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The electrooxidation of methanol is a research topic of great concern for the development of high performance Direct Methanol Fuel Cells (DMFC). Platinum electrodes have been reported to be the most active for this reaction, but their activity is not satisfactorily high. It is well known that the reaction on platinum is retarded by strongly adsorbed organic intermediates (poisons) produced from CH_3OH itself. Considerable decrease in this poisoning effect is observed with the presence of oxides.

This thesis focuses on the electrocatalytic activity of precious metal-oxides for the oxidation of methanol in alkaline media. The oxides studied are as follows: $BaPtO_3$, Sr_4PtO_6, Sr_3NiPtO_6, $PtO_2.H_2O$, PdO, IrO_2 and RuO_2. Carbon-based (Vulcan XC72) electrodes using these electrocatalysts were prepared and subjected to Cyclic Voltammetry (CV) in 1M NaOH+1M CH_3OH electrolyte at room temperature (~24°C). Sr_4PtO_6/C electrode showed slightly higher

activity than Pt/C electrode for the electrooxidation of methanol. Cyclic voltammetry conducted for a repeated number of cycles for all these electrodes showed essentially no poisoning effects in marked contrast to Pt/C electrode. $PtO_2.H_2O/C$ and PdO/C electrodes were found to show excellent characteristics with appreciable activity even at -600mV Vs SCE. The enhancement of activity for $PtO_2.H_2O/C$ electrode may be attributed to the presence of Pt and OH species at the reaction sites. Chronoamperometric studies were conducted on these electrodes to measure their stability. The current density values observed in the case of $PtO_2.H_2O/C$ and PdO/C electrodes were almost double those of the Pt/C electrode. A maximum current density value of approximately $45mA/cm^2$ was observed for $PtO_2.H_2O/C$ electrode at 100mV Vs SCE. Surface area measurements revealed the fact that the increased catalytic activity of PdO and $PtO_2.H_2O$ could not be just attributed merely to surface area effects.

Study of Precious Metal-Oxide Based Electrocatalysts for the Oxidation of Methanol

by

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Chapter 1

Introduction to Direct Methanol Fuel Cell

1.1 Introduction

Fuel cells are electrochemical devices that convert chemical energy into direct current electrical energy without intermediate steps. The best known example is the Hydrogen-Oxygen fuel cell, in which hydrogen is oxidized to protons and oxygen is reduced to water (figure 1.1 & eqn.1.1)[1].

$$H_2 \Rightarrow 2H^+ + 2e$$

$$O_2 + 4H^+ + 4e \Rightarrow 2H_2O \qquad (1.1)$$

The overall reaction is then :

$$H_2 + 1/2\,O_2 \Rightarrow H_2O \qquad (1.2)$$

which is essentially the combustion of hydrogen to water, but with the energy directly converted into electrical energy and not into heat. The Direct Methanol Fuel Cell (DMFC) functions in an analogous fashion by oxidizing the liquid fuel (methanol) to carbon dioxide & water[2].

Sir William Grove (1811 - 1896) must be regarded as the inventor of the fuel cell. He described in 1839[3] an experiment in which electricity was generated by supplying hydrogen & oxygen to two separate electrodes in sulfuric acid. Tietelbaum in 1910 was the first to convert the chemical energy of

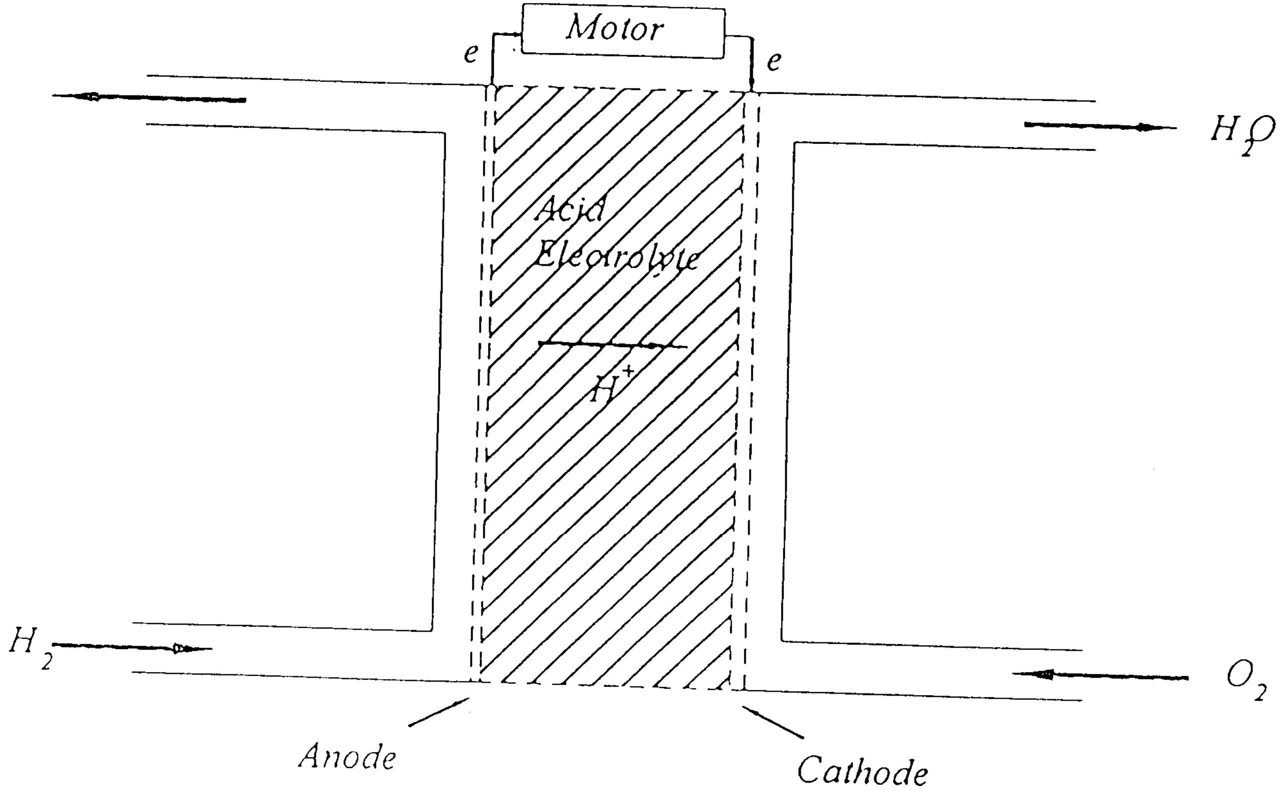

Figure 1.1 Schematic representation of a simple Hydrogen-Oxygen Fuel Cell.

liquid fuels like petroleum, in a galvanic cell into electricity[4]. The use of fuels like alcohols was proposed later by Kordesch & Marko[5] and by Justi *et al* [6].

Methanol, a liquid fuel, is made readily available from natural gas, oil, wood & coal. It can be easily transported & stored. Methanol is reported to have high energy density of the order of 2392 Wh/Kg[7] and has been proved to be the only alcohol that can be easily oxidized electrochemically to carbon dioxide and water[8].

Methanol can be electrochemically oxidized at a fuel cell anode either directly or indirectly. In the indirect method, methanol is initially reformed to give hydrogen in a high temperature step. However, the reactor required to accomplish this both lowers practical power densities and raises the inherent thermal signature of the overall power flow system. As a consequence there are incentives for developing fuel cells which directly use methanol as a fuel in their anode compartment.

1.2 Advantages and applications

The Direct Methanol Fuel Cell functions by oxidizing the liquid fuel to carbon dioxide and water. This removes the need for an external hydrogen fuel supply and offers the prospect of producing compact systems ranging in size from a few watts to several kilowatts (~15kW). This is one of the most desirable fuel cell systems for small scale power units. Methanol is completely miscible in acid and alkaline electrolytes and is relatively plentiful. The DMFC uses only methanol and air, usually produces only carbon dioxide & water and is therefore pollution free and hence environmentally benign.

The potential markets of DMFCs are both as an alternative to storage batteries and also as an independent power generator where high output is required. Probable applications include use in video cameras & recorders, and in boats & RVs, where in many cases batteries can only be used for short operating periods before recharging is required, whereas fuel cells are supplied with the fuel. DMFCs have the advantage of using a relatively safe liquid at a low operating temperature and in the long term they could find application as alternative power sources for vehicle propulsion.

1.3 Reasons for using methanol

Generally an ideal fuel should have the following properties:

1. Cheap and ready availability.
2. Liquid state over a wide range of temperature of operation.
3. Chemical stability and solubility in strong acids or alkaline.
4. Low viscosity.
5. High calorific value.
6. Formation of inoffensive gaseous reaction products.
7. Rapid oxidation at a suitable anode.
8. Minimum overvoltage.

9. Easy conversion into final oxidation products such as carbon dioxide and water.
10. Inertness at the cathode.

A few liquid fuels can be considered to possess most of the properties, though in practice, no single substance is likely to exist having all the above properties. Liquid fuels suggested to date include: glycol, glycerol, formaldehyde, hydrazine, methanol, isopropyl alcohol, etc. Of these methanol has attracted most interest due to the following reasons:

1. It has a low carbon content.
2. It has high solubility in aqueous electrolytes.
3. It possesses a readily oxidizable hydroxyl group.
4. It is inexpensive and readily available compared to other alcohols.
5. Ease of retrieval from its sources.
6. It can be distributed to the consumer very easily.
7. It is the most electroactive organic fuel, undergoing electrooxidation at the fuel cell electrode at temperatures below 80°C.

1.4 Methanol electrooxidation in acid medium

In an acidic electrolyte the two half cell reactions given in eqn.(1.3) occur. The theoretical voltage difference between the electrode potentials of the two reactions is 1.2V which corresponds to a ΔG (reaction) of -702.5 kJ/mol [9].

$$CH_3OH + H_2O \Rightarrow CO_2 + 6H^+ + 6e$$

$$O_2 + 4H^+ + 4e \Rightarrow 2H_2O \qquad (1.3)$$

The total reaction of the cell is given in eqn.(1.4)

$$CH_3OH + 3/2\,O_2 \Rightarrow CO_2 + 2H_2O \qquad (1.4)$$

Acid electrolytes are generally used for the oxidation of methanol to avoid the build up of carbonate in the electrolyte (section 1.5). In contrast, alkaline electrolytes offer superior electrochemical performance and improved fuel cell output compared to acid systems. A schematic representation of an acid electrolytic DMFC is shown in figure 1.2.

Probably the first operating direct methanol fuel cell was built by Shell Research in 1965[10]; this cell gave only 0.25V at 30mA/cm^2, i.e., less than one fourth of the theoretical value. More recent research[11] on a laboratory scale fuel cell gave 0.5V at 300mA/cm^2 at a temperature of 90°C.

Although the maximum voltage attainable from the overall reaction in the methanol-air cell is in theory 1.2V; in practice this is not achieved. There are several reasons for this reduced voltage :

(a) The reversible methanol oxidation potential is not observed due to the occurrence of additional reactions involving formaldehyde and formic acid species and a mixed potential results.

(b) The overpotential required to achieve useful currents is very high due to poisoning of the catalyst.

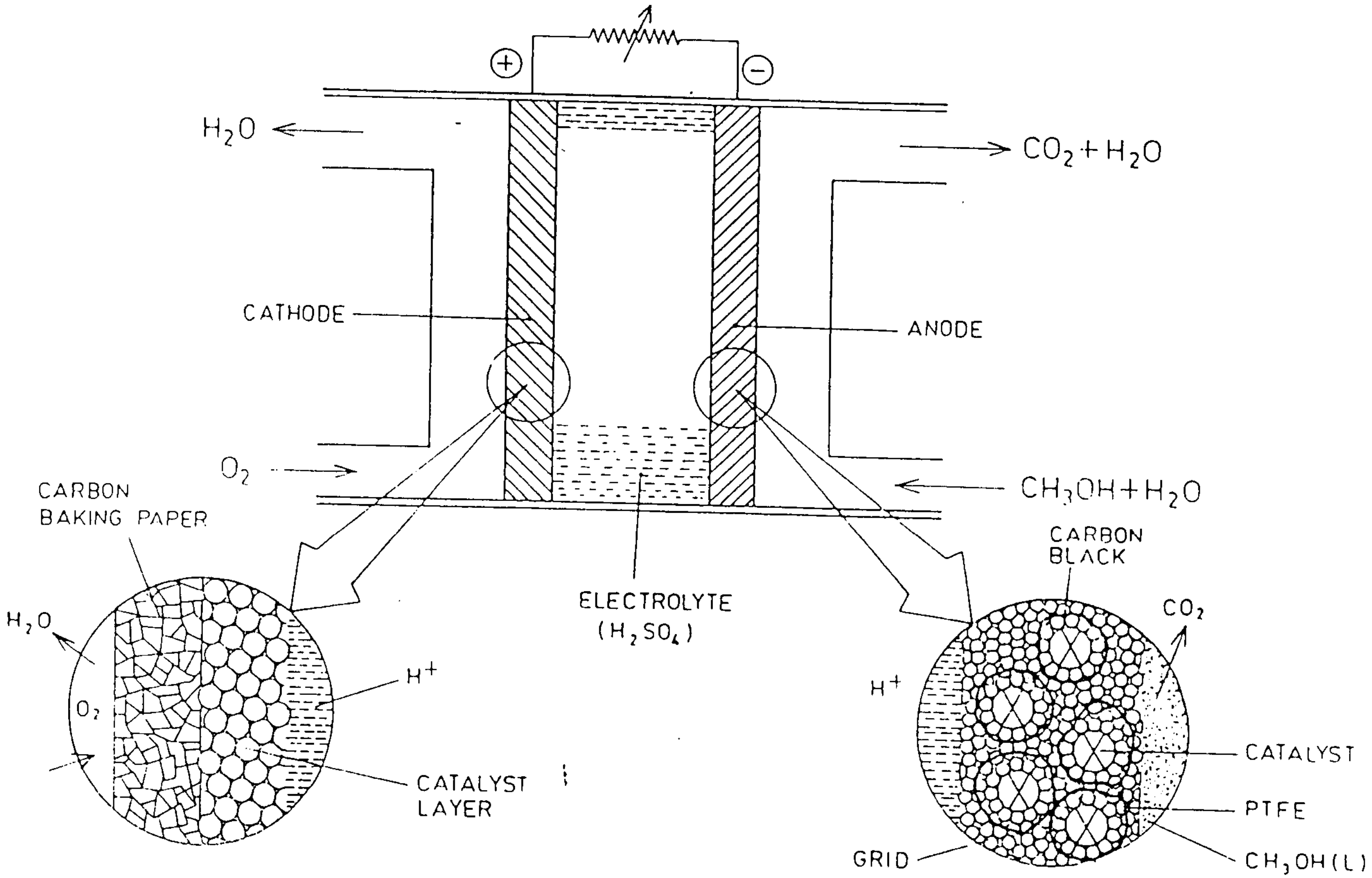

Figure 1.2 Principle model for Direct Methanol Fuel Cell in acid electrolyte.

(c) The oxygen reduction electrode also has a mixed reversible potential due to peroxide formation and suffers from a high overpotential, although not as severe as the methanol electrode.

The main problem, in spite of extensive research in the last 30 years in DMFC, is primarily electrocatalytic and is associated with the need to reduce substantially the overpotential at the anode. To explain the nature of the problem, it is necessary to look at the generally accepted reaction mechanism for the oxidation of methanol on a platinum electrode. This has been reviewed in detail in literature[12,13], and a brief outline is given in the next chapter.

1.5 Methanol electrooxidation in alkaline medium

Oxidation of methanol in alkaline solution leads to the production of carbonate according to the following reaction :

$$CH_3OH + 8OH^- \Rightarrow CO_3^{2-} + 6H_2O + 6e \qquad (1.5)$$

Due to the carbonate build up in the anode compartment, continuous replenishment of the electrolyte in practical cells is required. But there are two major incentives that prompted researchers to study methanol oxidation in alkaline solution :

(1) Potential use of inexpensive non-noble metal electrocatalysts, and

(2) The higher reaction rates compared with acid electrolyte, especially at room temperature.

The latter has been attributed to a slower rate of adsorption of the poisoning intermediates on the electrode surface[14] and to a reaction mechanism which is less complex than in acid medium due to the formation of adsorbed CO which is more easily oxidized than the strongly adsorbed C-OH species present in acid.

In general, noble metals and their alloys display the highest activities for methanol oxidation in alkaline medium. Other catalysts reported in the literature are Raney Nickel, nickel oxide and nickel alloys[15].

Chapter 2

Literature Review

2.1 Mechanism for the electrooxidation of methanol

Through the years a number of review articles on the electrooxidation of methanol have appeared[7,8,16,17] and the generally accepted mechanism for the oxidation of methanol is given in figure 2.1.

From aqueous solutions, methanol is adsorbed to the Pt surface via the carbon atom. Franaszcuk *et al* [18] suggest that hydrogen bonding takes place between the alcoholic group and the water molecules. This is in contrast with gas-phase adsorption at low temperatures for which they[18] and others[19] have shown that the methoxy species is formed at the catalyst surface; here the bonding occurs via oxygen.

The methanol residue is oxidized to carbon dioxide by adsorbed hydroxy species. The presence of these hydroxy species appears to be essential for the methanol electrooxidation. The problem is that these species are only formed in appreciable amounts at relatively high potentials (>0.74V *vs.* Reversible Hydrogen Electrode (RHE)). On the other hand methanol cannot adsorb on the platinum oxides which are formed as well at these potentials. Burke and co-workers[20,21] suggest that a hydrous oxide is the oxygen delivering species. This hydrous-oxide is however not very likely to play a role in the methanol oxidation, because of extreme condition which are necessary to generate these

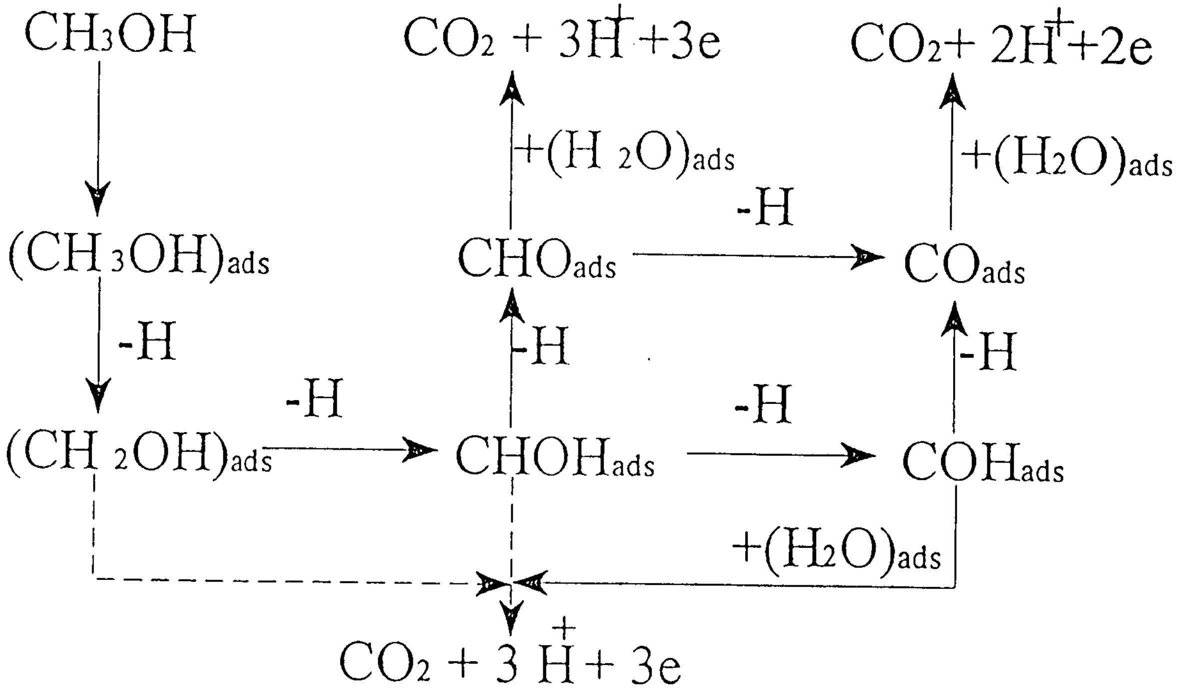

Figure 2.1 Mechanism for the electrocatalytic oxidation of methanol on Pt in acidic electrolytes.

species. Vassiliev *et al* [22] concluded on the basis of measurements in pure methanol that water molecules are needed for the dehydrogenation of the methanol molecules, because no dehydrogenation takes place in pure methanol.

