

ANODE MATERIALS FOR DIRECT METHANOL FUEL CELL

M AULICE SCIBIOH, B RAJESH AND B VISWANATHAN

Department of Chemistry, Indian Institute of Technology, Madras-600 036. (India)

(Received 21 December 2000; After Revision 14 May 2001; Accepted 8 October 2001)

A status report on anodic materials employed in direct methanol fuel cell (DMFC) with their relevant fundamental and applied chemistry are the subject matter of this review. State-of-the-art in the fields of its methodology, catalysis, electrolytes and electrode performance are considered. An emphasis is placed on catalytic metal micro/nano particulates dispersed in/on conducting polymers and an insight is provided regarding the molecular level interactions. These diverse attempts will merge as far as the objective is concerned namely how to extract the best possible performance out of a given amount of noble metal incorporated in a particular catalyst?

Key Words: Anode Materials; Direct Methanol Fuel Cell; Electrode Materials; Carbon; Conducting Polymers; Metal-Support Interactions; Nanomaterials

1 Introduction

Fuel cells - A nineteenth century invention, twentieth century technology development and twenty first century energy demand! A fuel cell is an electrochemical cell, which can continuously and directly converts the chemical energy of a fuel and an oxidant to electrical energy (Scheme.1) by a process involving essentially invariant electrode-electrolyte system¹.

Thermal energy conversion → Mechanical energy conversion

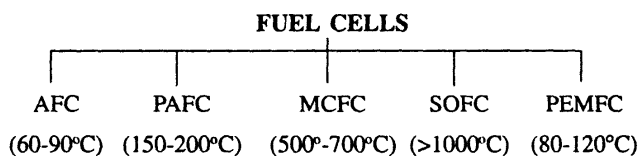
↑ Fuel Cell ↓

Chemical energy of the fuels → Electrical energy conversion

Scheme 1 Direct energy conversion with fuel cells in comparison to conventional indirect technology

Fuel cells can be classified according to the working temperature: high, medium and low (ambient) temperature systems, or referring to the pressure of operation: high, medium and low (atmospheric) pressure systems. They may be further distinguished by the fuels and/or the oxidants employed: (1) gaseous reactants (such as hydrogen, ammonia, air and oxygen), (2) liquids fuels (alcohols, hydrazine, hydrocarbons) or (3) solid fuels (e.g., coal, hydrides). For practical reasons fuel cell systems are simply distinguished by the type of electrolyte used and

the following names and abbreviations are now frequently used in publications: Alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC) and proton exchange membrane fuel cells (PEMFC).



Subsequent classification of the systems is: if the electrolyte of an alkaline or acidic fuel cell is for instance in liquid form, then it is called a mobile electrolyte system; if the electrolyte is soaked up in a porous material, it is called immobile or matrix system.

Fuel cells are bound to play a key role in the near future for world energy scenario. Their important characteristics such as high efficiency, very low emission and noise levels are mandatory in the coming generation of power plants. These days, few types of fuel cells approach commercial viability. Possible configurations of fuel cells and their relative merits are given in Table I.

Organic fuels may be used either directly or indirectly in fuel cells. In the direct method, the fuel is the anodic reactant. In the indirect method, the organic compound is reformed chemically in a separate reactor into hydrogen or a mixture of hydrogen and CO, which

Table I
Configuration of fuel cells

Fuel Cell System	Temperature range	Efficiency (Cell)	Electrolyte	Advantages	Disadvantages	Application Area
Alkaline Fuel Cell (AFC)	60-90° C	50-60%	35-50% KOH	<ol style="list-style-type: none"> 1. Low temperature operation 2. Rapid O₂ reduction kinetics 3. Non-noble electrocatalysts 	<ol style="list-style-type: none"> 1. Do not reject CO₂ 2. Pure H₂ & O₂ are required 	Space applications/ Traction application
Polymer Electrolyte Fuel Cell (PEFC)	50-80° C	50-60%	Polymer membrane (Nafion/Dow)	<ol style="list-style-type: none"> 1. Electrolyte-good proton conductor 2. Minimum corrosion problem 3. Long life period 4. Able to withstand large pressure differentials 	<ol style="list-style-type: none"> 1. Water management is critical, limitation in operating temperature 2. Higher catalyst loadings than PAFC both in anode & cathode 	Space applications/ Traction applications
Phosphoric Acid Fuel Cell (PAFC)	160-220°C	55%	Concentrated phosphoric acid	<ol style="list-style-type: none"> 1. Operate at high acid temperature range 2. Water management is easy 	<ol style="list-style-type: none"> 1. Phosphoric acid is poor ionic conductor at low temperature 2. CO poisoning at Pt catalyst 	Dispersed power applications (50-500kW, 1MW, 5MW, 11MW)
Molten Carbonate Fuel Cell (MCFC)	620-660° C	60-65%	Molten carbonate melts (Li ₂ CO ₃ /Na ₂ CO ₃)	Noble metals are not required	High operating temperatures	Power generation
Solid Oxide Fuel Cell (SOFC)	800-1000° C	55-65%	Yttrium-stabilized zircon dioxide (ZrO ₂ /Y ₂ O ₃)	<ol style="list-style-type: none"> 1. Noble metals are not required 2. Rapid O₂ reduction kinetics 	High operating temperatures	Power generation

are then led into the anode chamber of the fuel cell. The advantage of the anode reaction is the oxidation of hydrogen, which is a well-known process; it is the reaction of a mixture of H₂ and CO at high temperatures, which is also fast. The competition at the present time between the direct and indirect methods of utilization of organic fuels lies with size, weight, cost and efficiency of the chemical reformers for the indirect method on one hand and the electrochemical activity and cost of the electrode materials for direct oxidation on the other². Some of the common fuels, their combustion reactions, experimental parameters and EMFs developed³ are given in Table II. Hydrogen is the most promising fuel because of its maximum energy density and the maximum voltage that can be derived, closer to the theoretical value. However, the use of hydrogen as fuel is always associated with the complexity in storing, and

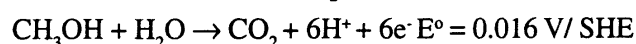
handling, which drives one to reflect on an alternative fuel.

Electrochemists are challenged to use a fuel, which is easily transportable and easily converted into energy from the liquid state. Methanol is the favoured fuel in the aspects of cost, efficiency, availability, existence in liquid state, stability, oxidizing ability, chemical inertness at the cathode and electrical yield per gram of fuel⁴. Methanol can be electrooxidised at a fuel cell anode either directly or indirectly. If used indirectly, methanol is initially reformed to give hydrogen in a high temperature step. The reactor required to accomplish this, however, both lowers practical power densities and rises the inherent thermal signature of the overall power source system. As a consequence, there are strong incentives for developing fuel cells that directly oxidize methanol as a fuel in their anodic compartments. The typical design of

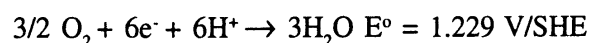
Table II
Chemical and electrochemical data on various fuels

Fuel	ΔG^0 (kcal/mol)	E^0_{theor} (V)	E^0_{max} (V)	Energy density (kWh/kg)
Hydrogen	-56.69	1.23	1.15	32.67
Methanol	-166.80	1.21	0.98	6.13
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic Acid	-68.20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	–
Propane	-503.20	1.08	0.65	–

a Direct Methanol Fuel Cell (DMFC) is shown in Fig. 1. It consists of an anode at which methanol is electro-oxidized to CO_2 through the reaction⁵



and a cathode at which oxygen (usually as air) is reduced to form water or steam



The electrolyte in this cell can be aqueous acid or alkali, the former being pioneered in the fifties and sixties by Shell and the latter by Exxon-Alstom. The advantages of the methanol-feed fuel cell over the cells designed for gas-feed⁶ are as follows:

- Elimination of fuel vapourizer and its associated heat source and controls,
- Elimination of complex humidification and thermal management systems,
- Dual-purpose use of the liquid methanol/water as fuel and as an efficient stack coolant, and
- Significantly lower system size, weight and temperature compared to other existing fuel cell systems.

In spite of these advantages, however, the DMFC remains not well developed compared to other fuel cells, and it has been suggested that the obvious advantages of methanol as a fuel should be harnessed by prior reforming of the methanol to yield hydrogen and CO_2 ⁷. Great difficulties that are encountered in improving the efficiency of the DMFC can be listed as:

- Acid electrolytes must be used because carbonate formation is a serious problem in alkaline solution, particularly at the current densities regarded as

commercially desirable. The acid electrolyte causes problems of corrosion and is responsible for the slow electrode kinetics of the reduction of oxygen at the cathode.

- Similar electrocatalysts were proposed for both anode and cathode, leading to the problem of mixed potentials at both electrodes and a marked reduction in efficiency. This is particularly difficult at the cathode and partitioning the cell with a membrane to avoid “chemical short circuits” will introduce a further source of inefficiency and resistance.
- The anode reaction is slow near the thermodynamic potential, with the catalysts that are currently used. A large over potential loss is therefore encountered⁸.
- The catalysts currently used for the anode are all based on a high platinum content. These catalysts are easily poisoned both by impurities and more seriously by the products of the anodic reaction itself.

Now a days, in fuel cell technology, especially in DMFCs, which is being considered for long as the most difficult fuel cell technology due to methanol cross over and catalytic inefficiency, steady progress has been made in various fields such as catalysis, electrolytes, electrode structure, theoretical understanding of gas diffusion and fuel cell engineering. This presentation is aiming not at the mere updation of the work in the field of DMFC, as excellent reviews are already available in the literature⁹⁻¹⁴, but to critically evaluate some of the vital issues in the development of DMFC particularly with respect to formulation, design and fabrication of anode materials. It is worth

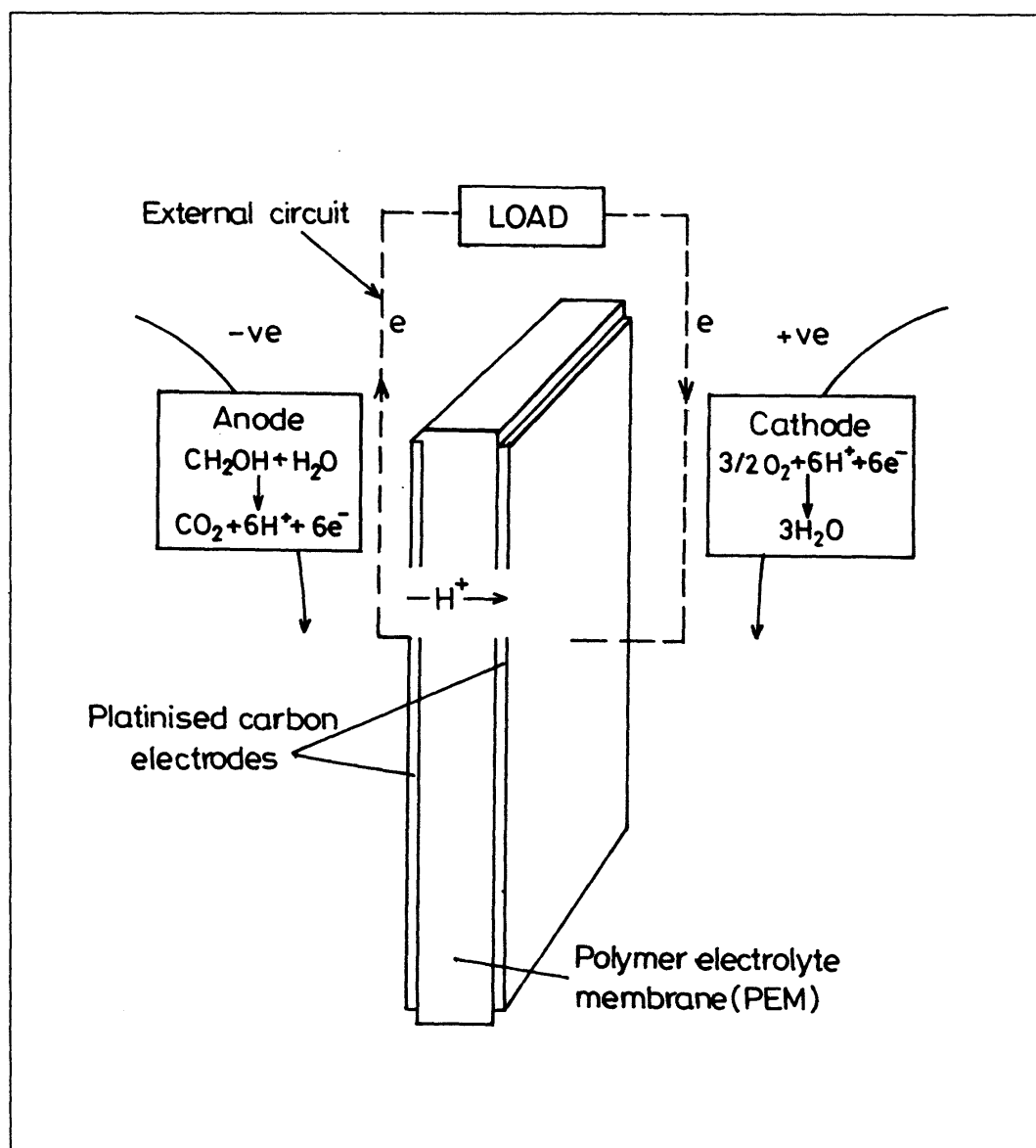


Fig. 1 Schematic representation of DMFC in operation

emphasizing on the areas where improvements would be highly advantageous:

- The activity of the anode must be further improved by identifying a suitable catalyst for use at ambient conditions.
- The current loadings of noble metals need to be reduced. In order to reduce the usage of precious metals and thus cost, the best possible performance has to be extracted from a given amount of the catalyst. This aspect can be subdivided into catalyst preparation, pretreatment and characterization. Other topics such as *catalyst-support interactions* and *choice of a suitable support* are also involved.

