行政院國家科學委員會專題研究計畫　期中進度報告

子計畫一：甲醇燃料電池新型電極材料之開發與應用(1/3)

計畫類別：整合型計畫
計畫編號：NSC93-2218-E-009-066-
執行期間：93年11月01日至94年11月30日
執行單位：國立交通大學材料科學與工程學系(所)

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報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中　華　民　國　95年6月16日

1. Introduction

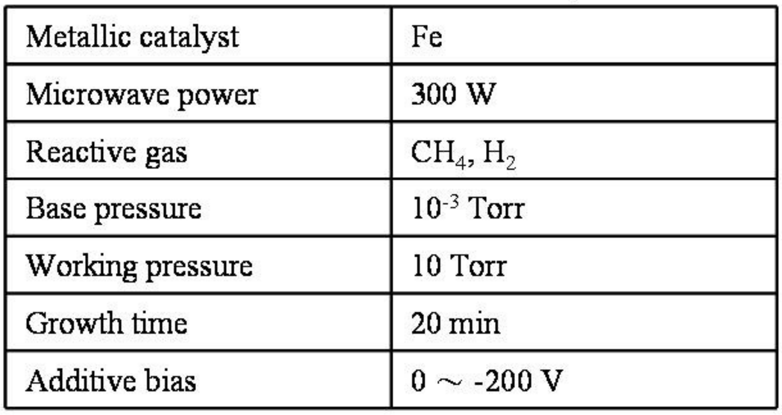
Carbon nanotubes and related materials have been investigated as catalyst supports for fuel cell applications in the past decades. The dispersions of Pt or Pt-Ru catalysts on CNTs have been widely reported recently, and shown the improvement of electrocatalytic properties by using CNTs as catalyst supports [1-7]. However, conventional dispersion approaches of Pt on CNTs based on wet impregnation and chemical reduction of the metallic precursors, which require a series of complex procedures and a lot of time. Also, the remove of chemical solvents and other contaminants is a crucial step for preventing the degradation of cell performance. It is everyone's expectation to find out a simple and convenient way for fulfilling the needs of catalysts deposition.

In this report, a fast, convenient and simple way to disperse Pt on CNTs supports is demonstrated by using a rf-magnetron sputtering system.

2. Experimental procedures

Multi-wall carbon nanotubes were fabricated directly on carbon cloth (E-TEK) by bias assisted microwave plasma enhanced chemical vapor deposition (MPECVD). Iron was first deposited on the carbon cloth with area of 1cm^2 by ion beam sputtering deposition for 10 min. It was mainly used as the catalyst for synthesizing carbon nanotubes. The reactive gas species were methane and hydrogen with a ratio of 1/4. The microwave power and the working pressure were set at 300W and 10Torr, respectively. The additive bias was adjusted from 0V to -200V. All of the experimental conditions for synthesizing MWCNTs are listed in Tab.1. An optical pyrometer was used to monitor the substrate temperature which was about 600^{o}C.

Polarization curves were obtained by the fuel cell testing system (BEAM 75M FC system) using a commercial single cell with a working area of 1 cm^2. 2M methanol solution was fed to the anode side at a flow rate of 3 ml min^{-1}. Oxygen was fed to the cathode side at a flow rate of 500 ml min^{-1}. The single cell was operated at 70°C.



Metallic catalyst	Fe
Microwave power	300 W
Reactive gas	CH_4, H_2
Base pressure	10^{-3} Torr
Working pressure	10 Torr
Growth time	20 min
Additive bias	0 ～ -200 V

Tab.1 Growth condition of MWCNT by MWCVD.

