CHAPTER 6

CARBON (CDX-975) BASED Pt ELECTRODES FOR DIRECT METHANOL FUEL CELL (DMFC) APPLICATIONS

6.1 INTRODUCTION

Direct methanol fuel cell (DMFC) has received considerable attention as a leading candidate for portable power source of the future due to its high energy-conversion efficiency, easy storage of the liquid fuel, ambient operating temperature and simple construction (Dyer, 2002). High energy density, easy handling, low cost, transportability and high solubility in aqueous electrolyte made methanol as a promising fuel in fuel cell application and an alternate energy source (Lamy *et al*., 2002). The development of active anode is of primary importance in DMFC. Platinum based catalysts are promising candidates as anode electro-catalyst for DMFC applications. The electro-oxidation process of methanol to CO_2 in DMFC occurs through an initial dehydrogenation step (Aricò *et al*., 2001) and the presence of Pt appears to be necessary in the DMFC anode due to its excellent dehydrogenation properties at low temperatures. Various attempts have been made to reduce the Pt content in the DMFC anode electrode. Ultra low Pt loaded electrodes (0.1 mg/cm^2) have been developed for DMFC application (Aricò *et al*., 2004). Even though Pt has been demonstrated as the only active and stable noble metal for methanol oxidation, particularly in acid medium, pure platinum gets readily poisoned by CO-like intermediates formed during the oxidation of methanol (Park *et al*., 2002). The convenient way to overcome CO poisoning is to employ Pt alloy with oxophilic

metals, which would function as sites for oxygen containing intermediate species, and promote their oxidation (Thomas *et al.*, 2002).

Unsupported and supported Pt-Ru bimetallic catalysts (Perez *et al.*, 1998) have been investigated as anode materials for methanol oxidation. Anodes with supported bimetallic catalysts display effective utilization of noble metal and a considerable interest has been focused on the development of suitable support materials. Carbon is widely employed as support material for anode electro-catalyst (Lee *et al.*, 2004; Lizacano-Valbuena *et al.*, 2003; Liu *et al.*, 2002). Other forms of carbon like carbon nanotubes (CNT), carbon nanofibres and mesoporous carbon have also been used as supports for both Pt and Pt-Ru catalysts for methanol oxidation (Che *et al.*, 1998; Rajesh *et a*l., 2002; Joo *et al.*, 2001). Polymers like polyaniline, polypyrrole, poly-3-methylthiophene, poly-3-ethylenedioxythiophene and composites based on polymers have also been studied as supports for metal catalysts (Qi and Pickup, 2002; Rajesh *et al.*, 2002; Choi *et al.*, 2003). Rajesh *et al* employed conducting polymeric nanocones supported Pt particle as anode electro-catalyst for methanol oxidation (Rajesh *et al.*, 2004). H-zeolite-Y supported Pt-Ru catalyst has been found to be active for methanol oxidation (Samanth *et al.*, 2004). Apart from Pt-Ru bimetallic catalysts, Pt-Ru-Nafion (Chu *et al.*, 2002), Pt-WO$_3$ supported on CNT (Rajesh *et al.*, 2003), Pt-Ru/Ti mini mesh (Cheng and Scott, 2003) and Pt-Sn/C (Zhou *et al.*, 2004) have been used as possible electro-catalysts for methanol oxidation. Guo and coworkers prepared nanosized Pt/C by employing citric acid stabilization method for the application of PEMFC (Guo *et al.*, 2005). The influence of the interaction between Pt and carbon on the activity for methanol oxidation has also been investigated in detail (Hall *et al.*, 2004).

Various reducing agents such as hydrazine, formic acid, sodium formate and formaldehyde have been used to prepare Pt loaded carbon catalysts (Ramesh *et al*., 1987; Lizacano-Valbuena *et al*., 2002; Hammett and Kennedy, 1988). However, formaldehyde reduction method is widely used to prepare noble metal electrodes for application in fuel cells and this method has the advantages of preparing Pt particles of uniform size without introducing impurity (Neto *et al.,* 2000). The main reason for using this method is that the reduction potentials of the various metal ions (namely, Ru^{2+} to Ru is 0.455 V, Rh^{2+} to Rh is 0.6 V, Pd^{2+} to Pd is 0.951 V and Pt^{2+} to Pt is 1.1 V) are appropriate for reduction by formaldehyde. The oxidation products of formaldehyde reduce different metal ions of the same valence states, or metal ions of different oxidation states.

Among the available carbon supports, Vulcan XC-72 (cabot) has been extensively used. However, CDX-975 (a carbon material marketed by M/s Columbian Chemicals Company) has similar colloidal properties as Vuclan XC-72. The sulphur level in CDX-975 (0.6%) is lower than that in Vulcan XC-72 (1%). Also, metal impurities such as Na, K, Fe, etc., are considerably lower than what is present in Vulcan XC-72. Due to these features, CDX-975 has been investigated as an alternate carbon support for electrode applications. The anode electro-catalyst (Pt/CDX-975) was prepared from CDX-975 and H_2PtCl_6 by employing formaldehyde as reducing agent.

In this chapter, Pt/CDX-975 (a carbon material marketed by M/s Columbian Chemicals Company) is evaluated as a possible anode electro-catalyst support for methanol oxidation in DMFC.

6.2 RESULTS AND DISCUSSION

6.2.1 Powder X-ray diffraction (XRD)

X-ray diffraction patterns of the catalysts prepared by formaldehyde reduction method are shown in Fig 1(a-d).   20 % Pt/CDX-975 and 40 % Pt/CDX-975 samples exhibit characteristic peaks for the (111), (200), (220) and (311) planes of Pt at 2θ values around 40, 47, 67 and 83, respectively, which correspond to the fcc structure of Pt (JCPDS, card 4-802).   These peaks are not observed for 5 % Pt/CDX-975 because of lower loading of Pt.   For the 10 % Pt/CDX-975 sample, a broad peak is observed at 2θ value of 44 corresponding to the (111) plane of Pt and this is attributed to the very small particle size of the supported Pt metal.   The average particle sizes of the catalysts have been determined from the peak at $2\theta = 40$ using Scherrer's equation (West, 1984).   The values of the average particle size for all catalysts are presented in Table 6.1.   A particle size of < 2 nm was observed in case of 10 % Pt/CDX-975.

