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Enhanced performance of ethanol oxidation on mesoporous carbon supported ternary Pt–Sn–Pd catalyst for membraneless fuel cell

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Abstract : The mesoporous supported ternary Pt–Sn–Pd catalysts synthesized by sodium borohydride reduction method. X-ray diffraction spectroscopy (XRD) demonstrated the representative characterization of a crystalline Pt face centered cubic (fcc) structure, evaluated with that of Pt/MP, the lattice parameter of Pt–Sn–Pd/MP catalysts enlarges, its diffraction peaks are shifted little towards a lower 2θ values. It designates to Sn and Pd be well incorporated into Pt alloy surface. Transmission electron microscopy (TEM) represents that the Pt–Sn–Pd nanoparticles among a crystallite size near to 3 nm are extremely dispersed on the surface of MP. The electro-catalytic performance of the combined catalysts for electro-oxidation of ethanol was examined with cyclic voltammogram (CV), and chronoamperometry (CA). The consequences designate that alter of Pd and support using MP could promote extensively the catalytic performance for ethanol electro-oxidation. The Pt–Sn–Pd/MC catalysts exhibit a higher intrinsic activity for ethanol electro-oxidation than Pt–Sn/MC, Pt–Sn–Pd/MC. The Pt–Sn–Pd/MC catalyst with a best among all different compositions for electro-oxidation, which may be attributed to the high surface area, good electrical conductivity and uniformly distribution of particles in the mesoporous carbon support materials. The single menbraneless ethanol fuel cell (MLEFC) experiment results demonstrate that Pt–Sn–Pd/MC given the high power density and current density among they prepared catalysts.

Keywords : Membraneless fuel cells, Platinum, Palladium, Tin, Sodium Perborate

Introduction

Fuel cell is electrochemical cell produced energy from fuel and oxidant flow continuously; energy production occurs without noise and side product formed only the water and heat[1]. Several type of fuel cell is present, membraneless fuel cell is the one of the growing technology for energy production. It is more advantages compared to proton exchange membrane fuel cell, such that anode and cathode stream continuously flow the single channel without disordered mixing, no ion exchange membrane required, sealing, manifolding, no need any special treatment for water management and operate at normal temperature [2,3]. Membraneless fuel cell applicable in very essential for the portable device such that DNA analysis, Blood diagnostics, iso-electric focusing, and circuit boards [4]. Ethanol recently attractive fuel energy production technology for fuel cell, due to be essential properties such that, easily handled, liquid, storage, transport and high energy density. MLEFCs have established remarkable interest from the educational and commercial for the huge reward that ethanol suggest as a fuel designed the anodic oxidation reaction [5].

Pt has been considered as best catalyst for electrochemical reaction obtained anode material for ethanol fuel cell. Even if Pt is very high cost and absorption of ethanol oxidation intermediate such that methane, acetaldehyde and carbon monoxide hindered electrochemical reaction[6]. Although regulate to overcome this limitation adding to the second metal into Pt surface it is increase the OH species ethanol oxidation reaction to bifunctional mechanism and electronic effect[7]. In order improve the cell performance several metal, such that

Ru, Sn, Mo, Rh, W and Pb added co catalyst into Pt surface to alloy formation [8,9]. Among them Pt–Sn/C catalyst improved electrochemical reaction at normal temperature due to OH molecules is formed on SnO_2 surface, easily oxidized adsorbed intermediate [10]. Zhou et.al found that Pt–Sn/C catalyst increase the cell potential compared to other binary catalysts [11]. Gonza et.al observed that Pt–Sn/C catalyst best catalytic activity for ethanol oxidation reaction compared to the ethylene glycol [12]. Furthermore ethanol anode reaction sufficient for fuel cell reaction due to Sn is migrating away from the Pt catalysts surface during the long time operation. To enhance the electrochemical activity of ethanol oxidation and increase the stability of Pt-Sn surface third metal added to Pt–Sn surface [13,14].