3. Result and discusions

3.1 Directly synthesis of CNTs on carbon cloth

Fig.1 shows the carbon nanotubes were directly grown on carbon cloth by MWCVD under different additive bias. Fig.2 (a) is the image of carbon nanotubes grown without applying bias. Fig.1 (b), (c),and (d) are images of carbon nanotubes grown on carbon cloth with applying negative bias of -100V,-150V and -200 V, respectively. It is easy to find that the length of CNTs is enlarged with the increasing negative bias voltage. It has been reported generally that applying negative bias could enhance the nucleation density of diamond [8-10].This might enhance the growth rate of carbon nanotubes result in the elongation of tube's length. However, the distance between carbon nanotubes under -200V is very small. This is difficult to deposit noble catalysts onto the surface of carbon nanotubes uniformly by sputtering. On the contrary, carbon nanotubes grown without applied bias shown poor growth rate. Therefore, we choose the condition of applied -100V as the optimal bias voltage for growing CNTs on carbon cloth in this chapter.

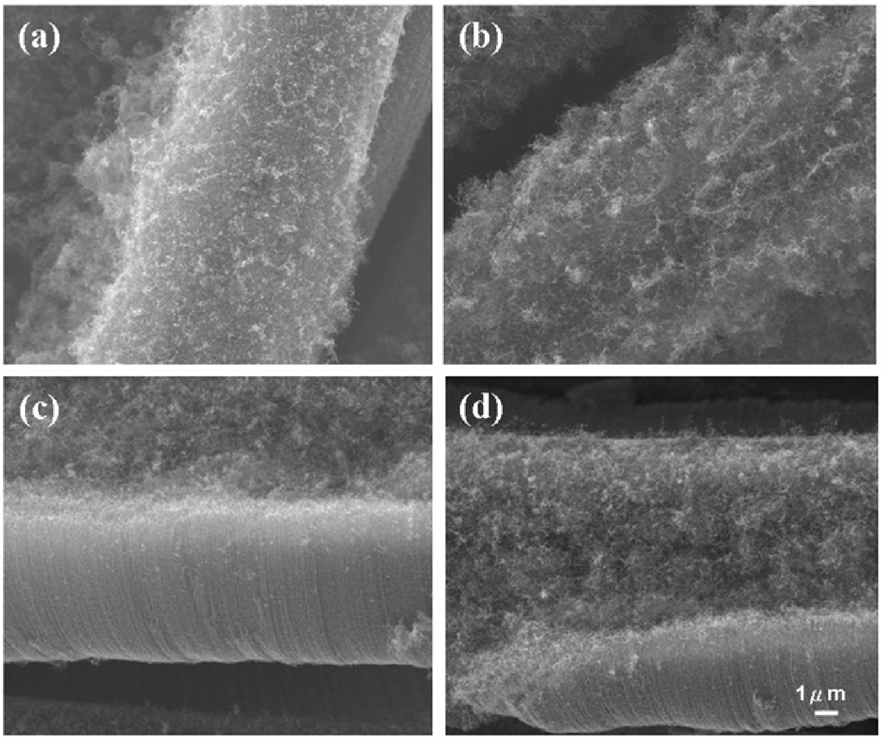


Fig.1 SEM images of different negative bias for synthesizing carbon nanotubes on carbon cloth: (a) 0V,(b)-100V,(c)-150V,and(d)-200V.

The nano-structure of the carbon nanotube grown under -100V is shown in Fig.2. The outer and inner diameter of carbon nanotubes are about 20 nm and 10nm, respectively. It is found that the amount of amorphous carbon around the outer shell of nanotube is very small; this indicates that the crystallinity of these carbon nanotubes is good.