Table 6.1 Average particle size of Pt loaded CDX-975 catalysts

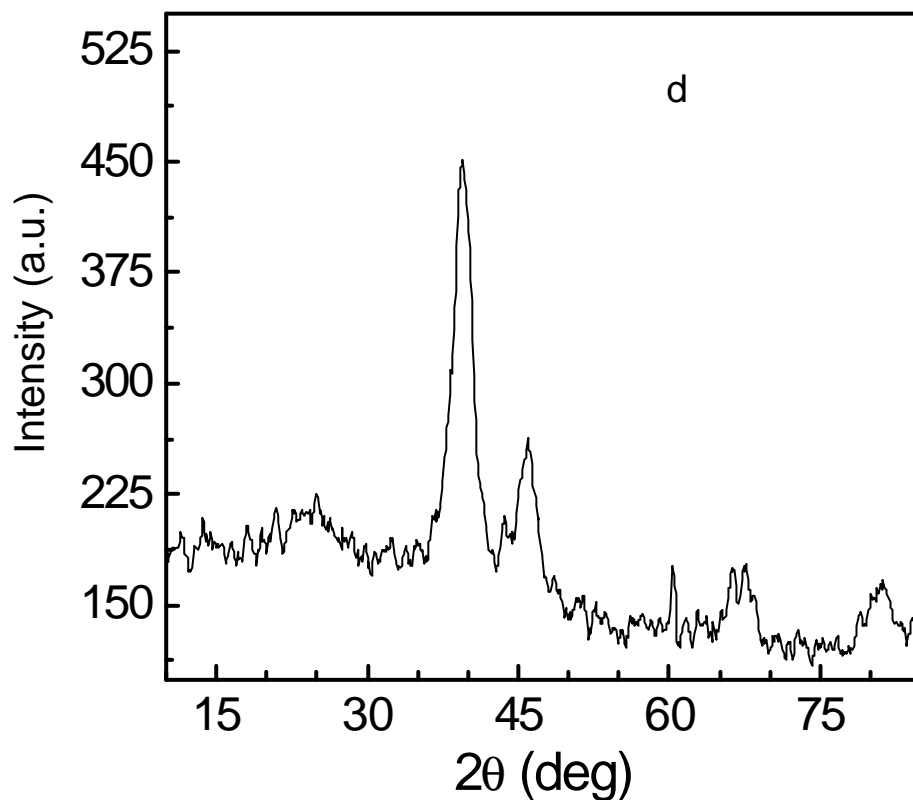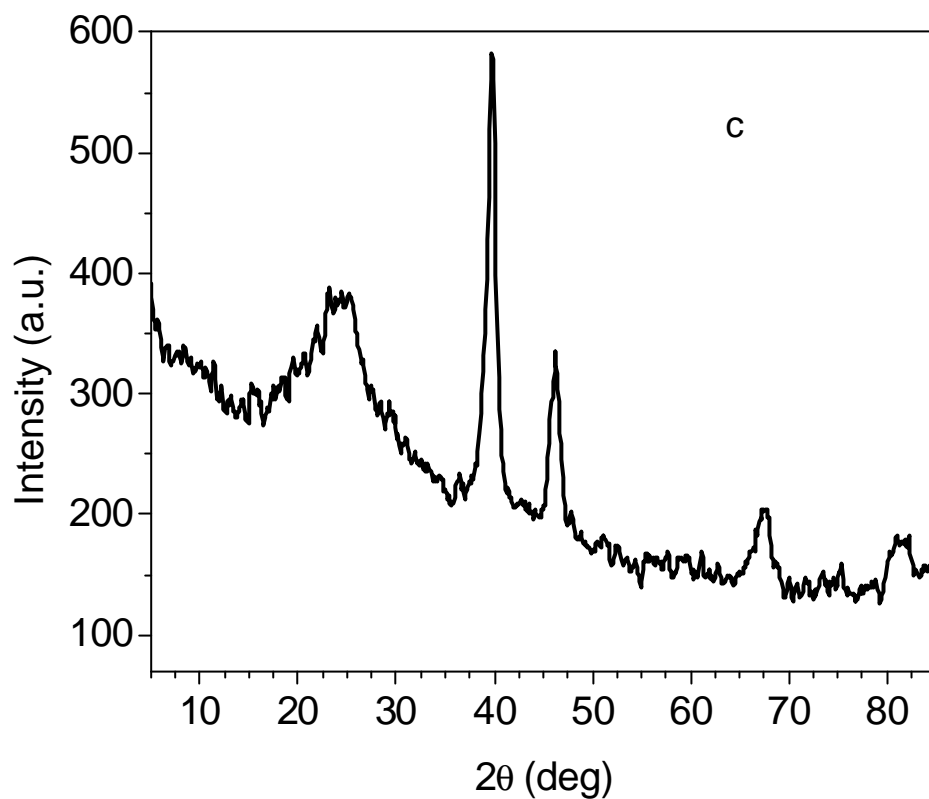| Catalysts	Average particle size (nm)
5 % Pt/CDX-975	-
10 % Pt/CDX-975	< 2
20 % Pt/CDX-975	11
40 % Pt/CDX-975	4
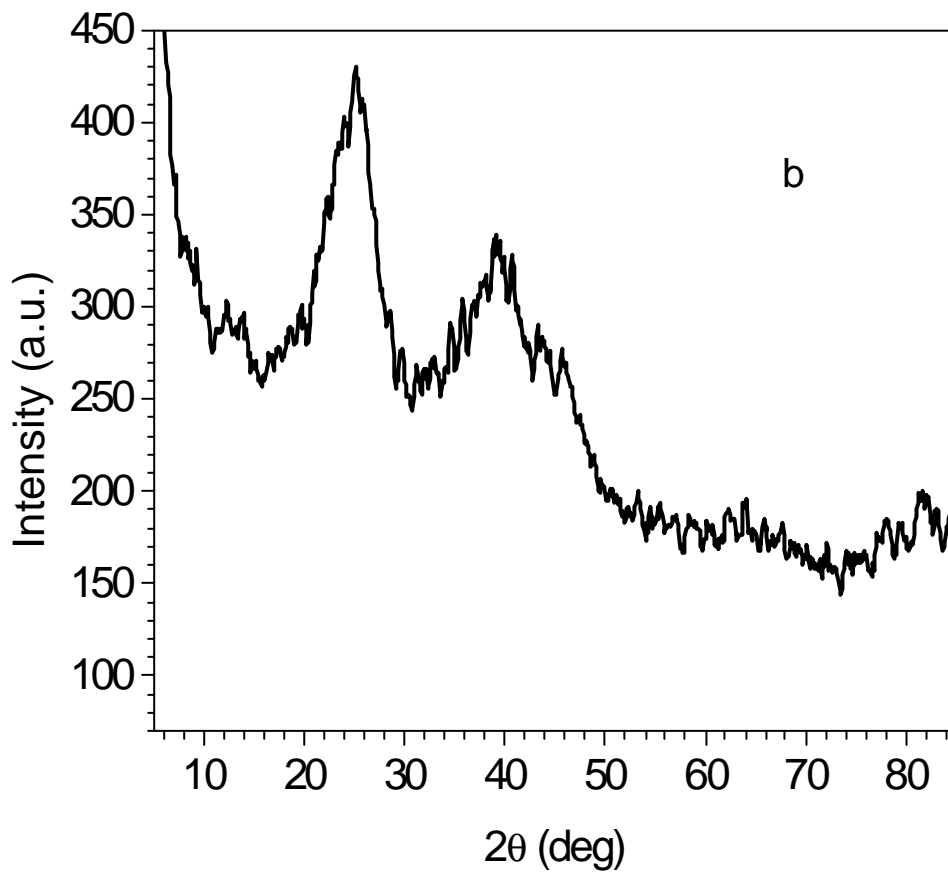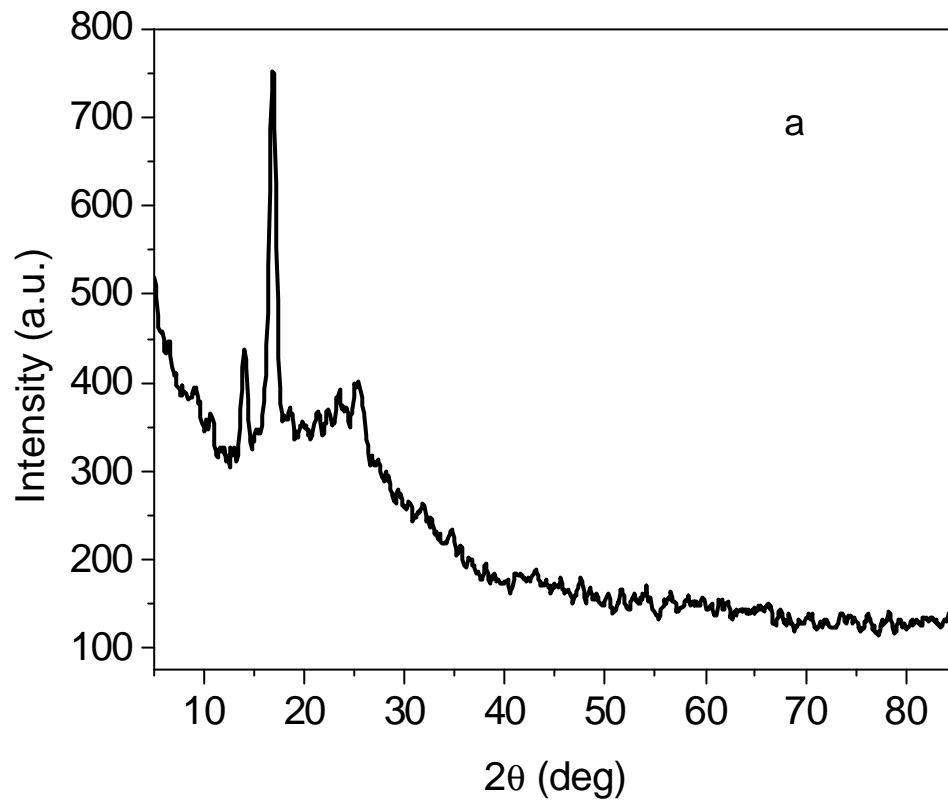
Fig. 6.1 **XRD patterns of Pt/CDX-975   a) 5 % Pt/CDX-975 b) 10 % Pt/CDX-975 c) 20 % Pt/CDX-975 and d) 40 % Pt/CDX-975**