Conversely, the catalysts by carbon support materials will stimulate a decrease in the active compound beneath extensive period operation. Moreoverthe major problems are through respect to the stability of membraneless fuel cell equipment [14]. Conventionally recommended to the use of carbon support materials by means of ordered configuration and elevated electrical conductivity enhanced the fuel cell performance, and since, numerous research group have lately made efforts toward synthesize and use dissimilaroriginal carbon supports such as nanofibers [15,] carbon microspheres [16], nanotubes [17], carbon aerogels and xerogels [18,],hard carbon spherules [19], and mesoporous carbon for fuel cell applications [20].In particular, mesoporous carbon (MC) have been widelystudies as catalyst support materials for the electro-oxidation of ethanol, mainly for their high surface area and their good electrical conductivity that formulate them good applicant to change the commercial Vulcan XC-72R support materials. In this paper discussed about the membraneless fuel cell, ethanol used as a fuel, sodium perborate[21-23] used as an oxidant and mesoporous supported Pt–Sn–Pd used as the catalyst.Catalysts were prepared by the sodium borohydride reduction method. Pd is the non noble metal, abundant is very high, cost is very less and added to the third metal in the Pt–Sn surface enhance the oxidation reaction. Prepared catalyst like that binary based catalyst Pt–Sn/MC (50:50) and Pt–Pd/MP(50:50)and ternary based catalyst Pt–Sn–Pd/MC(50:35:15) and Pt–Sn–Pd/MC were characterized by the physical method, such that X-ray diffraction method, energy dispersive analysis, transmission electron microscopy analysis and chemical method for cyclic voltammetric analysis and chronoamperometric technique represent the mesoporous support ternary based catalyst shown the best performance for the ethanol oxidation reaction in membraneless fuel cell. The Single cell performance results also representthe mesoporousternary based catalyst exhibit the high power density and cell potentials.

Experimental

Materials

The precursors used for the preparation of catalysts were H_2PtCl_6. $6H_2O$, $SnCl_2$. $2H_2O$, $(NH_4)_2PdCl_4$and mesoporous carbon (MC), Vulcan XC-72 carbon support.Graphite plates (3 cm long and 0.1 cm wide,from E-TEK) were used as substrates for the catalyst to prepare the electrodes. Deionized water (DI) and isopropanol mixed solution was used as the solvent; Nafion® (DE 521, DuPont USA) dispersion was used to make the catalyst slurry. Ethanol (from Merck), sodium perborate(from Riedel) and H_2SO_4 (from Merck) were used as the fuel, the oxidant and as the electrolyte for electrochemical analysis, respectively; all the chemicals were of analytical grade.Pt/C (40-wt%, from E-TEK) was used as the cathode catalyst.

Preparation of Catalysts

Pt–Sn–Pd/MC catalyst is prepared by sodium borohydride reduction method. The metal sourcesand supportof mesoporouscarbon was dissolved in water and propanolcombination solution. The metal precursor was dissolved in deionized water and carbon support dispersed solution was added to the precursor solution. The obtained solutions are ultrasonicated for 10minutes, after the sodium borohydride solution added drop wise and stirred for numerous hours at normal temperature. Finally the mixture was filtered, washed with deionized water repeatedly and dried at 70° C for 2h[24].The resulting catalyst was characterized by physical and chemical methods.Above mentioned same procedure followed by the preparation of the mesoporous carbon support Pt/MC, Pt–Sn/MC, Pt–Pd/MC and Pt–Sn–Pd/MC based catalysts.