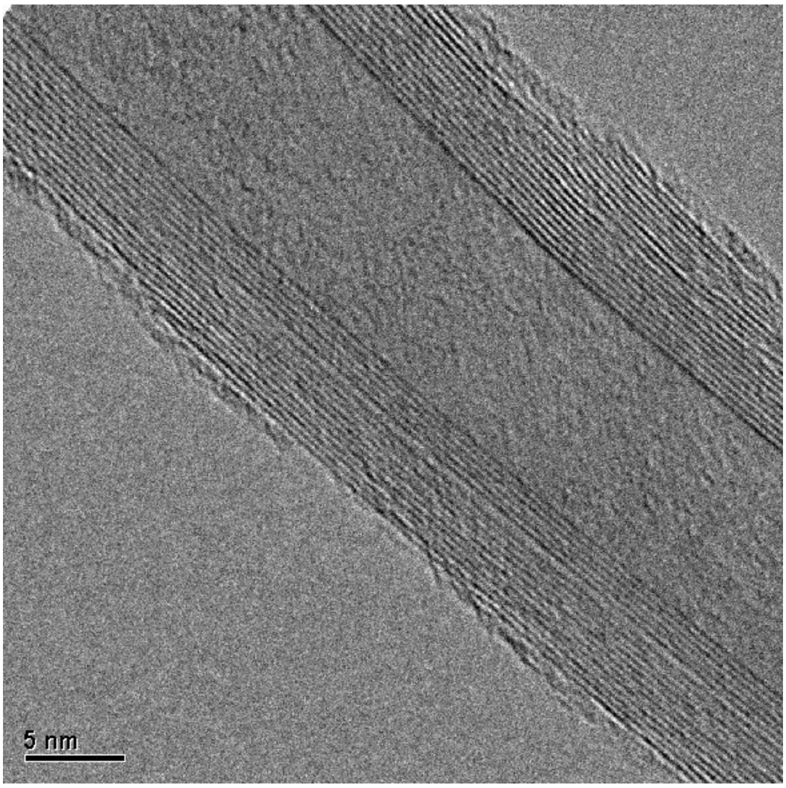


Fig.2 TEM images of carbon nanotubes growth with applied -100V.

3.2 Characterizations of sputtered Pt/CNTs

The deposition of platinum nanoparticles on carbon nanotubes was carried out by means of a rf-magnetron sputtering (SYSKEY rf-magnetron sputtering) The metal loading of Pt/CNTs catalyst can be easily controlled by varying sputtering time, which depicts in Fig.3. The metal loading was measured by TGA and EDX. Based on MWCNTs will totally burn out at 900oC in O_2 atmosphere, and the residues should be Pt nanoparticles. We can identify the metal loading of Pt by TGA.