At a platinum electrode, the reaction of the COH with OH species adsorbed, occurs as follows[23] :

$$Pt_3COH + PtOH \Rightarrow Pt_2CO + H_2O$$

$$Pt_2CO + PtOH \Rightarrow PtCOOH + 2Pt$$

$$PtCOOH + PtOH \Rightarrow 2Pt + H_2O + CO_2$$

The above mechanism assumes that the catalyst is direct functional, that is to say, that it must electrosorb methanol and water at the same site.

The identity of the adsorbed species and of the reaction intermediate in the methanol electrooxidation has been the subject of considerable controversy over the past 20 years. In recent years the detection and identification of these intermediates has been aided by the development of in-situ Infra Red (IR) and Mass Spectroscopic (MS) techniques. All the IR techniques give the possibility of detecting an intermediate as a function of the electrode potential, although the various methods differ in the way to achieve this. The techniques most used are EMIRS[24] (Electrochemically Modulated Infrared Spectroscopy), SNIFTIRS[25] (Subtractively Normalized FTIRS), PMIRRAS[26] (Polarization Modulated IR Reflection Absorption Spectroscopy), SPAIRS[27] (Single Potential Alteration IRS) and LPSIRS[28] (Linear Polarized Sweep IRS). With the MS techniques the intermediates can be either detected indirectly by on-line determination of products as function of potential (Differential Electrochemical Mass Spectroscopy (DEMS)[29]), or directly by transferring the electrode to a vacuum chamber and performing temperature programmed desorption (Electrochemical Thermal Desorption Mass Spectroscopy[30]).

In spite of extensive research, there is still no overall consensus on the intermediates involved in methanol electrooxidation over platinum (mono- or polycrystalline). Although IR, DEMS and electrochemical methods all show that CO (either linear or bridge bonded) and/or COH are present, it is still not clear under what circumstances which adsorbate is present. With IR measurements, the presence of CHO has been claimed too. The small amounts of bridge/multi-bonded CO found with IR seems to be due to the small cross-section of these species. But, it is yet to be determined whether either CO or COH or both are found to be present on the electrode surface.

2.2 Effects of electrolyte

Figure 2.2 shows the effect of varying the electrolyte type, when using Pt/Ru catalysts. Although greatly enhanced activity is obtained by using electrolytes of high pH, they suffer the drawback of becoming carbonated both by carbon dioxide released as a reaction product from the anode and by naturally occurring CO_2 in the air passed over the cathode.

Anion adsorption is also known to occur on Pt catalysts in electrolytes. The activity of Pt for methanol oxidation in H_2SO_4 is well below that in $HClO_4$[31-

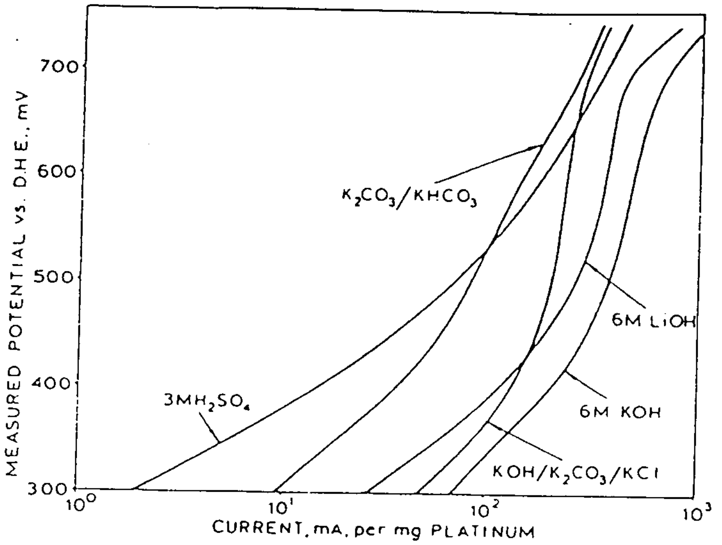

Figure 2.2 The performance of the methanol oxidation electrode can be influenced by changing the electrolyte. In alkaline solution, that is at high pH, the reaction is enhanced significantly but alkaline electrolytes suffer the disadvantage of carbonation which ultimately causes deactivation.[2]

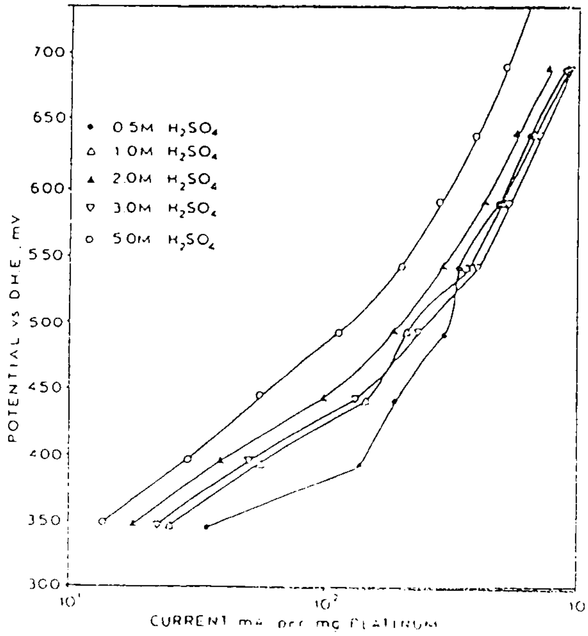

Figure 2.3 The activity of an acid Direct Methanol Fuel Cell is increased as the concentration of the electrolyte is lowered. In practice a compromise between the anode and cathode activity and electrolyte conductivity must be achieved.[2]

33]; this effect is strongest for Pt(111)[34,35], while no effect is found for Pt(110)[36]. Castro Luna *et al.* [37] have shown that the values of maximum coverage of the organic species defined as θ_{org}^{max}, for electrodispersed Pt, attained in different electrolytes are 0.82, 0.74 and 0.62 for 1M $HClO_4$, 0.5M H_2SO_4 and 0.3M H_3PO_4 respectively, thus showing the influence of the electrolyte anion on the maximum available surface coverage. In $HClO_4$ a higher coverage of the poison is reached and the rate of poisoning is faster; so on the whole, there is no clear advantage of $HClO_4$ over 0.5M H_2SO_4. The concentration of sulfuric acid has a great influence on the catalytic activity (figure 2.3) for the methanol electrooxidation and a concentration of about 0.5M is the optimum. For the high current densities required in fuel cell applications, however, a compromise is necessary between activity and solution conductivity. In this case, the optimum is at a concentration of about 3M[8,2]. Surface oxide formation is also influenced by the nature of the acid anion. It has been shown[32,33] that in $HClO_4$ the surface oxidation starts at lower potentials than in H_2SO_4, leading to a lower potential for the start of the methanol oxidation.

2.3 Effects of temperature

The performance of the direct methanol fuel cell anode is profoundly affected by temperature (figures 2.4 & 2.5). The slopes of the Arrhenius plot for platinum and platinum-ruthenium co-deposited catalysts are parallel, indicating a similar mechanism.

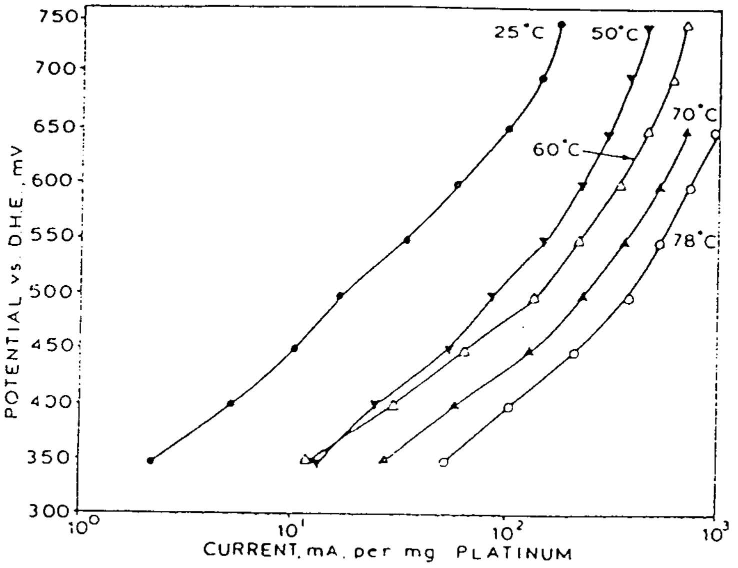

Figure 2.4 The performance of the direct methanol fuel cell may be enhanced by increasing the stack operating temperature, although the temperature increase must be limited to prevent methanol loss by vaporization.[11]

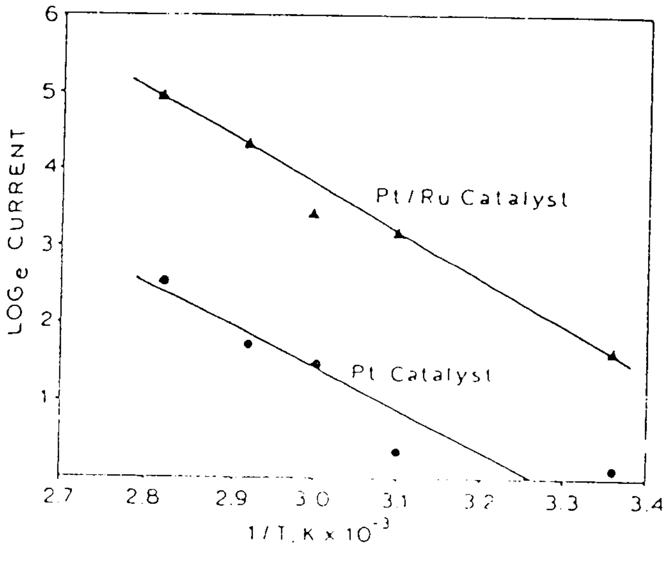

Figure 2.5 An Arrhenius plot for platinum and platinum/ruthenium catalysts indicates that ruthenium promotes the activity of platinum but does not change the mechanism of the anode reaction.[11]

The upper limit of operation for small practical fuel cells is determined by the high vapor pressure and low boiling point of methanol fuel. Temperatures below 60°C are required to avoid excessive evaporative losses. For larger cells, more sophisticated engineering solutions, such as system pressurization may become feasible[38].

2.4 Electrocatalysts studied

2.4.1 Platinum

Precious metals were found to be good electrocatalysts for the oxidation of methanol. The most widely used electrode/substrate material is, platinum.

In order to use Pt as a catalyst in practical fuel cells, the surface area must be large, which can be achieved by depositing small Pt particles on a conducting support or by electrochemically roughening the surface of platinum. EMIR Spectra show[39,40] that on electrochemical roughened platinum surface, the amount of adsorbed CO decreases, even at potentials (0.3V Vs RHE) at which smooth Pt is known to be covered nearly completely with CO. Also the amount of CO appears to decrease with increase in the electrode roughness. Beden *et al.*[39] suggest that this is due to the presence of mainly Pt(111) faces, and the development of these faces has been deduced from X-Ray diffractometry on electrodispersed electrodes[41].

Research on Pt single crystal surfaces[31,16] has shown that the behavior of Pt(111) differs markedly from Pt(110) and Pt(100). On repetitive oxidation and reduction cycling noticeable decreases in current are observed on Pt(100) and Pt(110), but not on Pt(111)[34]; this agrees with the fact that less CO can be seen on Pt(111), assuming that this is the poisoning species. Lamy *et al* [42] suggested multibonded CO to be the poisoning species and this species is preferentially bonded on Pt(110), the surface which shows the fastest deactivation[36].

2.4.2 Carbon supported platinum

It is well known that by decreasing the particle size, one can increase the surface area and also change the catalytic behavior of a material. Hence, high surface area carbon powders are used as the conducting support to disperse platinum particles. Carbon blacks, active carbon and graphite are the commonly used supports. Most popular for fundamental studies is a high surface area carbon black: Vulcan XC-72, with a specific surface area of 300m^2/g.

The type of the carbon support can affect the catalytic behavior due to differing metal-support interaction. On the basis of ESR and XPS studies[43,44], it has been concluded that electron donation by platinum to the carbon support takes place, and it is believed that the extent of donation is influenced by the particle size of the platinum. The particle size in turn depends upon the Pt/C preparation method. The widely used methods are as follows:

1. The impregnation method: the support is impregnated with H_2PtCl_6 which is then reduced with a strong reducing agent such as $NaBH_4$[45].
2. The ion exchange method: the carbon support is oxidized to form carboxylic acid groups and then ion exchanged with $Pt(NH_3)_4(OH)_2$[46].
3. The colloidal method: a monodispersed Pt sol(prepared by reducing H_2PtCl_6 with e.g. sodium citrate) is added to the support[47].
4. Chemical vapor deposition: the platinum is vaporized on a substrate e.g. glassy carbon[48].
5. Electrodeposition of platinum on Teflon bonded carbon support[49].

The high performance of carbon supported Pt is probably due to a relatively low potential of formation of an adsorbed hydroxy species. The particle size effect on methanol electrooxidation has been investigated by McNicol *et al.*[50] employing Pt catalysts prepared in a variety of ways. They report that the activity decreases for very small and very large particles. This variation is explained as follows: For larger particles the activation of water still takes place at a relatively high potential, so that the coverage of the hydroxy species (θ_{OH}) is still relatively low at the potential at which the comparison is made. Decreasing the particle size results in OH formation at lower potentials, and so enhances the reaction rate. However, for very small particles, activation of water takes place at such low potentials, that even at relatively low overpotentials the surface coverage with OH is already so substantial, that the CH_3OH adsorption step begins to suffer. That is, decreasing the particle size too much results in a change of rate determining step with a concomitant decrease in the specific activity. However, this particle size effect cannot be fully separated from the metal-support effect, which has indeed been found to influence the methanol oxidation activity[51].

In summary, Pt/C catalysts do have a higher specific activity for the methanol electrooxidation than smooth Pt and they are more stable. This is mainly due to the effect of particle size on water activation and the decrease in CO_{ad} poisoning.

2.4.3 Bimetallic catalysts

The activity of Pt can be enhanced by introducing a second metal like Ru or Sn[52]. Although there is no consensus about the actual mechanism of this promotion effect, different explanations have been proposed:

1. An electronic (ligand) effect[53] where the second metal alters the electronic state of platinum in such a way that the activation of water is increased and/or the methanolic residue is less strongly bonded.
2. A geometric (third body) effect: the second metal blocks certain adsorption sites on the surface, so as to prevent/retard the build-up of poisoning species.
3. A bifunctional effect: the second metal specifically takes care of the activation of water, thus increasing the oxidation rate of methanol residue.

4. A redox effect of the metal ion, where the oxidized form oxidizes the methanol residue, upon which it is regenerated by water.

The geometric effect, however can be discarded, because of the different metals with similar metal overlayer structures should have a similar effect on the methanol oxidation. This was not the case as shown by Janssen and Moolhuysen[54] and Leiva and Giordano[33,55].

Platinum-Ruthenium[56-61] and Platinum-Tin[52,54,62,63] alloys have been the most extensively studied bimetallic catalysts for the electrooxidation of methanol. Janssen and Moolhuysen prepared PtSn electrodes by immersion, alloying and electrodeposition and found a 50-100 times increase in activity at low potentials (<0.5V Vs RHE) with respect to unpromoted Pt electrodes.

Although the reason for enhanced methanol oxidation activity due to the addition of Ru to Pt is not completely clear, the existence of a ligand effect suggests that it may be due to a weakening of the bond between Pt and the methanolic adsorbate. On the other hand there is now increasing evidence that the addition of Ru results in an increased facility of water activation[58-61,64].

In the case of PtSn, the effect of Sn on methanol oxidation activity of Pt turns out to be rather variable. A point however on which there appears to be a consensus is that in the presence of Sn a large amount of oxygen is present on the surface. Whether this is due to the activation of water by Sn itself, or due to an electronic effect through which Pt can activate water more easily, is still a matter that is open for discussion. Carbon supported electrodes of these alloys i.e., PtRu/C and PtSn/C are also more active for methanol electrooxidation than Pt/C[11,65,66].

Other metals have been suggested as promoters too. Small increases in activity were found for Mo[67,68,69], Nb_2O_5, TiO_2[70], ZrO_2[71] and platinum containing Ni-Nb alloys[72]. Furthermore, it has been shown that Au[73], Cu[35], Ag, As, Pb[55,33], Bi[74,75] and Sb[76] result in a decrease in the methanol oxidation activity.

2.5 Supports other than carbon

2.5.1 Solid polymer electrolytes(SPE)

The introduction of SPE membranes as electrolytes and support systems has led to the extensive investigation of Pt-SPE electrodes for methanol oxidation[77,78]. Although Pt supported on aSPE shows less activity per real cm^2 than platinised platinum electrode, Aramata and Veersai[79,80] found that the activity of the SPE supported catalyst does not decrease. A reasonable explanation for the long-term stability is the stabilization of Pt-oxides. From XPS data it appears that the ratio of Pt^{2+}/Pt is greater on Pt-SPE than on platinised platinum[80]. It is suggested that the Pt^{2+} species is stabilized by the SPE matrix, which is the same effect that has been reported for $Pt\text{-}SnO_2$.

2.5.2 Tungsten oxides

Tungsten oxides have been examined as a supporting material for Pt based electrodes both as pure tungsten oxides and as rare-earth metal tungsten bronzes(Ln_xWO_3). Machida *et al.*[81] found that the pure rare-earth tungsten bronzes do not show any activity, Pt doped systems($PtDy_{0.1}WO_3$) however do. Tseung *et al.*[82,83] reported an increase in the methanol oxidation activity for co-deposited Pt-WO_3 systems compared to electrodeposited Pt on a platinum surface. The effect of WO_3 was ascribed to an increased water activation. It has also been suggested[81] that the higher activity is due to the removal of strongly adsorbed species (CO) by a WO_3/WO_3^+ redox couple; however, no clear relationship between the redox potential of this couple and the specific activity was found.

2.5.3 Polyaniline and polypyrrole

Considerable interest has also been shown in polyaniline as a support for Pt[84,85,86]. Earlier results show that the main oxidation product was HCHO. But the addition of Ru[87] and Sn[88] result in a more efficient oxidation and an increase in activity. A higher activity than Pt alone was also reported for Pt in polypyrrole[89], the activity however being given for the geometric surface area.

2.5.4 Tungsten carbide

According to Levy and Bourdart[90] the electronic structure of WC is similar to that of Pt which implies that WC could be a catalyst for methanol oxidation. The major problem is that WC does not easily adsorb methanol, whereas water is adsorbed very strongly[91], which is the opposite behavior to Pt itself. Some methanol oxidation activity was however found[92,93], especially in the presence of Mo[94,95].

It is clear that WC has an activity that is far too low for practical purposes. It might however be suitable as a support for Pt based catalysts.