6.2.2 Determination of Pt loading for the catalysts using UV-Visible Spectroscopy

The amount of Pt loaded in different Pt/CDX-975 catalysts was estimated using UV-Visible spectroscopy. A calibration graph was obtained by using standard solutions of H_2PtCl_6 and 5 % $SnCl_2$ solution. The absorbance was measured at 403 nm for all standard and unknown solutions. The procedure involves heating 50 mg of catalyst at 1173 K for 10 h and extraction of the resulting residue with aqua regia. To the extracted solution, HCl was added and evaporated to dryness and this was repeated four times and was finally made up to 50 ml. 5 ml of 5 % $SnCl_2$ was added to 10 ml of the made up solution and was diluted to 100 ml in a standard flask. The absorbance of the resulting solutions were compared with the standard solution and the amount of platinum loaded in the catalysts were calculated from the calibration graph and given in Table 6.2

Table 6.2   Amount of Pt loading in the catalysts estimated using UV-Visible Spectroscopy

Catalysts	Pt loading (%)
5 % Pt/CDX-975	4.94
10 % Pt/CDX-975	10.0
20 % Pt/CDX-975	20.0
40 % Pt/CDX-975	39.5

6.2.3. Evaluation of electro-active surface area (EAS)

Cyclic voltammetry was employed to obtain electro-active surface area of the electrode materials in order to account for the higher current response in methanol oxidation. Fig. 6.2 a–d depicts the cyclic voltammograms obtained in 1 M H_2SO_4

between – 0.25 V and 1.2 V Vs Ag/AgCl$_{(saturated KCl)}$ at a scan rate of 25 mV/sec for Pt/CDX-975. All the prepared catalysts exhibited the hydrogen adsorption and hydrogen desorption peaks between – 0.2 V and 0.1 V. Pt is capable of forming platinum oxide in aqueous solution. The formation of platinum oxide is shown in Fig. 6.2 b. The formed platinum oxide can be reduced reversibly. The potential of platinum oxide formation is shifted towards the cathodic direction when Pt loading decreases. The active Pt surface area of the electrodes was evaluated from the columbic charge for hydrogen desorption (Q_H) of the electrode. The value of Q_H was calculated as the mean value between the amounts of charges exchanged during the electro absorption (Q′) and desorption (Q″) of hydrogen on Pt sites (Pozio *et al.,* 2002). The electrochemical active surface areas [EAS] for all electrodes were (Lee *et al.,* 1998) calculated using the Eq. (1) and are presented in Table 6.3

$$EAS = Q_H [Pt] \times 0.21 \qquad\qquad (6.1)$$

Where [Pt] represents the platinum loading (mg/cm^2) in the electrode, Q_H the charge for hydrogen desorption (mC cm^{-2}) and 0.21 is charge required to oxidize a monolayer of hydrogen on bright Pt. 10 % Pt/CDX-975 (173 m^{2}g^{-1}) displayed the higher electro-active surface area compared to other Pt loaded CDX-975 catalysts and this may be due to the lower particle size of the Pt as observed from XRD data. The electro-active surface area of 20 % and 40 % Pt/CDX-975 was found to be comparable with reported values for similar Pt supported carbon catalysts prepared by formaldehyde reduction method (Umeda *et al.,* 2003).

Calculation of Pt loading for EAS evaluation

The procedure for the calculation of electro-active surface area of the electrodes was illustrated with 5 % Pt/CDX-975 catalyst. [Pt] loading on a GC electrode of area 0.07 cm^2 was calculated to be 0.280 mg/cm^2.