Physical and Chemical Characterization

The prepared catalyst morphology was found used the transmission electron microscopy(Philips CM 12) while the particle dispersion and mean particle size also determined. The X-ray diffraction (XRD) analyses be used to find out crystal structure of the prepared catalyst using a Rigakumultiflex diffractometer(model RU-200 B) with Cu-$K_{\alpha l}$ radiation source ($\lambda_{k\alpha l}$ = 1.5406Å) operating temperature. The tube current was 40mA with a tube voltage 40kV. The 2θ angular regions between 20° and 90° were recorded at scan rate of 5° min^{-1}. The crystallite size was found out Scherrer's equation [25].The diffraction peak of Pt lattice (111), (200), (220), (311) and (222) shown five plan but crystallite size calculated by given formula only for (220) plane due to avoided the carbon distraction.

$$D = \frac{0.9\lambda_{k\alpha l}}{\beta_{2\theta}\cos\theta_{max}} \qquad \rule{8cm}{0.4pt} \qquad (1)$$

Where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at the maximum intensity (FWHM) in radians and θ is the Bragg angle, 0.9 is the shape factor for spherical crystallite and D is the crystallite size. Crystallite size must be smaller or equal to the grain size [26, 27] .The lattice parameter of the prepared catalyst determined given the equation.

$$a = \frac{\sqrt{2}\lambda_{k\alpha l}}{\sin\theta_{max}} \qquad \rule{8cm}{0.4pt} \qquad (2)$$

The composition ratios were evaluated by energy-dispersive X-ray (EDX) method using an integrated TEM (Transmission Electron Microscope) instrument.The particle size of prepared catalyst is observed by TEM.

Electrochemical measurements were carried out using the thin porous coating technique [36 28]. For the electrochemical measurements, 20 mg of the catalyst dispersed in a solution of 50 ml of water containing three drops of 6% polytetrafluoroethylene (PTEF) suspension. The mixture was treated in an ultrasound bath for 10 min and shifted to the hole of the working electrode. Electrochemical analysis were worked about the three-electrode cell with on CH instruments, model (CHI6650, USA) controlled by a personal computer using the CHI software, at normal temperature. Cyclic voltammetry (CV) and chronoamperometry (CA) technique was used for the measurements. Catalyst coated glass carbon electrode (GCE, 3mm diameter and 0.071 cm2 of electrode area, from CHI, USA) was used as the working electrode. Ag/AgCl in saturated KCl was used as the reference electrode (RHE). The catalyst slurry was ten drop-cast on to a glassy carbon electrode and allowed to dry at 100°C for 30 minutes. In cyclic voltammetry and chronoamperometry experiments, the current values (I) were expressed in amperes and were normalized per gram of platinum. The quantity of platinum was calculated considering the mass of the catalyst present in the working electrode multiplied by its percentage of platinum. Cyclic votammetrytest were performed in 0.5M $H_2SO_4$and 1MC_2H_5OH while the chronoamperommetry test of the prepared catalysts were analyzed the cell potential at 0.8V in 0.5M H_2SO_4 and 1M C_2H_5OHsolution at normal temperature. During the testing time every 30 minutes after argon gas passed through the electrolyte and ethanol solution due to the removal of oxygen free molecule.

Result and Discussion

X-Ray Diffraction (XRD)

Fig.1 show XRD pattern of prepared catalyst Pt/MP (100), Pt–Sn/MC (50:50), Pt–Pd/MC(50:50) Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC (50:35:15) while prepared catalysts showed the typical structure of Pt. 25° to 35° reflection plan showed the carbon support of Vulcan-72 R. The configuration of the crystalline and alloyed phase of Pt catalyst has been established by the (111), (200), (220) and (311) plans. Additional peak attributed to 33° and 51° represented the tetragonal structure of tin oxide [28, 29]. The prepared catalyst 2θ value of Pt/MC compared to binary catalysts Pt–Sn/MC (50:50) catalyst shown that lower value and Pt–Pd/MP catalyst shown the higher value[30]. Supplementary ternary based Pt–Sn–Pd/MC represent higher 2θ value compared to binary Pt–Sn/MC and Pt–Sn–Pd/MC, due to small evenly distributed support materials. No characteristic of palladium and palladium oxide are detected. The crystallite size of prepared catalyst range is 3-4 nm.