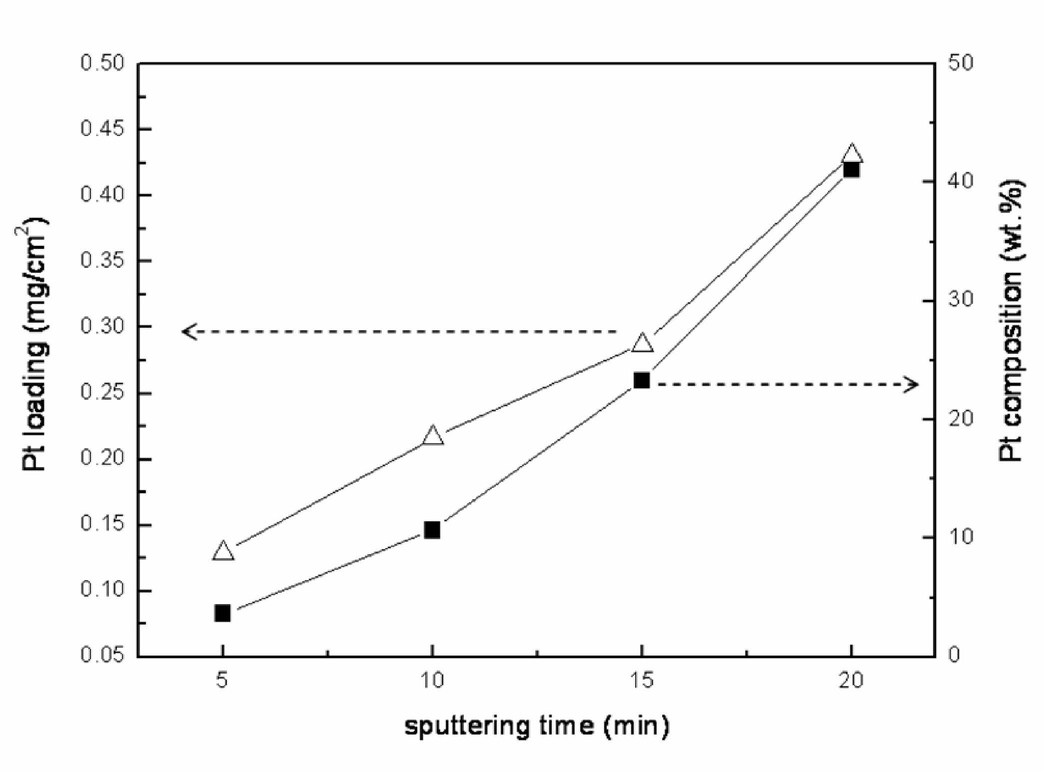


Fig.3 The metal loading and wt.% of sputtered Pt/CNTs

The morphologies of sputter-deposited Pt/CNTs under various sputtering time observed by SEM were given in Fig.4. The Pt particles become large from several nanometers to dozen of nanometers with the increasing sputtering times. It can be seen that Pt particles will aggregate when the sputtering times is over 10 minutes.

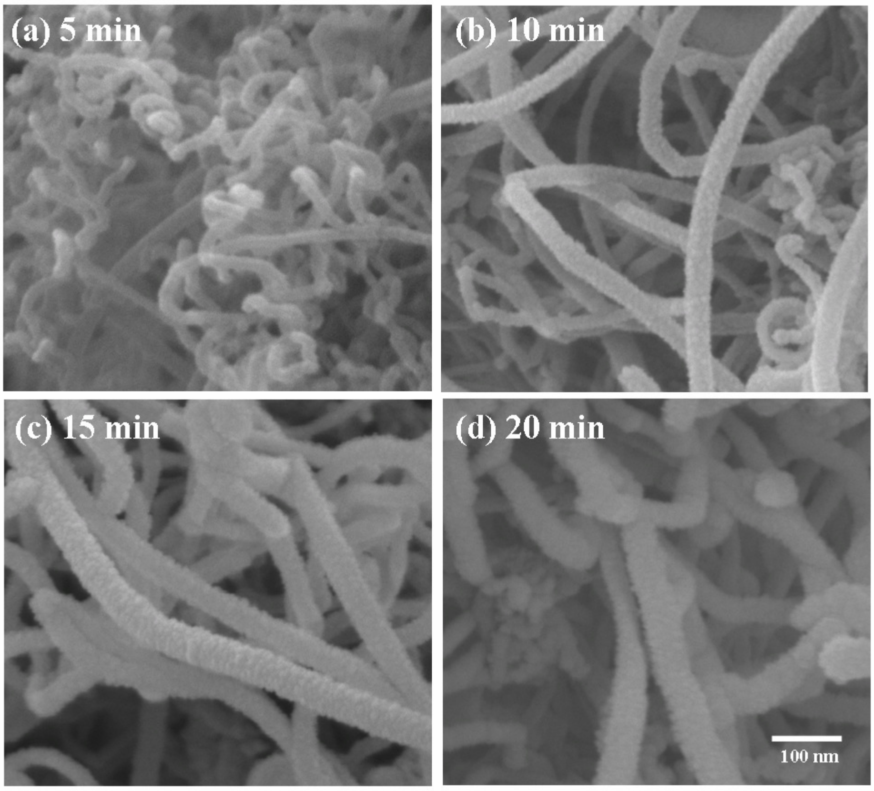


Fig.4 SEM images of platinum catalysts deposited on carbon nanotubes by sputtering for (a) 5min, (b) 10 min, (c)15 min and (d) 20 min.

Fig.5 depicts the histogram of Pt nanoparticles distribution of sputter deposited Pt/MWCNTs, which was made by randomly calculating 100 grains of Pt nanoparticles from TEM micrograph. This indicates that sputter deposited Pt/MWCNTs shows a narrow size distribution from Fig.6 and average diameter of Pt nanoparticle is 3.4 nm.