2.6 Introduction to platinum-oxides

Platinum, though chemically inert and stable to high temperatures, has been known to react with alkali and alkaline earth metals to form ternary platinum oxides when used as a container in several synthesis experiments [96-99].

Platinum oxides have been of interest due to the potential use of their catalytic and electrochemical properties[100,101]. Even minor amounts of platinum substituted into an oxide with the perovskite structure results in an appreciable increase in catalytic activity[102]. Also the discovery of high conductivity in some ternary platinum oxides containing chain of platinum atoms[103-106] has led to the investigations of the relationships between their crystal structures, chemistry and physical properties[107,108].

The only investigation on ternary platinum oxides as electrocatalysts for the oxidation of methanol was carried out by White and Sammells[109]. They prepared and studied high surface area perovskite electrocatalysts of the general composition ABO_3(A= Sr, Ce, Sm, Pb or La and B= Co, Pt, Pd or Ru). According to them, $SrRu_{0.5}Pt_{0.5}O_3$ dispersed as an electrocatalyst onto a polymer electrolyte gave up to 28mA/cm^2 at 0.45V Vs SCE at 87°C for the oxidation of methanol. The potential ability of these perovskite anode electrocatalysts for maintaining enhanced long-term activity may be related to their capacity towards supplying basic surface oxide ions for dehydrogenation of adsorbed methanol and for subsequent oxidative reaction towards chemisorbed intermediates which otherwise poison electrocatalytic reaction sites.

Chapter 3

Scope and objectives

3.1 Introduction

It is evident from the literature review that the problem of poor catalytic activity remains the main barrier to the success of the direct methanol oxidation fuel cell. The work described in this thesis is aimed towards the improvement of the catalytic activity for the electrooxidation of methanol using metal oxide catalysts.

3.2 Choice of electrocatalyst

The use of base-metal oxides especially the Group IV - VI transition metal oxides as gas-phase catalysts for a wide variety of oxidation reactions including the partial oxidation of methanol to formaldehyde[110] and the oxidative dimerisation of methane[111] is now well known. As a consequence of the fact that most of these oxides are poor electrical conductors very little is known about their ability to catalyze electrochemical reactions, although there is evidence to suggest that some conducting metal oxides are electrochemically active[112,113]. Deposition of insulating transition metal oxides on a conductive support, such as carbon black, does potentially offer a method of utilizing their catalytic ability in electrochemical reactions.

For the oxidation of methanol, both adsorption of the fuel from solution and oxygen atom transfer must take place. Although, in principle, oxides could supply the latter, it is very unlikely that methanol will adsorb preferentially on oxide surfaces. Hence a lot of oxides have been examined as catalysts only by incorporating platinum as a co-catalyst[114-116].

White and Sammells[109] were the first to study ternary platinum oxides suchas $SrRu_{0.5}Pt_{0.5}O_3$, as electrocatalysts for the oxidation of methanol. Based on their results, we decided to investigate some more ternary Pt-oxide electrocatalysts. A literature review showed that there was no study conducted on other precious metal oxides. Hence, the electrocatalysts put under study in this work were as follows :

$BaPtO_3$, Sr_4PtO_6, $PtO_2.H_2O$, $H_2Pt(OH)_6$, PdO, IrO_2 and RuO_2.

3.3 Choice of electrolyte

The long range goal of fuel cell research is the development of fuel cells that operate on inexpensive fuels, converting chemical energy into electrical energy with high efficiencies at practical current densities using inexpensive electrode materials They must have long operational life and a low cost of replacement of aging parts. A preliminary assessment of electrode materials has indicated a failure to identify suitable electrocatalysts other than Pt for the air/oxygen reducing electrode in DMFC employing acid electrolytes. Though alkaline electrolytes result in the formation of carbonates as the product of oxidation of methanol that poison the electrodes, it can be slowed down to a value below the tolerable limit.

Alkaline electrolytes show higher catalytic activity for the oxidation of methanol and also give the opportunity to investigate electrocatalysts other than platinum. Moreover, more oxides are stable in alkaline medium than in acid. Hence, all the investigations in this work were carried out in alkaline medium.

3.4 Choice of electrocatalyst support

A high performance for the oxidation reaction requires the fabrication of porous electrodes using substrates that have high surface area on which the catalyst can be effectively dispersed. Moreover, the effective surface area must not be degraded by normal operating conditions. Degradation may be caused by: (1) chemical attack of the electrolyte on the electrodes & current collector (2) poisoning intermediates getting adsorbed on the electrode surface resulting in loss of surface area and high overpotential losses (3) mechanical collapse of the porous electrode structure and (4) sintering due to heat from the internal losses. Therefore, great attention must be directed to the choice of substrate material and the method of electrode fabrication.

Selection of a suitable substrate material is dictated by at least six factors: cost, inertness in the operating medium, ease of fabrication, high electrical conductivity, electrochemical stability and inertness to unwanted side reactions. Various types of active (high surface area) carbon have been reported in the literature as catalyst supports in electrodes used for both oxygen reduction and methanol oxidation in acid and alkaline solutions[117]. The studies have indicated that Vulcan-XC72 from M/s Cabbot Corporation, USA, which has a low ash content, functions as an excellent electrode support material. Also teflon-bonded electrodes of this material are mechanically stable in both acid and alkaline medium. All electrodes in this work were prepared using VulcanXC-72 as the catalyst support.

3.5 Experimental methods

3.5.1 Cyclic Voltammetry

Cyclic voltammetry is probably the most widely used technique for the electrochemical characterization of catalysts. The theoretical as well as experimental aspects have been extensively covered (see for example refs 118-120). A short description will be given here with attention to the application of this technique for the characterization of, and the study of the methanol electrooxidation on, Pt based catalysts.

A schematic representation of the electrochemical cell that is used for cyclic voltammetry is shown in figure 3.1. A three electrode system is used, where the potential of the working electrode is changed with respect to the fixed potential reference electrode, according to the potential program in figure 3.1. In the experiments described in this thesis, a standard calomel electrode has been used. This reference electrode, which is denoted as SCE has a potential of E= 0.24V Vs RHE(Reversible Hydrogen Electrode).

Cyclic voltammetry was used to study Pt in an acid electrolyte for the first time by Will and Knorr[121]. The result of the cyclic voltammetric experiment on Pt in 0.5M H_2SO_4 is shown in figure 3.2. In the presence of 0.1M CH_3OH, the cyclic voltammogram changes, as shown in figure 3.3. First, it can be noted that the hydrogen adsorption/desorption regions (i.e., regions A & B in figure 3.2) are suppressed considerably due to the formation of adsorbed methanolic residues which block the surface for hydrogen adsorption. Furthermore, in the anodic direction a current peak is seen due to the oxidation of methanol; the potential of this peak coincides with potential of oxide formation (eqn.3.1) in the absence of CH_3OH (region C in figure 3.2).

$$\mathrm{PtOH} \Rightarrow \mathrm{PtO} + \mathrm{H}^+ + e \qquad (3.1)$$

The oxides block the surface from further methanol adsorption, and the current due to methanol oxidation diminishes as the surface becomes totally blocked by oxides. In the reverse scan, the methanol oxidation starts at the potential where the Pt-oxide is reduced; thereby free platinum sites are created for methanol adsorption and its oxidation until the potential is too low for the formation of an oxygen delivering species which is necessary for the oxidation of the methanol adsorbates.

Cyclic voltammetry is a dynamic technique, which implies that the activities (or currents) that are measured for the methanol oxidation depend on the rate at which the potential is changed. In this thesis, cyclic voltammetry was

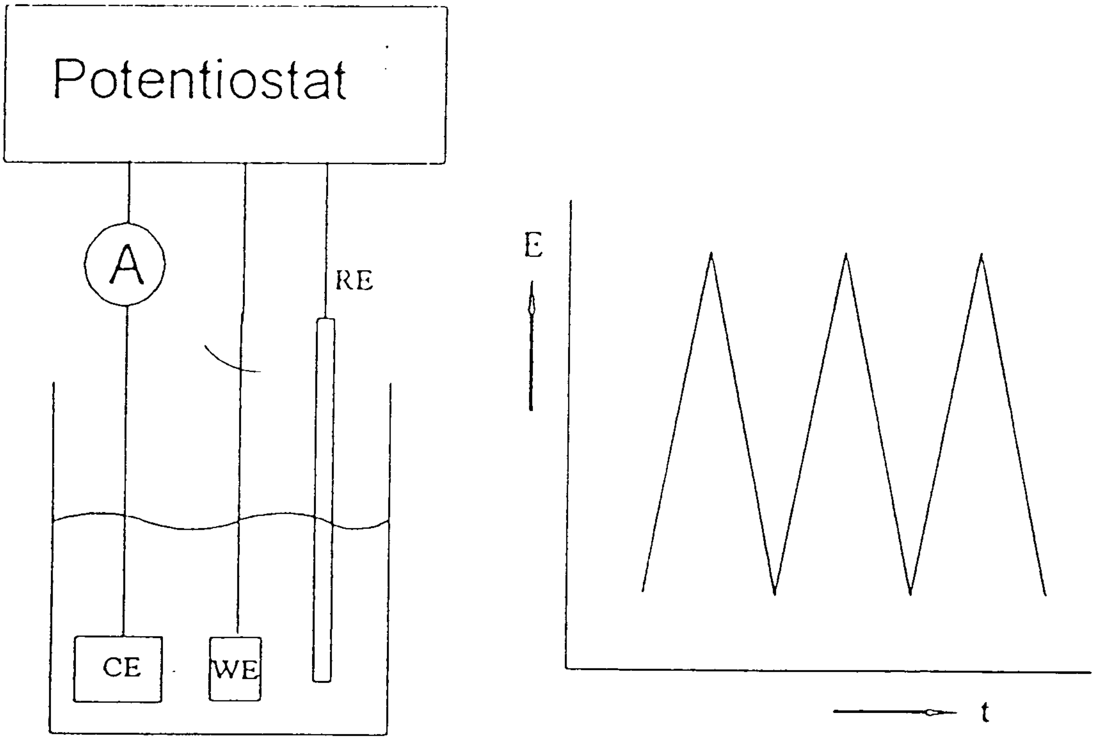

Figure 3.1 Three electrode system for cyclic voltammtery (left) and the potential program for cyclic voltammetry (right). WE=Working electrode; CE=Counter electrode; RE=Reference electrode.

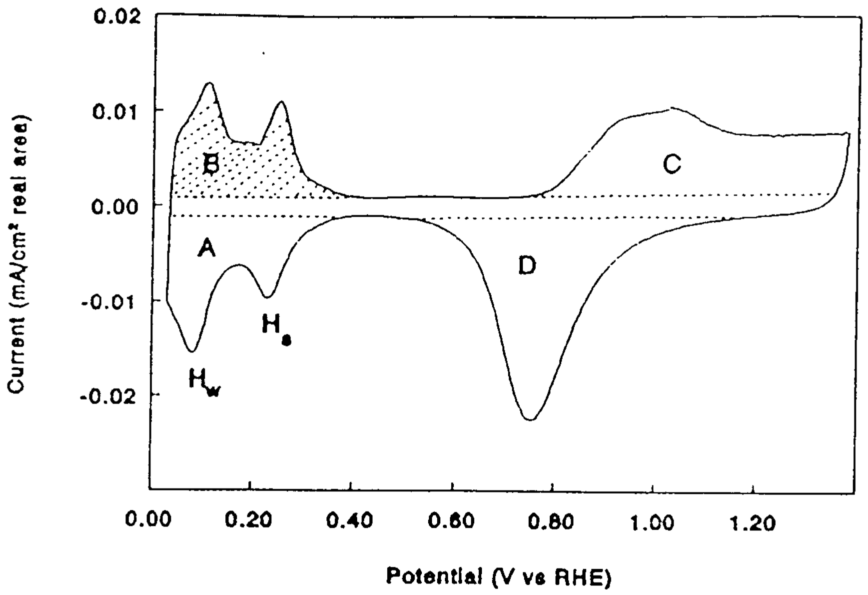

Figure 3.2 Example of a cyclic voltammogram of a Pt electrode in 0.5M H_2SO_4. v=10mV/s.

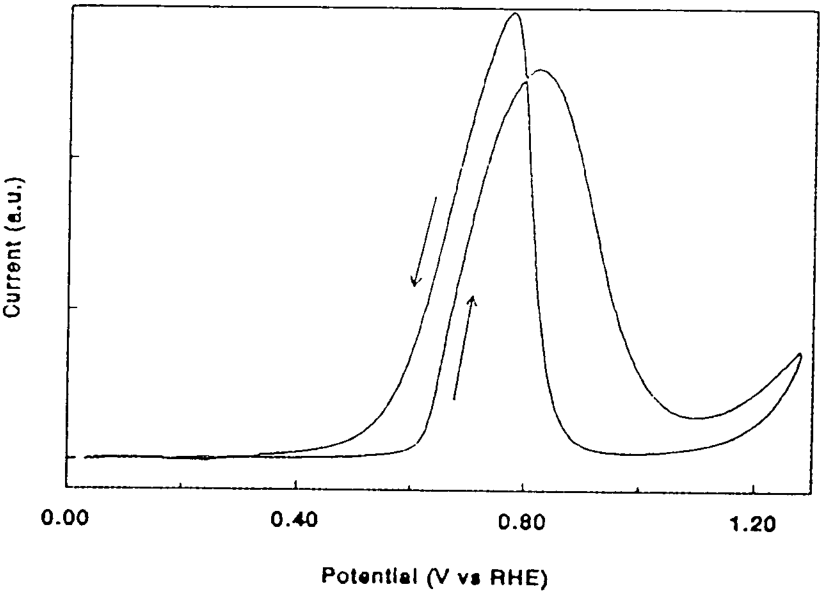

Figure 3.3 Example of a cyclic voltammogram of Pt electrode in the presence of methanol. 0.5M H_2SO_4, 0.1M CH_3OH, v=10mV/s.

carried out at a scan rate of 10mV/s to compare the catalytic activity of the different oxide electrocatalysts.

3.5.2 Chronoamperometry

The technique of voltammetry for studying the redox behavior of electrodes in solutions has several serious drawbacks which arise from the fact that the experimental variables are changing with time and potential, and that rate constants and coverages (either of poison or adatoms) are potential dependent. The oxidation of the fuel and the poison will be occurring simultaneously with further formation of the poisoning intermediate. When a potential step perturbation is applied there is only the element of time to consider since all potential dependent quantities will be constant. It is for these reasons that some workers consider chronoamperometry to be a preferable technique[122,123]. Chronoamperometry is a potential step technique, in which the potential of the working electrode is maintained at a constant value with respect to a reference electrode and the variation of current is measured with respect to time. Chronoamperometry, in the experiments described in this thesis is mainly used as a measure of stability of the oxide electrocatalysts.

Chapter 4

Experimental

4.1 Preparation of the electrocatalysts

4.1.1 Platinum oxides

The principal aim of the current work was to prepare simple oxides with a general formula ABO_3 with platinum on the B-site. The only such compound reported in the literature is $BaPtO_3$; Gallagher *et al.*[124] followed two approaches for its preparation. The first involved the conventional technique of mixing the appropriate oxides (PtO_2 & BaO_2) in the proper amounts and then heating to achieve a complete reaction. It was recognized that, because of the tendency of platinum(IV) towards reduction, this would require a high pressure of oxygen at the reaction temperatures. The second approach was to seek a suitable precursor of the proper stoichiometry such as $BaPt(OH)_6$ which would readily decompose and subsequently react at a sufficiently low temperature that high pressure facilities would not be needed.

The use of oxides as electrocatalysts, requires the selection of a preparation technique that produces high surface area powders. Hence the precursor method was chosen with slight changes in the preparation technique. Stoichiometric amounts of BaO_2 (Atomergic Chemetals Corp.) and $H_2Pt(OH)_6$

(Alfa Aesar) powders were mixed thoroughly, placed in a platinum crucible and heated in air at 600°C for 16 hours.

All attempts to prepare $SrPtO_3$ in the same method were unsuccessful and instead led to the formation of Sr_4PtO_6. Hence stoichiometric amounts of SrO_2 (Pfaltz & Bauer inc.) and $H_2Pt(OH)_6$ were mixed and heated in air at 800°C for 16 hours in a platinum crucible to obtain single phase Sr_4PtO_6. Sr_3NiPtO_6 was also prepared in the same way using stoichiometric amount of NiO (J.T.Baker inc.) along with other reagents.

4.1.2 Other oxides

The other precious metal oxides used were reagent grade and are as follows: $PtO_2.H_2O$ (Cerac inc.), PdO (Cerac inc.), IrO_2 (Strem chemicals) and RuO_2 (Strem chemicals).

4.1.3 Pt/C

Platinum dispersed carbon electrocatalyst powder was prepared by the reduction of chloroplatinic acid. The platinum loading was maintained at 8% by weight.

The required amount of Carbon powder (Vulcan XC-72) was suspended in hot water and a calculated volume of chloroplatinic acid (corresponding to 8wt% of Pt) was added to this solution. The solution was then allowed to boil for one hour. A stoichiomteric volume of 37wt% HCHO (reducing agent) was then added and the entire mixture was allowed to boil and dry. The resulting mass was washed repeatedly with hot distilled water, filtered and dried in an oven at 110°C.

4.2 Preparation of porous carbon electrodes

The porous carbon electrodes were prepared by simple compaction technique. It is shown schematically in figure 4.1.

Initially porous carbon electrodes using only carbon and teflon were prepared to optimize the fabrication technique. The carbon used for this purpose was fuel cell grade carbon, namely Vulcan XC-72 from Cabot Corporation with its characteristic non-wetting property. The ash content of this carbon was reported to be about 0.05% which is significantly lower than the values of 1.5-6% reported for several other carbons. The other physical properties of the carbon are as follows :

Surface area: 254 m^2/g.
mean particle size: 30 nm.
Apparent density: 96 Kg/m^3

The optimum amount of teflon binder required was found to be around 30wt%. Carbon powder was fixed to a 62wt% and the electrocatalyst metal to 8wt%. The amount of the oxide electrocatalysts were calculated based on 8wt% of the metal. The total weight of the electrocatalyst and carbon was around 100 mg.

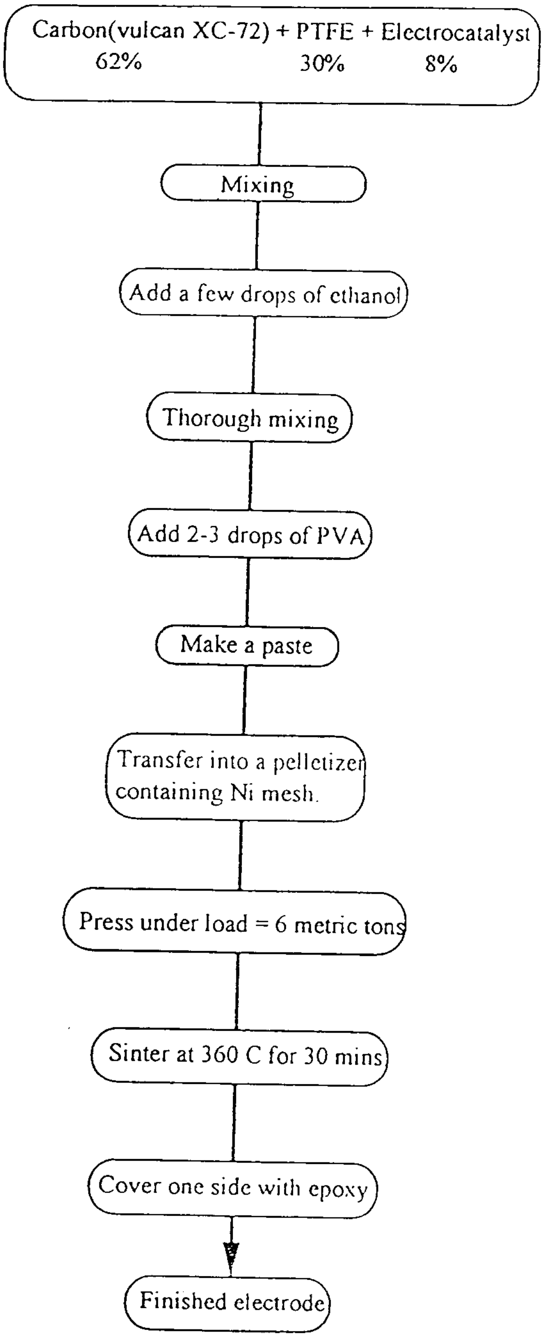

Figure 4.1 Flow chart for the preparation of Carbon-based electrodes.