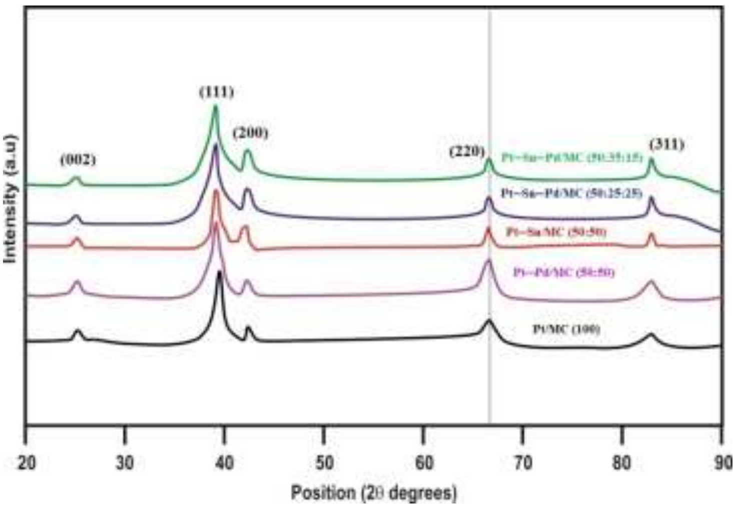

Fig.1. XRD patterns for the prepared catalysts a)Pt/MC (100), b)Pt–Sn/MC (50:50), c)Pt–Pd/MC(50:50), d)Pt–SnPd/MC(50:35:15), f) Pt–Sn–Pd/MC.

Table 1 shown lattice parameter value of Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC catalyst were lattice parameter calculated used the Schrrer formula. It is explained binary Pt–Sn/MC lattice parameter is (0.3945) indicated lattice expansion and Pt–Sn–Pd/MC lattice parameter is (0.3913) indicated that lattice contraction but Pt–Sn–Pd/MP showed the lattice expansion compared to Pt/MC. Both value clearly shown Sn and Pd metals incorporated into Pt surface.

Table 1.The EDX composition, lattice parameters, and the particle size obtained for Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC (50:35:15) different atomic ratios of catalysts.

Electrocatalyst	**Nominal atomic ratio**			**EDX Atomic ratio**			**Lattice parameter (nm)**	***2θ***	**Crystallite size (nm)**	**Particle size from TEM (nm)**
	Pt	Sn	Pd	Pt	Sn	Pd				
Pt/MC	100	-	-	-	-	-	0.3916	67.54	-	-
Pt–Sn/MC	50	50	-	52	48	-	0.3945	66.98	4.5	4.1
Pt–Pd/MC	50	-	50	54	-	46	0.3903	67.82	4.3	4.0
Pt–Sn–Pd/MC	50	35	15	49	38	13	0.3913	67.60	3.1	2.9
Pt-Sn-Pd/MC	50	34	16	48	39	13	0.3915	67.62	2.9	2.7

Transmission Electron Microscopy (Tem)

The fig.2 shown the tem image of prepared Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC (50:35:15) catalyst. The morphology of prepared catalyst represents spherical shape and uniformly dispersion of particle on carbon support, average particle size of all the catalyst is 3-5 nm. Table 1 shown that ternary based Pt–Sn–Pd/MP catalyst has smaller particle size compared to among those catalysts. XRD result also showed that Pt–Sn–Pd/MP smaller crystallite size. Both experiment value confirmed that ternary catalyst have smaller size compared to all the prepared catalysts.