2 A Glimpse at Methanol Oxidation

The presentation is organized in four sections with suitable appropriate subsections in two of them. As a logical sequence the details of methanol oxidation on Pt/C this being the best studied system has been taken up in section 2 with subsections enumerating the studies on bulk Pt, on Pt particles and Pt based alloys in this sequence. Section 3 deals with the results reported on supported systems, especially on the conventional carbon support as well as on the conducting polymer supports. The subsections in this section deal with each of the known individual systems or with the possible variables in the case of carbon

support. Section 4 deals with a perception on the status of polymer based electrodes while section 5 outlines some directions for future studies. It may be clear that this strategy that we have followed in the presentation is to evolve a logical comprehension of the development in this area so as to evolve what future studies are needed to improve the comprehension as well as to push the frontier further in this area.

2.1 Methanol Oxidation on Bulk Platinum

The reported studies on bulk platinum lead to the following essential features:

- Electrosorption of methanol is slow on bulk platinum at lower potentials, with activation energy of 35kJ/mol¹⁴.
- Sequential proton stripping from methanol takes place, giving a series of multiply bonded intermediates that eventually converted to linearly bonded CO. Evidence for short-lived hydrogenated intermediates on platinum arises from IR¹⁵, DEMS¹⁶, time- resolved¹⁷ and product studies¹⁸.
- At potentials above ~ 0.5 V/NHE, there is a steady loss of adsorbed CO from the surface of the platinum and a gain of CO₂. Above 0.7 V, the surface is almost free of CO_{ads}^{14, 19}
- Morphology appears to play an important role in determining the activity of platinum²⁰, with roughened platinum showing higher activity²¹ and this increased activity is associated with (i) Easier adsorption of methanol at energetically favoured sites such as steps. (ii) Formation of isolated low-coordinate platinum ad-atoms, which take place during roughening²². It was also suggested that such platinum atoms may be easily oxidized as evidenced by XPS, giving rise to a Pt-O species at potentials far below than that required for planar platinum atom²³. (iii) A decrease in strong specific adsorption of HSO₄⁻ on large planar areas of the platinum is known to inhibit methanol adsorption²⁴.
- Methanol adsorption is inhibited quite generally by adsorption of anions such as chloride, bromide, iodide²⁵, perchlorate²⁶ and phosphate²⁷.
- Studies on methanol adsorption and oxidation on single-crystal surfaces of platinum show considerable sensitivity to the Miller indices of these surfaces: (i) The rate of methanol adsorption is highest on Pt (110) surface^{28,24b}, with instantaneous potential-step measurements giving currents as

high as 156 mA/cm² for the initial chemisorption process. (ii) The adsorption of methanol to form linearly bonded CO is most extensive on Pt (100) and surfaces with (100) terraces. (iii) Substantial multi-bonded adsorbate is present on Pt (211) surface and this is applicable to Pt (111) and Pt (110) in sulphuric acid electrolyte²⁹.

- Studies on electrochemical kinetics are associated with surface pre-treatment and control over the surface coverage of intermediates³⁰. Kinetic analyses suggest two extreme types of mechanism for methanol oxidation on platinum: one involves attack of water on CO molecules on the outside of the chemisorbed CO from the edges of the islands in a type of Reppe process, and the second involves rate-limiting migration of CO from the edges of the islands to active sites, perhaps to Pt-O, as identified by XPS. Currents are always higher on roughened platinum than on equilibrated platinum, at least for potentials below about 0.55-0.6 V/NHE. Above this potential, CO_{ads} is oxidized rapidly from the platinum surface, and FTIR studies³¹ suggest that intermediates such as Pt₃COH may be oxidized directly to CO₂ at higher potentials. This change of mechanism at higher potentials has also been detected by the presence of formyl radicals using spin-trap EPR studies³². The listing of essential features of the studies on bulk platinum indicates the geometry and reactivity of the active sites for methanol oxidation.

2.2 Methanol Oxidation on Platinum Particles

The oxidation of methanol on platinum particles is of technological importance than that on bulk platinum. The essential findings are:

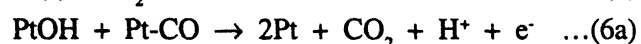
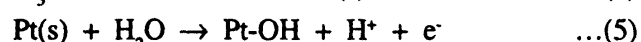
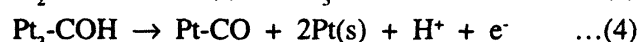
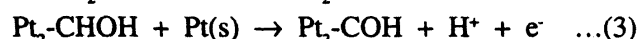
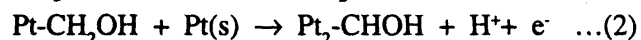
- Considerable controversies exist regarding the “size-effect” towards methanol oxidation. Shell³³ suggested the existence of size effect, with an optimal Pt diameter of 3nm. Kennedy, Goodenough and Bruke *et al.*²³ report an optimal diameter of 2 nm. This size effect is a consequence of structure-demanding nature of the adsorption process. However, Watanabe *et al.*³⁴ do not find any evidence for size effect and commented on the earlier findings that they were flawed by failure to control the inter-particle distance.
- Spectroelectrochemical studies such as *in situ* IR for Pt particles revealed a decrease in linearly

bonded CO with an increase in the bridged form at higher coverages.³⁵

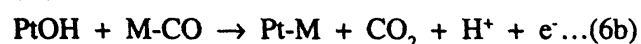
- Christensen *et al.*³⁶ showed that the rate of chemisorption of methanol on Pt particles is faster than that on bulk platinum at lower potentials suggesting that methanol chemisorption is favoured on steps or at defective crystallographic sites.

2.3 Methanol Oxidation Mechanism

Several reports were centred around understanding the oxidation of methanol and its mechanisms at different catalyst systems under well characterized conditions such as different single crystal orientations and foreign metal clusters on polycrystalline or single crystal surfaces^{8,9,11-13,16,20,24b,37-63}. The mechanism for methanol oxidation can be viewed in terms of two basic functionalities: (a) Electrosorption of methanol onto the substrate and (b) Addition of oxygen to adsorbed carbon-containing intermediates to generate CO₂, which can be alternatively facilitated by the second metal in alloy systems. Few electrode materials are capable of adsorbing methanol; in acid medium only platinum and platinum-based catalysts are showing sensible activity and stability. Adsorption of methanol seems to take place through a sequence of steps. In the following general mechanism, proposed steps (1) – (4) are associated with the electrosorption process and the subsequent steps involve oxygen transfer or oxidation of surface bound intermediates. Though the mechanism of methanol oxidation almost remains the same in both platinum and platinum based catalyst (Pt-M), the adsorption of water and further decomposition to give the oxophilic species takes place at a lower potential on the bimetallic surface (M), which leads to the easy removal of the oxidation intermediates (Step 6b)

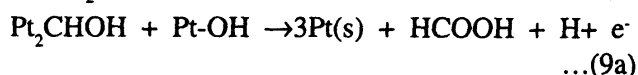


(or)

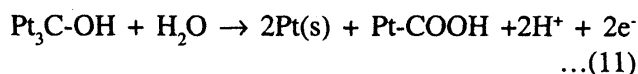
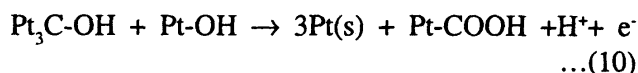
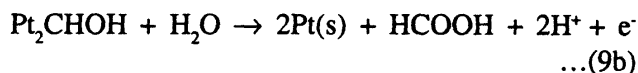


(or)

where M=Ru, Mo, Sn



(or)



2.4 Methanol Oxidation on Pt Based Alloys

Although platinum is overwhelmingly the most active catalyst for electrooxidation of methanol, the high loading necessary for commercial performance fuelled the search for other materials based on methanol oxidation mechanism, that could combine with platinum, with the latter used to chemisorb methanol followed by the action of promoter which could provide oxygen in 'active' form to facilitate oxidation of the chemisorbed CO, the process known as 'bi-functional' mechanism. Since, the oxidation of methanol involves various stages, i.e., dehydrogenation, chemisorption of CO-like species, adsorption of OH species, chemical interaction between the adsorbed CO and OH and CO₂ species evolution, one of these stages may behave as the rate-determining step (rds) according to the particular catalyst surface. The choice of multifunctional catalyst is to increase simultaneously the rate of various stages, avoiding particular steps becoming the rate determining process. The search for possible catalyst materials has been focused sometime upon binary and ternary alloys.

In 1976, Janssen *et al.*⁵⁰ prepared a large number of Pt based binary catalysts by deposition of sub-monolayer amounts of second components on to the surface of Pt via an immersion method and in some cases, where immersion method failed to yield stable binary catalysts, the preparation of Raney-type and true alloy catalysts was adopted. In a number of cases, the adsorbed second element was unstable and such systems include: Cu, Zn, Cd, B, Al, In, Tl, Cr, Mn, Fe, Co, Ni, all rare earths except Dy and Th. For Si, P, Hf and Ta no adsorbed phase was obtained.

There are number of reviews available on electrooxidation of methanol on noble and non-noble metal combinations of platinum for the years 1973-

1999^{8,50,64-75}. In general, the following approaches were addressed in an attempt to promote the activity of platinum.

- i. A simplest method for enhancing oxidative activity is to generate more Pt-O species on Pt surface by incorporation of another metal by alloy modification and that subsequent dissolution leads to highly reticulated and active surfaces. Alloys such as Pt₃Cr and Pt₃Fe exhibit higher activity by virtue of this process⁷⁴.
- ii. A second approach is the use of surface ad-atoms, deposited by upd (under potential deposition) on Pt surface. The role of ad-atoms were: (a) blocking of hydrogen adsorption, (b) the ability to modify the electronic properties of Pt, (c) the ability to act as redox centres, (d) blocking of poison adsorption sites, (e) to induce Pt-O formation on neighbouring sites, creating additional active sites for oxidation of CO_{ads}'

These have been studied extensively^{50,71,72} with Au^{71a}, Sn^{71b} and Bi⁷². The ability of Sn and Bi ad-atoms to enhance electro oxidation of methanol was discussed latter by Campbell *et al.*⁷² and reported that under carefully controlled conditions, the adsorption of these metals inhibited methanol oxidation although Herrero *et al.*⁷³ studies showed evidence that Bi adsorption also inhibited the formation of adsorbed CO.

- iii. *Use of alloys of platinum with different metals, where the second metal forms a surface oxide in the potential region for methanol oxidation.*

This approach is the basis for the studies of Pt-Sn, Pt-Ru, Pt-Os, Pt-Ir etc.⁷⁴. In this study, Ir and Os found to act as promoters, while Au and Pd inhibit the reaction. Pd was active in alkaline medium and not found to be useful in acidic conditions⁷⁵. Cathro⁷⁶ showed that electrodeposited Pt-Re alloys exhibiting substantial activity among the non-noble metals. Reports of strong enhancement for electrodeposited Mo on Pt have been reported⁷⁷, especially at low currents, where different mechanism found to operate. Troughton *et al.*⁷⁸ used Pt/Ru/Sn system, and found that alloying Pt/Ru with Sn tends to expel the Ru, leading to no advantage. Other multimetallic systems of this type include carbon supported and unsupported Pt/Ru/Sn/W⁷⁹.

- iv. Another type of approach is the use of combination of Pt with a base metal oxide.

Hammnet *et al.*⁸⁰ found Nb, Zr and Ta to promote Pt activation, particularly at higher currents. Later, Hammnet *et al.*⁸¹ attempted to use ZrO₂ to promote Pt/Ru, but was unsuccessful. Hammnet *et al.*⁸⁰ identified WO₃ as an inhibitor but latter, Shen and Tseung^{82a} found that hydrous WO_{3-x} as a promoter for Pt when electrodeposited on its surface and this result was further confirmed separately by Shukla^{82b}. A 1 mg Pt/ 1 mg WO₃ codeposited on gold foil gave a steady state performance of 100 mA/cm² at 200 mV/SCE, 0.5 M H₂SO₄, 1 M MeOH at 333K. On the other hand a platinized gold electrode of similar Pt loading gave 10 mA/cm² at 450 mV/SCE, but poisoned within 20 mins. Similar catalysts were prepared by doping tungsten bronzes of the structure Ln_{0.1}WO₃ with Pt.^{82c} Mixed oxides of In/Pb on carbon also exhibited considerable activity but poor stability^{82d,e}. Tseung *et al.*^{82f} reviewed on the experimental evidence and mechanism of 'hydrogen spill-over' on Pt/WO₃ and the application of this system for various electrocatalytic reactions. Lasch *et al.*^{82g} studied the electro oxidation of methanol using ternary alloys by introducing transition metal oxides such as WO_x, MoO₃ and VO_x to Pt-Ru catalysts and the results are compared to binary Pt-Ru alloy catalysts. The materials were prepared via the modification of Adams method and the Pt-Ru particles size were ~ 3-5 nm. In the metal oxide containing ternary catalysts a lower polarization of methanol oxidation was observed and were capable of sustaining large current densities. However, deactivation of catalysts occurs above 750 mV/RHE and this might be due to the formation of catalytically inactive surface oxide. The ternary compound apparently influences the rate of methanol oxidation and surface oxide formation. The most prominent effect of catalytic activity was found with Pt-Ru-VO_x and methanol oxidation starts at 360 mV/RHE, which is almost identical to Pt-Ru electrode (380 mV).