 [Pt] loading   = 0.280 mg/ cm^2

Charge (Q′) calculation for the forward peak (Fig. 6.2 a)

Charge during the forward peak = 108 mA $\times$ mV / 25 mVsec^{-1} = 4.32 mAsec

Glassy carbon area = 0.07 cm^2

Therefore, the charge during the forward peak = 4.32 mAsec/[0.07 $\times$ 60 $\times$ 60]

$$= 0.0171 \text{ mAh/cm}^2$$

(Since 26.8 Ah = 1F = 96, 500C)

96,500/26.8 $\times$ 0.0171/1000

Charge (Q′) on the forward peak = 61.82 mC/cm^2

Charge (Q″) calculation for the reverse peak

 Following a similar procedure,

Charge (Q″) on the reverse peak = 59.86 mC/cm^2

Calculation of Electrochemical Active area of platinum

EAS = Q$_H$ / [Pt] x 0.21

Q$_H$ = [Q′+ Q″]/2

Q$_H$ = [61.82+ 59.86]/2 = 60.84 mC/cm^2

[Pt] = 0.280 mg/cm^2

EAS = 60.84/[0.280 x 0.21] = 1035 (mC/cm^2)/[mg/cm^2 x mC/cm^2]
$$= 1035 \text{ cm}^2/\text{mg}$$
$$= 1035 \times 10^{-4} \text{ m}^2/10^{-3}\text{g}$$
$$= 103.5 \text{ m}^2/\text{g}$$