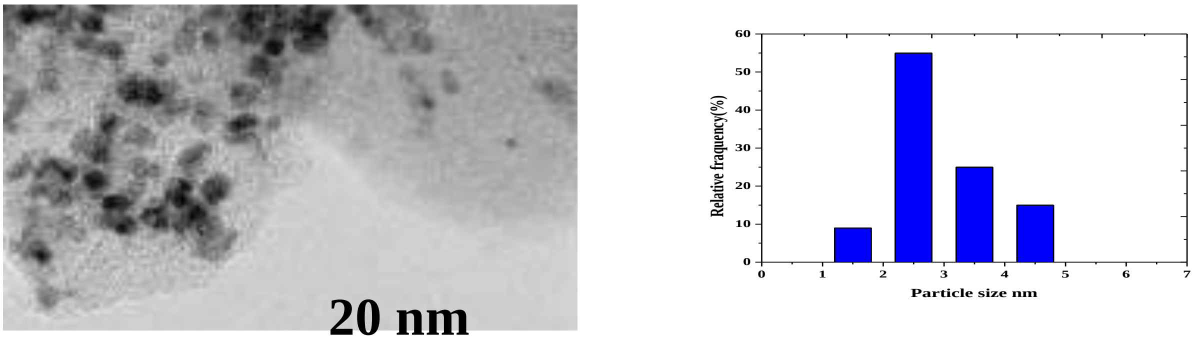

Fig. 2. Tem images for the prepared catalyst Pt–Sn–Pd/MC.

Energy Dispersive X-Ray Spectroscopy (EDX)

Fig. 3 shown the energy dispersive X-ray spectrum of the Pt/MC, Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC and Pt–Sn–Pd/MC (50:35:15). EDX analysis used to determine the chemical composition of prepared catalyst. The composition of prepared catalyst shown table1 and represent the theoretical and experimental percentage is better as matched. Although confirmed that metal precursors are reduced to metal particles showed the given spectrum.

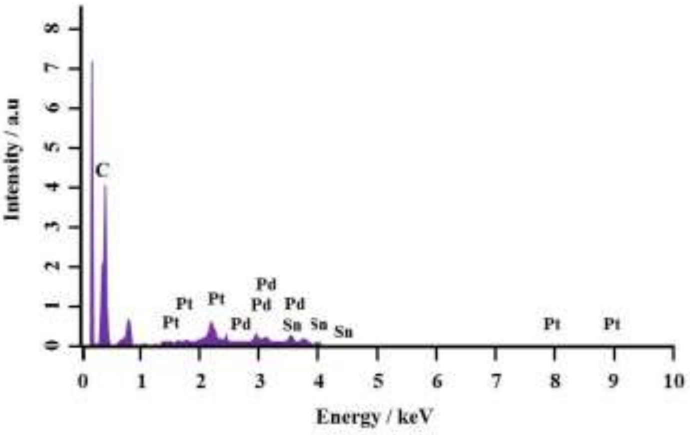

Fig .3.EDX spectra of a) Pt–Sn–Pd/MC.

Cyclic Voltammetry

The fig. 4a represents the hydrogen adsorption and desorption peak of Pt/MC, Pt–Sn/MC, Pt–Pd/MC, Pt–Sn–Pd/MC and Pt–Sn–Pd/MCcatalyst in 0.5M H_2SO_4. A hydrogen adsorption –desorption region clearly absorbed 0.05-0.35V. Pt/MC and Pt–Sn/MC catalysts shown well known hydrogen adsorption regain, although Pt–Sn/MC double layer adsorption at 0.05 -0.8V [31]. Pt–Pd/MC and Pt–Sn–Pd/MC shown the good hydrogen adsorption region compared to the Pt/MP and Pt–Sn–Pd/MC due the presence of the Pd increases the OH adsorption in the double layer region, since Pd is small size compared to that Pt and Sn [32 33]. This result demonstrates that Pt–Sn–Pd/MC shown better adsorption and desorption region compare to among the catalyst.