- v. *Incorporation of Pt onto Oxide Structures*

In addition to electrodeposition of Pt onto an oxide surface, incorporation of Pt directly on to oxide structures was also attempted. For instance, perovskite-based oxides, such as SrRu_{0.5}Pt_{0.5}O₃^{83a}

and $\text{Dy}_x\text{Pt}_3\text{O}_4$ ^{83b} are of this category. However, there exists ambiguity about their long-term stability in acidic environments. It was presumed that they undergo reductive decomposition through methanol adsorption to give fine platinum particles at the surface, which act as catalytic sites.

vi. Replacing Pt with other Noble Metals

Other noble metal catalysts such as Ir have been investigated^{84a} but are found to be less active than Pt. Okamoto *et al.*^{84b} found that WC when annealed with carbon in He atmosphere shows very little activity for methanol oxidation, compared to platinum. Amorphous metal alloys such as NiZr^{84c} were active, by forming a thick passivating oxyhydroxide film on which electro oxidation of methanol takes place, and were stable in acidic conditions. Kawahima *et al.*^{84d} used alloys of NiZr and NiTi with few percentage of platinum and were found to be active for methanol oxidation.

Although binary alloys of Pt with many other oxophilic elements have been studied, none is more active than high-surface area Pt-Ru and it is known that the catalytic action of PtRu proceeds mainly by the so-called bi-functional mechanism. Several reports are available in literature using Pt-Ru for electrooxidation of methanol and the key findings are summarized as follows.

- The electrocatalytic activity of Pt-Ru alloys for methanol oxidation was investigated in 1960's but at that time, the cause for the enhancement was not clear.^{85a} Watanabe *et al.*⁸⁶ proposed bi-functional theory for electro catalysis and further showed that ad-electrode has same electrochemical characteristics as the alloy electrode for the oxidation of methanol.
- Later, Watanabe *et al.*⁸⁷ prepared Pt+Ru binary catalyst by co-deposition method, which has three times larger specific surface area ($80 \text{ m}^2 \text{ g}^{-1}$) than that prepared by conventional methods. The supported alloy (Ru/Pt=1/1) exhibited high catalytic activity of 200 mA/cm^2 at 0.4 V/NHE and a limiting current of more than 1.0 A/cm^2 .
- The alloying of Ru and Pt has been postulated to give rise to an electronic effect in which electrons are transferred from Ru to Pt.⁸ But, the suggested direction of electron donation has been challenged latter, particularly from FTIR studies

on well-defined bulk alloy⁸⁸ and on Pt-Ru particles,⁸⁹ both of which show a reduction in CO_{ads} coverage at the electrode at any given potential and an increase in the absorption frequency of bound CO; this latter effect must be electronic in origin and consistent with CO being less strongly adsorbed through a reduction in the back π -bonding from Pt to the $\text{CO}\pi^*$ orbital. The reduction in π -back bonding will also lead to a higher positive charge on the carbon atom, rendering to more liable to nucleophilic attack by water and permitting oxidation of CO at lower potential. This effect was confirmed by DEMS studies⁹⁰.

- A second role of Ru is to increase the coverage of Pt-Ru surfaces by oxy species. An XPS study⁹¹ revealed that the presence of Ru enhanced the amount of Pt-O species, and this observation was confirmed by later work.^{23a,92a,b} Mössbauer data by the same authors⁹³ showed that in co-deposited Pt-Ru particulate electrodes Ru was present in the form of an oxyhydroxide rather than a well-defined RuO_2 species, and the decrease in activity of the catalyst made in this method was attributed to transformation of the hydrous oxide to more inactive anhydrous phase⁹⁴.
- In Pt-Ru catalyst, Ru sites adsorb oxygen-containing species at 0.2-0.3 V lower potentials than pure Pt surface: the adsorbed carbonaceous species are preferentially oxidized at these sites by surface diffusion from sites where adsorption occurs. Pt-Ru sites adsorb more active form of oxygen containing species than Ru-Ru pairs or Ru clusters. The optimum surface composition of Ru maximizes the Pt-Ru pair sites within the constrain of the optimum ensemble for adsorption of the molecule. In case of CO and HCOOH adsorption is equally facile at Ru-Ru, Pt-Pt and Pt-Ru sites and the optimum surface composition is 50 atomic per cent of Ru. For methanol, the situation is quite different as adsorption occurs through consecutive dissociative steps. In terms of geometry, the optimum adsorption site seems to be a C_{3v} Pt ensemble and the composition which simultaneously maximizes the number of these ensembles and Pt-Ru pairs is 10 atomic per cent of Ru^{95a-e}.
- Studies on well defined alloy surfaces, with known surface compositions^{95a,96} have shown that low Ru coverages lead to facile chemisorption of methanol

but, as expected rate limiting oxidation of CO_{ads} , with the rds being CO migration to active Ru clusters. It has been a puzzle that practical Pt-Ru electrodes are optimized at 50 atomic per cent and this puzzle was solved with the observation that Ru has a high activation energy for methanol chemisorption; But above 333 K, methanol can adsorb on both platinum and ruthenium^{95a} and the reduction that is found in adsorption rate at room temperature for Pt-Ru alloys as compared to pure Pt is not found at 333 K at very low methanol concentrations..

- Chrzanowski *et al.*⁹⁷ carried out the electrooxidation of methanol on ruthenium deposits with various Pt single crystal faces such as Pt (111), Pt (100) and Pt (110) and found that all deposits are catalytically active and at low potentials catalytic enhancements are much pronounced in Pt (111)/Ru.
- Rolison *et al.*⁹⁸ found by using surface and bulk analyses that although practical Pt-Ru blacks have diffraction patterns consistent with an alloy arrangement they are primarily a mix of RuO_2 , RuO_xH_y , Pt, PtO_x and PtO_xH_y . Hydrous ruthenium oxide is a mixed proton and electron conductor and innately expresses Ru-OH speciation. These properties are of key importance in methanol oxidation. Since, Ru-OH is a critical component of the bifunctional mechanism that it is oxygen transfer species that oxidatively dissociates $-\text{C}\equiv\text{O}$ fragments from the Pt surface. The catalysts and membrane electrode assembly should not be exposed or processed at >423 K as such conditions deleteriously lower the proton conductivity of ruthenium hydroxide and thus affect the ability of the Ru component of the electro catalyst to dissociate water. That is a mixture of Pt metal, Pt oxides, and Ru oxides control the relevant interphase and catalyst-ionomer structure that then acts in the operating fuel cell as the reaction environment for the electro chemical oxidation of methanol.
- Iwasita *et al.*⁹⁹ compared the activities of different types of PtRu catalysts for methanol oxidation such as: UHV-cleaned PtRu alloys, UHV-evaporated Ru on to Pt(111) as well as adsorbed Ru on Pt (111) prepared with and without additional reduction by hydrogen. Catalytic activities were found to be different according

to the preparation routes and UHV-STM data showed the formation of two- and three-dimensional structures depending on the surface coverage. *In situ* IR data suggested that the probable rate-determining step might be reaction of adsorbed CO with Ru oxide.

- For methanol oxidation at 333 K in 2.5-3 M H_2SO_4 /1 M CH_3OH on Pt-Ru at 0.4 V, $\sim 40 \mu\text{A}/\text{cm}^2$ was found for real surface area. For lower concentration of acid, where there is less competitive anion adsorption, values near $160 \mu\text{A}/\text{cm}^2$ was observed at the same temperature^{95A,100}. Given an activation energy of 60 kJ mol^{-1} , this would correspond to $\sim 200 \text{ mA}/\text{cm}^2$ for loading of $1 \text{ mg}/\text{cm}^2$ at 333K and would increase by a factor of 3.5 at 353 K and by a factor of 10 at 373 K.

PtSn is another catalyst system, probably only second to that in PtRu. Theoretical studies suggest that Sn alloyed into Pt is inactive in generating OH_{ads} ¹⁰¹. It was found experimentally that PtSn alloys are not active, while electrosorbed or electro deposited Sn on Pt is a reasonably good catalyst for methanol oxidation^{76b, 95b, 102}. However, the conclusion that PtSn alloys are inactive for methanol oxidation is disputed¹⁰³. The contradiction might be due to two reasons: It is some times unclear whether the binary system is an alloy or just a mixture of two metals, and Sn may leach out in acidic conditions, and in turn re-adsorbed electro catalytically at Pt sites. In less well-controlled experimental conditions, the latter effect may simulate a catalytic activity of PtSn mixtures or alloys. Generally, it was assumed that adsorbed Sn acts in a similar fashion as Ru alloyed in to Pt by activation of adsorbed water^{95b,102b,c}. The fact that adsorbed Sn on Pt is active, while it is not for PtSn alloys and this might be due to the ionic nature of adsorbed Sn.

Despite nearly three decades of research and optimization, the best-known electrocatalysts are binary Pt-Ru alloy and Pt-Ru-Os ternary alloy. Ley *et al.*¹⁰⁴ found the beneficial effect of Os substitution into Pt-Ru using CO adsorption data, methanol oxidation data and *in situ* FTIR. CO tolerance and methanol oxidation studies on single phase arc-melted electrodes and on dispersed high surface area catalysts incorporated in to full DMFC, suggest that a bifunctional ternary catalyst in the Pt-Ru-Os system with nominal composition Pt-Ru-Os (65:25:10) was superior to Pt-

Ru (1:1) catalysts for DMFC anodes. Steady-state voltammetric data of the arc-melted alloys at 298K confirmed that Pt-Ru-Os (65:25:10) was superior to Pt-Ru (1:1) (at 363K, 0.4 V; 340 mA/cm² with Pt-Ru-Os vs 260 mA/cm² with Pt-Ru). This work must be qualified in that it was restricted to single-phase electrodes prepared by borohydride reduction of metal chloride salts and not in high surface area electrodes. Within this regime, Pt-Ru-Os is superior to Pt-Ru. Reddington *et al.*¹⁰⁵ proposed a combinatorial screening method for electrode materials for anode catalysis in DMFCs. They found several good catalysts by screening combinations of five elements (Pt, Ru, Os, Ir and Rh) in unexpected regions of composition space and identified a quaternary catalyst with significantly higher activity than the best previously known binary Pt-Ru catalyst.

The use of Pt with non-noble metals alloys as anodic materials for methanol electro-oxidation is associated with the limitations such as (i) They might not show long-term stability and (ii) The active surface area of these alloys is uncertain, possibly even changing with time due to a leaching out effect.

3 Methanol Oxidation on Supported Metal Particles

Dispersed micro/nano particles of noble metals supported on high surface area materials are of considerable interest to catalysis, in part due to their unique physical and chemical properties^{106,107}. The primary function of the support is to separate the individual particles physically in order to diminish the rate of agglomeration. The physical properties of nanoparticles depend strongly on the perturbations that arise from the large fraction of metal atoms residing at the particle surface, may show a marked difference from those characterizing the bulk solid state. The support plays a major role, determining the mechanical and thermal stability of the particles while helping them in a highly dispersed state.

The choice of a suitable support is a factor, which affects the performance of supported catalysts. Interactions between the catalyst and the support have been identified to modify the intrinsic catalyst activity. In studies of methanol oxidation, the supports so far employed for dispersing catalytic metal particulates are carbon and conducting polymers. For instance, in the case of carbon supports, nature of functional

groups i.e., lower concentrations of acid/base groups and carbons with sulfur and nitrogen-based functionalities have shown enhanced catalytic activity. However, till today, to the best of our knowledge there is no report available which precisely deals with molecular level interactions that are taking place between the conducting polymer support and supported metal particles. Despite the extensive efforts of research to date, such an understanding has yet to evolve.

3.1 Noble Metals on Carbon Supports

The use of carbon as catalyst support is continuously growing and there are number of reports available¹⁰⁸⁻¹¹⁴ as an attempt to relate metal dispersions with the properties of the support. Carbon and graphite possess unique combination of chemical and mechanical properties that are attractive in electrochemical technologies¹⁰⁵. Due to the unique role of platinum catalysts in fuel cells, studies have been reported on the synthesis of platinum particles supported on matrices including carbon and conducting polymers. Traditionally, dispersed platinum is produced by impregnation methods (chemical reduction or thermal decomposition of platinum compounds). Electrochemical methods also provide an attractive way to produce dispersed platinum electrodes. Earlier studies on a Pt-carbon system in which the support was a graphitized carbon black (V3G) subjected to various levels of carbon burn off in air had shown the differences in Pt dispersion as a function of carbon burn off^{110,111}. The increase in the Pt dispersion with the extent of gasification of the carbon support was related to (i) an increase in surface heterogeneity—which in turn increases the potential energy barrier for the diffusion of Pt species across the carbon surface during sample preparation¹¹⁰ and (ii) an increase in the surface area of the support—the number of surface Pt atoms per unit area of the support was almost constant and independent of the extent of carbon burn off¹¹¹. On the other hand, Ehrburger^{113,114} analyzing the dispersion of small particles on carbon surfaces with other metals/V3G systems, has pointed out the importance of active surface area on the dispersion of metal on carbon. The apparent discrepancy about the factor conditioning the Pt dispersion may be due to a lack of knowledge of the surface chemistry of the carbon support. In fact, during the gasification of V3G and subsequent cooling to room temperature in air, the chemical nature of the carbon support could

have changed progressively with burn off. Therefore, a systematic study of the effect of chemical nature of carbon support on the characteristics of the final catalysts seems appropriate.