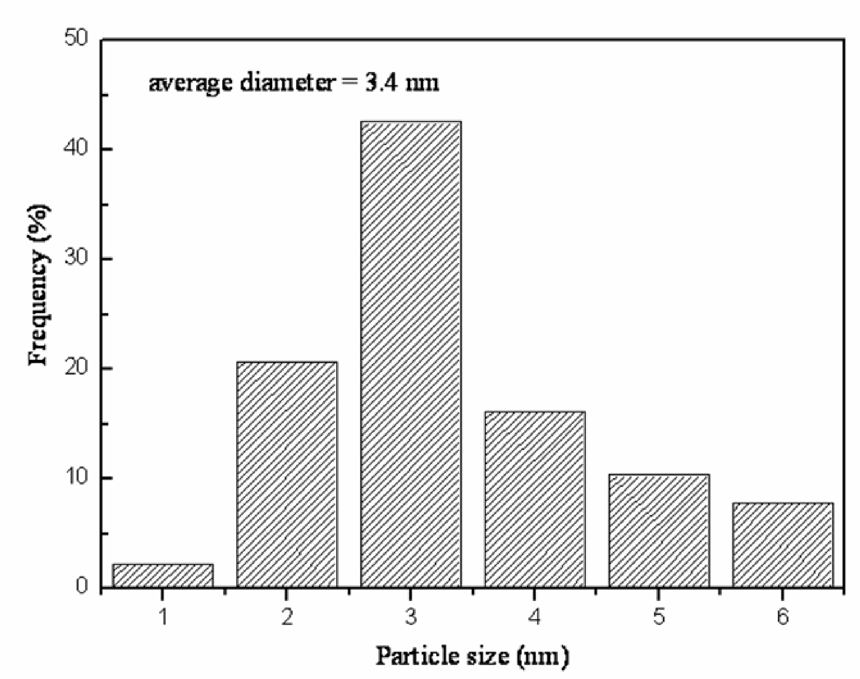


Fig.5 Histogram of Pt nanoparticle diatribution of sputter deposited Pt/MWCNTs

Fig.6 shows CVs of Pt5/CNTs, Pt10/CNTs, Pt15/CNTs and Pt20/CNTs immersing in deaerated 1M H2SO4 solutions. Two peaks, corresponding to weak H-adsorption and strong H-adsorption are observed during cathodic potential sweep between 0.4 and 0.05 V. The strong, medium and weak H-desorption peaks between 0.4 and 0.05 V are also observed under anodic sweep [11]. By using the charge passed for H-adsorption QH, surface area of Pt (SPt) can be estimated from the equation below [12].

SPt /cm2= QH/210 (μC/cm2) (1)

The constant 210 in equation (1) is surface charge density of Pt. Each electrode was taken with a triangular potential sweep (50 mVs-1) between 0 and 1.0 V (vs. SCE) in 1 M H_2SO_4 solution for the determination of the surface area of Pt. Obviously, the great improvement of electrochemical property can be seen after using carbon nanotubes as the catalyst support. The H-adsorption peak has stronger intensity for Pt/CNTs due to the better dispersion and smaller particle size when compared with Pt/CC.