Fig 4. Shown typical cyclic voltammograms obtained with Pt binary and ternary catalyst deposited on the different carbon supports presence in the 0.5M H_2SO_4 and 1M C_2H_5OH. Pt/MC catalyst shown the onset potential is more than 0.4V due to strongly adsorption of CO in Pt surface [34 35]. Binary based catalyst Pt–Sn/MC onset potential is 0.30V and Pt–Pd/MC ethanol oxidation start at above 0.5V. Pt–Sn–Pd/MC onset potential started at 0.25V is low compared to Pt–Sn binary catalyst. Mesoporous supported Pt–Sn–Pd/MC (50:35:15) onset potential is very low compared to among all the catalyst;this could be ascribed to the ordered porous structureand good electrical conductivity of the support that permitanimproved electron transfer and distributionof the reactive and by products. Pt–Pd/MC shown the very high onset potential compared to Pt/MC for the reason that Pd is best performance occur only formic acid reaction and more active to the alkaline medium [36]. Even though addition of Pd on Pt–Sn surface is enhance ethanol oxidation reaction. Here Pd role is activating the Pt–Sn catalyst, not involved the ethanol oxidation reaction and also Pd is small easily incorporated to the Pt–Sn surface reduce the adsorption of the intermediate. The result demonstrate that ternary based Pt–Sn–Pd/MCshown the higher potential and low onset potential, hence enhance the ethanol oxidation reaction in membraneless fuel cell.

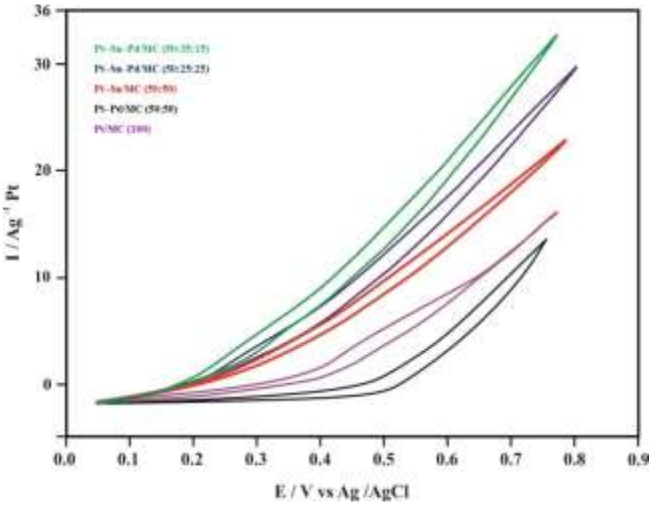

Fig.4. Cyclic voltammograms for ethanol oxidation for Pt/MC (100), Pt–Sn/MC(50:50), Pt–Pd/MC(50:50), Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC (50:35:15) in 0.5M H_2SO_4 + 1.0M CH_3CH_2OH solution at normal temperature.

Table 2.Pt/MC (100), Pt–Sn/MC (50:50),Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15) in 0.5M H_2SO_4 + 1.0M CH_3CH_2OH solution at normal temperature

Catalyst	**Scan rate 10 mV/s^{-1}**	
	Positive peak potential (mV vs. Ag/AgCl	Peak current density (mA/cm^2)
Pt/MP (100)	780	12.73
Pt–Pd/MC (50:50)	756	15.8
Pt–Sn/MC (50:50)	726	21.3
Pt–Sn–Pd/MC (50:35:15)	738	29.76
Pt–Sn–Pd/MC(50:35:15)	742	36.41

Chronoamperometry

Stability test of prepared catalyst carried at 0.500V for 2h shown fig 5. Estimate performance of catalysts and poisoning effect of catalyst during the experiment conditions. Fig 5 represent that first five minutes, a quick diminish in current density, go after slow diminish to current standards for throughout long periods experiment. The 0.500V potential applied to ethanol solution first, the ethanol molecule adsorbed to water then converted into intermediate like that, CO, CHx and acetaldehyde. Further oxidation of acetaldehyde into acetic acid and carbon dioxide require water molecule [37]. Although initially absorbed intermediate block absorption of the water molecule into Pt surface, in this reason, starting decay of stability of the catalysts. Consequently results obtained due to strongly adsorbed intermediate causes poisoning of prepared catalysts. The ternary Pt–Sn–Pd/MC catalysts give better result than Pt–Sn/MC,Pt–Pd/MC, Pt/MC and Pt–Sn–Pd/MC (50:35:15) catalysts. Nevertheless, superior activity acquired for ternary catalysts could be elucidated by action of beneficial synergistic effect between tin and palladium. Additionally, introduction of Pd into Pt–Sn binary catalysts can direct to a raise in surface oxophilic nature.