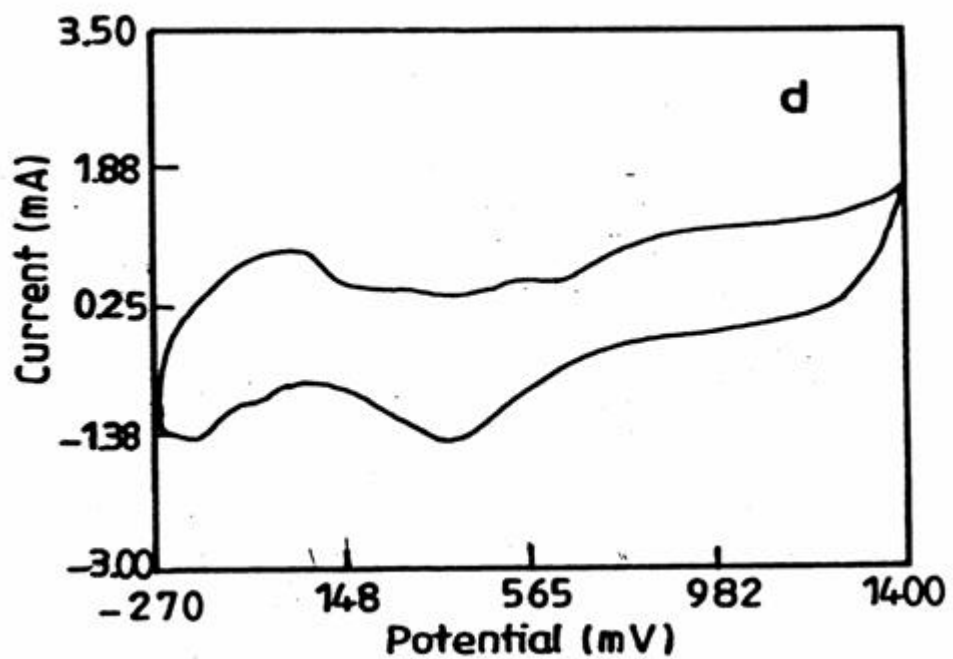**Electro-active surface area of 5 % Pt/CDX-975 = 103.5 m^2/g**
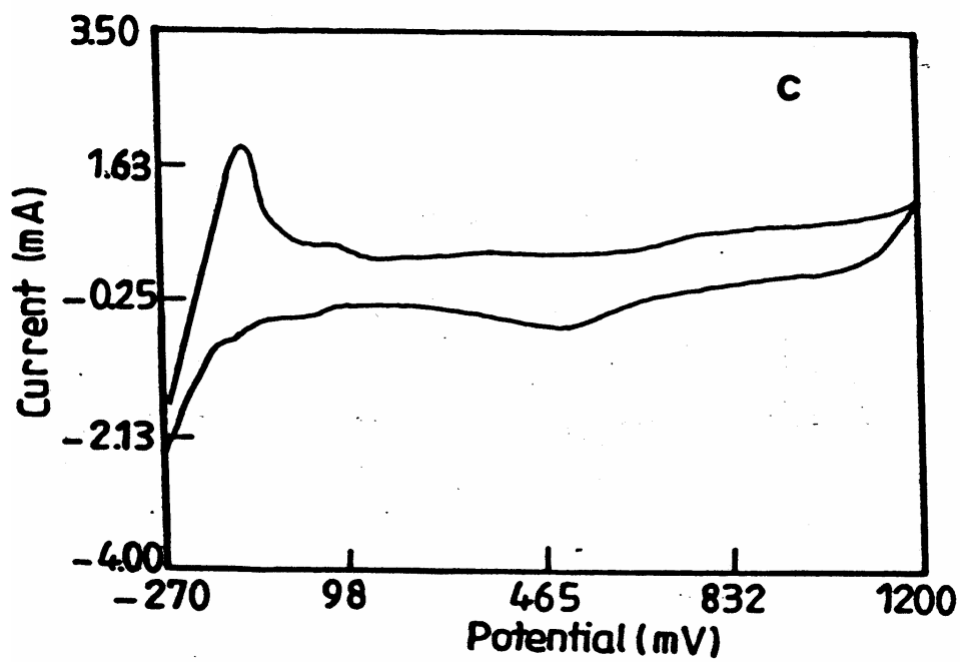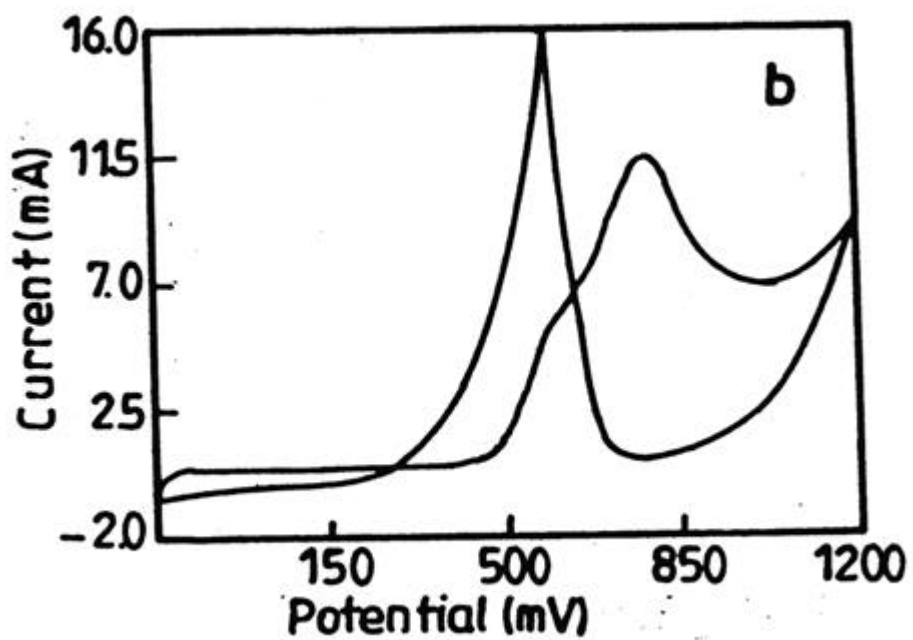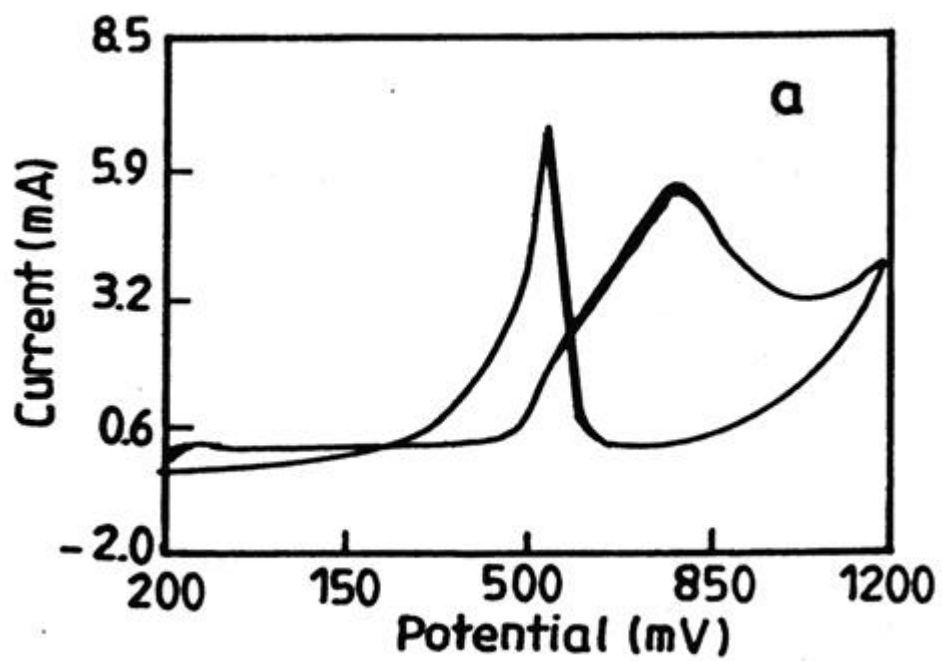
147
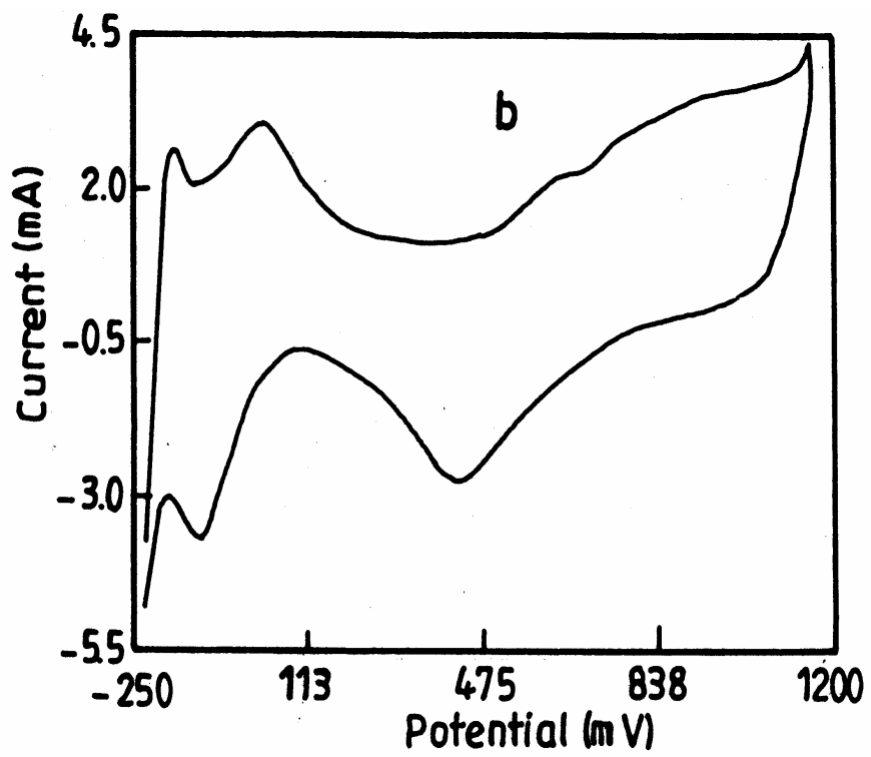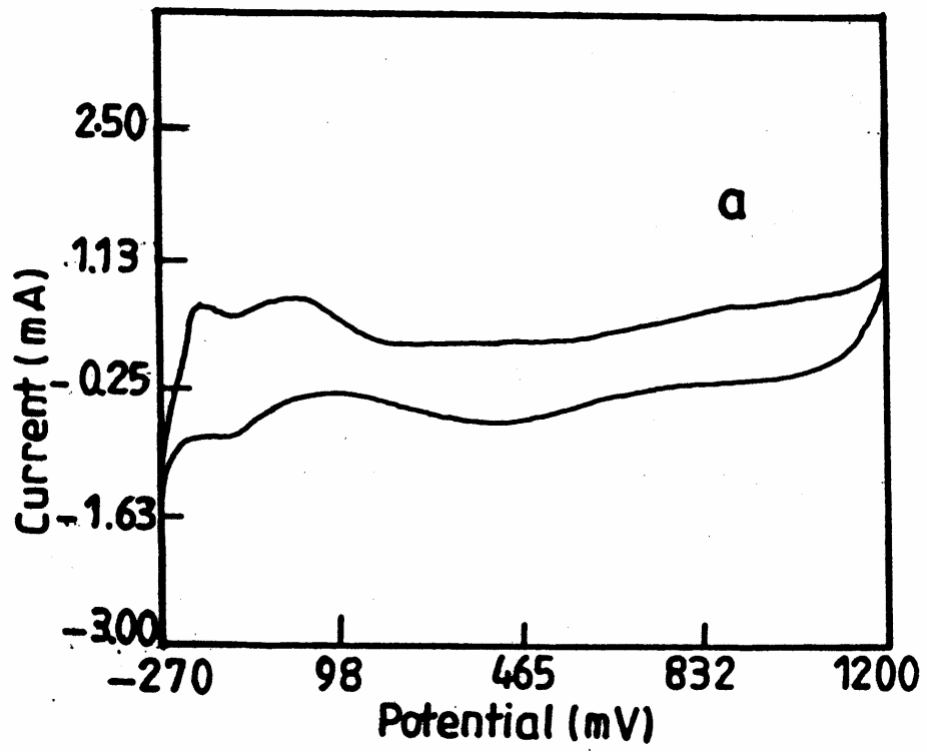
Fig 6.2   Cyclic Voltammograms of Pt/CDX-975 in 1M Sulfuric acid a) 5% Pt/CDX-975 b) 10%Pt/CDX-975 c) 20% Pt/CDX-975 d) 40% Pt/CDX-975