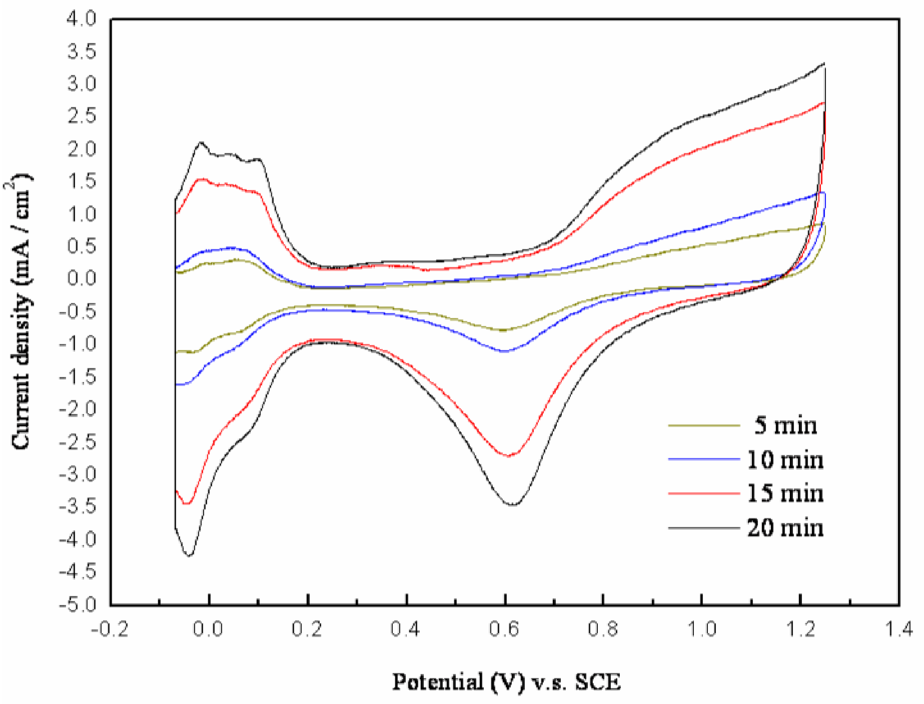


Fig.6 Cyclic votammograms of Pt/CNTs electrode with different sputtering times in 1.0 M H_2SO_4 aqueous solution.

Characteristics of the Pt/CNTs in methanol solution, which were performed by cyclic voltammetry were measured in a deaerated 1M CH3OH + 1 M H2SO4 solution between 0 and 1.0 V with a scan rate of 50 mVs-1. Methanol-oxidation current peaks are clearly observed at 0.8 V in the anodic sweep and at 0.6 V in the cathodic sweep from all samples, which represent the reactions of equation (2) and (3) [13].

Pt-(CH3OH)ads →Pt-(CO)ads + 4H++ 4e- (2)

Pt-CO+Pt-OH→2Pt+CO2 + H++ e- (3)

From Fig.8, the peak current density of all CNTs supported electrocatalysts is obviously higher than that of Pt10/CC. The improvement in electrocatalytic activity was attributed to the present of carbon nanotubes supports, the small size distribution and good dispersion of Pt on carbon nanotubes. Pt20/CNTs exhibits the maximum current density, which is about 19.1 mA cm^{-2} according to the highest Pt loading of all Pt/CNTs samples. However, Pt10/CNTs shows higher mass efficiency than Pt15/CNTs and Pt20/CNTs, which could be observed in Tab.2. The degradation of the electroactivity of Pt15/CNTs and Pt20/CNTs can be explained as the aggregation of Pt nanoparticles during long sputtering times. Various electrochemical properties of these samples are listed in Tab.2. Tab.2 listed various calculated values of Pt loading (L_{Pt}, mg), working surface area of Pt (S_{Pt}, cm^2), methanol oxidation current density at 0.8V (i, mA cm^{-2}) of samples and mass efficiency of Pt (Me, mA mg^{-1} Pt).

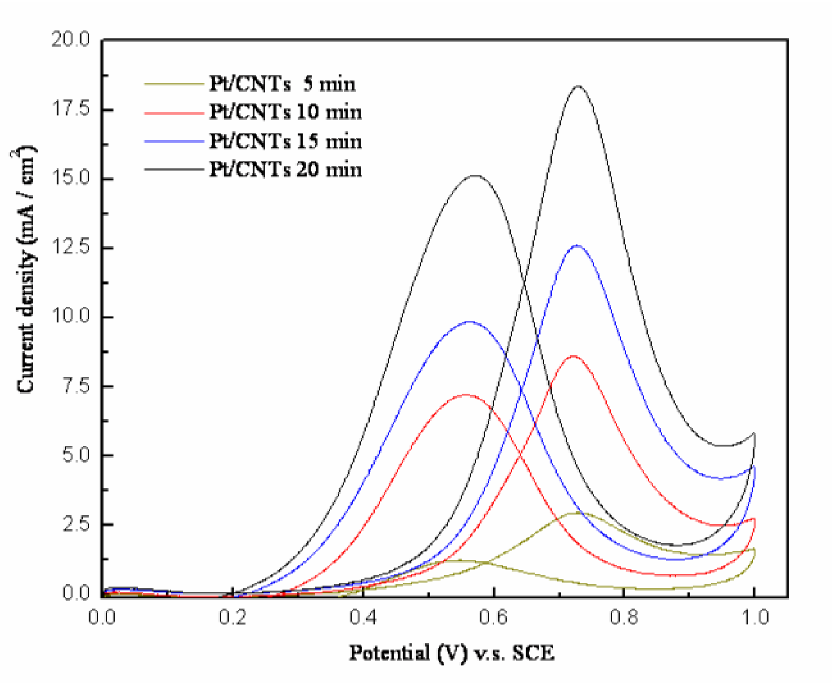
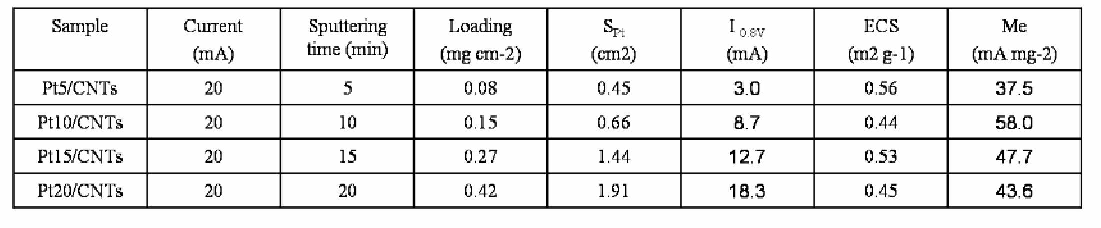