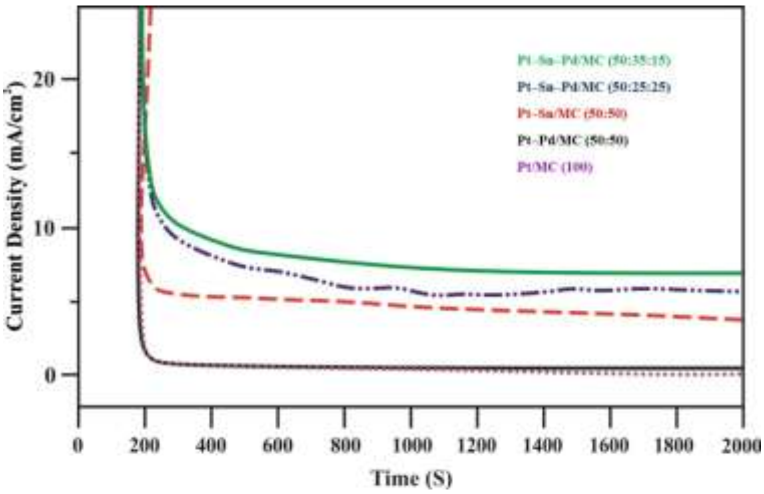

Fig.5.Chronoamperometry result for ethanol oxidation for Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15), Pt–Sn–Pd/MC (50:35:15) in 0.5M H_2SO_4 + 1.0M CH_3CH_2OH solution at normal temperature.

Single Cell Performance

Fig.6 shows polarization graph of optimized Pt/MC (100), Pt–Pd/MC (50:50), Pt–Sn/MC (50:50) and Pt–Sn–Pd/MC (50:35:15) Pt–Sn–Pd/MC (50:35:15) used membrane less ethanol fuel cell (MLEFC) anode catalyst. In single cell experiment tested by 1M ethanol solution used as fuel and 0.5M sodium perborate solution used as an oxidant and prepared catalyst for ethanol oxidation reaction. The open circuit voltage of prepared catalyst obtained for Pt–Pd/MC and Pt/MC catalysts is 0.487V and 0.543V, correspondingly, while the ternary catalyst Pt–Sn–Pd/MC, binary Pt–Sn/MC catalysts is 0.723V and 0.632V and Pt–Sn–Pd/MC (50:35:15 supporting materials 734V. Table 3 clearly shown that ternary catalysts Pt–Sn–Pd/MC (35.58mWcm^{-2}) is high power density than that of the binary Pt–Sn/MC (22.26mW cm^{-2}).

Table 3.Summary of performance of single fuel cell tests using Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC(50:35:15).

Anode Catalysts	Open circuit voltage (mV)	Maximum power density (mW/cm^2)	Current density at maximum power density (mA/cm^2)
Pt/MC (100)	0.543	4.65	43.76
Pt–Sn/MC (50:50)	0.632	22.26	135.55
Pt–Pd/MC (50:50)	0.487	11.5	89.20
Pt–Sn–Pd/MC (50:35:15)	0.723	33.28	180.15
Pt–Sn–Pd/MC (50:35:15)	0.734	35.56	200.15

The highest catalytic activity of Pt–Sn–Pd/MC could be ascribed to the synergy between the elements of catalystsand supporting materials attributed to the unique structural propertiesmakes them more accessible surface area of the ethanol oxidation reaction. It might be coupled a change in Pt electronic effect related with formation of Pt–Sn–Pd alloys that also attributed to a bifunctional mechanism in which Pt influence ethanol adsorption and dissociation[38]. Experimental results determined addition of Pd to anode catalyst can reduce quantity of Pt without any diminish in the cell performance.