The following sub-sections deal with the role and influence of various aspects such as preparation method, particle size, carbon functionality, effect of ad atoms effect and morphology of carbon support towards the final catalytic activity of catalyst particulates toward electrooxidation of methanol. Various aspects

associated with these issues are carefully analyzed and comparisons of results are made by mass normalization approach. The data are given in Table III, to facilitate the reader to get a quick grip on the associated issues.

3.1.1 Role of Preparation Method

Common methods of preparation of electrocatalysts supported on carbon include impregnation, adsorption and ion exchange.

Table III
Evaluation of Methanol Oxidation Performance on Noble Metal(s) supported on Carbon Electrodes

S.No	Metal(s)	Type of carbon	Activation treatment	Performance		Reference
				Pot (V/NHE)	Mass Sp. Activity (mA/mg)	
1	Pt Black	–	–	0.48	85.0	23b
2	Pt	Vulcan XC-72	CO ₂	0.43	180.0	
3	Pt	PG coated Carbon fibre paper	H ₂	1.0	103.3	120
			Air	1.2	30.5	
4	Pt	"	H ₂	0.55	100*	128
5	Pt	Boron doped Diamond (BDD)	–	0.41	2.0	133
6	Pt-Ru	–	–	0.54	20.0	92a
	Pt-Ru	VulcanCX-72	CO ₂	0.48	250.0!	
7	Pt-Ru	"	"	0.60	240.0!	174
8	Pt	VulcanXC-72	CO ₂	0.74	150	74
	Pt-Au	"	"	0.79		
	Pt-Os	"	"	0.64		
	Pt-Ir	"	"	0.64		
	Pt-Pd	"	"	0.87		
	Pt-Ru	"	"	0.56		
9	Pt-Au	GC	Rf sputtering	0.26	1.25*	176
10	Pt-Pbo-Ir ₂ O ₃	Graphite	–	0.5	2.0	82e
	Pt-Pbo-Ir ₂ O ₃ /Au		–	0.5	2.75	
11	Pt	Graphite	–	0.4	15.0*	177
	Pt/Ru/WO ₃	"	–	0.35	55.0*	
12	Pt-Ru	VulcanXC-72	Colloidal preparation	0.5(0.4)	100(20)	135
	Pt-Ru	"	Etek	0.5(0.4)	75(12)	
	Pt	"	"	0.5(0.4)	60(0.2)	
13	Pt	GC	–	0.43(0.14)	0.65*	178
	Pt-MoO ₃		–	0.45(0.14)	0.54*(0.4)*	
14	Pt-Ru	GC		0.8	25.7	82g
	Pt-RuWO _x	"	Chem prep	0.8	32.14	
	Pt-RuMoO _x	"		0.8	44.3	
	Pt-Ru VO _x	"		0.8	57.14	
15	Pt	CNT	CVD-based	0.527	71.43	185
	Pt-Ru	"	template synthesis	0.427	53.6	

* Current Density (A/cm²); # Current (mA); ! At 333 Ks

In impregnation technique, carbon support is in contact with a solution containing the salt of a metal catalyst. Impregnation occurs by capillary action, drawing the salt solution into the porous structure of the support and subsequent evaporation of the solution results in precipitation of metal salt in the pores of the support. In the case of supported metal catalysts, dispersion and distribution of the active phase are largely determined by the impregnation step. A limitation of the impregnation technique is that the surface area of metal particles (m^2/g) decreases as metal loading increases. This occurs when the metal salt concentrates in a fixed number of pores; as the salt concentration increases, a larger mass of salt is precipitated in each pore (pore-concentration mechanism), and larger metal particles are obtained when the metal salt is reduced. The surface area of Pt per unit weight of catalyst (A) often follows the relationship $A = N^{1/3} \rho^{-2/3} W^{-2/3}$, where N is the number of crystallites, ρ is the density of Pt and W is the Pt loading in weight percentage of the catalyst¹¹⁶. For Pt supported on graphitized Vulcan XC-72¹¹⁶, which is obtained by impregnation in $\text{Pt}(\text{NH}_3)_4(\text{NO}_2)_2$ solution, the surface area is $100 \text{ m}^2/\text{g}$ Pt for a Pt loading of 5 wt%. When the loading is increased to 20wt%, the surface area is only about $35 \text{ m}^2/\text{g}$ Pt. These results were explained by pore-concentration mechanism and data fitted appropriately to the above equation. In the case of platinized carbon, the precursor most often used is hexachloroplatinic acid (H_2PtCl_6), since this compound usually yields a better metal dispersion than for example, platinum ammine complexes¹¹⁷. The later precursors result in high dispersions only when the carrier was specially pretreated to increase its ion exchange capacity¹¹⁸. From aqueous solutions, H_2PtCl_6 is adsorbed strongly on to activated carbons (up to ~10 wt% of Pt, depending on the nature of activated carbon). The adsorption is less strong when organic solvents were used¹¹⁹.

Ion exchange technique is based on the surface property of carbon¹¹⁶. Several of the surface groups on carbon undergo ion exchange reactions with ionic species in solution providing highly dispersed electrocatalysts on carbon supports. Ion exchange is achieved with metal ions in solution as cation complexes, which exchange with hydrogen from carboxyl or phenol groups on carbon surface. The extent of ion exchange and metal loading are controlled by pH of the solution and contact time. This technique

was successfully employed to obtain Pt catalyzed carbon fibres¹²⁰. An advantage of the ion exchange method over the impregnation method is that a relatively high surface area can be obtained, even at a high metal loading. A constant surface area of $\sim 100 \text{ m}^2/\text{g}$ Pt is obtained by the ion exchange method on graphitized Vulcan XC-72 with Pt loadings of about 20 wt%, whereas the surface area obtained at these high loadings by impregnation method is lower¹¹⁶. Blurton¹²¹ prepared supported Pt catalysts by variation in the ion exchange technique.

Adsorption of colloidal Pt on carbon black is described in patents by Petrow and Allen^{122,123} and in reviews by Ciapetta and Plank¹²⁴ and Davis and Klabunde¹²⁵. A catalyst of Pt on carbon is prepared from Pt particles obtained by reducing a H_2PtCl_6 solution with a reducing agent such as hydrogen gas, sodium citrate, sodium borohydride, formaldehyde, acrolein, hydrogen peroxide, or hydrazine. When H_2PtCl_6 is reduced by borohydride, formaldehyde or hydrogen¹²⁶, the Pt surface area varied from 8 to $43 \text{ m}^2/\text{g}$ and the Pt particle sizes are $\sim 350\text{-}65 \text{ \AA}$.

Studies on activity of noble-metal catalysts supported on pyrographite-coated carbon-fiber paper (PG-coated CFP) for electrochemical oxidation of methanol was reported by Atwood *et al.*¹²⁷. These catalysts were prepared by oxidation of CFP to produce acidic surface groups followed by impregnation or ion-exchange with a cationic platinum salt. The catalyst was dried, heating in air or hydrogen decomposed the platinum salt and the catalyst was finally reduced electrochemically. X-ray photoelectron spectroscopic studies revealed that Pt $4f_{7/2}$ binding energies of air-activated and hydrogen-activated samples were 72.2 eV and 70.0 eV respectively, which were higher than that reported for bulk Pt. Electrochemical measurements and XRD indicated that the hydrogen-activated catalysts have surface area in the range $120\text{-}280 \text{ m}^2/\text{g}^{-1}$, corresponding to a mean crystallite size of $<2.0 \text{ nm}$, whereas air-activated catalysts have area in the range $70\text{-}120 \text{ m}^2/\text{g}^{-1}$, corresponding to a mean crystallite size of $<5.0 \text{ nm}$. A commercial unsupported Adams Pt catalyst has an electrochemical surface area of $\sim 45 \text{ m}^2/\text{g}^{-1}$, corresponding to a mean crystallite size of $\sim 8.0 \text{ nm}$. The air-activated catalysts had higher intrinsic activity for methanol electro oxidation than unsupported platinum. Hydrogen activation produced larger platinum surface area resulting in intrinsic catalytic activities

that were not only substantially lower than that for air-activated catalysts but also lower than for unsupported platinum. Catalysts activated in air or hydrogen both exhibit a decrease in the Pt surface area as determined by electrochemical measurements after prolonged cycling in the range 0 and 1.6 V, showing such treatment could produce sintering of Pt crystallites. The specific activity of air-activated catalysts decreases as Pt surface area falls whilst the intrinsic activity was almost constant. For the hydrogen activated catalysts, the total current produced increased as the surface area of the metal was reduced by cycling, i.e., both specific and intrinsic activity increased with decreasing surface area, until the surface area fell below $40 \text{ m}^2\text{g}^{-1}$ when a decrease in activity was observed. In a later paper, Atwood *et al.*^{33b} proposed two possible explanations for these observations: (a) smaller Pt crystallites in hydrogen-activated samples were less active for methanol oxidation and upon cycling, converted into larger, more active crystallites (b) cycling treatment produces oxidation of the carbon substrate during anodic sweep and Pt was then recomplexed with the carbon via surface groups.

Stoyanova *et al.*¹²⁷ prepared carbon supported Pt catalysts (Pt/C) by treatment of PtO_2/C under different conditions such as (i) heating at 653K in air, argon and hydrogen, (ii) electrochemical reduction in H_2SO_4 ; and (iii) reduction with NaBH_4 . The effect of preparation conditions on the structure and the catalytic activity of the catalysts for the electrooxidation of methanol in acid media was studied. The highest activity was achieved for the catalyst treated in air. Jakikozawa *et al.*¹²⁸ found that for Pt/C catalyst for methanol oxidation, the face (110) possesses the highest activity.

In general, gas pre-treatment of the carbon substrate is found to increase the activity of the electrode. Goodenough *et al.*¹²⁹ utilized CO_2 treated platinumized high surface area VulcanXC-72 carbon as anode for methanol oxidation. Galvanostatic studies of an argon saturated 1.0 M methanol in 2.5 M H_2SO_4 at 333 K showed that the supported Pt electrode not only exhibited much lower overpotential (-172 mV/RHE) than Pt black (-122 mV/RHE), but is also capable of showing higher current densities with relatively low loadings of Pt (For 8% Pt on VulcanXC-72, at potential +182 mV/RHE, $I = 600 \text{ mA/cm}^2$, 180 mA/mg; whereas for Pt black, at potential +132 mV/RHE, $I = 290 \text{ mA/cm}^2$, 85 mA/mg). Lifetime performance

study revealed that compared to rapid poisoning (4h) observed for Pt black, the platinumized-carbon electrode showed a considerable improvement (stable till 28h). The enhanced activity of these electrodes compared with Pt black was explained in terms of the unusual surface properties of small Pt crystallites and of the strong metal-support interactions between the carbon substrates and Pt crystallites. XPS investigations of these electrodes showed the presence of both Pt^0 and oxidized Pt species. The overpotential for methanol oxidation on platinumized-carbon anodes compared with Pt black suggested that the increased activities could be attributed to the formation of active Pt-O groups rather than a weakening of the Pt methanol interaction. This weakening could result in increased activity of the anode by lowering the stability of the Pt-CO species and hence resulting in less ready poisoning of the surface. A gradual decrease in activity observed on prolonged polarization was correlated with an increased amount of oxidized Pt observed in the XPS, suggesting that the oxidized Pt so formed was an inactive strongly bound Pt oxide, which is formed on methanol adsorption sites. While other workers have identified the need for active Pt-O groups¹³⁰, this study was the first one to show the presence of two types of Pt-O groups, viz active Pt-O at the B_5 or similar sites and a strongly bound Pt-O which are competing for methanol adsorption. B_5 sites are defined as surface sites on which an adatom is coordinated by five surface atoms¹³¹. A Pt_{B_5} site would be particularly susceptible to attack by water to give the reaction, $\text{Pt} + \text{H}_2\text{O} \Rightarrow \text{Pt-O} + 2\text{H}^+ + 2\text{e}^-$ and as the Pt_{B_5} sites occur on surface steps they would not compete for the chemisorbed methanol molecules. Their susceptibility to attack by water would be enhanced if the B_5 sites were relatively poor in electron density. This may be achieved via electron donation from Pt particle to the substrate, which would be possible at the carbon-Pt interface and the adjacent layer of Pt atoms. It is likely that one effect of gas pretreatment is to increase the extent of this electron transfer between the Pt particle and the substrate.

van Dam *et al.*¹³² prepared Pt/C catalyst using chemically modifying commercially available extruded activated carbon Norit ROX 0.8, by nitric acid or air oxidation or thermal decarboxylation. It was shown that the proper choice of preparation conditions lead to Pt/C catalysts of high metal loading (5%) and a high metal dispersion (60%). However, Norit ROX

0.8 type carbon was not employed so far for methanol oxidation, and therefore we confine ourselves with just a mention about this study to facilitate an understanding on the design and preparation of Pt/C with desired properties.