Calculated amounts of the carbon powder, electrocatalyst and teflon powder (Goodfellow) were mixed thoroughly. A few drops of ethanol was added for further homogeneous mixing. 2 to 3 drops of 5wt% Poly-vinyl alcohol (PVA) was added to make a thick paste.

A nickel mesh(40 mesh woven from 0.13mm dia wire, supplied by Alfa Aesar) was cut to the desired shape in order to fit inside a pelletizer. This was spot welded with a Ni wire and place inside the pelletizer, which had a small slit to keep the wire intact.

The thick paste obtained after PVA addition was transferred into the pelletizer and pressed using a hydraulic press to a pressure of 6 metric tons. The pellet was carefully removed, placed between two ceramic plates and sintered in air at 360°C for 30 minutes. After cooling the electrode in air, its thickness was measured and recorded. One side of the electrode was covered with epoxy, along with a glass tube to extend the Ni wire to the potentiostat probe, thus exposing only one side of the electrode to the electrolytic solution.

4.3 Electrochemical characterization

4.3.1 Experimental setup

All the electrochemical experiments were conducted using a computer controlled Versastat^{TM} potentiostat (EG&G, Princeton Applied Research(PAR)).

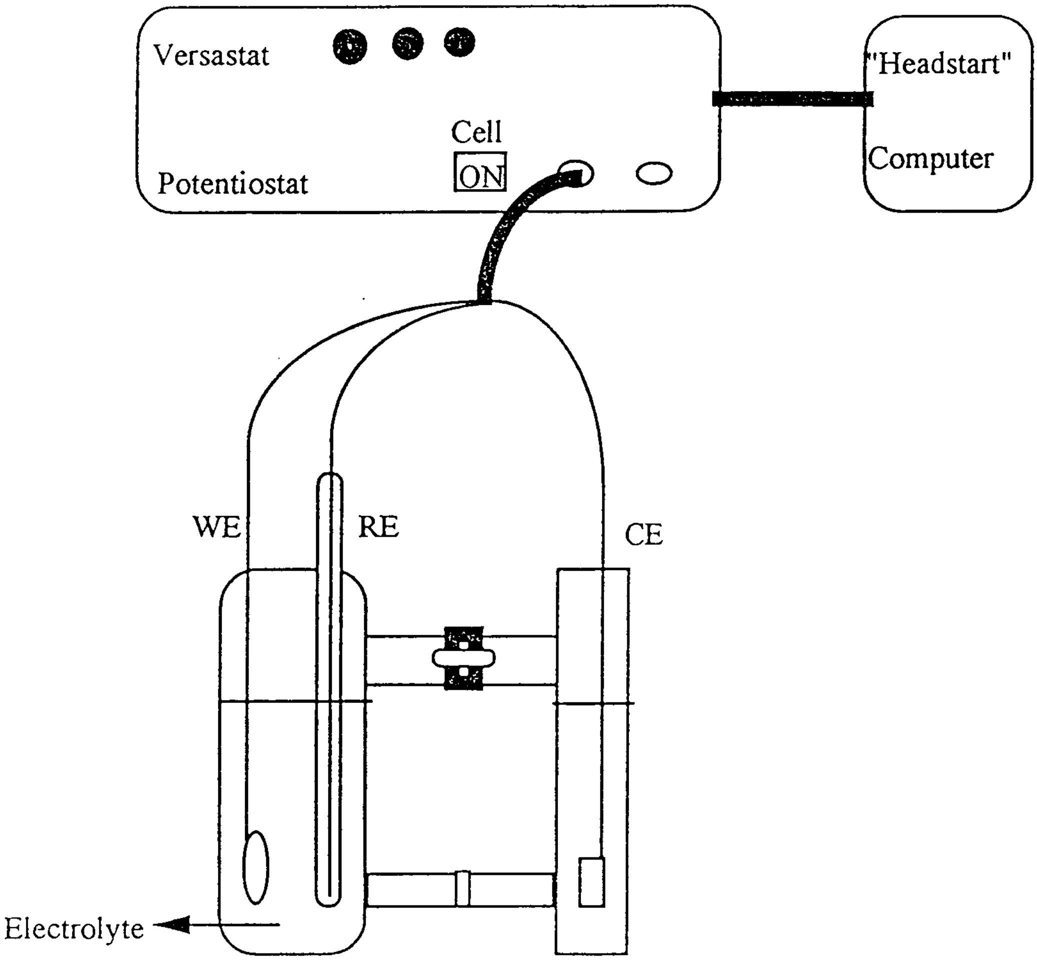

Figure 4.2 Experimental setup for the electrochemical characterization.

The software used for this purpose was headstart, supplied by EG&G, PAR. The working electrode(porous carbon electrode) was connected to the positive terminal and a platinum mesh counter electrode to the negative terminal. All potentials are reported against standard calomel reference electrode.

4.3.2 Cyclic Voltammetry

1M NaOH standard solution was prepared using AR Chemicals and double distilled water. The solution was de-aerated with Ar gas bubbling for 45 minutes. This solution was used as the electrolyte for all cyclic voltammetric experiments, except when the effect of electrolyte concentration was studied. Standard solutions of 0.1M, 0.25M, 0.5M & 0.75M NaOH were prepared to study the effect of electrolyte concentration.

The cyclic voltammetric experiments were carried out under the following conditions :

Working Electrode(WE)	C-based electrodes.
Counter Electrode(CE)	Pt-mesh.
Reference Electrode(RE)	Standard Calomel Electrode(SCE).
Temperature	Room Temp.(~24°C).
Scan range	-1000mV to 100mV *vs*. SCE.
Scan rate	10mV/s.
Number of scans	5.

4.3.3 Chronoamperometry

After CV studies the electrodes were subjected to chronoamperometry in order to measure their stability by holding the electrode at a constant potential *vs.* SCE. The conditions under which this was carried out were as follows:

Working Electrode(WE)	C-based electrodes.
Counter Electrode(CE)	Pt-mesh.
Reference Electrode(RE)	Standard Calomel Electrode (SCE).
Temperature	Room Temp.(~24°C).
Potentials held	-200, -100, 0 & 100mV *vs*. SCE.
Duration	600 seconds.
Time interval between readings	10 seconds.
Electrolyte	1M NaOH + 1M CH_3OH.

4.4 BET characterization

Surface areas of a few of the electrocatalysts were measured using the ASAP 2000 accelerated surface area and porosimetry system. A sample of the electrocatalyst was weighed accurately and degassed for 15 hours. BET analysis was carried out using Nitrogen.

Chapter 5

Results and Discussion

5.1 XRD characterization

The prepared catalyst powders were characterized using a Siemens D5000 Diffraktometer (CuKα radiation) for 2θ values of 2 to 60°. $BaPtO_3$, which was obtained as a light gray powder showed only broad peaks implying that the sample was composed of small crystallites. The pattern (figure 5.1) showed a good match with the values available in the database (34-0850)[124] confirming the major crystalline phase to be $BaPtO_3$. Sr_4PtO_6 and Sr_3NiPtO_6 powders were light purple and dark gray in color, respectively. XRD patterns of these powders (figures 5.2 & 5.3) showed a good match to the standards. Attempts were also made to record XRD patterns of the reagent grade $PtO_2.H_2O$, PdO, IrO_2 and RuO_2 powders. IrO_2 (figure 5.4) powder was found to be single phase and highly crystalline. The small crystallite sizes of $PtO_2.H_2O$ and PdO resulted in very broad peaks (figures 5.6 & 5.7). RuO_2 was found to be essentially amorphous (figure 5.5). The XRD pattern for Pt/C powder is shown in figure 5.8. The presence of Pt was confirmed by the presence of sharp peaks that correspond to the platinum metal peaks. The broad peaks are due to carbon.

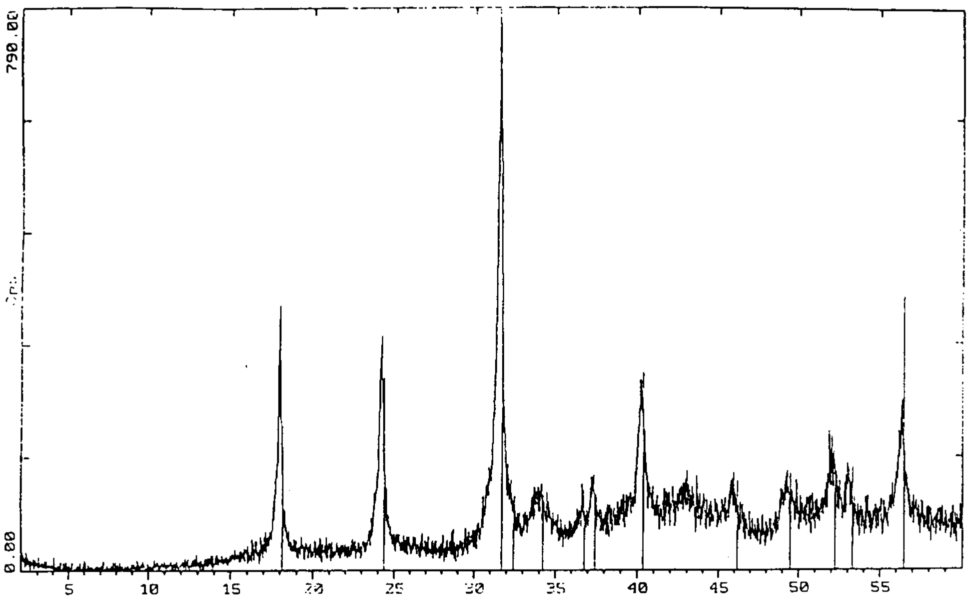

Figure 5.1 X-Ray Diffraction pattern for $BaPtO_3$[124].

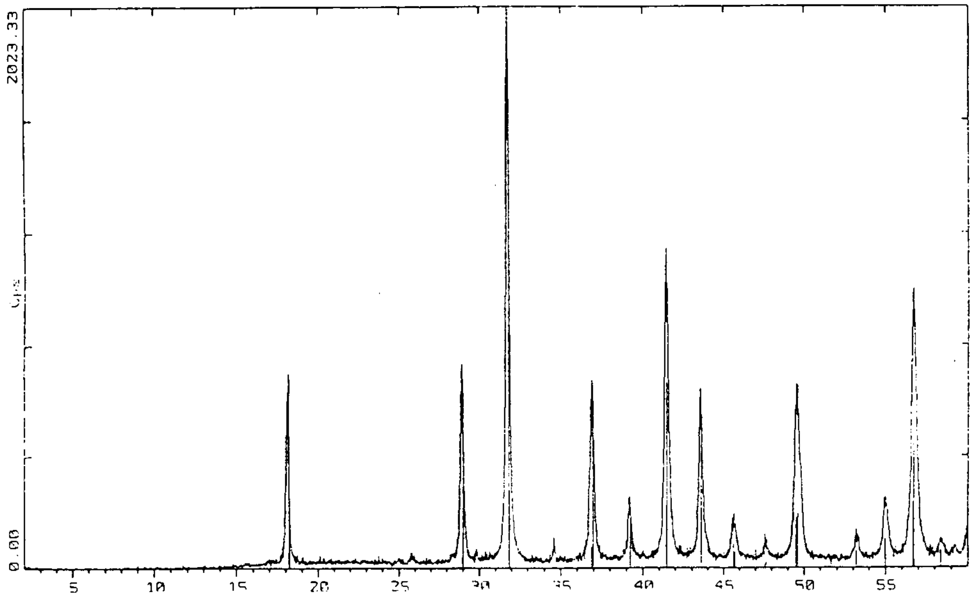

Figure 5.2 X-Ray Diffraction pattern for Sr_4PtO_6[125].

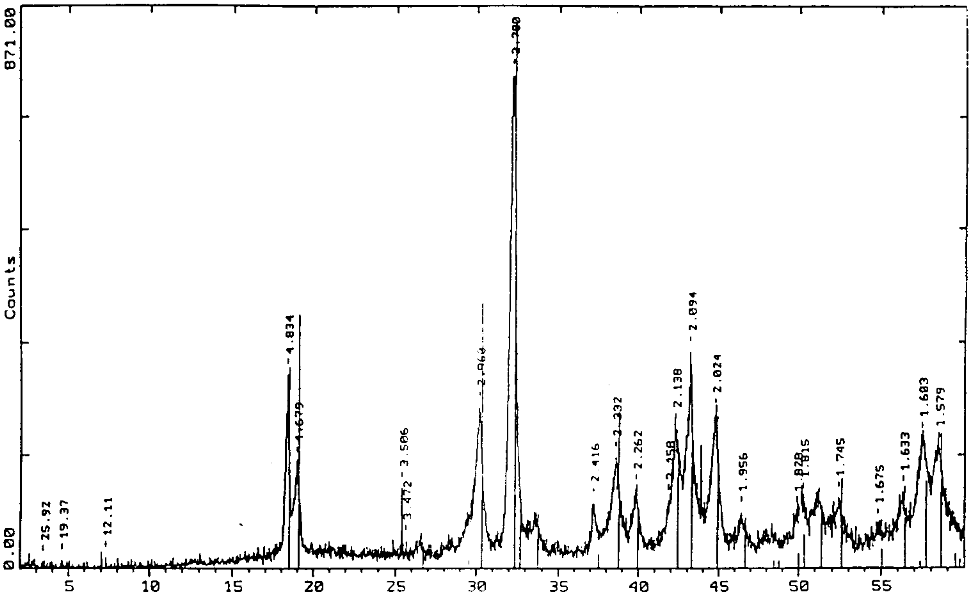

Figure 5.3 X-Ray Diffraction pattern for Sr_3NiPtO_6[126].

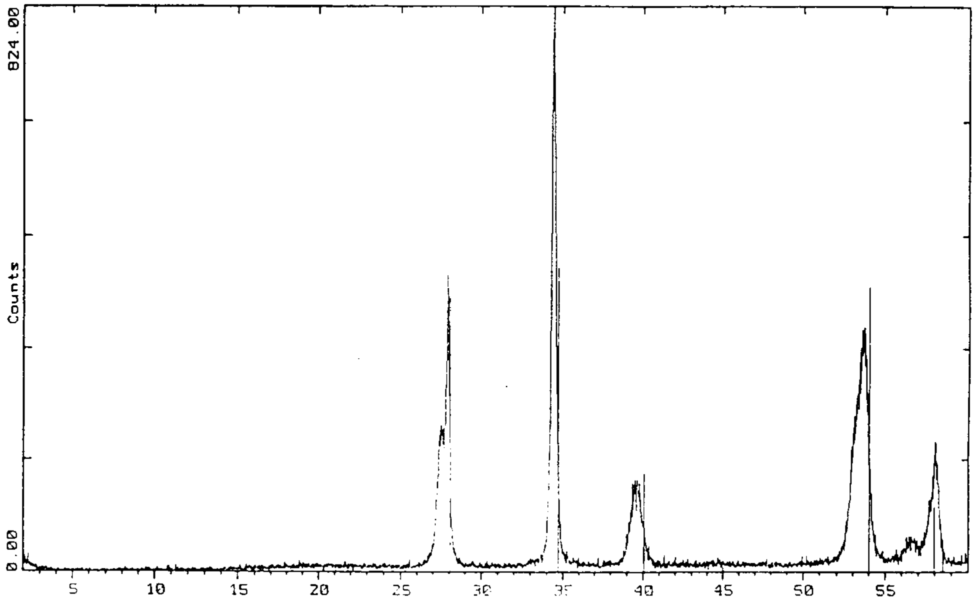

Figure 5.4 X-Ray Diffraction pattern for IrO_2.

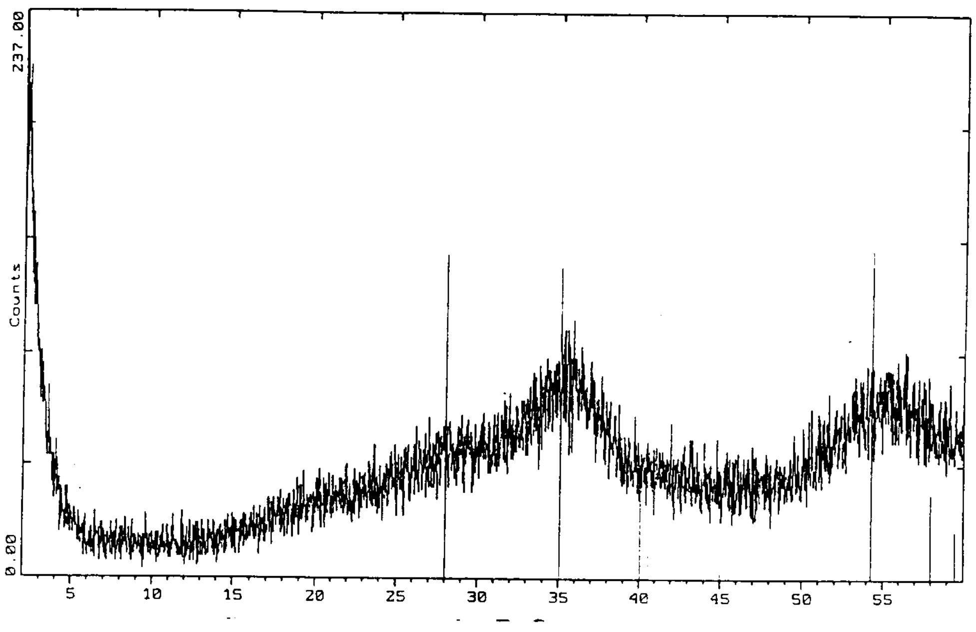

Figure 5.5 X-Ray Diffraction pattern for RuO_2.

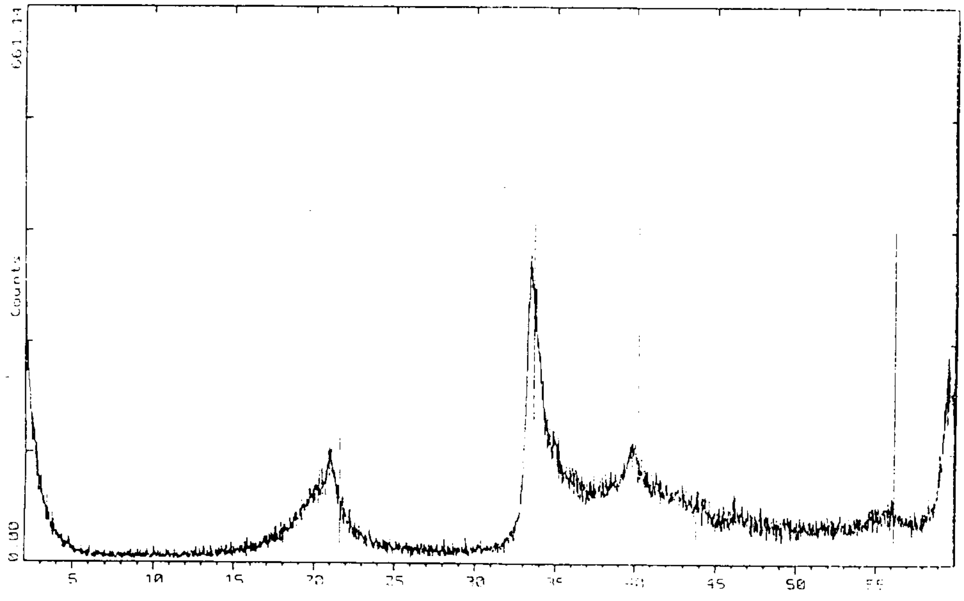

Figure 5.6 X-Ray Diffraction pattern for $PtO_2.H_2O$.