148

Table 6.3   Electrochemical active surface area (EAS) of Pt/CDX-975

Catalysts	EAS (m^2/g)
5 % Pt/CDX-975	103.5
10 % Pt/CDX-975	173.4
20 % Pt/CDX-975	35.0
40 % Pt/CDX-975	15.5

6.2.4   Methanol electro-oxidation activity

Cyclic voltammometry was carried out in 1 M sulfuric acid and 1 M methanol solution between – 0.2 V and 1.2 V at the scan rate of 25 mV/sec Vs Ag/AgCl$_{(saturated}$ $_{KCl)}$ to evaluate the electro catalytic activity of the catalysts for methanol oxidation. Cyclic voltammograms of all four catalysts namely 5%, 10%, 20% and 40% Pt on CDX-975 are shown in Fig. 6.3.   In the case of 10 % Pt/CDX-975, the methanol oxidation peak was observed at 0.7 V with a peak current of 11.7 mA which is found to be higher than that of other Pt loaded CDX-975 catalysts.   Higher electro-active surface area and smaller particle size (~ 2 nm) of the metallic particles are the possible reasons for the higher methanol oxidation activity of 10 % Pt/CDX-975 catalyst. Methanol oxidation potential is found to be dependent on the platinum loading (> 10 %) on the catalyst.   As the platinum loading increases, the peak potential is shifted towards anodic direction.   The current densities and the observed methanol oxidation potentials for all the catalysts are given in Table 6.4.
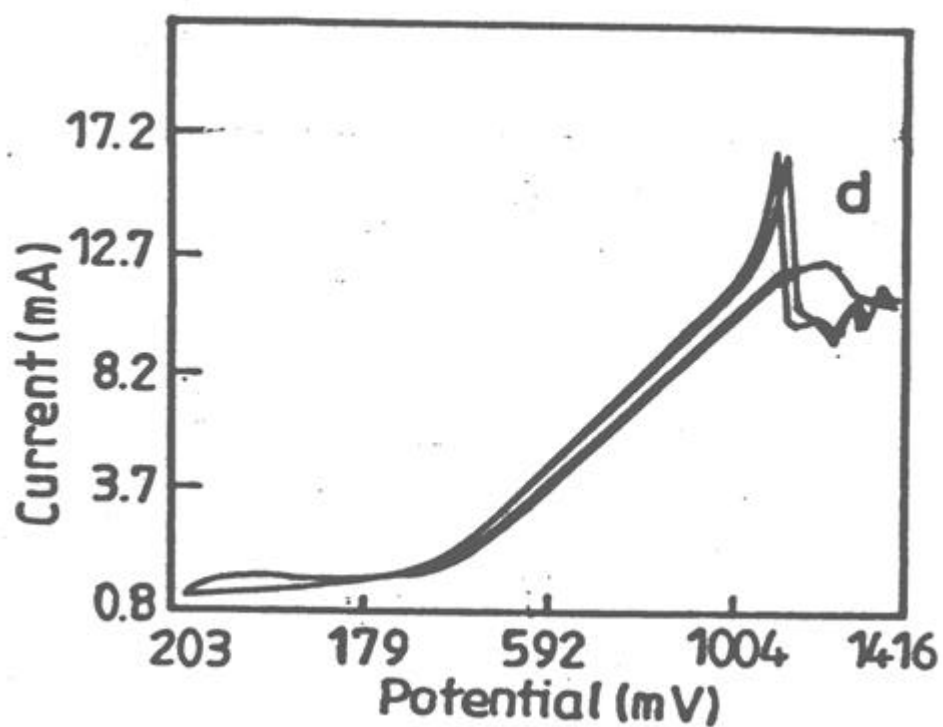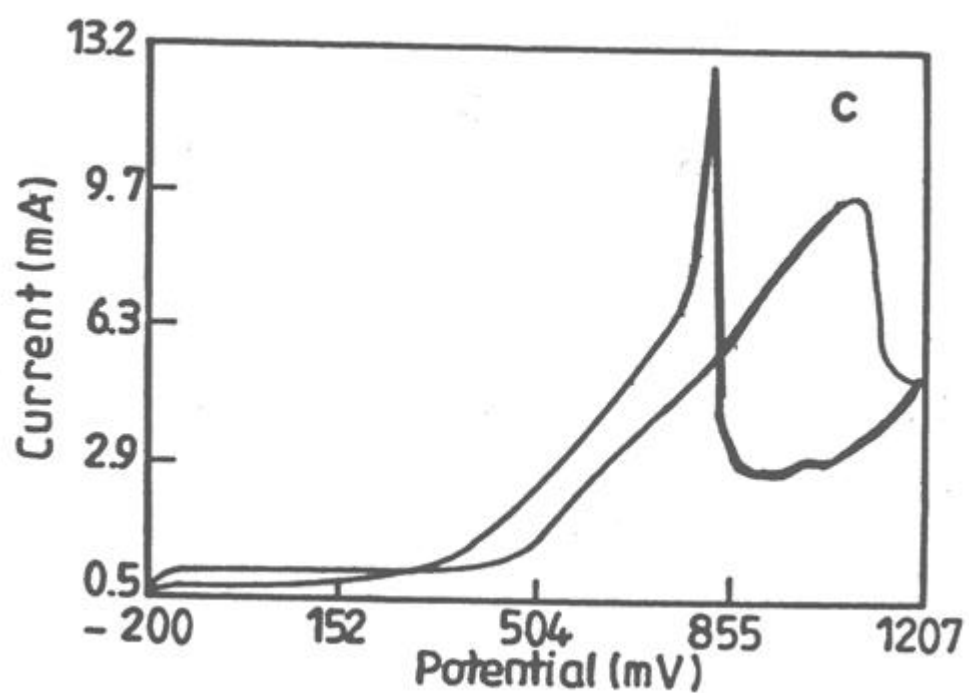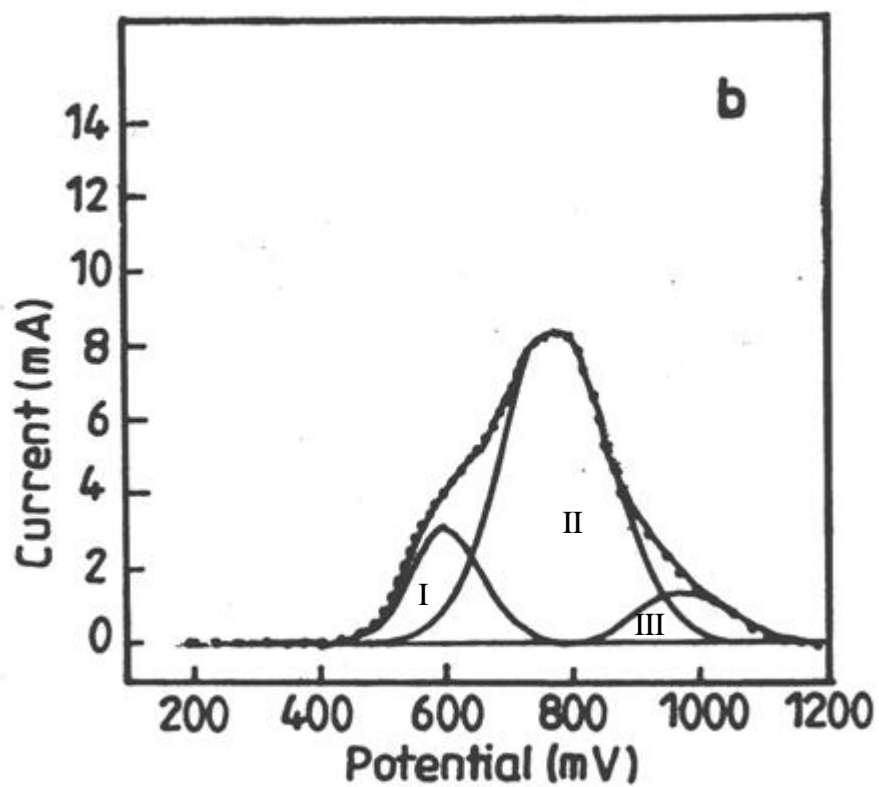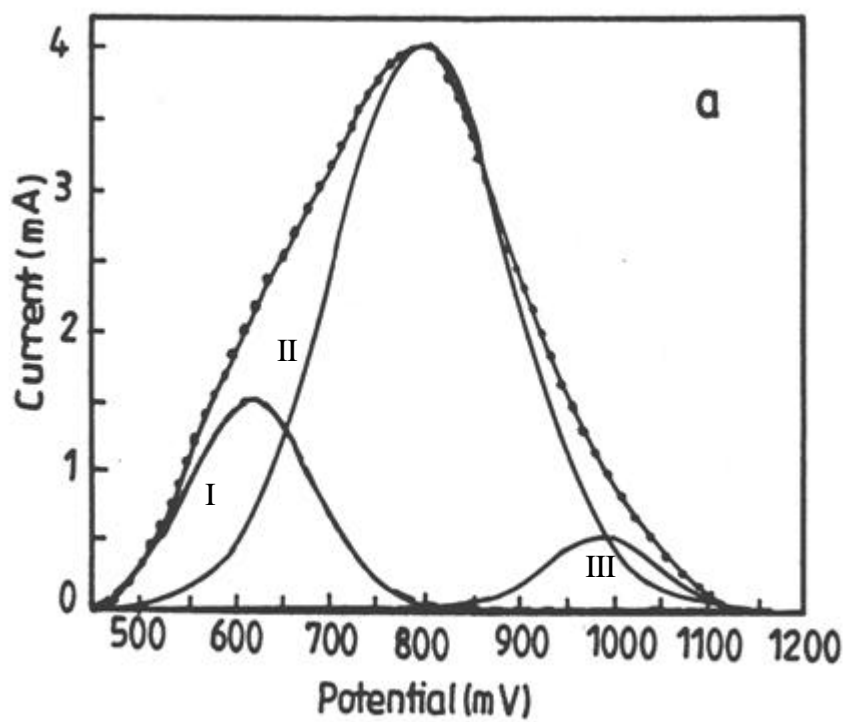
Fig 6.3 **Cyclic voltammograms of Pt/CDX-975 in 1 M sulfuric acid and 1 M methanol a) 5 % Pt/CDX-975 b) 10 % Pt/CDX-975 c) 20 % Pt/CDX-975   d) 40 % Pt/CDX-975**