Conductive diamond film electrodes are new materials for electrochemical applications offering good conductivity, chemical inertness, thermal stability, corrosion resistance and electrochemical stability. Wang *et al.*¹³³ incorporated Pt particles into the surface region of boron doped diamond thin films using microwave assisted chemical vapour deposition method. Diamond differs from sp^2 carbon electrodes, in that the oxidation is confined to the surface. The high atomic density and strong sp^3 bonding within the lattice inhibit bulk oxidation under all but the most severe conditions (oxygen plasma treatment). This morphological or microstructural damage contrasts with the severe bulk damage that occurs with most of sp^2 carbon electrodes during oxidative treatment. This damage is caused by combination of intercalation, oxidation and gasification reactions. Metal particles were well anchored and ranged from 10-500 nm in size. The active Pt metal loading was 200-400 ng/cm^2 . However, the real catalyst loading was 0.1 mg/cm^2 . The dispersed Pt particles were extremely stable as no loss in activity was observed after 2000 potential cycles between the oxygen and hydrogen evolution regime in 0.1 M $HClO_4$. Pt containing film was electroactive for methanol oxidation with a maximum current density of 1 mA/cm^2 or 2 mA/mg active Pt at 0.1M methanol concentration and the start potential was 400 mV and reached a maximum at 650 mV. A second maximum was observed at the reverse scan at 400 mV showing Pt-oxides were reductively removed making sites available again for coordinating with methanol. These dimensionally stable, corrosion-resistant, well faceted micro crystallites may be efficiently utilized for methanol oxidation by reducing the metal particle size and increasing the degree of dispersion over the diamond surface and by using mixed metals such as PtRu.

Guo *et al.*¹³⁴ electrodeposited Pt particles on amorphous carbon surface and sol-gel modified carbon surface on gold grids and studied their microstructure and morphology using TEM and EDS techniques. Faceted polytetrahedral crystals were formed on the C/Au surface with oriented crystallization in the former case, while 2D dendritic cauliflower-like

Pt aggregations consisted of smaller particles with high surface area were found on the latter case, allowing advantageous for the preparation of highly active noble metal catalysts at a reduced cost.

Schmidt *et al.*¹³⁵ studied the electrocatalytic activity of bimetallic $Pt_{0.5}Ru_{0.5}N(Oct)_4Cl$ colloids supported on VulcanXC72 toward the oxidation of CO and CO/H_2 mixtures. At 333K the electrochemical activity of PtRu colloid catalyst toward the oxidation of 2% CO in H_2 was found to be slightly higher than that of a commercial PtRu (E-TEK).

Chen *et al.*¹³⁶ prepared a series of carbon supported electrocatalysts such as Pt/C, Pt/ WO_3 /C, Pt-Ru/C and Pt-Ru/ WO_3 /C as Teflon-bonded electrodes and used in 0.5M H_2SO_4 to study their CO tolerance capacity towards anodic oxidation of impure hydrogen containing 100 ppm of CO at 353K. The first three catalysts were gradually poisoned and the performance was less than 100 mA/cm^2 whereas no change in the performance of the teflon-bonded Pt-Ru/ WO_3 /C electrode at 220 mA/cm^2 was observed over a test period of 6h. The carbon used was Vulcan XC-72R. Though co-deposited Pt/ WO_3 electrodes can ensure uniform dispersion of Pt around the WO_3 particles¹³⁷, it was not possible to use codeposition method to make Pt/ WO_3 powder for the fabrication of Teflon-bonded electrodes. Therefore all catalysts were prepared by freeze-drying technique to ensure uniform dispersion of Pt crystallites on the carbon surface. Recently, Chen *et al.*¹³⁸ compared the performance of Pt-Ru/ WO_3 /C catalyst prepared by two methods such as hydrogen reduction at 573 K and thermal decomposition at 723 K. The former technique provided Pt loading of 2.07 mg with an active surface area of 80.2 m^2/g , whereas the later technique provided Pt loading of 2.17 mg with an active surface area of 50.3 m^2/g .

Roman-Martinez *et al.*¹³⁹ prepared a bimetallic PtSn/C catalysts on two activated carbon supports (commercial carbon GA-160 and oxidized carbon using aqueous H_2O_2 at room temperature) with different surface chemistry by two different preparation procedures namely, co-impregnation or successive impregnation to identify the effect of support surface oxidation and the preparation procedure on the interaction of platinum with the support and/or with tin atoms. Their findings were: (i) EXAFS revealed clear differences in structure of catalysts that arise as a consequence of preparation method and surface

chemistry of the support. (ii) in dried samples, the interaction of platinum is stronger with the oxidized support. Co-impregnation method results in a weaker interaction with the support for Pt than the successive impregnation method, probably since Cl⁻ ions inhibit the adsorption process; (iii) in dried samples tin does not affect the electronic state of Pt atoms. (iv) the presence of bimetallic PtSn phases, Pt particles and Pt-O-Sn²⁺ species were found and the catalytic activity of bimetallic catalysts was determined by the relative concentrations of these surface species and their distribution in the support. However, they did not study its catalytic activity toward methanol electrooxidation.

3.1.2 Particle Size Effect

In both electrocatalysis and gas-phase heterogeneous catalysis there are numerous examples of reactions where the catalytic activity is dependent on the crystallite size of the catalytically active metal atoms. Where a reaction is so dependent on crystallite size, it has been termed demanding or structure-sensitive and where no such dependence the reaction has been termed facile or structure-insensitive. As crystallite size decreases so the number of edge and corner atoms increases dramatically. Such sites with low coordination numbers might be expected to have different reactivities from that of a regular lattice position atom. The influence of Pt crystallite size on the activity of Pt arises since the coordination number of the surface atoms depends on the crystallite size. In addition, account must be taken of the possible loss of metallic character in crystallites where most metal atoms are surface atoms. It is known that surface area of an electrocatalyst increases with decrease in size of the particles. In electrocatalysis the role of platinum crystallite size in determining activity has been investigated for a number of reactions and some data are conflicting. The electrocatalytic reduction of oxygen on Pt was shown to be structure insensitive on catalysts where the mean Pt crystallite size varied between 3 and 40 nm. Blurton *et al.*¹⁴⁰ prepared a highly dispersed platinum catalysts on a conductive carbon support by localizing the platinum ions through exchange with ions in a commercial ion exchange resin and subsequently reducing the metal ions by resin pyrolysis in an inert atmosphere. These doped carbons were made in to Teflon bonded fuel cell electrodes for oxygen electroreduction in acid electrolyte and the specific activity of the dispersed Pt was about

twenty times less than that of crystalline Pt black. The lower activity of this catalyst compared to Pt black was attributed to difference in Pt crystallite size and/or the influence of support on Pt activity. However, Blurton *et al.*¹⁴⁰ showed that Pt crystallites with diameter <1.5 nm had significantly lower activity for this reaction than large crystallites.

Lundquist and Stonehart¹⁴¹ observed the existence of a crystallite size effect in the reduction of oxide layers of Pt and surprised to see the effect to persist in crystallite size >10nm. Analogous crystallite size dependences were found for the gas-phase formation of Pt oxides and oxide poisoning of heterogeneous reactions of Pt. Stonehart and Lundquist¹⁴² also demonstrated a strong crystallite size effect in the electrooxidation of chemisorbed hydrogen atoms on Pt. But the electrooxidation of hydrogen molecules on Pt was shown to be structure-insensitive. The role of particle size on the electrochemical behaviour of supported metal particles has been extensively discussed in the literature¹⁴³⁻¹⁵⁹.

Considering all these results, no definite conclusions have been drawn on the influence of particle size towards the performance of carbon supported Pt for methanol oxidation. Frelink *et al.*¹⁵⁹ carried out a systematic study on oxidation of methanol at Pt/C catalysts with different particle sizes. Carbon black (Vulcan XC 72) with the specific surface area (BET) of 340 m²/g was used as a support. The catalysts were obtained by different preparation methods such as ion-exchange, impregnation, colloidal and impregnated- sintered catalysts. The particle sizes ranges between 1.2 and 10 nm. The specific activity was found to decrease with the decrease in particle size in the range 4.5 to 1.2 nm. The dependence of the activity on the particle size was explained in terms of either its effect on the formation of an adsorbed hydroxy species or its effect on the number of methanol adsorption sites.

3.1.3 Role of Carbon Functionality

The physicochemical properties of carbon are strongly influenced by the presence of chemical species on the surface. In addition, the surface structure of carbon affects its physicochemical properties because the reactivity of carbon atoms with unsatisfied valences on edge sites is greater than that of carbon atoms in the basal planes. Consequently, the chemical properties of carbon vary with the relative fraction

of edge sites and basal-plane sites on the surface. Because carbon blacks have a high surface: volume ratio, chemical species are readily adsorbed on the surface and they have a major impact on the chemical properties of the carbon black. Numerous reviews are available on this topic¹⁶⁰. It is known that surface groups have a pronounced effect on the formation of dispersed metal phase of supported catalysts. The surface of carbon black support is composed of graphene layers. Functional groups, which are predominantly oxygen, nitrogen or sulfur based, are located at the edges of the graphene planes, or present as heteroatom functionality within the planes¹⁶¹. The design of supported catalysts, such as Pt/C is in advanced stage by information concerning metal-support interactions between surface carbon functional groups and the particulate metal. A considerable amount of literature centered on the metal-support interaction between carbon functionality and particulate Pt and the influence it has on particle size and dispersion¹⁶². Chemical nature of oxygen surface groups of carbon was the subject of many investigations.

A systematic study of the effect of chemical nature of the carbon support—on the characteristics of the final catalysts is essential. Carbon treated with oxidizing aqueous solutions at room temperature mainly contains acidic groups¹⁶³. Boehm¹⁶⁴ carried out a detailed analysis of acidic groups and found that the important functional groups were (in the order

of decreasing acidity): carboxylic acid and anhydride groups, phenolic hydroxyl groups, and quinonic carbonyl groups. The more acidic species decomposed on heating to give CO₂ and the weaker species, phenolic acid and quinonic groups decomposed to give CO.

Chemical nature of oxygen surface groups of carbon was the subject of many investigations. A representation of oxygen surface functional groups present on carbon is given in Fig. 2. Burguete *et al.*^{162c} studied the role of oxygen surface groups of carbon supports on Pt dispersion, maintaining all other variables concerned with the support and catalyst preparation as constant. The different supports employed were: (i) carbon C, a furnace carbon black (ii) carbon C (H₂), resulting from a heat treatment in pure hydrogen and (iii) & (iv) carbons C (H₂) 8N and C (H₂) 12 N, obtained from C (H₂) by treatment, for 48 h, with 8 N and 12 N solutions of H₂O₂. The characterization of porous texture of carbons was carried out by physical adsorption of N₂ at 77 K in a conventional gravimetric system¹⁶⁵. The adsorption isotherms for supports were almost coincident in the whole range of relative pressures showing that either the heat treatment in H₂ or the treatment in H₂ followed by oxidizing treatment in H₂O₂ did not change appreciably the porous texture of the carbon. The oxygen surface groups of carbon were determined using temperature-programmed desorption technique in helium atmosphere. It was known that the oxygen