Fig.7 Cyclic votammograms of Pt/CNTs electrode with different sputtering times (a)5 min, (b)10 min, (c)15 min and (d)20 min in 1.0 M H_2SO_4 + 1.0 M CH_3OH aqueous solution.

Tab.3 Electrochemical properties of sputtered Pt/CNTs



Sample	Current (mA)	Sputtering time (min)	Loading (mg cm-2)	S_{Pt} (cm2)	$I_{0.8V}$ (mA)	ECS (m2 g-1)	Me (mA mg-2)
Pt5/CNTs	20	5	0.08	0.45	3.0	0.56	37.5
Pt10/CNTs	20	10	0.15	0.66	8.7	0.44	58.0
Pt15/CNTs	20	15	0.27	1.44	12.7	0.53	47.7
Pt20/CNTs	20	20	0.42	1.91	18.3	0.45	43.6

The polarization curves and power density curves of the MEA with sputtered Pt/MWCNTs cathode catalyst layer were show in Fig.8 and Fig.9, respectively. Obviously, the power density is increasing with the increasing of sputtering times. However, the power density of Pt20/MWCNTs cell is slightly higher than Pt15/MWCNTs cell, which is consistent with the results of CVs.

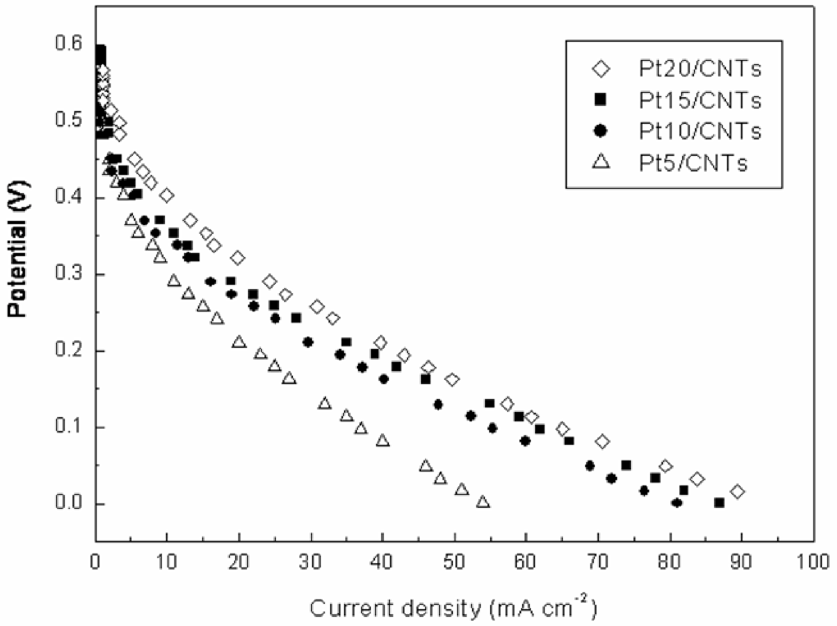


Fig.8 Polarization curves of the Pt/CNTs in 1cm2 single cell with CH3OH/O2 at flow rates of 50/500 sccm and 70oC