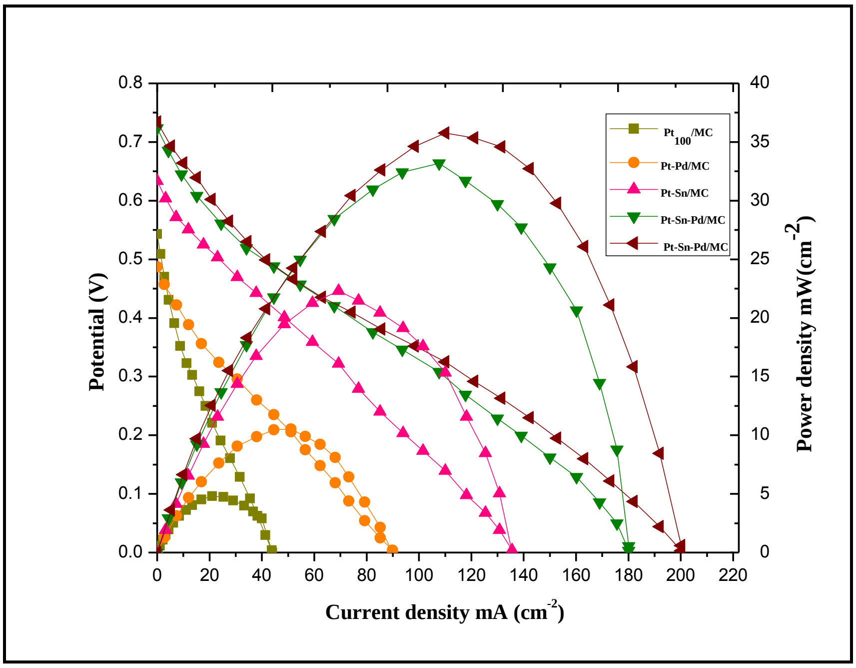

Fig.5. Polarization and power density cure of prepared catalysts for Pt/MC (100), Pt–Sn/MC (50:50), Pt–Pd/MC (50:50), Pt–Sn–Pd/MC (80:10:10), Pt–Sn–Pd/MC (50:35:15).

Conclusion

In this present study membraneless ethanolfuel cell demonstrate that Pt/MC (100), Pt-Pd/MC (50:50), Pt–Sn/MC(50:50),Pt–Sn–Pd/MC (50:35:15) and Pt–Sn–Pd/MC (50:35:15) catalysts were synthesized by sodium borohydride reduction method. The electrochemical result of cyclic votammetry and chronoamperometry experiment attributed that ternary based catalyst Pt–Sn–Pd/MC represent excellent electrochemical activity for ethanol oxidation reaction. Additionally the physical characterization of the transmission electron microscopy evaluation represent that metal nanoparticles were uniformly dispersed on the mesoporous support material. X-ray diffractograms experimental results confirmed that prepared catalyst all are shown Pt alloy formation, crystallite size of the ternary catalyst small and this observation coordinate with the TEM analysis experiment. Energy dispersive X-ray analysis experiment also demonstrates that experiment composition better as same the theoretical composition. The membraneless ethanol single cell test of polarization graph demonstrates that ternary Pt–Sn–Pd/MC catalysts superior power density (35.56mW cm^{-2}) than Pt–Sn–Pd/MC (50:35:15), Pt–Pd/MC, Pt–Sn/MC and Pt/MC. The enhanced performance of Pt–Sn–Pd/MC (50:35:15) catalyst showed that in membraneless fuel cell, combination of bifunctional mechanism and combination of Pd and mesoporous support which directed to formation of intermediate changed to the desired product. The membraneless ethanol fuel cell is an environmentally friendly and higher energy production system for future portable devices.

Acknowledgments

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