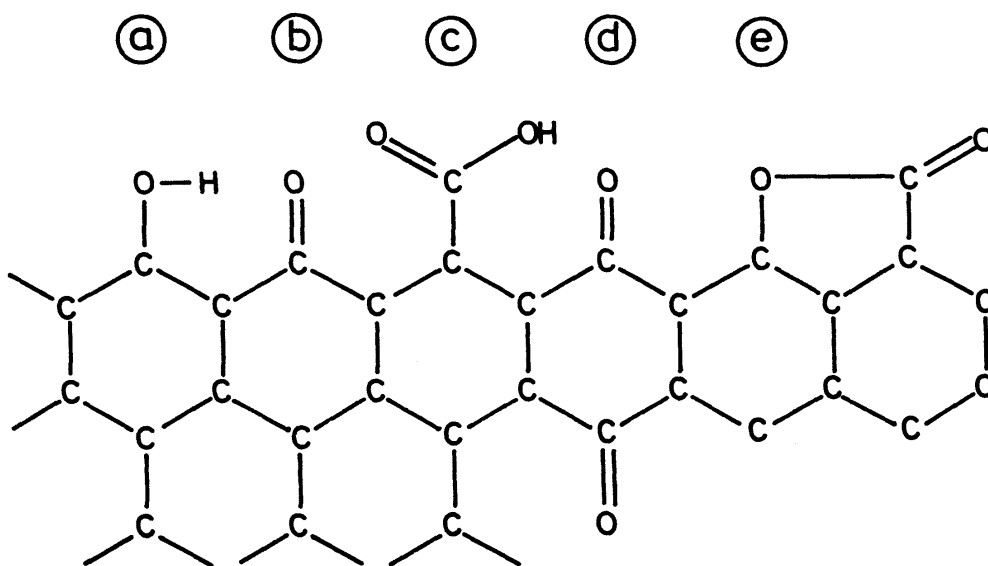


Fig. 2 Schematic representation of surface oxygen functional groups on carbon: (a) phenol (b) carbonyl (c) carboxyl (d) quinone (e) lactone

surface groups of a carbon decompose to CO and CO₂ upon heating in an inert atmosphere. CO₂ was desorbed at lower temperatures than CO. Catalysts were prepared by impregnation method and Pt loading was measured using UV spectrophotometry (261.8 nm) by burning away the carbon in air at 973K. The number of Pt surface atoms on the catalysts was determined by chemisorption of H₂ at 298K. The size of Pt particulates were in the range of 2.5 nm and the H/Pt ratio increased with the increasing amount of surface groups. Since the carbon supports had similar porous textures and catalysts were prepared by same procedure the increase in metal dispersion was attributed to the role of surface oxygen groups. The dispersion on catalyst type (iii) was more than twice that of catalyst type (ii) because of the larger amount of surface groups of the former. The final state of dispersion of catalyst depended on (keeping all other factors constant) the interactions of the precursor with the carbon support at the different stages of preparation. The dependence between Pt dispersion and amount of surface groups was attributed to the following: (i) Metal precursor distribution throughout the carbon support was an important aspect in impregnation technique; both solvent-carbon interactions and charge on impregnating metal complex can play an important role. The solvent-carbon interaction was more important because the acidic nature of the carbon was not favourable to the anionic character of the metal precursor. Since, the metal precursor- H₂PtCl₆ .6H₂O was in aqueous solution, the change in hydrophobicity of the carbon upon treatment with H₂O₂ was important because acidic groups were introduced in the carbon. These surface groups increased the wettability of the carbon facilitating the access of the aqueous solution to the internal pore structure. This in turn led to more homogeneous distribution of the precursor than in non-oxidized carbon. This finding is some what related to the finding of Machek *et al.*¹⁶⁶ on the effect of solvent polarity in the adsorption of hexachloroplatinic acid on activated carbon and Al₂O₃, that non-polar solvents led to a high dispersion than polar solvents for activated carbon. For Al₂O₃ (since its surface is hydrophilic) the distribution of the precursor was found to be more homogeneous and the dispersion of Pt was larger in aqueous solution^{166b}. (ii) when once the metal precursor is distributed on the carbon support, the maintenance of this distribution during the reduction stage is also important. Metal and/or its precursor

might interact with the support through its surface groups hindering a redistribution and agglomeration of the metal and affecting its final states of dispersion. This interaction could be important during the reduction of precursor if the metal-support interaction is weak. Flynn *et al.*¹⁶⁷ pointed out that the sintering of Pt catalyst may start at temperatures as low as 573K. Ehrburger *et al.*¹⁶⁸ studied the dispersion and sintering of iron phthalocyanine and found that the oxygen surface groups of the support acted as anchorage centers, maintaining the metal dispersion. Similarly, for H₂PtCl₆ the oxygen surface groups may act as chemical anchorage centres, through the formation of some Pt-O complex on the surface. This work allowed one to relate the dispersion with a type of surface oxygen group; more stable the surface group, more effective the anchorage of Pt and larger the metal dispersion. An increase in the number of oxygen surface groups may produce an increase in the interaction of the metal precursor or the metal particles with the support, thus increasing the dispersion. The sintering resistance increased noticeably with the content of CO complex; the migration of Pt was prevented because of the enhanced interaction with the carbon surface. Antonucci *et al.*^{162a} showed that an increase in the concentration of oxygenated carbon functional groups (-COOH, -OH) decreases Pt surface area for a given loading, by increasing Pt crystallite size.

Roy *et al.*¹⁶⁸ found that carbon blacks with nitrogen, sulfur and phosphorus functionalities initiate the formation of particulate Pt with reduced dimensions relative to untreated carbon blacks. The size decrease was attributed to strong binding between the Pt particles and carbon support during catalyzation process. For untreated, N, S- functionalized carbons the mean potential of methanol oxidation was reported to be 604, 554, 633 mV, respectively, at +50 mA/cm² and the corresponding Pt particle size was 2.5, 1.5, 1.0 nm (O > N > S/P) (at all electrodes Pt content = 0.7 mg/cm²). Electrocatalysts prepared with nitrogen-functionalized carbon showed highest activity toward methanol oxidation. The sulfur functionalized electrode showed lowest activity toward methanol, suggesting the existence of a specific interaction between Pt and sulfur on the carbon support, which inhibit the rate of the reaction. N-functionalization was accompanied by an increase in basicity of carbon support, while sulfur functionalization resulted in increase in acidity. XANES technique was employed to identify the

specific types of carbon functionality, which interact with Pt. In the case of nitrogen-functionalized support pyridinic and pyrrolic groups were present, while in sulfur functionalized support aromatic S-H functionality and inorganic sulfate species were present. The nitrogen functionality in the carbon support determines the size of Pt by bonding with lone pairs of electrons at the nitrogen site in an sp^2 hybridized orbital in the plane of the ring. These N-sites, which predominate in untreated carbon black were less negative than oxygen sites. The assumption was that during catalyzation, Pt might bind more strongly to pyridinic sites, thereby preventing Pt particles from sintering to the extent observed on untreated carbons. The increased electron donation from pyridinic N-functionality to Pt might be responsible for enhancement in kinetics of methanol oxidation. Compared with untreated carbon, Pt binds more strongly to less electronegative sulfur sites. There was no poisoning effect from sulfate, which is present in untreated carbon but sulfur functionalized carbon where poisoning was observed is attributed to organic type sulfur generated from P_4S_{10} or residual phosphorous.

Vulcanized carbon (VC) is a standard catalyst support despite its innate sulfur content, because of its favourable electrochemical properties. Organically bound sulfur native to VC has both advantageous and disadvantageous effects on Pt catalytic activity. Sulfur hetero atoms improve the dispersion and surface area of Pt catalysts supported on carbon by serving as nucleation sites or anchors for Pt clusters¹⁶⁹. Recently, Swider *et al.*¹⁷⁰ probed the interaction between nanoscale Pt and the sulfur in vulcanized carbon (XC-72). Adsorption of sulfur on the surface of Pt changes its surface energy, including both adverse and favourable effects. In hydrogenation catalysis, a small amount of sulfur can completely poison the activity of the Pt catalyst¹⁷¹, whereas, when controlled the adsorbed sulfur enhanced other Pt catalyzed reactions¹⁷². It was found that the PtO_x present at the surface of nanoscale Pt oxidize the organosulfur in VC to SO_2 in the presence of H_2O ¹⁷³. In the presence of oxygen, PtO_x catalytically oxidizes SO_2 to SO_3 , which immediately undergoes acid-base reaction with any water present to form sulfate, which is not a catalyst poison. Chemical-state and electroactive studies indicated that nanoscale Pt remain electrochemically active if it is heated with VC in aqueous mixture but the Pt is poisoned by organosulfur when Pt and VC were heated in the absence of water.

Water was not necessary in the fabrication protocol if Pt was mixed with electrodesulfurized VC or sulfur-free acetylene black. It was shown that high sulfur content carbon improves Pt catalyst dispersion but this carbon associated sulfur can have deleterious effects on oxidation reactions involving CO or hydrogen showing the importance of using carbons with low sulfur content to retain the electro activity of supported nanoscale Pt. By using low sulfur-content carbon the lifetime of Pt catalyst may be extended and new non-aqueous methods can be employed to prepare electrodes containing Pt or Pt based multicomponent catalysts for use in DMFC.

3.1.4 Multimetallic Systems

Goodenough *et al.*^{92a} studied the electrooxidation of methanol on unsupported Pt+Ru and compared the performance of this electrode with highly dispersed Pt+Ru on a teflon bonded carbon electrode (CO_2 activated Vulcan XC-72). For unsupported Pt+Ru the open circuit voltage was -570 mV / MSE, which was closer to the theoretical thermodynamic potential for methanol oxidation (-630 mV). When small anodic current was passed, the potential shifted to -350 mV at a current density of 10 mA/cm². The maximum current density per mg of precious metal achieved on this unsupported material was very low 20 mA/mg; this was achieved only at very high over potentials. Co-deposition of Pt and Ru on a CO_2 -treated conducting-carbon support followed by reduction treatment similar to that for the unsupported material gave dispersed particles of reasonably uniform size, with mean diameter of ~ 6.5 nm. The carbon supported Pt+Ru electrode has an improved performance per gram of precious metal with over 250 mA/mg, but an increase of over 200 mV in overpotential at low current density. The higher open circuit voltage was attributed to the equilibrium coverage of small Pt+Ru crystallites, which were more biased towards the potential reactions like oxide formation and reduction rather than low potential reactions involving hydrogen or methanol. The shift in the bias was attributed to the ability of carbon support to promote the interaction of oxygen, which was important for oxygen reduction on platinized electrodes.

Kennedy *et al.*¹⁷⁴ studied the electrooxidation of methanol on Pt: C and Pt+Ru: C electrodes (C = CO_2 treated VulcanXC-72) in 1.0 M MeOH + H_2SO_4 solution at 333 K and found that the Pt+Ru: C electrode was active for 100 h at a load of 25 mA/cm². XPS

studies and the life performance studies of the electrodes using periodic potential relaxation steps revealed the presence of two types of Pt oxides, one a tightly bound inactive group and second a more labile moiety. In this study, the identification of nature of the surface groups present on Ru is lacking.

Radmilovic *et al.*¹⁷⁵ employed high resolution electron microscopy (HREM) and energy dispersion X-ray spectroscopy (EDS) to characterize the composition, size, distribution and morphology of Pt-Ru particles with nominal Pt: Ru ratio of 1:1 and 3:1 supported on carbon black (VulcanXC-72R). The particles were predominantly single nanocrystals with diameters in the order 2.0 to 2.5 nm. Twinned particles were also observed occasionally. Two-dimensional projection in high-resolution images showed that the well-resolved particles were of cubooctahedral shape and the facets were mainly based on (200), (111) and (113) planes.

Hamnett *et al.*⁷⁴ studied the electrooxidation of methanol on porous carbon electrodes (CO₂ treated VulcanXC-72) impregnated with bimetallic platinum group catalysts, Pt/M (M = Au, Os, Ir, Pd and Ru) in H₂SO₄ electrolyte. Au and Pd were found to inhibit the reaction while Ir, Os and Ru were acting as promoters. The presence of metal oxides was found by XPS and the role of the second metal in promoting or inhibiting the methanol oxidation reaction was attributed to the ease of formation of "active oxygen" groups. The potential in V/MSE at current 150 mA/mg for methanol oxidation in 2.5M H₂SO₄ at 333K was +0.25, +0.175, +0.125, +0.025, +0.02 and -0.125 at electrodes Pt/Pd-C, Pt/Au-C, Pt/C, Pt/Ir-C, Pt/Os-C and Pt/Ru-C respectively.

Morita *et al.*¹⁷⁶ prepared Au-Pt bimetallic catalyst on smooth glassy carbon (GC) support by RF sputtering method and studied its catalytic activity for electrooxidation of methanol in 0.01 M H₂SO₄. The particle size of Pt was in the range 1-10nm. Cyclic voltammetry exhibited a maximum current at potential 0.5 V /SCE for all the electrodes such as Pt/GC (30%)-Pt/GC and Au (70%)-Pt/GC, the current densities were found to be 2.5, 1.25 and 1.1mA/cm² respectively. The modification of Pt/GC by small amount of Au, scarcely affect the performance and the peak currents per apparent surface area of the electrode decreased with an increase in Au coverage. The activity per Pt site reached a maximum at 70-80% Au coverage and a further increase in Au was

equivalent to that of pure Au film (i.e., pure Au has no activity for methanol oxidation in acidic medium) suggested a complete coverage of the Pt surface.

Biswas *et al.*^{82e} studied the electrocatalytic activity of a graphite based Pt electrode modified with In+Pb mixed oxide towards methanol oxidation in 0.5 M H₂SO₄. A more negative zero-current potential around 70 mV/RHE was realized on a Pt/In+Pb mixed oxide/GC with Au compared with 95 mV/RHE for Pt/In+Pb mixed oxide/GC without Au. These were close to the theoretical oxidation potential ~ 30 mV in acidic solutions.

Viswanathan *et al.*¹⁷⁷ studied the electrocatalytic oxidation of methanol on Pt and Pt-Ru-WO₃ deposited on graphite electrodes in H₂SO₄ medium. A maximum apparent current density on Pt/C electrode was found to be 15 mA/cm² at 0.4 V/NHE for 1.0 M H₂SO₄ +1.0 M MeOH. Whereas for codeposited Pt-Ru-WO₃/C, maximum apparent current density was found to be 55 mA/cm² at 0.35 V/NHE. This enhanced activity was attributed to the availability of Pt, Ru and WO₃ on adjacent sites. Polarization studies revealed that the best activity was exhibited at Pt/C and co-deposited Pt-Ru-WO₃/C electrodes in the potential range ~ 0.5 - 0.6 V/SCE, and it was reasoned out that below and above this potential region, the oxidation of methanol was less favoured or Pt was blocked by SO₄²⁻ ions.

Zang *et al.*¹⁷⁸ prepared Pt/MoO_x/C composite electrode by co-deposition method and carried out electro oxidation of methanol in acidic medium. XPS data revealed the presence of Mo in 6, 4 & 3 oxidation states. The composite electrode exhibited better performance than platinized carbon electrode. A surface redox mechanism which involves (i) Mo (VI)/(IV) couple in substoichiometric lower valence MoO_x (2 < x < 3) and (ii) the proton spill over effect from hydrogen molybdenum bronzes were two proposed explanations for the enhanced catalytic activity of this system.