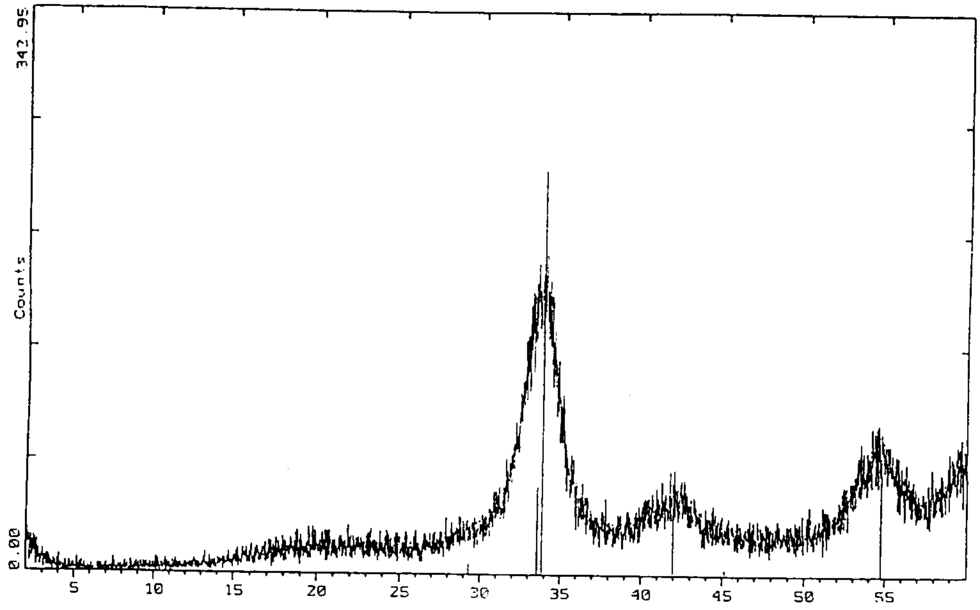

Figure 5.7 X-Ray Diffraction pattern for PdO.

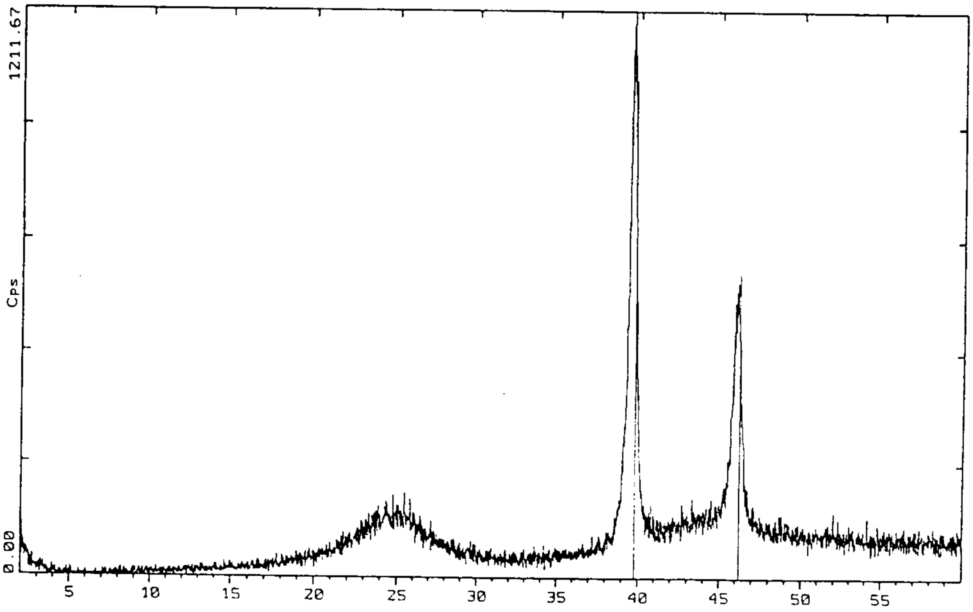

Figure 5.8 X-Ray Diffraction pattern for Pt/C catalyst powder (8wt% Pt).

5.2 Cyclic Voltammetry

In order to study the electrocatalytic activity of platinum for the oxidation of methanol, CVs were performed with Pt foil in 0.5M H_2SO_4+1M CH_3OH and 1M NaOH+1M CH_3OH (figures 5.9 & 5.10). They were found to be identical to those reported in the literature[127,128]. The CV in figure 5.9 has several characteristic features: the inhibition of the hydrogen adsorption/desorption peaks due to the chemisorption of methanol, a relatively low methanol oxidation current at potentials in the double layer region, a peak in the oxidation current near 0.7V *vs* SCE on the anodic scan, followed by a decline as the surface is blocked by the formation of the oxide. Increasing the potential further drives the oxidation of methanol on the oxide surface. On the returning (cathodic) scan, stripping the oxide layer gives rise to the auto-oxidation current as methanol is oxidized on the freshly revealed bare Pt surface. But as potential goes down to 0.5V *vs* SCE, inhibition occurs via the formation of strongly adsorbed methanolic fragments. A similar behavior is also observed in alkaline medium (figure 5.10). But the electrocatalytic activity seems to be better in alkaline medium since an adsorbed species such as (CO^{-}_{ads}) is more easily oxidized to carbon dioxide, compared to the strongly bound poisoning species (such as COH) that is formed in acid medium.

A carbon (Vulcan XC72) electrode was subjected to CV (figure 5.11) to find out the stability window for C-based electrodes. The electrode was found to be stable in the potential range of -1000 to 100mV *vs* SCE. This potential

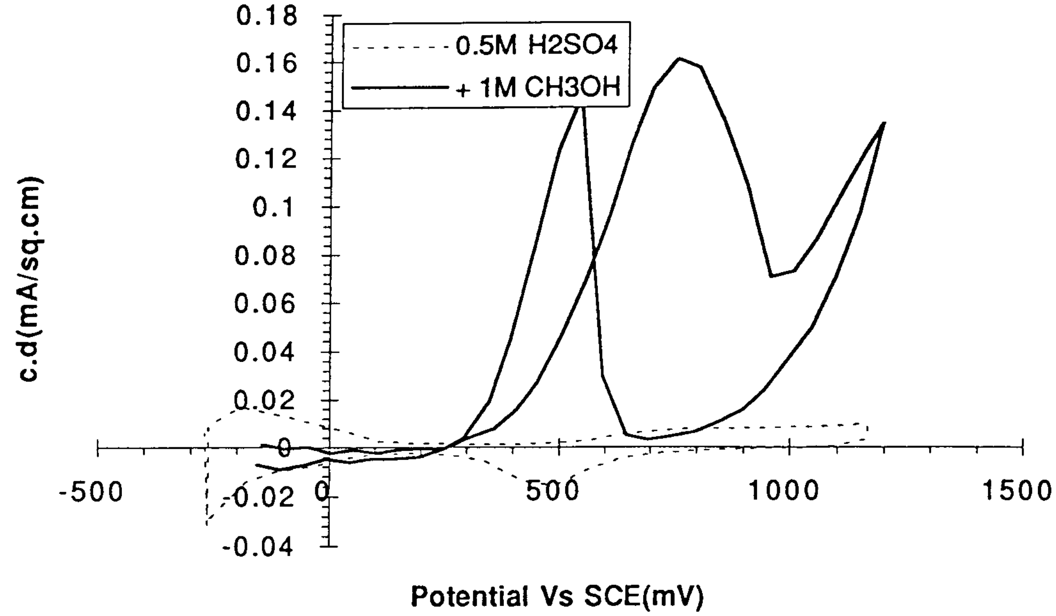

Figure 5.9 Typical cyclic voltammograms for a Pt foil showing the electrocatalytic activity for oxidation of methanol in acidic medium.

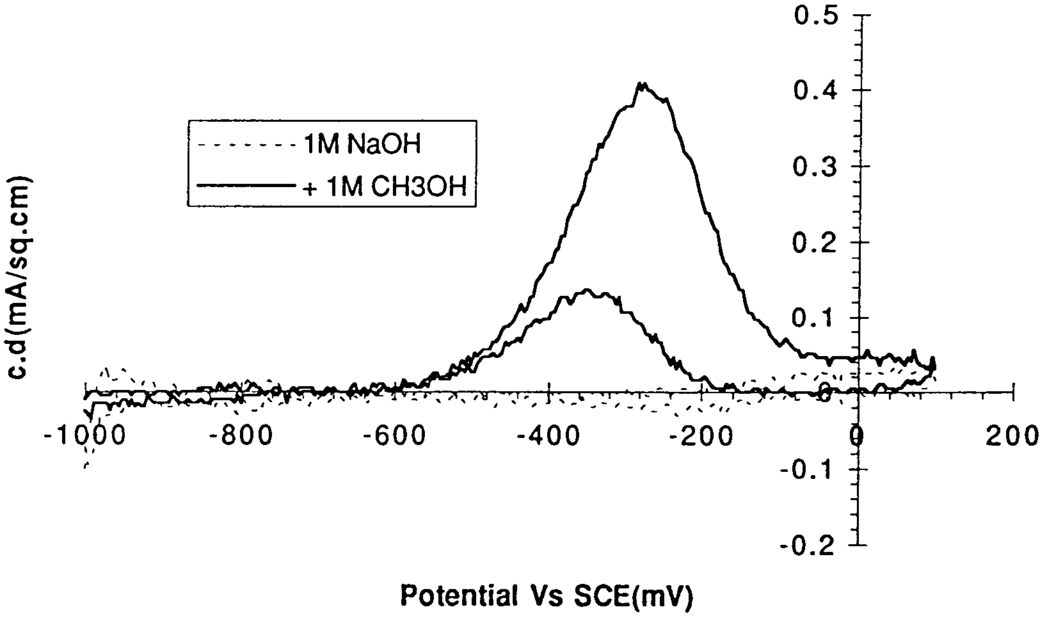

Figure 5.10 Cyclic voltammograms of a platinum electrode showing electrocatalytic activity for the oxidation of methanol in alkaline medium.

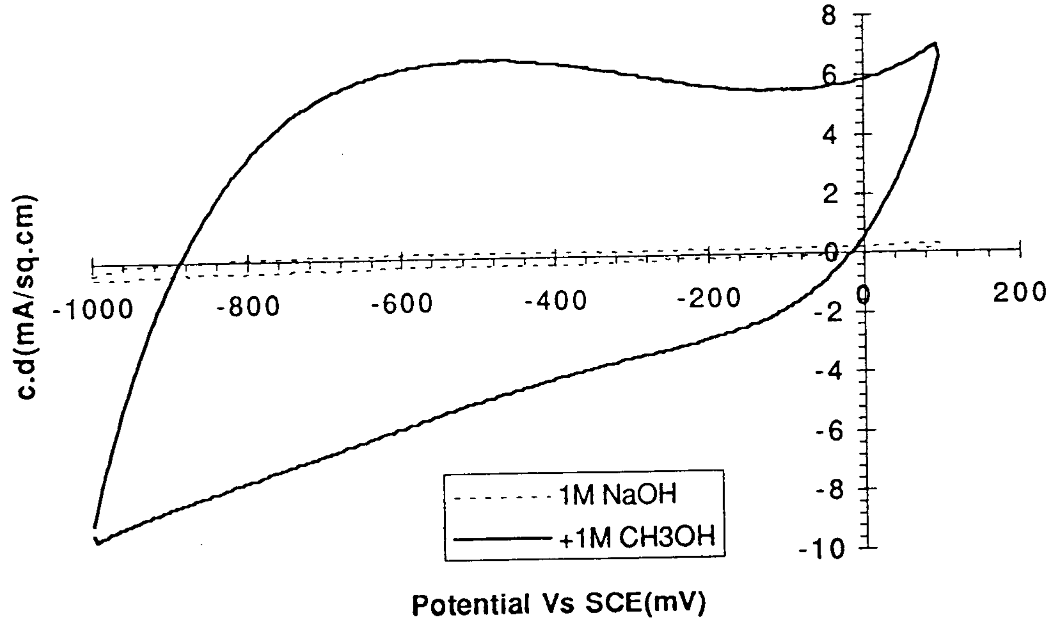

Figure 5.11 Cyclic voltammograms for Carbon (Vulcan XC72) electrode.

window is enough to study the electrocatalytic activity for methanol oxidation i.e.,

$$CH_3OH + 8OH^- \Rightarrow CO_3^{2-} + 6H_2O + 6e \qquad E° = -0.99V \ vs \ SCE$$

Beyond these potential values the electrodes were found to disintegrate.

Ni mesh, which is used as the current collector in all experiments was subject to CV studies in both alkaline (figure 5.12) and acid (figure 5.13) electrolytes. Figure 5.12 shows a redox couple in the 200 to 400mV *vs* SCE potential region. Also in the presence of methanol there is an increase in current showing some catalytic activity for the oxidation of methanol. But the overpotentials are rather very high. In acidic electrolytes, Ni is highly unstable and oxidizes to Ni^{2+} which is shown in figure 5.13. Hence all the experimental studies were limited only to alkaline electrolytes.

5.2.1 Pt/C, Sr_4PtO_6/C, $BaPtO_3$ electrodes

Figure 5.14 shows the CVs for Pt/C electrode in 1M NaOH and 1M CH_3OH+1M NaOH. It can be seen that the poisoning effect due to the adsorption of intermediates is drastically reduced and also the current densities are 30 to 40 times higher than that for the Pt foil.

The dotted and solid curves in figures 5.15 & 5.16 show typical CVs of $BaPtO_3$/C and Sr_4PtO_6/C electrodes in 1M NaOH and 1M NaOH+1M CH_3OH solutions respectively. Comparison of these curves with figure 5.14 show that

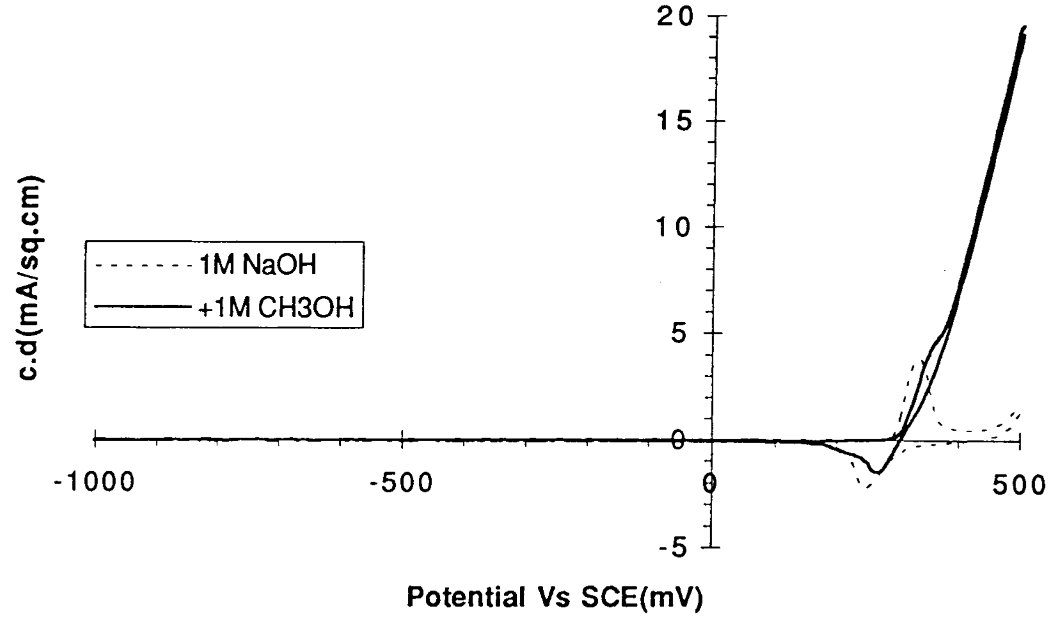

Figure 5.12 CVs for nickel mesh in 1M NaOH and 1M CH_3OH + 1M NaOH.

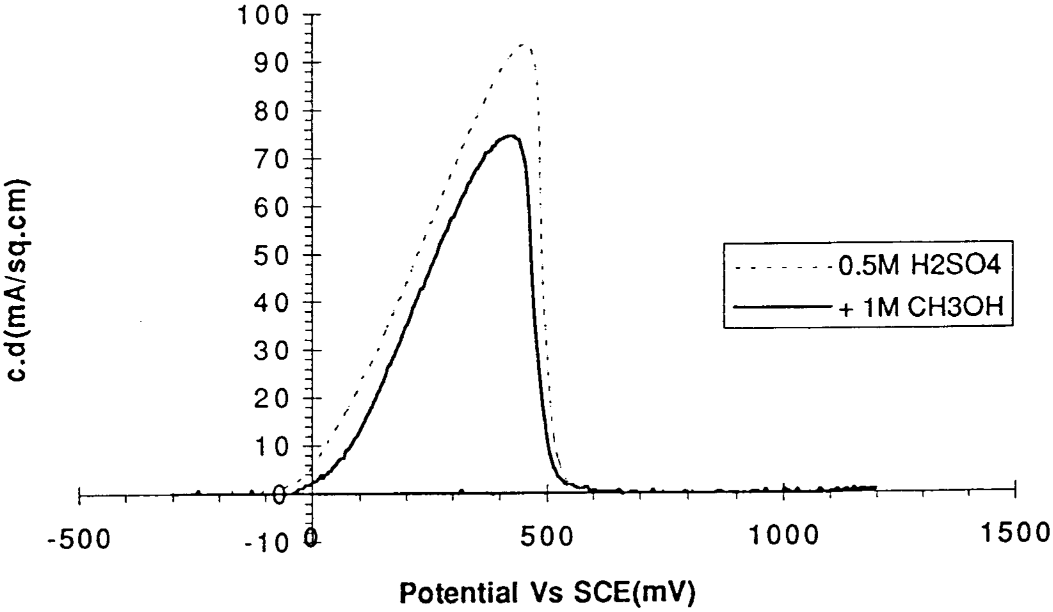

Figure 5.13 CVs for nickel mesh in 0.5M H_2SO_4 and 1M CH_3OH + 1M H_2SO_4.

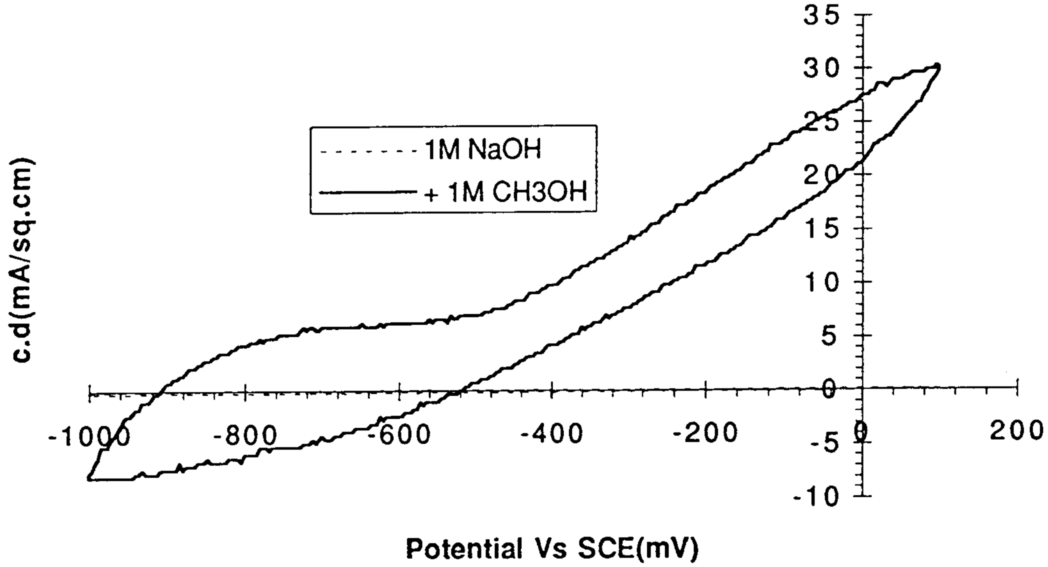

Figure 5.14 Typical cyclic voltammograms for Pt/C (8wt% Pt) electrode.