Table 6.4 Methanol oxidation activities of Pt/CDX-975 catalysts

Catalysts	Forward peak			Reverse peak		
	Potential (V)	Current (mA)	Current Density (mA/cm^2)	Potential (V)	Current (mA)	Current Density (mA/cm^2)
5% Pt/CDX-975	0.814	5.56	79.4	0.564	6.58	94.0
10% Pt/CDX-975	0.788	11.74	167.7	0.589	15.51	221.6
20% Pt/CDX-975	1.072	9.98	142.6	0.819	12.72	181.7
40% Pt/CDX-975	1.160	10.25	146.4	1.094	14.00	200.0

6.2.5 Effect of formaldehyde reduction

The cyclic voltammograms observed for methanol oxidation have been deconvulated and are shown in Fig. 6.4 a-d.   It is seen that methanol oxidation peaks can be resolved into three components and the current responsible for this observed activity of methanol oxidation has been attributed to oxidized form of Pt ions (Peak I), Pt in the zero-valent state (peak II) and some Pt complex species (peak III) generated from the oxidation products of formaldehyde used for the reduction of Pt ions from H_2 $PtCl_6$.   All these species are found to be present in the electro-catalysts obtained and are active for the oxidation of methanol.   It is seen from the data given in Table 6.5 that the extent of reduction of Pt ions decreases with Pt loading.   It is therefore deduced that formaldehyde reduction method is appropriate for the preparation of Pt electro-catalysts with lower loadings.
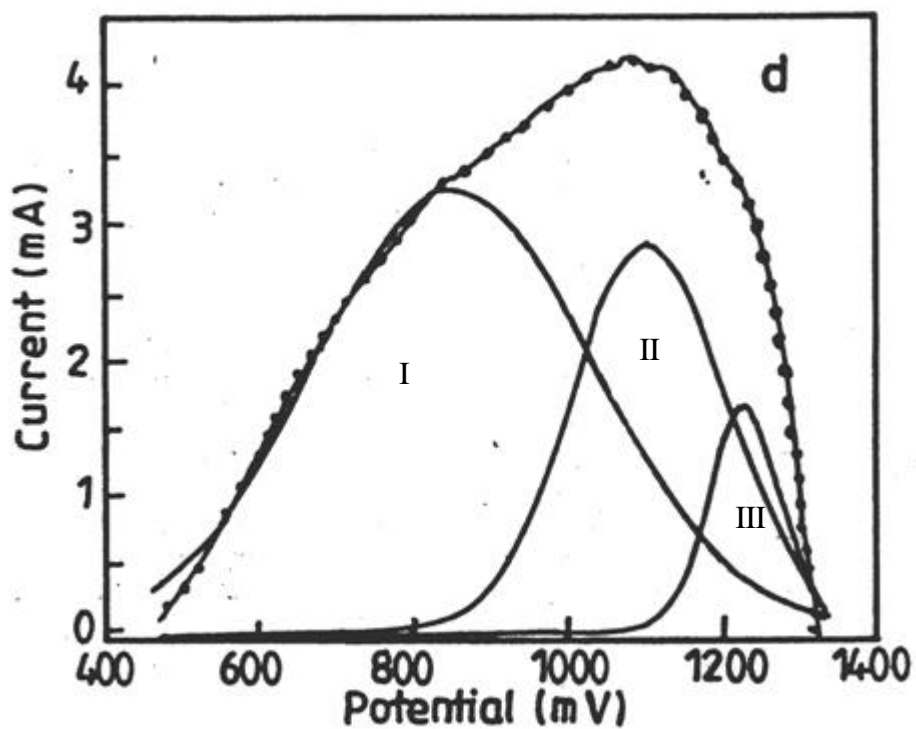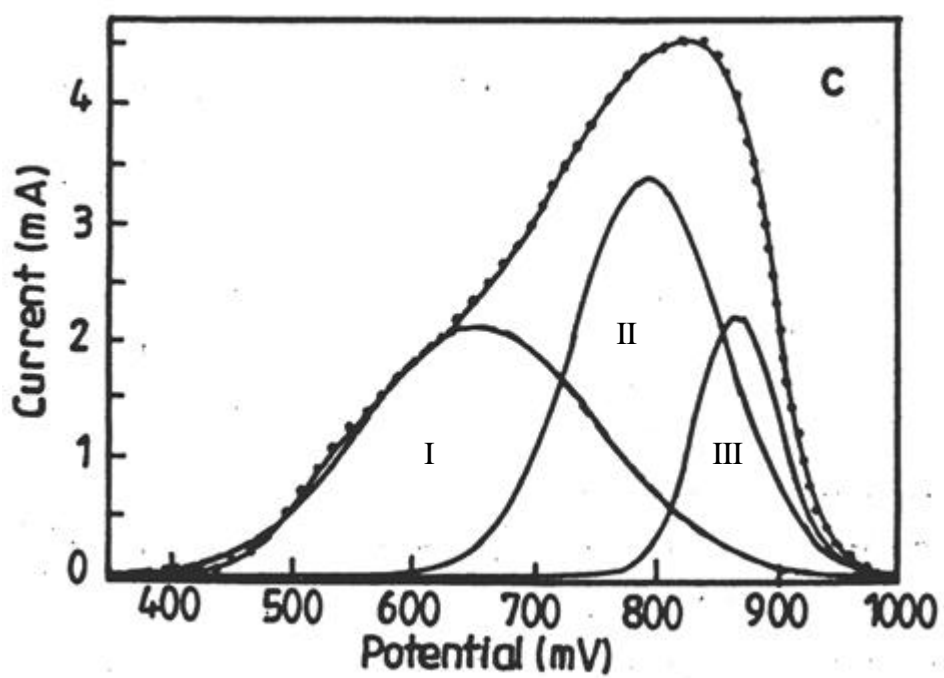
Fig 6.4. **Deconvulated cyclic voltammograms of Pt/CDX-975 in 1M sulfuric acid and 1 M methanol a) 5% Pt/CDX-975 b) 10%Pt/CDX-975 c) 20% Pt/CDX-975   d) 40% Pt/CDX-975**

