation in alkaline media" Catalysis Communications,Vol. 10, 2009,pp. 1893-1897.

20. G. Zhou, M. Lu and Z. Yang,"Aqueous synthesis of copper nanocubes and bimetallic copper/ palladium core-shell nanostructures", Langmuir,Vol. 22, 2006, pp.5900-5903.

21. P.-X. Hou, C. Liu and H.-M.Cheng, "Purification of carbon nanotubes", Carbon, Vol. 46, 2008, pp. 2003-2025.

22. A. S. A. Khan, R. Ahmed and M. L. Mirza, "Comparison of catalytic activities of carbonsupported Pt and Pt-Ru catalysts for methanol oxidation in neutral and basic media by cyclic voltammetry", Turkish Journal of Chemistry, Vol. 32, 2008, pp. 743-753.

23. J. C. Huang, Z. L. Liu, C. B. He and L. M. Gan, "Synthesis of PtRu nanoparticles from the hydrosilylation reaction and application as catalyst for direct methanol fuel cell", Journal of Physical Chemistry B, Vol. 109, 2005, pp. 16644-16649.

24. R.N. Singh, A. Singh and Anindita, "Electrocatalytic activity of binary and ternary composite films of Pd, MWCNT and Ni, Part II: Methanol electrooxidation in 1M KOH", International Journal of Hydrogen Energy, Vol. 34, 2009, pp. 2052-2057.

25. R. Pattabiraman, "Electrochemical investigations on carbon supported palladium catalysts" Applied Catalysis A General, Vol. 153, 1997, pp. 9-20.

26. N. Rusnaeni, W. Purwanto, M. Nasikin and L. Hendrajaya, "The Influence of Pt Atomic Ratio in the Activity PtNi/C Nanocatalysts for the PEMFC", ITB Journal of Engineering Science, Vol. 43, 2011, pp. 1-10.

27. S. Yan, S. Zhang, Y. Lin and G. Liu, "Electrocatalytic performance of gold nanoparticles supported on activated carbon for methanol oxidation in alkaline solution", Journal of Physical Chemistry C, Vol. 115, 2011, pp. 6986-6993.

28. Z. P. Sun, X. G. Zhang, Y. Y. Liang and H. L Li, "Highly dispersed Pd nanoparticles on covalent functional MWNT surfaces for methanol oxidation in alkaline solution" Electrochemistry Communication, Vol. 11, 2009, pp. 557-561.

29. Z. X. Zheng, Y. L. Du, Z. Wang, F. Zhang and C. Wang,

"Highly dispersed Pd nanoparticles on covalent functional MWNT surfaces for methanol oxidation in alkaline solution", Journal of Molecular Catalysis A: Chemical, Vol. 363-364, 2012, pp. 481-488.

30. A. S. A. Khan, R. Ahmed and M. L. Mirza, "Cyclic voltammetric study of electro-oxidation of methanol on platinum electrode in acidic and neutral media", The Nucleus, Vol. 44, 2007, pp. 133-141.

31. R. N. Hegde, B. E. K. Swamy, B. S. Sherigara and S. T. Nandibewoor, "Electrooxidation of atenolol at a glassy carbon electrode", International Journal of Electrochemical Science, Vol. 3, 2008, pp. 302-314.

32. E. A. Franceschini, M. M. Bruno, F. A. Viva, F. J. Williams, M. Jobbagy and H. R. Corti, "Mesoporous Pt electrocatalyst for methanol tolerant cathodes of DMFC", ElectrochimicaActa, Vol. 71, 2012, pp. 173-180.