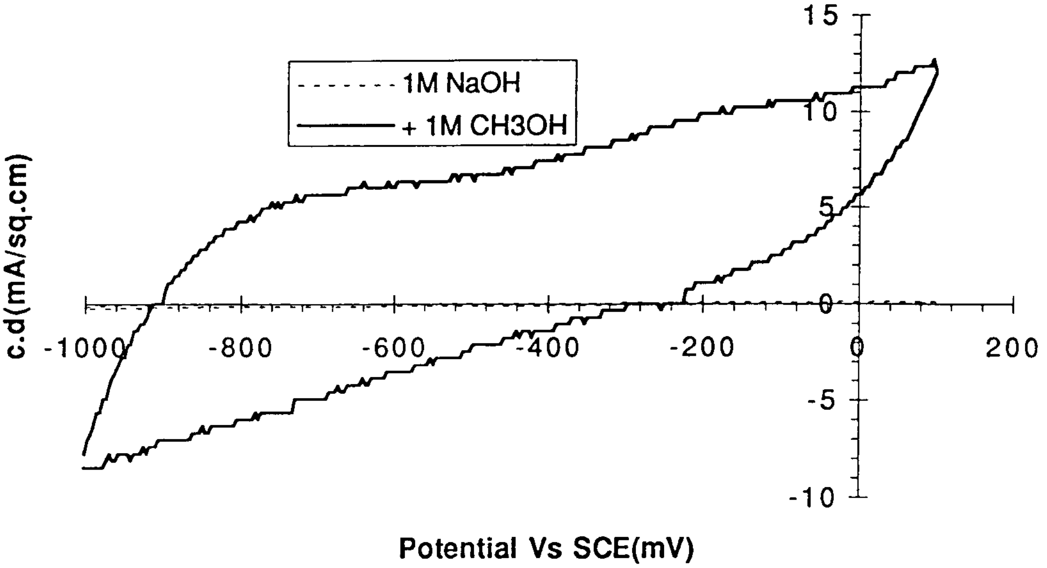

Figure 5.15 CVs for $BaPtO_3/C$ (8wt% Pt) electrode.

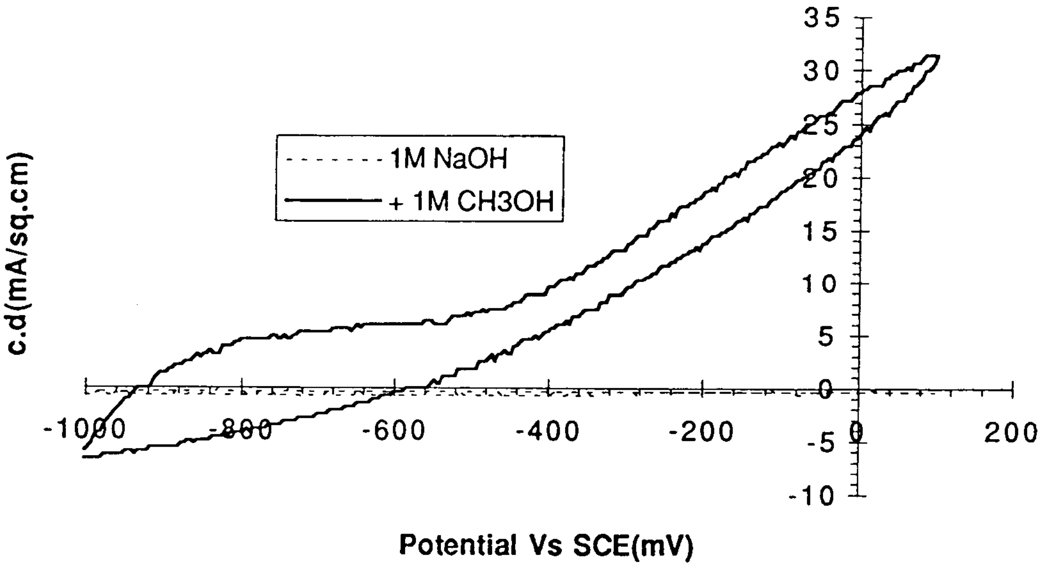

Figure 5.16 CVs for Sr_4PtO_6/C (8wt% Pt) electrode.

the catalytic activity of $BaPtO_3/C$ electrode is lower than Pt/C. However, Sr_4PtO_6/C electrode shows a slight increase in the electrocatalytic activity.

It should be noted here that the true surface areas of $BaPtO_3/C$ and Sr_4PtO_6/C electrodes could not be evaluated owing to the absence or barely detectable presence of hydrogen adsorption-desorption peaks on the CVs obtained in the background solution. Therefore the catalytic activity of these electrodes cannot be compared with that of Pt/C electrode on the basis of true surface area. However, the relative catalytic activities of these electrodes can be estimated by maintaining the Pt loading in all these electrodes at a constant value. The amount of Pt incorporated in all these electrodes was 8wt%.

5.2.2 Effect of electrolyte concentration

Figures 5.17, 5.18 & 5.19 show typical CVs for Pt/C, $BaPtO_3/C$ and Sr_4PtO_6/C electrodes in 1M CH_3OH and 0.1M, 0.25M, 0.5M, 0.75M & 1M NaOH solutions. The general trend observed in all these figures is an increase in the current density (c.d.) values as the pH increases. As expected the catalytic activities go higher as the pH is increased. But in the case of Pt/C electrode, there is a decrease in the activity when the electrolyte is 1M NaOH+1M CH_3OH. This effect can be attributed to the repeated usage of the same electrode leading to the poisoning of the catalyst due to strongly adsorbed intermediate species. This effect was not observed for Sr_4PtO_6/C & $BaPtO_3/C$ electrodes.

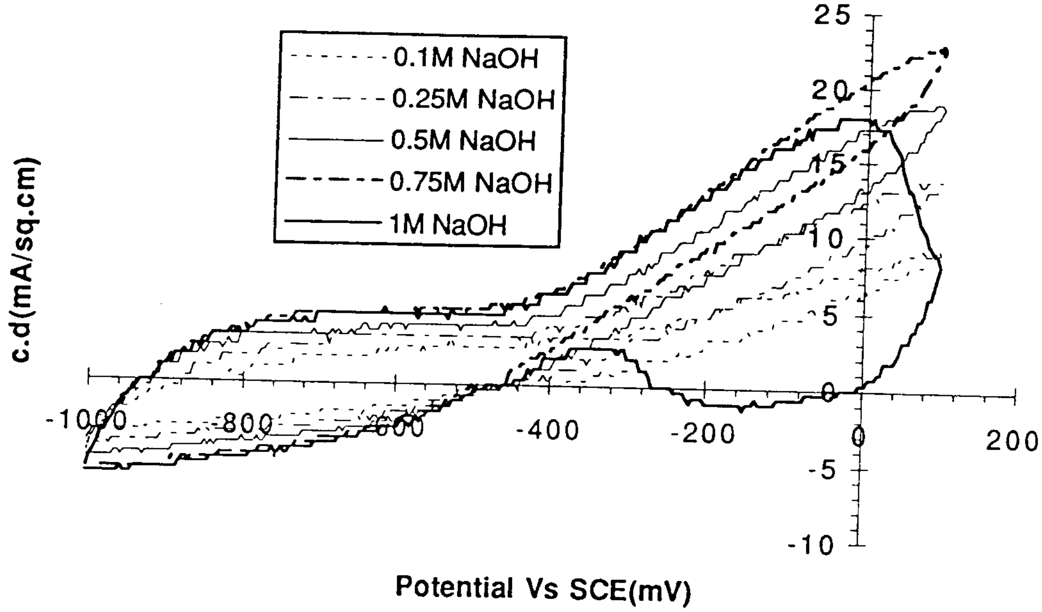

Figure 5.17 CVs showing the effect of electrolyte concentration for the electrooxidation of methanol on Pt/C electrode.

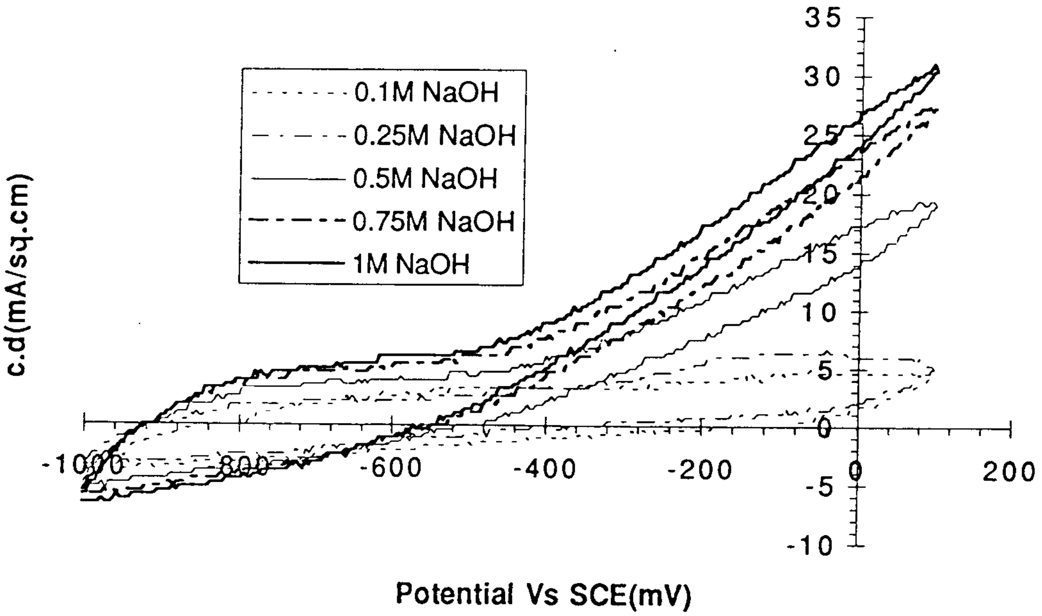

Figure 5.18 CVs showing the effect of electrolyte concentration for the electrooxidation of methanol on $BaPtO_3$/C electrode.

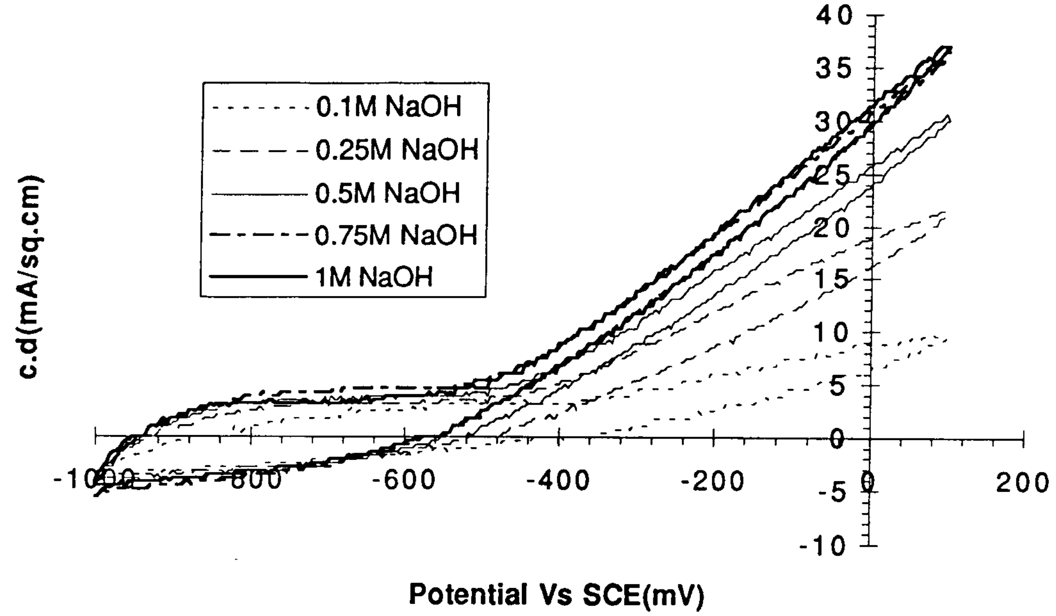

Figure 5.19 CVs showing the effect of electrolyte concentration for the electrooxidation of methanol on Sr_4PtO_6/C electrode.

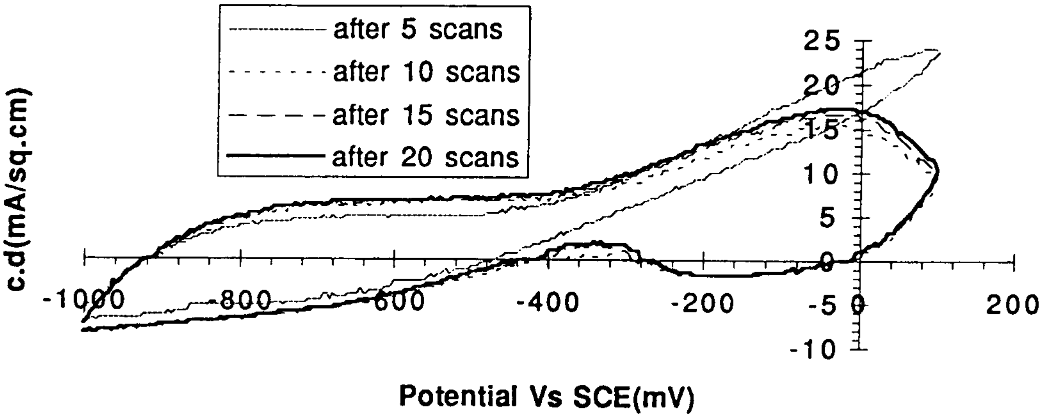

Figure 5.20 CVs for Pt/C electrode in 1M NaOH + 1M CH_3OH for a repeated number of scans at a scan rate of 10mV/s.

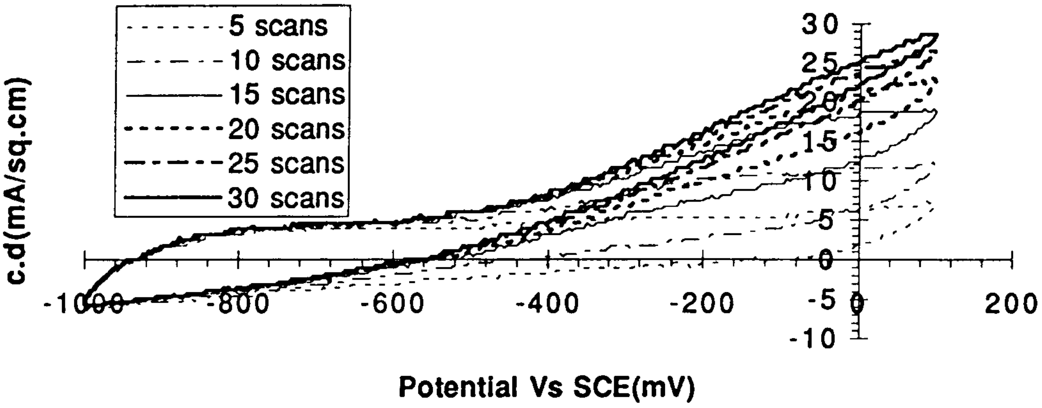

Figure 5.21 CVs for $BaPtO_3/C$ electrode in 1M NaOH + 1M CH_3OH for a repeated number of scans at a scan rate of 10mV/s.

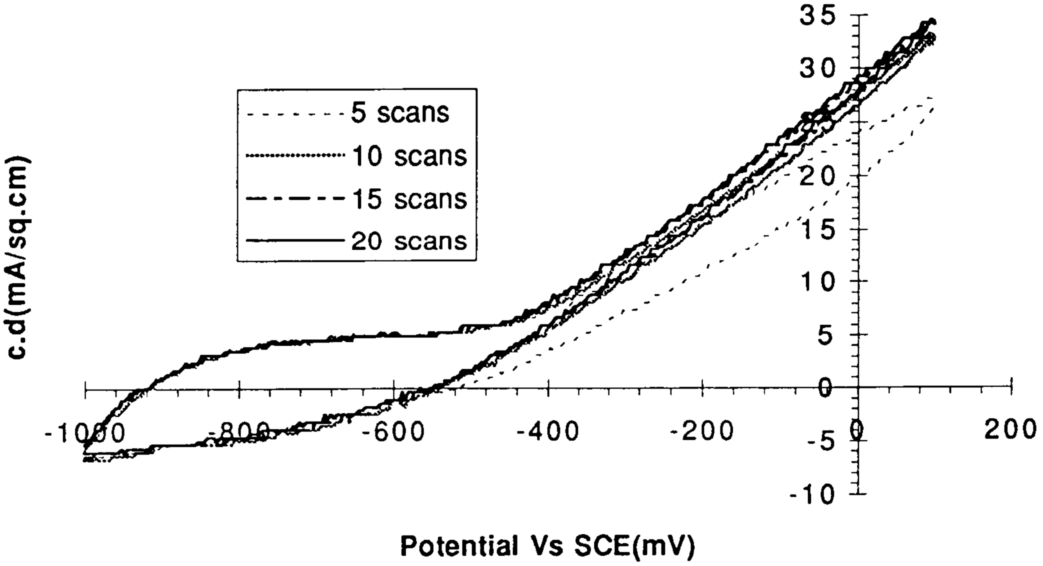

Figure 5.22 CVs for Sr_4PtO_6/C electrode in 1M NaOH + 1M CH_3OH for a repeated number of scans at a scan rate of 10mV/s.

5.2.3 Effect of number of scans

In order to investigate the poisoning effect observed in Pt/C electrode, CVs were performed in 1M NaOH+1M CH_3OH electrolyte for repeated number of cycles. Figures 5.20, 5.21 & 5.22 are the CVs for Pt/C, $BaPtO_3$/C & Sr_4PtO_6/C electrodes respectively. It is evident that Pt/C electrode does gets poisoned as the number of scans is increased leading to a decrease in the catalytic activity. On the other hand, Sr_4PtO_6/C electrode shows a slight increase and then for successive number of scans its almost constant. In the case of $BaPtO_3$/C electrode the electrocatalytic activity increases with the number of scans and the c.d. values become comparable to that of Pt/C electrode.