Table.6.5 Percentage contribution of the various Pt species to the total activity observed for methanol oxidation

Catalyst	Peak I (%) Pt (ion)	Peak II (%) Metallic Pt	Peak III (%) Pt complex of oxidized product of HCHO
5 % Pt/CDX-975	19.3	75.0	5.7
10 % Pt/CDX-975	18.1	73.1	8.7
20 % Pt/CDX-975	41.3	43.2	15.0
40 % Pt/CDX-975	61.8	30.0	8.1

6.2.6 Chronoamperometry response of electrodes

Stability of the electrode under potentiostatic conditions is essential for oxidation of methanol for the possible application in DMFC.   Chronoamperometric studies were performed to evaluate the stability of the electrodes for methanol oxidation.   A plot of current Vs time behavior under potentiostatic condition in 1 M H_2SO_4 and 1 M methanol over a certain period of time was used to derive the stability of the electro-catalysts.   Chronoamperometric response observed in 1 M H_2SO_4 and 1 M methanol for all the prepared catalysts for a time period of 3 h is shown in Fig. 6.5.   It is seen that there is constant decay in the current with respect to time possibly suggesting the poisoning of the electrode by CO.   In case of 10 % Pt/CDX-975, though there is a gradual decay of current for a period of 4000 sec, the current appears to be stable afterwards, suggesting better tolerance of 10 % Pt/CDX-975 (Fig. 6.5 b) electro-catalyst compared to other catalysts.
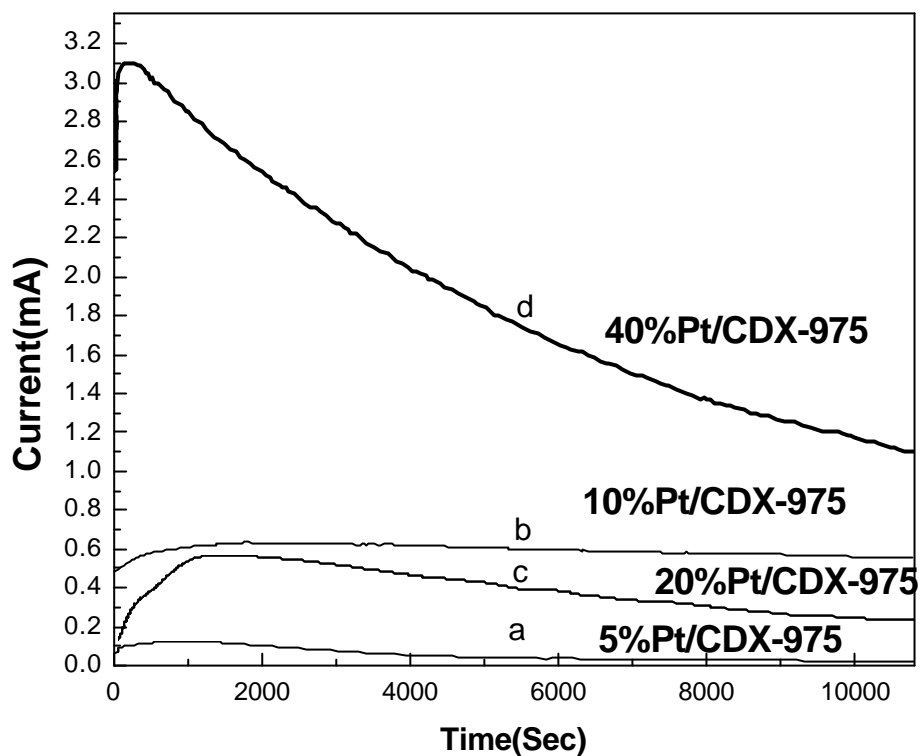
Fig 6.5 **Chronoamperometric response of electrodes in 1 M sulfuric acid and 1 M methanol a) 5 % Pt/CDX-975 b) 10 % Pt/CDX-975 c) 20 % Pt/CDX-975   d) 40 % Pt/CDX-975**

6.3 CONCLUSION

CDX-975 is identified to be a promising support for electrode application in DMFC. The platinum loading on CDX-975 was varied to identify the optimized catalyst for methanol oxidation.   The optimum loading was found to be 10 % Pt/CDX-975. The higher methanol oxidation activity of 10 % Pt/CDX-975 correlated well with smaller particle size (XRD), high electro-active surface area and sustained chronoamperometric response.