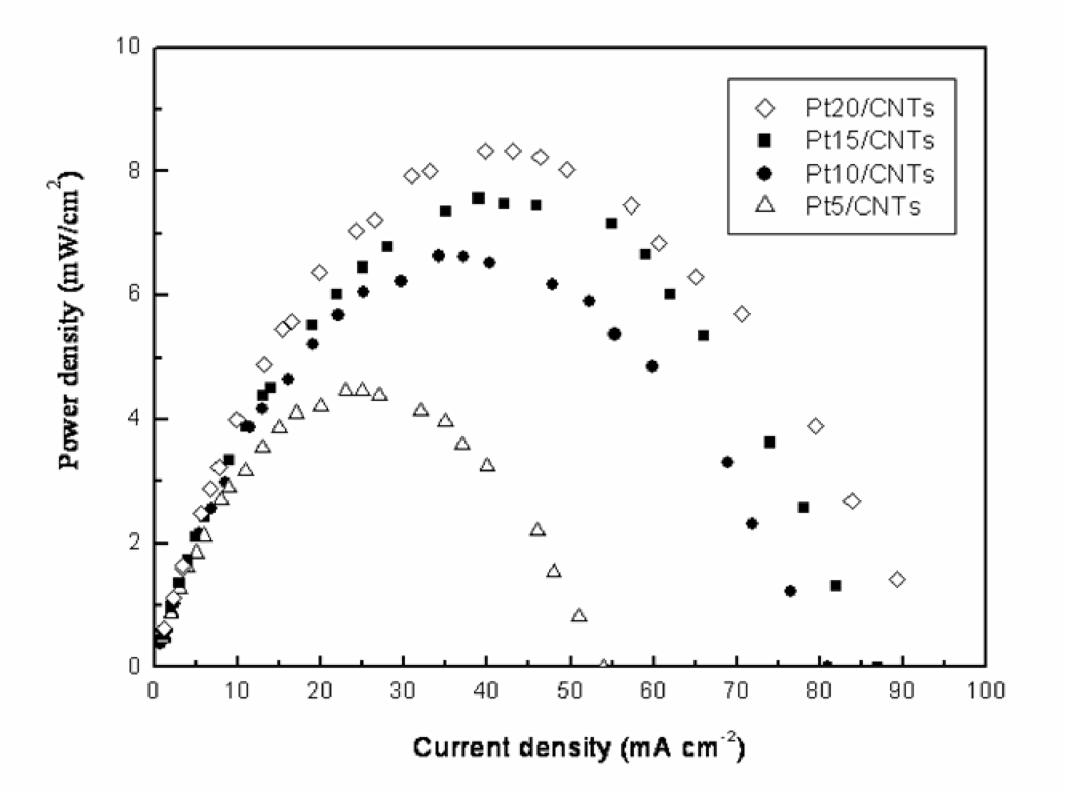


Fig.9 Polarization curves of the Pt/CNTs in 1cm^2 single cell with CH_3OH/O_2 at flow rates of 50/500 sccm and 70°C.

4 Conclusions

Platinum nanoparticles were uniformly dispersed by sputtering on carbon nanotubes support as the cathode for a DMFC. The platinum surface area measured from the H-adsorption charge obtained by cyclic voltammetry has a maximum surface area of 17.90 cm2 at 0.42 mg cm^{-2} Pt loading. The maximum current density is considered to be based on the surface area of Pt, which is 18.3 mA cm^{-2} from the measurement of cyclic voltammetry. The improvement in electrocatalytic activity was attributed to the present of carbon nanotubes supports, the small size distribution and good dispersion of Pt on carbon nanotubes. These results show that sputtering deposition is a feasible and convenient method for dispersing the electrocatalysts on catalyst support.

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