5.2.4 Sr_3NiPtO_6/C electrode

Figure 5.23 shows typical CVs for a Sr_3NiPtO_6/C electrode in 1M NaOH+1M CH_3OH. Suprisingly, the electrocatalytic activity for the oxidation of methanol is very low when compared to Sr_4PtO_6/C electrode. Search for a good reason for this decrease in activity led to the discovery that A_4PtO_6 compounds undergo slow hydrolysis. Figure 5.24 compares the crystallographic structures of Sr_4PtO_6 and Sr_3NiPtO_6. The figure shows views down the [010] of Sr_4PtO_6 and Sr_3NiPtO_6. Sr_4PtO_6 crystallises in the trigonal space group $R\bar{3}c$ and contains isolated PtO_6octahedra surrounded by Sr ions. In Sr_3NiPtO_6 however there are

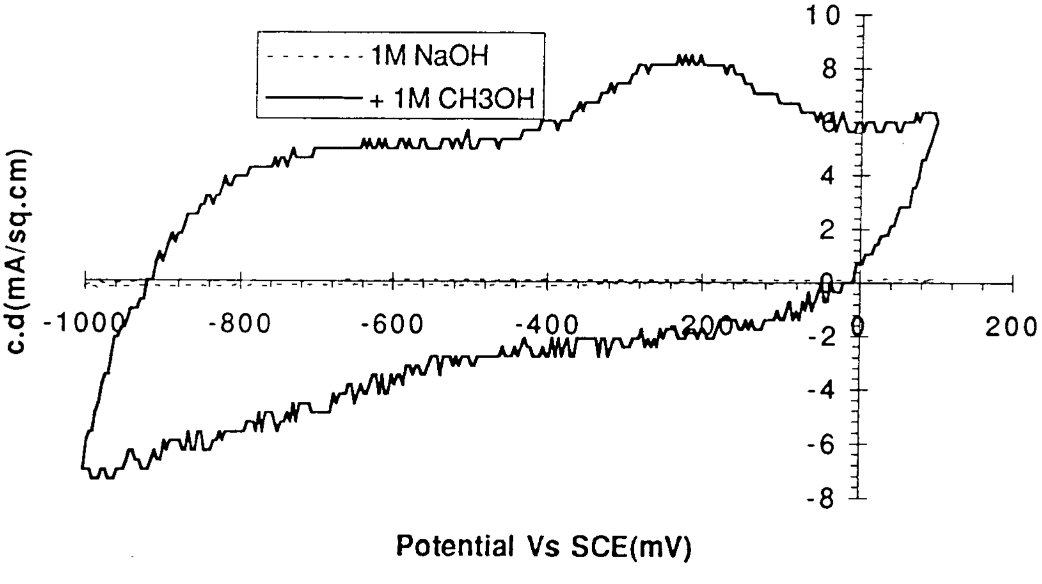

Figure 5.23 Cyclic voltammograms for Sr_3NiPtO_6/C (8wt% Pt) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

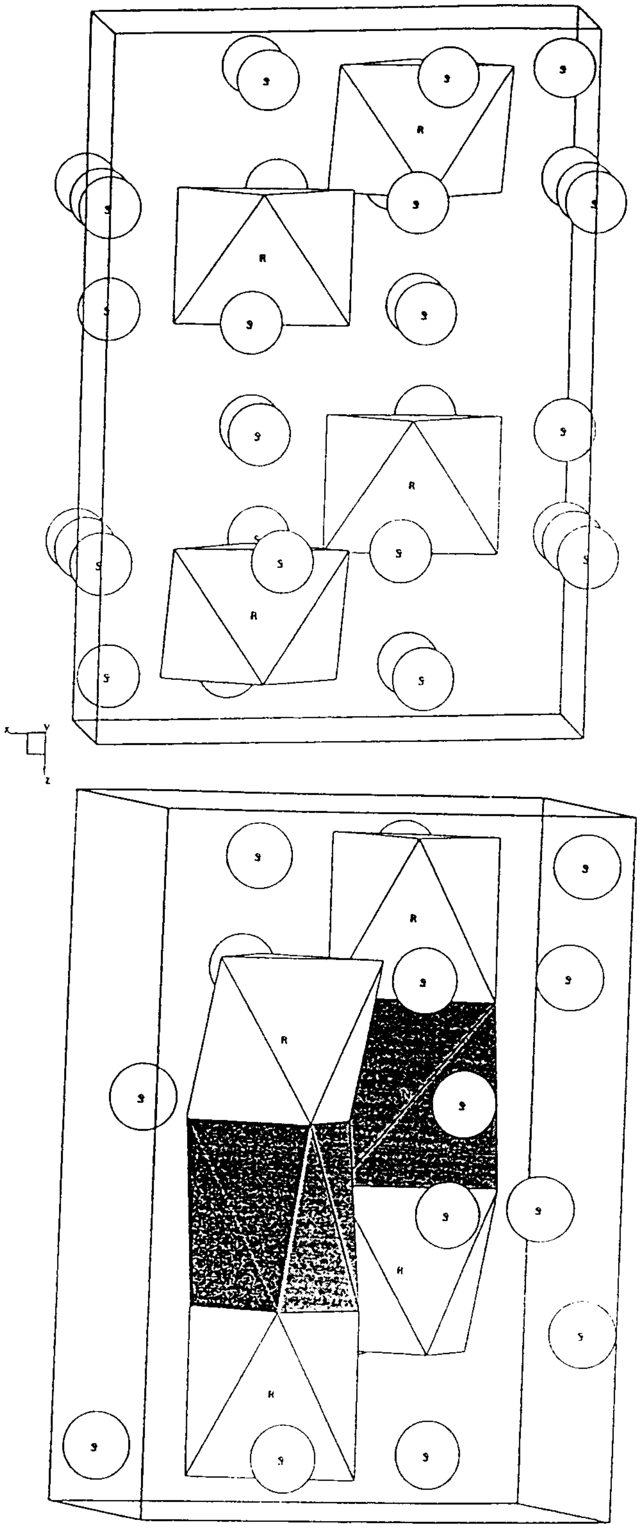

Figure 5.24 Crystallographic structures of Sr_4PtO_6 (top) and Sr_3NiPtO_6 (bottom).

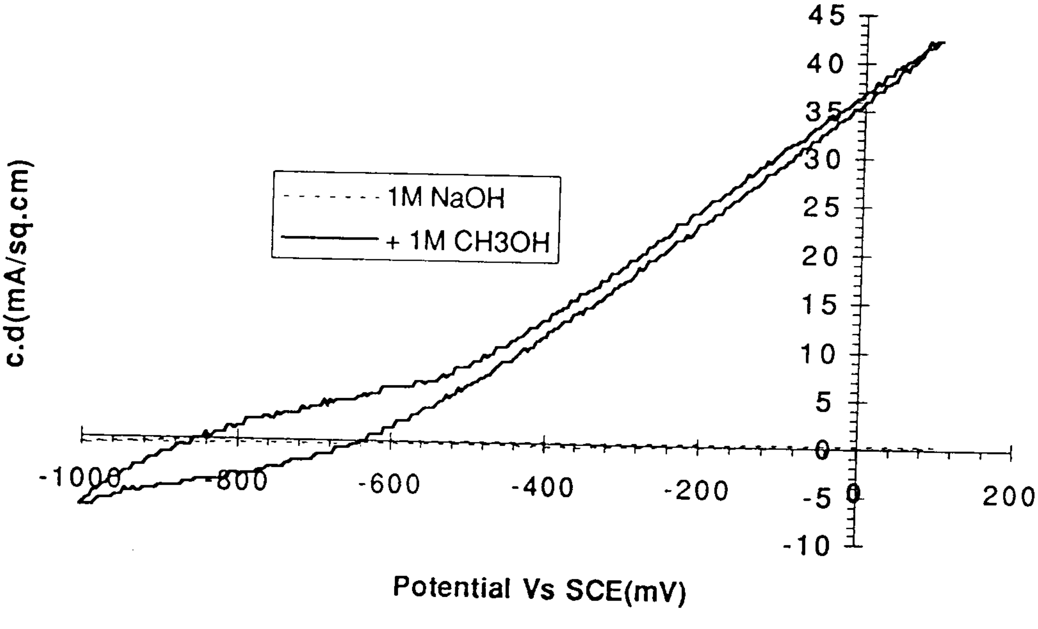

Figure 5.25 Cyclic voltammograms for $H_2Pt(OH)_6/C$ (8wt% Pt) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

extended chains of NiO_6 and PtO_6 octahedra. The presence of these extended chains appears to slow the rate of hydrolysis of this compound.

Based on these results, it was concluded that the product of hydrolysis was responsible for the electrocatalytic activity. But, it was very difficult to characterize the hydrolysis product due to its amorphous nature. It could be speculated to be $Sr(OH)_2$ and $H_2Pt(OH)_6$. Hence an electrode was made using $H_2Pt(OH)_6$ as the electrocatalyst. Figure 5.25 shows the CVs for $H_2Pt(OH)_6$/C electrode in 1M NaOH & 1M CH_3OH+ 1M NaOH. The overpotentials decreased by 200mV and the c.d. values observed were almost doubled in comparison with a Pt/C electrode.

5.2.5 $PtO_2.H_2O$/C, PdO/C, IrO_2/C & RuO_2/C electrodes

Figures 5.26, 5.27, 5.28 & 5.29 show the CVs of $PtO_2.H_2O$/C, PdO/C, IrO_2/C and RuO_2/C electrodes in 1M NaOH & 1M CH_3OH+1M NaOH respectively. IrO_2/C and RuO_2/C electrodes do not show any appreciable activity for the oxidation of methanol. On the other hand $PtO_2.H_2O$/C and PdO/C electrodes show excellent characteristics. The c.d. values for $PtO_2.H_2O$/C were found to be the highest of all the electrocatalysts studied.

It is well known that the presence of hydroxy-species is essential for the oxidation of the poison (CO or CHO) that is formed during the electrooxidation of methanol. The reason for $PtO_2.H_2O$/C electrode showing higher catalytic activity could be speculated as due to the hydration of PtO_2 to form $PtO_2.3H_2O$.

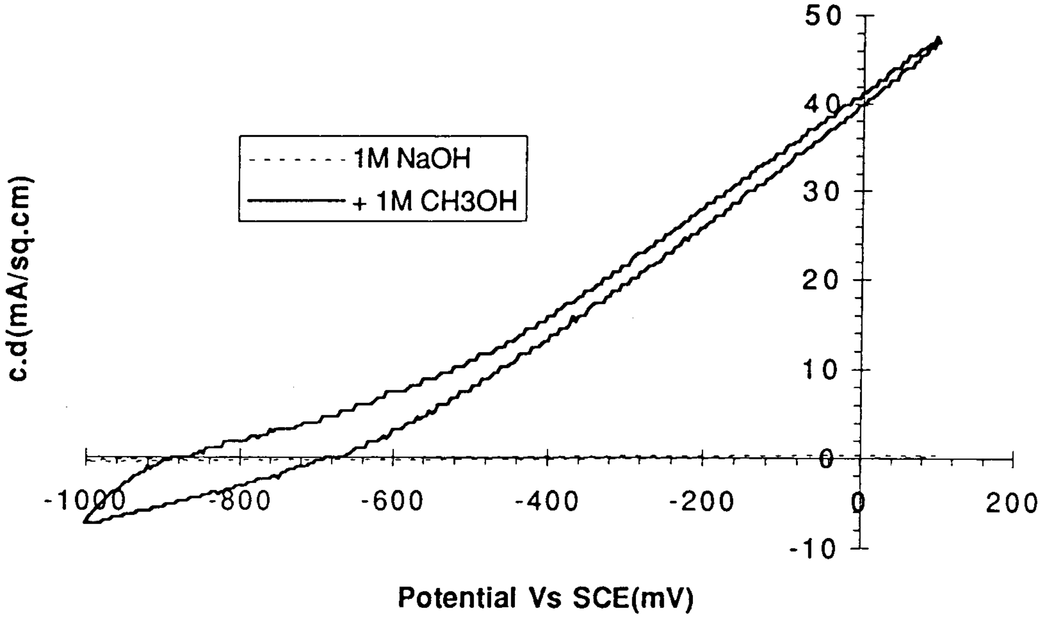

Figure 5.26 Cyclic voltammograms for $PtO_2.H_2O/C$ (8wt% Pt) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

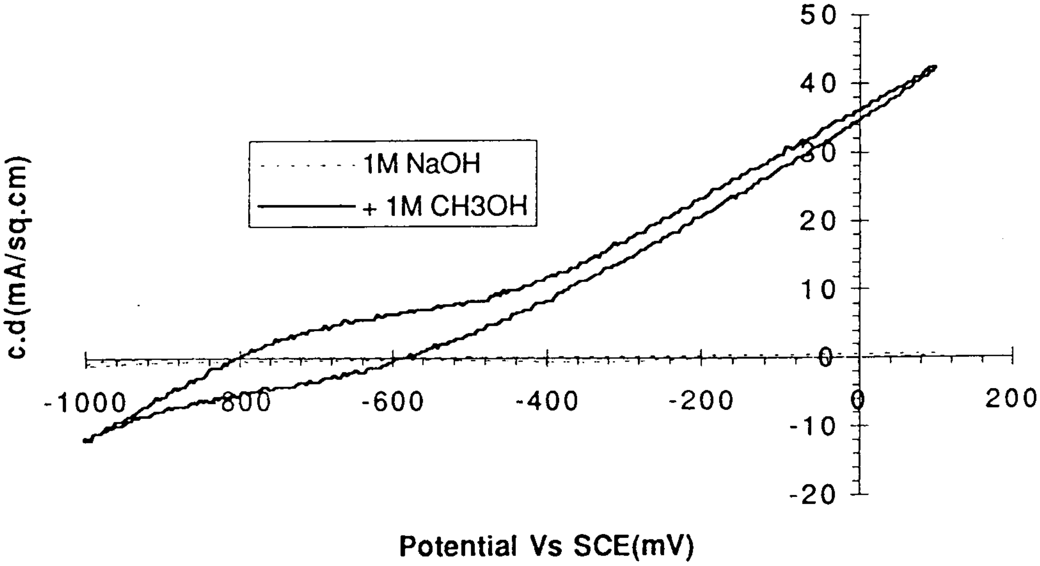

Figure 5.27 Cyclic voltammograms for PdO/C (8wt% Pd) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

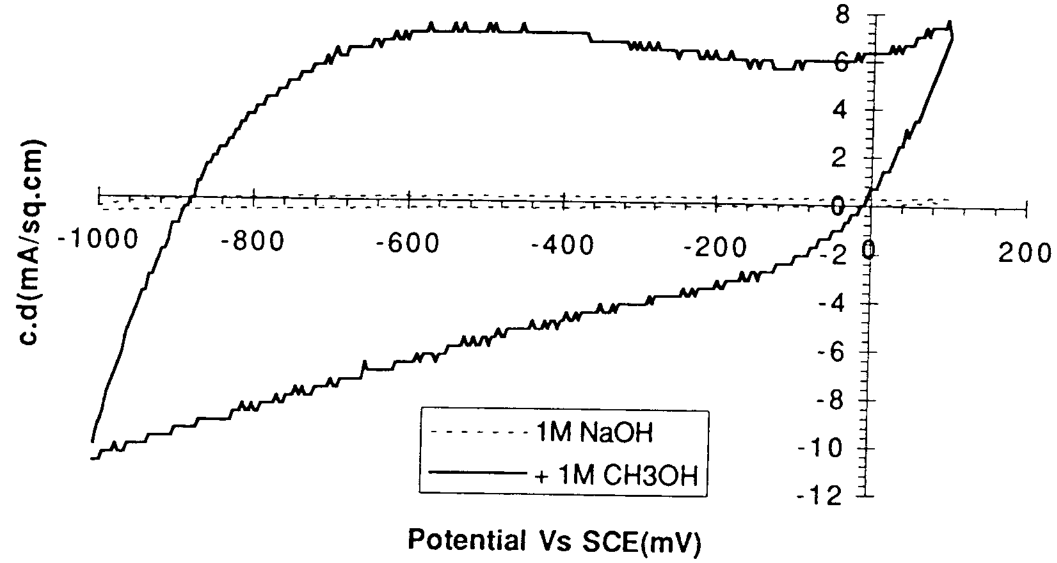

Figure 5.28 Cyclic voltammograms for IrO_2/C (8wt% Ir) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

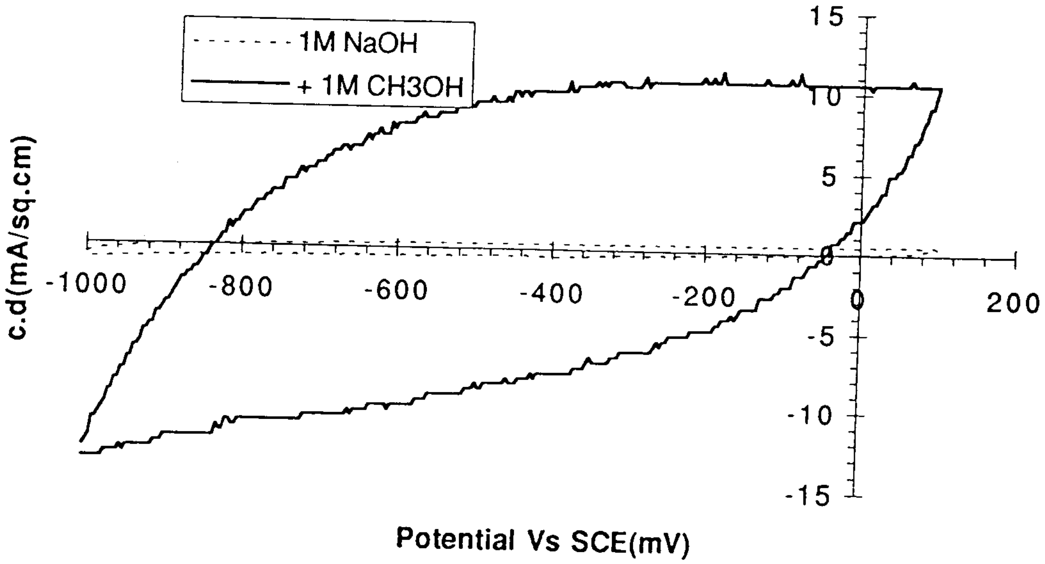

Figure 5.29 Cyclic voltammograms for RuO_2/C (8wt% Ru) electrode in 1M NaOH and 1M CH_3OH + 1M NaOH.

The presence of both platinum and hydroxy species at the reaction sites could be the reason for an improved catalytic activity. Another possible mechanism that is proposed is as follows:

Step 1: Reduction of Platinum oxide.

$$PtO_2 + 2CH_3OH + 8OH^- \Rightarrow 2CO_2 + 8H_2O + Pt + 8e$$

Step 2: Adsorption of methanol on to Pt.

$$Pt + CH_3OH + 4OH^- \Rightarrow Pt\text{-}CO(ad) + 4H_2O + 4e$$

Step 3: Oxidation of the intermediate.

$$Pt\text{-}CO(ad) + 2OH^- \Rightarrow Pt + CO_2 + H_2O + 2e$$

5.3 Chronoamperometry

Chronoamperometry (CA) was performed on selected electrodes in order to measure their stability in comparison with Pt/C electrode. Figure 5.30 shows the results of CA carried out on a Pt/C electrode for a duration of 10 minutes at potentials -200, -100, 0 & +100 mV *vs* SCE. The current density (c.d.) values decrease steadily at potentials -200 & -100 mV *vs* SCE. But on further polarization of the same electrode the c.d. decreases very rapidly.