Hills *et al.*¹⁷⁹ studied the support interactions experienced by two different compositions of Pt-Ru nanoparticles prepared from PtRu₅(CO)₁₆ and Pt₂Ru₄(CO)₁₈ molecular precursors (the latter of which lacks a central stabilizing carbide core) by activation in H₂ at 673 K, supported on various carbons including carbon black, fullerene soot and desulfurized carbon black. The morphology, average size and composition of the supported nanoparticles were found from first

shell coordination numbers determined using EXAFS data. The average coordination number of $[\text{PtRu}_5]$ supported on carbon black, fullerene soot and desulfurized carbon black were found to be 6.3 ± 1.0 , 6.4 ± 2 and 6.5 ± 1.0 and for $[\text{Pt}_2\text{Ru}_4]$ supported on carbon black and fullerene soot were 6.6 ± 1.0 and 7.5 ± 1.3 respectively. These values are considerably lower than the anticipated value of 12 for an fcc structure. This reduction in first shell coordination is directly related to the finite size of the nanoparticles, since the fraction of the surface sites with lower coordination numbers increases as the particle size decreases. An average coordination number of 6.3 correspond to a hemispherical particle with a diameter of 1.2nm. The following observations were made on fullerene-soot-supported nanoparticles: (i) Presence of Ru-low-Z-atom (i.e, C or O) interactions. (ii) Metal-carbon interactions were highly disordered contributing little magnitude to the EXAFS signal. (iii) Heating the molecular precursor in H_2 resulted in reductive condensation. Two models were proposed, the first one suggesting a possible higher symmetry of the fullerene soot leading to differences in the disorder characterizing its interactions with the nanoparticles and the second model suggesting the formation of Ru carbide phase at the support-nanoparticle boundary. In carbon black supports, both PtRu_5 and Pt_2Ru_4 precursors gave a uniform population of C- supported alloy nanoparticles according to the initial compositions. The final states reached on C-black supports were consistent with metallic ensembles of Pt atom and also surface segregation of Pt was found on both the systems. The structures of the particles formed on carbon black are not sensitive to the heteroatom content of the support, suggesting these interactions do not exert a dominating influence over the activation process involved in the nanoparticle nucleation and growth. The metal-carbon interactions present on these supports were highly disordered.

Arico *et al.*^{79a} studied the electro oxidation of methanol using carbon-supported Pt-Ru-Sn-W catalyst prepared by liquid-phase reduction method. XPS and XRD data showed that the catalyst was composed of metallic Pt, microcrystalline RuO_2 and SnO_2 phases and amorphous WO_3/WO_2 species. In the half-cell measurements the activity of the catalyst increases with the concentration of methanol and reached a maximum at 2.0 M methanol. IR-free polarization curves showed that the activity of the quaternary catalyst was superior to Pt metal/C samples having

the same amount of Pt. The presence of semi-insulating metal-oxides such as RuO_2 , SnO_2 and WO_3 on the electrode surface exhibited a significant uncompensated resistance. The single cell performance was found to be lower than that predicted by half-cell measurements and this was attributed to the methanol cross-over through the Nafion membrane.

Childers *et al.*¹⁸⁰ investigated the formation of formaldehyde during methanol electrochemical oxidation on supported Pt and Pt-Ru catalysts, showing that on solid Pt electrodes, the formaldehyde yield from methanol oxidation was ~30% at low potentials and ~2 % on C- supported catalysts in Nafion. The low yield of formaldehyde observed in the latter case was attributed to the reaction environment within the Nafion film consisting of a three dimensional network of catalyst particles. The ability of soluble partial oxidation products to undergo multiple encounters with the array of catalyst sites in the film increases the chances for reactions to progress towards completion. The low yield was also attributed to formaldehyde entrapment within the Nafion or adsorption to the carbon support. The different formaldehyde yields on solid Pt electrodes and metal nanocrystals dispersed in Nafion raise questions about relationship between results of electrochemical experiments with solid metal electrodes and the processes these studies aim to mimic in fuel cells. It appears that, in addition to the effect of surface structure and composition, model studies should also consider how product distributions could be influenced by the arrangement of metal catalyst particles on the micro/nanometer scales.

Electrochemical oxidation of methanol in alkaline medium has also been investigated¹⁸¹⁻¹⁸³. These studies have been directed towards correlation of activity with various physico-chemical properties of the metallic systems or to identify the binary systems exhibiting highest activity. Due to the practical difficulties encountered in alkaline medium such as insoluble carbonate formations, catalytic systems in alkaline medium were not employed for DMFC applications.

3.1.5 Noble Metals on Carbon Nanotubes

Carbon nanotubes (CNT) are unique materials, with interesting mechanical and electronic properties. Due to their closed topology and tubular structure, they find number of applications in nanoelectronic devices, for storage of hydrogen and other gases and as a catalyst support¹⁸⁴. Metal filled carbon nanotubes

attracted applications in heterogeneous catalysis. Many of these proposed applications require membranes that consist of monodispersed-aligned nanotubes. Typical procedures used to synthesize carbon nanotubes however, usually produce a random orientation of each nanotubes with closed ends. Che *et al.*¹⁸⁵ explored a template-synthesis method for the preparation of micro- and nanostructured materials with cylindrical pores of uniform diameter. Che *et al.*¹⁸⁶ and Kyotani *et al.*^{187a-c} used a combination of chemical vapour deposition (CVD) and template-synthesis methods to synthesize carbon nanotubes with highly aligned ensembles of uniform hollow tubes (20-200 nm) with open ends, which make them suitable for filling with desired materials. Che *et al.*¹⁸⁶ used metal (electrocatalytic materials such as Pt, Ru & Pt/Ru) filled carbon nanotubes for the studies of electrooxidation of methanol. Both C/Pt/Nafion and C/Pt-Ru/Nafion nanocluster membrane electrodes exhibit high electro catalytic activity for methanol oxidation and the current density of methanol oxidation at C/Pt nanocluster membrane electrodes was ~ 20 times higher than bulk Pt electrodes. This enhancement in current density was attributed to both the high surface area and high electrocatalytic activity of nanoclusters dispersed inside the CNTs.

Rajesh *et al.* prepared Pt-Ru catalyst supported on CNT using template carbonization of polypyrrole^{188a} and polyphenyl acetylene^{188b} and the size of Pt-Ru particles were 1.5 and 1.7 nm as detected using high resolution transmission electron microscopy. These materials are currently being explored as the anode material for direct methanol fuel cells. Though, Che *et al.*¹⁸⁵ reported a higher activity in CNT, it is necessary that the actual surface area of the CNT has to be evaluated in order to correlate with catalytic activity. Recently Bessel *et al.*^{188c} have reported a 400% higher activity for methanol oxidation of Pt supported on graphite nanofibres compared to the activity of Pt supported on Vulcan XC 72 carbon and it is interesting that the self poisoning also decreases by 48%. It has been proposed that the physiochemical environment of Pt and the structure of the graphite nanofibers might play a predominant role for the observed higher activity and stability. But the oxidation mechanism still to be probed for the higher stability.

It is appropriate to evaluate the performance of various metal electrodes supported on carbon on a single parameter and such data generated from the results which are given in Table III. It is seen the

mass specific activity varies from a few milli amps to nearly 200-300 mA/mg for the various system studies. Electrodes based on Pt or Pt-Ru supported on carbon shows higher activity of the order of 100-300 mA/mg while other systems generally show lower activity. However these parameters depend on the pretreatment given to these electrodes though most of them have similar potential window for methanol oxidation. These results in general reflect on the relative activity on the various systems but not on the performance since the later parameter depends on the active lifetime of the electrode and the geometrical retention of the active particles with respect to use. The data presented in this Table can be taken as an indicator for selection of active materials for anode preparation.

It is known that the interaction between carbon support and catalyst modify the catalyst activity, and these interactions depend on nature of surface atoms on carbon. In the case of carbon supports, there is a lack of uniform distribution of surface atoms and only gross level estimation of different heteroatoms in the surface is possible. Further, it is difficult to reproduce the exact surface composition. Since the overall electronegativity on support surface governs the dispersion of catalytic particles, one has to have a control over the surface heteroatoms with respect to their amount and distribution.

An alternative is to develop a catalyst support that is permeable to gases and water, while conducting both protons and electrons efficiently. These requirements make it mandatory that the catalyst layer be very thin and placed close to the hydrophobic diffusion layer. Such material could replace carbon in the catalyst layer and should provide enhanced performance. Conducting polymers with heteroatoms offer good performance over the above addressed issues: There is uniform distribution of heteroatoms in conducting polymers as there are repeating monomer units with a regular fashion. Further, unlike carbon the morphology of the polymer could be varied by controlling the deposition parameters. The catalytic particles can be incorporated either in two- or three-dimensional fashion according to the preparation methods adopted.

3.2. Noble Metals on Conducting Polymers

By imbedding the metal particles in polymeric films, the reduction of catalytic activity or efficiency

due to physical or chemical loss of the catalyst can be suppressed. Polymer films are frequently more effective than monolayers of adsorbed or covalently bound catalyst since they display better stability and a higher active site concentration. In the case of electrocatalysis at modified electrodes, good electronic/ionic conductivity of the film or support is also necessary. Efficient electrocatalytic systems would require mutual metal support interactions leading to activation of both dispersed metal and a matrix toward electrode processes¹⁸⁹. Modification of electrode surfaces provides an attractive way of confining active catalytic species at the effective spatial region and combines the experimental advantages of heterogeneous catalysis with the benefits of a three dimensional distribution of active centers typically characteristic of homogeneous catalysis. In practice, a good electrocatalyst should exhibit both high reactivity towards the substrate molecules in solution and have the ability to transfer electrons rapidly in the microstructure in order to avoid transport limitations. It is essential to identify the conditions (choice of matrix, reactive components and rigid anchoring groups) for preparation of thin but three-dimensional polymeric films, which are active for the electrooxidation of methanol. A great deal of research aims at providing the right morphology of catalytic surface in order to reduce CO poisoning.

Despite twenty years of studies on the basic aspects of conducting polymers, many issues such as the film formation process, the charging/discharging mechanism, and the interplay between structure, properties and synthesis conditions still remain unresolved. One method of gaining insight regarding conducting polymers is to extrapolate the properties from structurally well-defined oligomers. However, the knowledge of the factors governing the electrochemical reactions and the formation of polymer structures is far from complete. Almost no definite conclusions have been drawn so far on how a single parameter influences the properties of the polymers or how interdependent the experimental variables are.

Various studies have examined the electrocatalytic activity of platinum microparticles dispersed on/in electronically conducting polymers such as polyaniline¹⁹⁰, polypyrrole¹⁹¹, poly (3-methylthiophene)¹⁹², poly (N-methylpyrrole)¹⁹³, poly (2-hydroxy-3-aminophenazine)¹⁹⁴, copolymer of

pyrrole-dithiophene¹⁹⁵ and polyacetylene¹⁹⁶ for electrooxidation of methanol. These studies eventually lead us to raise the following questions: (1) Why these polymers alone are selected for electrooxidation of methanol? Can we use any other conducting polymers possessing desirable electronic/ionic conductivity, stability (chemical, thermal & mechanical) and desirable range of electroactive domain? (2) What is the molecular level interaction, which stabilizes and activates the dispersed metal particles? (3) How the structural backbone of these polymers contribute to the effective dispersion and functioning of platinum/metal towards methanol electrooxidation? (4) What is the electronic relationship between the active metal site and morphology of the polymer? (5) Where does the metal get anchored onto the polymer? How is the electrochemical active area of metal site influenced by the polymer backbone? (6) What are the criteria that determine the suitability of a conducting polymer for electrooxidation of methanol? These insights may help us to choose the appropriate conducting polymer in electrode fabrication for electrooxidation of methanol and to understand their role at molecular level interactions.

Most of the conducting polymers used in the studies of electrooxidation of methanol contain S, N and/or O heterocycles in their backbone. Polyacetylene has also been used which has extensive delocalization due to the presence of double bonds and exhibits excellent conductivity (1000 S/cm). For electrooxidation of methanol on polymer supports, the dispersed metal used was Pt with or without ad atoms.