Figures 5.31 & 5.32 show the CA plots for $BaPtO_3$/C and Sr_4PtO_6/C electrodes respectively. It can be seen that the current densities observed at each potential in these electrodes are higher than that of a Pt/C electrode. At potentials -200 & -100 mV *vs* SCE, unlike Pt/C electrode, these electrodes do

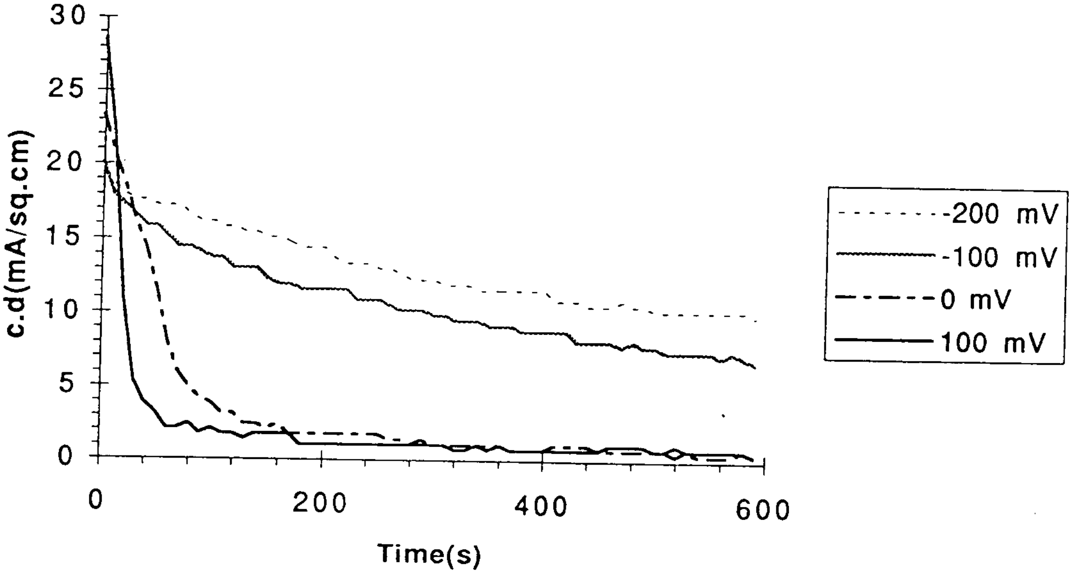

Figure 5.30 Variation of oxidation current density of Pt/C electrode with time at 24°C in 1M NaOH + 1M CH_3OH.

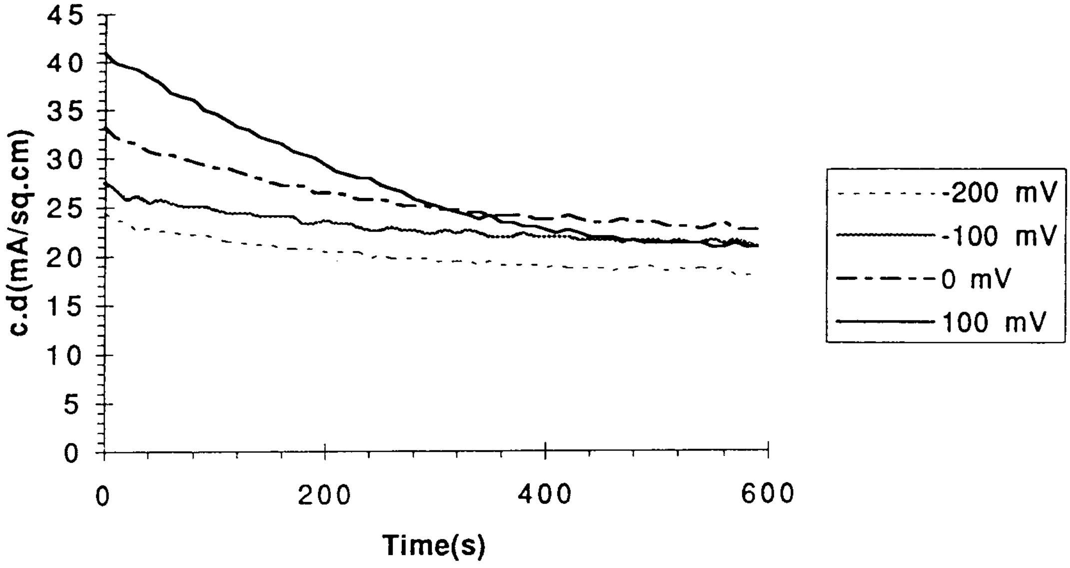

Figure 5.31 Variation of methanol oxidation current density with time for $BaPtO_3/C$ electrode in 1M NaOH + 1M CH_3OH.

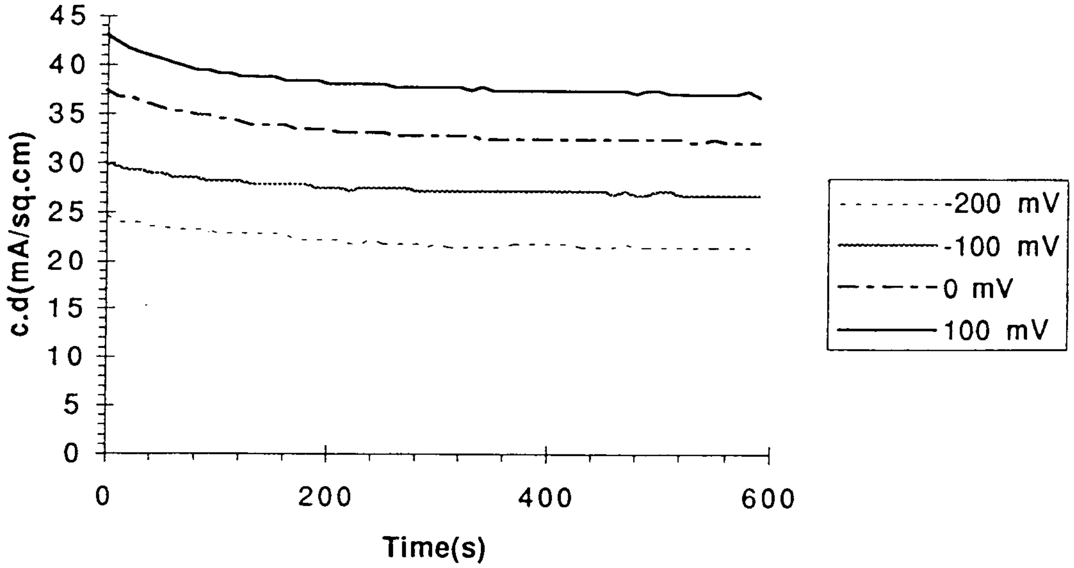

Figure 5.32 Variation of methanol oxidation current density with time for Sr_4PtO_6/C electrode in 1M NaOH + 1M CH_3OH.

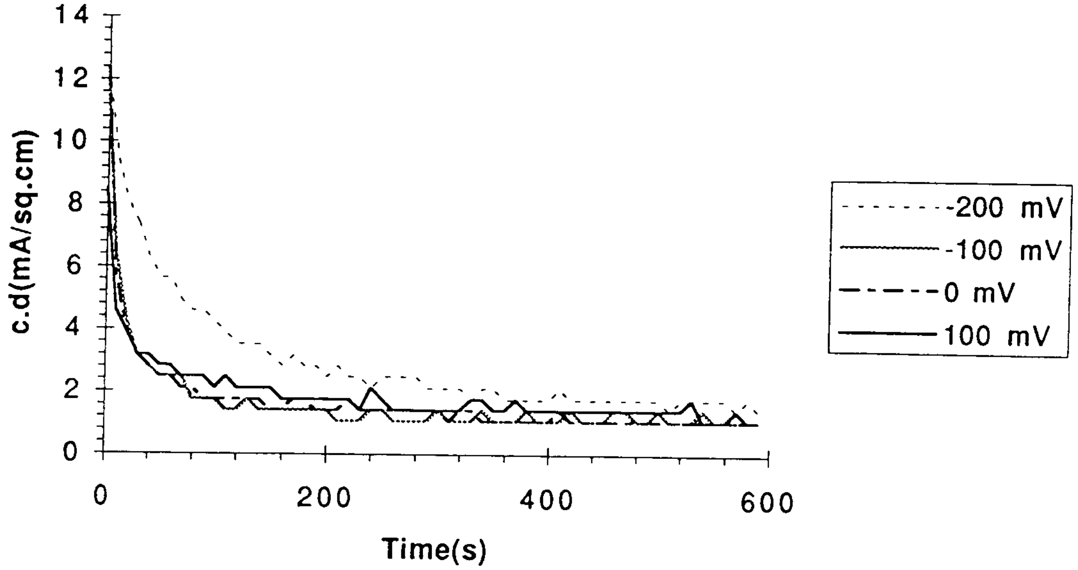

Figure 5.33 Chronoamperometric plots for Sr_3NiPtO_6/C electrode in 1M NaOH + 1M CH_3OH.

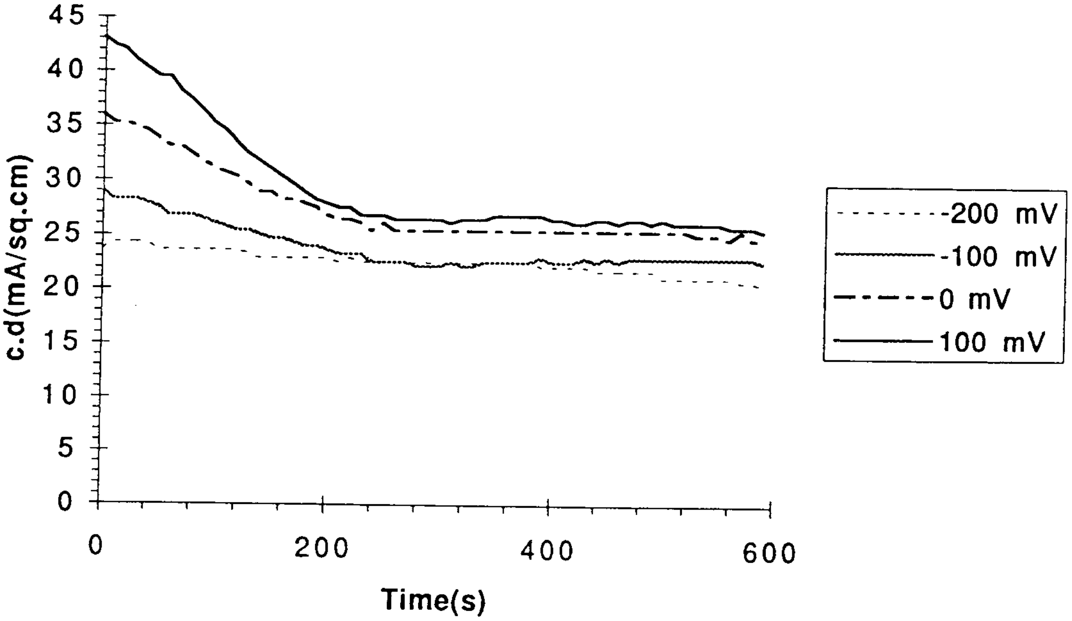

Figure 5.34 Chronoamperometric plots for $H_2Pt(OH)_6/C$ electrode in 1M NaOH + 1M CH_3OH.

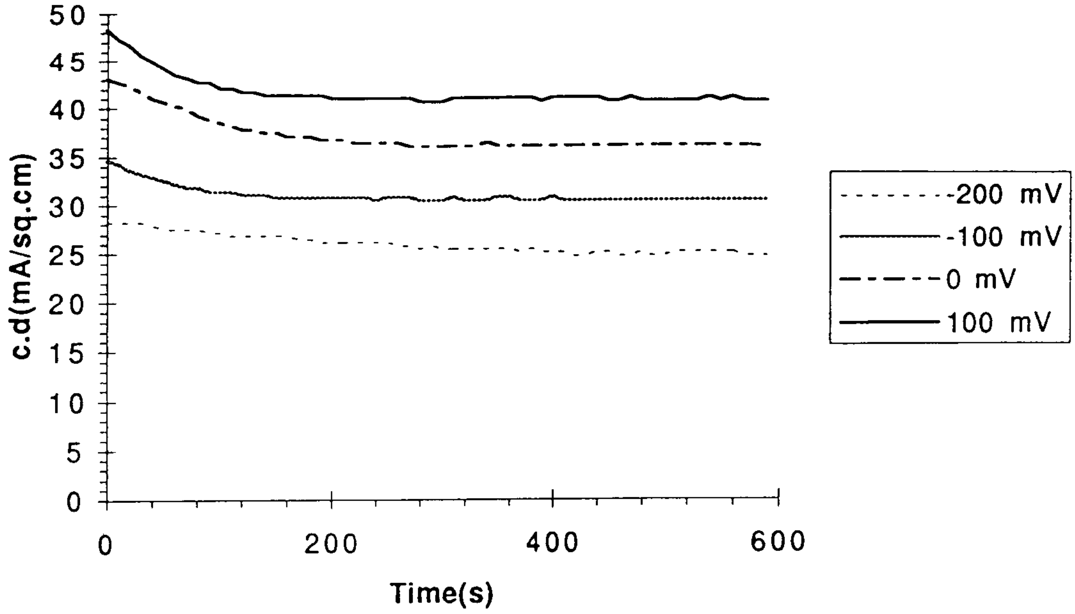

Figure 5.35 Variation of methanol oxidation current density with time for $PtO_2.H_2O/C$ (8wt% Pt) electrode in 1M NaOH + 1M CH_3OH.

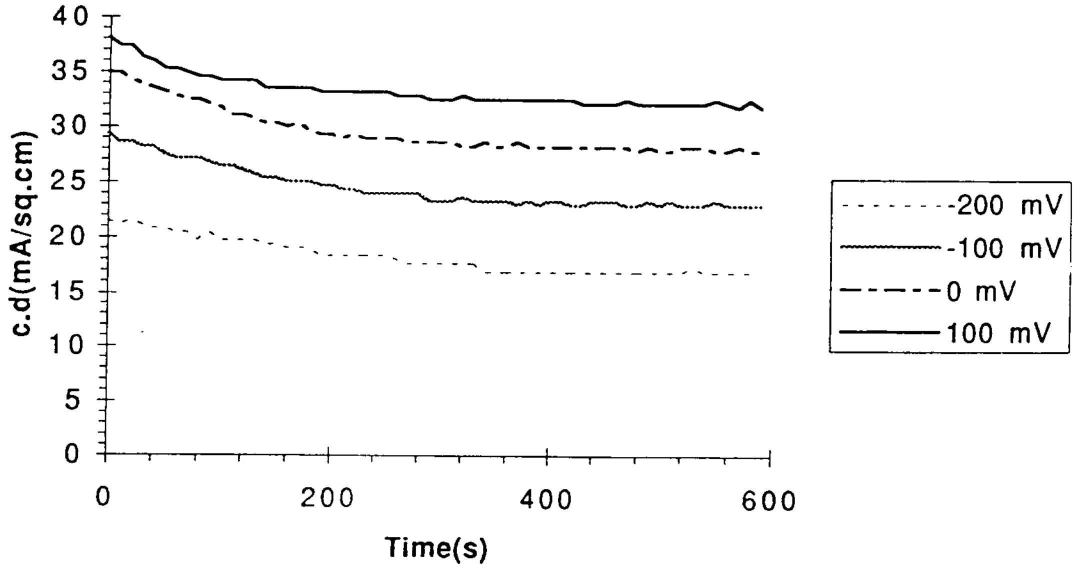

Figure 5.36 Variation of methanol oxidation current density with time for PdO/C (8wt% Pd) electrode in 1M NaOH + 1M CH_3OH.

not show any decrease in c.d. with time. $BaPtO_3$/C electrode at 0 & 100 mV *vs* SCE shows a slight decrease in c.d. and then attains a constant value. The Sr_4PtO_6/C electrode, however does not show any decrease in c.d. values at these potentials and remains constant with respect to time.

The CA plot for Sr_3NiPtO_6/C electrode is shown in figure 5.33. As expected, no appreciable current densities are observed. $H_2Pt(OH)_6$/C electrode shows higher and steady c.d. values than Pt/C electrode (figure 5.34). Although there is a slight decrease in the c.d. values at 0 & 100 mV *vs* SCE, it attains a steady value later with respect to time.

Among the other oxides studied only $PtO_2.H_2O$ and PdO showed electrocatalytic activity for the oxidation of methanol. Figures 5.35 & 5.36 show the CA plots for $PtO_2.H_2O$/C and PdO/C electrodes respectively. No decrease in c.d. values was observed for these electrodes. Also the current densities observed for $PtO_2.H_2O$/C electrode were the highest of all the electrodes studied.

5.4 Surface area measurements

One of the possible explanations for a higher catalytic activity of $PtO_2.H_2O$ and PdO powders could be high surface area in comparison to Pt/C powder. BET surface area measurements were carried out on C, Pt/C, $PtO_2.H_3O$ and PdO electrocatalysts and the results are as follows:

Electrocatalyst	*Surface area (m^2/g)*
Carbon (Vulcan XC72)	245.85
Pt/C (8wt% Pt)	215.26
$PtO_2.H_2O$	84.78
PdO	34.59

The surface area of platinum was calculated based on the peak width of the Pt peaks observed in Figure 5.8. The Pt particle size was found to be 4 nm and the surface area was 69.93 m^2/g (assuming the particles to be spherical in shape). Using these results the approximate surface area contributed by the electrocatalysts were calculated based on the amount of these materials used in the electrode preparation. The calculated surface areas are as follows:

Pt:	0.5594 m^2
$PtO_2.H_2O$:	0.8520 m^2
PdO:	0.3183 m^2

It is evident that there is an increase in surface area for $PtO_2.H_2O$ and PdO shows a decrease in surface area, in comparison to Pt. But both $PtO_2.H_2O/C$ and PdO/C electrodes show higher catalytic activity than Pt/C electrode. Hence the increase in activity of these electrodes is not thought to be due to surface area effects alone.

Chapter 6

Conclusions

Single phase powders of $BaPtO_3$, Sr_4PtO_6 and Sr_3NiPtO_6 were prepared and characterized using XRD. Carbon-based electrodes were prepared using these powders as electrocatalysts with a Pt loading of 8wt%. Cyclic voltammetric experiments were conducted on Pt/C, $BaPtO_3$/C, Sr_4PtO_6/C and Sr_3NiPtO_6/C electrodes, to study their electrocatalytic activity for the oxidation of methanol in 1M NaOH + 1M CH_3OH electrolyte. It was found that the Sr_4PtO_6/C electrode showed slightly higher activities than Pt/C electrode itself. Search for a plausible explanation led to the discovery that Sr_4PtO_6 slowly undergoes hydrolysis and the product of hydrolysis is responsible for the electrocatalytic activity. A $H_2Pt(OH)_6$/C electrode was therefore prepared and studied. It indeed showed very good characteristics for the electrooxidation of methanol. This hydrolysis effect was not observed for Sr_3NiPtO_6 possibly due to the absence of isolated PtO_6 octahedra required for the facile hydrolysis. Cyclic voltammetry conducted for a repeated number of cycles in the same electrolyte for these electrodes revealed that the poisoning effects observed for Pt/C electrode were not observed in the other electrodes.

Among the other oxides studied (i.e., $PtO_2.H_2O$, PdO, IrO_2 and RuO_2), $PtO_2.H_2O$/C and PdO/C electrodes showed excellent characteristics for the electrooxidation of methanol. The presence of both Pt and OH species at the reaction sites could be a reason for the increased activity of $PtO_2.H_2O/C$ electrode.

Chronoamperometric studies were conducted on Pt/C, $BaPtO_3/C$, Sr_4PtO_6/C, Sr_3NiPtO_6/C, $H_2Pt(OH)_6/C$, $PtO_2.H_2O/C$ and PdO/C electrodes in order to measure their stability. All oxide derived electrodes, except Sr_3NiPtO_6/C showed good and stable c.d. values even at 0 & 100 mV *vs* SCE. This is in marked contrast to the Pt/C electrode. A maximum c.d. values of about $45mA/cm^2$ was observed for the $PtO_2.H_2O/C$ electrode at 100mV *vs* SCE.

Surface area studies using BET method on Carbon, Pt/C, $PtO_2.H_2O$ and PdO powders suggest that the increased activity of $PtO_2.H_2O/C$ and PdO/C electrodes are intrinsic effects and not merely related to differences in catalytic surface areas..

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