3.2.1 *N-Containing Polymers*

3.2.1.1 *Polyaniline*

Polyaniline (PANI), is an interesting material, easy to synthesize in aqueous medium, generally homogeneous, strongly adherent to the support and chemically stable in acid medium¹⁹⁷. PANI has attracted much attention because of its special doping mechanism, good solubility and high stability in air. Examination on PANI films using SEM studies showed that it has a rough morphology and porous texture providing high surface area. But compared with other conducting polymers, such as polypyrrole (PPY) and polythiophene (PTH) the conductivity of PANI is poor. i.e., about 1-40 S/cm at room temperature for PANI prepared by common methods. The conductivity of PANI films doped with camphor sulphonic acid (CSA)

in *m*-cresol can reach as high as 300 S/cm. Recently¹⁹⁸, a new 'doping-dedoping-redoping' method is proposed to prepare doped PANI films with high conductivity (about 200-300 S/cm) at room temperature using HCl, H₂SO₄, HClO₄, H₃PO₄ and *p*-toluene sulphonic acid. PANI can be prepared by chemical oxidations¹⁹⁹, or by electrochemical techniques. Of the electrochemical techniques, the potential cycling method is a good choice²⁰⁰, since this technique provides various parameters related to the degree of growth. This allows one to have maximum amount of control over the quality of the PANI films. The physical and electrochemical properties of electrochemically grown PANI was well discussed in the report of Stilwell *et al.*²⁰¹ and the references cited therein. Promising results have been reported for electro oxidation of methanol on Pt based particles dispersed in PANI film¹⁹⁰. Kost *et al.*^{190d} studied the electrooxidation of methanol on Pt particles deposited on PANI films. They exhibited higher catalytic activity by a factor of 3 than bulk platinum electrode. Moreover, a drastic decrease in poisoning effect was shown by Laborde *et al.*^{190f} using *in situ* electrochemically modulated infrared reflectance spectroscopic (EMIRS) studies, which showed no significant CO_{ads} signal. Napporn *et al.*^{190j} studied the usefulness of PANI for the electrooxidation of oxygenated molecules containing one carbon atom (methanol, HCHO, HCOOH) at highly dispersed Pt based electrodes (Pt, Pt-Ru, Pt-Sn and Pt-Ru-Sn) and showed that electrodes composed of particles of Pt and of a second (or a third) metal inserted in conducting polymer matrix exhibit weak poisoning effects compared with pure Pt particles.

3.2.1.2 Polypyrrole

Since the initial report in 1979²⁰², that thick, uniform and adhesive films of polypyrrole (PPY) was first prepared, the interest in PPY began to expand, prompting a large body of literature relating to the various properties of this conducting polymer²⁰³. PPY has found particular utility in the rapidly expanding field of chemically modified electrode. It has a conductivity of 100 S/cm. Polypyrrole (PPY) has been modified with a variety of metals, including Pd, Pt, Pb, Cu, Ni, Sn and Au^{204, 205}. PPY has molecular weight 800-1000 and many of the observed effects of PPY are interdependent on various factors. For example, diffusion co-efficient of any depolarizer not only depends on film thickness but also on the surface morphology and the bulk structure of the material.

This will in turn affect the measured conductivity and doping levels seen for given conditions, but are themselves dependant on polymerization conditions used. Number of factors which affect the conductivity of material can be explained in terms of steric interactions which affect the conjugation of the *p*-system. i.e., by disrupting the planarity of the polymer back bone and by affecting the degree of orbital overlap, or due to structural changes involving coordination of the ion. These include, nature of substituents on pyrrole ring, the positions at which the monomers are linked and the nature of the dopant anion. Holdcroft *et al.*²⁰⁶ studied the preparation and electrocatalytic properties of PPY films containing Pt micro particulates. Recently, Zhou *et al.*²⁰⁷ observed a structural diversity of PPY during electro-polymerization of pyrrole and proposed diverse mechanisms for various events occurring during film formation process. Strike *et al.*^{191b}, utilized PPY film coated on Au electrode to disperse Pt particles for electrooxidation of methanol. The Pt was deposited either at a constant potential or by using a pulse train. From cyclic voltammetric studies, it was found that in the absence of methanol, the Pt does not have a dramatic effect upon the electrochemical properties of PPY film over the range 0.1 to 0.7 V/SCE and this observation was in agreement with previous literature for galvanostatically grown films. A considerable difference was seen between the electrodes Au/PPY/Pt and Au/PPY in the presence of methanol. The Au/PPY electrode (300 nm PPY) displayed no apparent methanol oxidation, while the Au/PPY/Pt (300 nm PPY, 200 μg/cm) exhibits the current of 1.5 mA. These modified electrodes exhibited both better electrocatalytic activity and an increased resistance to poisoning when compared to bulk platinum.

3.2.1.3 Poly-N- Methylpyrrole

Poly-N- methylpyrrole (PMPY) has conductivity of 0.001 S/cm at room temperature, which is five orders of magnitude less than PPY. The ionization potential value of 3.9 eV reported for PMPY is identical to PPY, which is expected. The methyl group is linked to the nitrogen atom and the nitrogen 2p_z orbital has no contribution to the top of the upper valence band, which determines the ionization potential value. Kuleza *et al.*¹⁹³ demonstrated the usefulness of poly-N- methylpyrrole as a matrix for the fabrication of a composite film containing spatially dispersed

platinum and highly reactive Ru oxo centres for electrooxidation of methanol. It is note worthy that this polymer is stable at positive potentials and, while oxidized attains a conducting state. By the introduction of polynuclear Ru/CNRu (cyanoruthenate), the overall stability of the composite film is increased and this is attributed to the strong interaction between anionic Ru/CNRu sites and positively charged cations in the rigid polymer (PMPY) matrix. These properties have allowed the preparation of fairly thick films in which active Ru oxo centers can be fully utilized for catalytic oxidations.

3.2.2 S-Containing Polymers

Poly 3-Methyl Thiophene (PMT): PMT is an electronically conducting polymer, stable in acid electrolytes and has good conductivity about 100 S/cm in the doped state but the resistivity increases by nine orders of magnitude when the polymer is not doped. Even though, many of the properties of polythiophene (PT) are similar to polypyrrole as in both cases the basic structure is essentially the same, PT has not been used so far for electrooxidation of methanol. One of the important reasons is that the electro-active domain of PT lies between 0.5 to 1.0 V/SCE, which is not the region for methanol oxidation. Structure of PT is essentially retained even when heavily doped, and chain lengths up to 300 have been calculated for poly (3-alkyl thiophene). Electrochemically prepared material was amorphous, eventhough it was suggested that polymer was basically granular or fibriallar (chemically prepared material was crystalline). The material was apparently quite porous, with columetric data providing evidence that thiophene polymers have a large internal surface area. Morphology depends on number of factors including nature of the substrate, the growth rate and the current and potential at which polymerization proceeds. Thin films were highly homogeneous and show little evidence for solvent incorporation but as the film thickness was increased the homogeneity was lost, possibly due to cumulative effect of structural defects such as chain folding, cross-linking, α - β coupling etc., or as a result of inhomogeneity of the electric field at the polymer surface. Use of high monomer concentration tends to produce powdery film. Electrochemically prepared PMT showed high degree of order, again with predominantly α,α -linking between thiophene rings, whilst unsubstituted PT has a much greater degree of disorder due to the possibility

of β -linkage. Sulfur of the thiophene ring does not play a large part in determining the electronic structure of the material (if the sulfur carried a significant portion of the charge on the chain, this symmetry would be disrupted), and that it merely stabilizes the lower energy form of the non-degenerate polymer chain of the backbone. Optical and XPS studies showed that unsubstituted and β -substituted polythiophenes have highly mobile spin in the polymer chains, and proposed that the conduction mechanism involves 3D variable-range hopping^{197a}. Swathirajan *et al.*^{192a} studied the electrooxidation of methanol using Pt-Sn particles dispersed on poly 3-methyl thiophene (PMT).

3.2.3 N, S - Containing Polymer

Copolymer of Poly (Pyrrole-thiophene): All conducting polymers have a defined domain of electroactivity and although polythiophene appears promising owing to it's excellent chemical and electrochemical stability but it's electroactivity potential range from 0.5 to 1.0 V /SCE does not fit with the electrooxidation of methanol. Thus, in order to extend this working range, copolymer poly (pyrrole-thiophene) has been used as a conducting matrix and this has been electroactive between 0.0 and 1.0 V/SCE. Laborde *et al.*¹⁹⁵ investigated the electrocatalytic properties of a conducting copolymer modified by the inclusion of a small amount of (0.1 mg/ cm²) dispersed platinum for electrooxidation of three molecules: hydrogen, formic acid and methanol. The onset potential for methanol oxidation was 0.55 V/RHE and the maximum current density of 1.0 mA/ cm² observed at 0.9 V/RHE.

3.2.4 N, O - Containing Polymer

Poly (2-hydroxy-3-aminophenazine): Poly (2-hydroxy-3-aminophenazine) (pHAPh) is a stable, redox active, ladder polymer with structure and properties closely related to those of poly (o-phenylenediamine) and poly (o-aminophenol). The electroactive potential range of pHAPh, like other polyaromatic ring chain films, poly (o-phenylenediamine) and poly (o-aminophenol)²⁰⁸ is wider than those of polyaniline, polythiophene and polypyrrole²⁰⁹. The electro-polymerization of HAPh on different electrodes was studied previously²¹⁰. Keladopoulou *et al.*¹⁹⁴ studied the electrooxidation of methanol on dispersed electrodes containing Pt, Pt-Sn and Pt/M (M = Pb, Tl & Bi). The details are subsequently considered in the latter section.

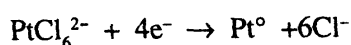
The following sub-sections deal with the role and influence of various aspects such as preparation method, metal loadings, film thickness of the polymer, particle size, ad atoms effect and morphology of polymer support towards the final catalytic activity of catalyst particulates in electrooxidation of methanol. Various aspects associated with these issues are analyzed and comparisons of results are made by mass normalization approach.

3.3.1 Role of Method of Preparation

Metallic particles were dispersed in electrically conducting polymer films in order to achieve multi-electron transfer processes in a three-dimensional matrix. Sufficient contact between the metal particles themselves and between metal particles and the electrode surface is essential to sustain large current densities. Organic conducting polymers are particularly suitable for holding metal particles; the facile flow of electronic charge through the polymer matrix obviates some of the limitations in film thickness and concentration of active catalyst that are otherwise encountered. However, these films become insulators at negative potentials. The motivation for incorporating metallic particles into porous matrices is to increase the specific area of these active materials and thus improve catalytic efficiency. In studies of such films, the effects of diffusion and permeation of solution species, catalyst loading and catalyst dispersion are paramount.

A simple and efficient method of dispersing catalysts is the electro-crystallization of metals producing catalytic materials based on the properties of small clusters. Thus, effective electrocatalysts are now routinely prepared by the electrodeposition and dispersion of metal crystals or crystal aggregates in conducting polymer films, previously electrodeposited on an inert electrode.

A common deposition technique employs the electroreduction of a metal salt, such as PtCl_6^{2-} .



In the case of redox polymer films, the redox couple may mediate the reduction of the metal salt. The electrochemical reaction is governed by the diffusion of electrons through the film, the rate of electrochemical reaction, the diffusion and permeation of the metal salt through the solution, and through the film. In the two extreme cases, metal is deposited on the polymer film surface, or on the electrode surface.

Since metal particulates entrapped in polymer films, act as catalytic sites for multi-electron transfer processes and thus differ from majority of the catalytic redox polymers.

Holdcraft *et al.*²⁰⁶ investigated the electrocatalytic properties of conductive polymer/metal catalyst films to examine the effect of variation in distribution and loading of the catalyst in the polymer matrix. Four different methods were employed to prepare polypyrrole films of various spatial distributions. Films were prepared in which Pt was deposited primarily at the polymer/solution interface, at the metal polymer interface, or uniformly through the film. Type 1 electrodes were prepared by the electrodeposition of Pt on bare electrodes from aqueous solutions of $\text{K}_2\text{PtCl}_6 + \text{KCl}$ at -0.2 V/SCE . Type 2 electrodes were prepared by the electrodeposition of Pt on to a preformed PP film from aqueous solution of $\text{K}_2\text{PtCl}_6 + \text{KCl}$ at 0.2 V/SCE . Type 3 electrodes were prepared by immersing a pre-reduced PP film into K_2PtCl_6 and placed in KCl followed by reduction by applying a potential step to -0.5 V/SCE . Type 4 electrodes were prepared by immersing an oxidized PP film into a K_2PtCl_6 and completely reduced in KCl by applying subsequent potential steps. Information on Pt distribution was obtained from C: Pt signal ratio in AES. Quantitative information was obtained from inelastic mean free path calculations and back scattered electron factors. It was found that homogeneous distribution of incorporated species was obtained only for Type 3 & 4 electrodes.

Strike *et al.*^{191b} studied the electrooxidation of methanol on Pt microparticles which were anodically deposited in polypyrrole. Anodic deposition allows the polymers to be prepared as a uniform coating over irregular surfaces and offers easy control over the film thickness. The platinum was deposited either at a constant potential or using a pulse train. The electrocatalytic behaviour of platinum deposited by the pulsed and potentiostatic methods was slightly different reflecting a different distribution or state of the metal deposited by the two protocols. Platinum was also deposited using a procedure in which a pre-oxidized PPY film was soaked in H_2PtCl_6 solution and then transferred to KCl for reduction at -0.2 V/SCE . However, the electrode was found to support very low current densities for methanol oxidation, perhaps resulting from the relatively low platinum loadings that this technique could provide for. Platinum was also deposited by sweeping the potential in

H_2PtCl_6 solution. This electrode displayed poor stability and decayed along the same path as thin film platinum electrodes. Another possible variable was length of time that the electrode was allowed to soak in the H_2PtCl_6 solution prior to the reduction, as well as the composition of that solution.

Following the observation of Vork *et al.*²¹² the current density during the metal deposition is also likely to be an important parameter. They employed polypyrrole films of 0.3 mm thickness deposited on a carbon or Pt substrate. Pt particles were deposited on this polymer layer in two ways. Firstly, by electro deposition of the particles in and on the polymer layer by reduction of Pt^{4+} ions after the formation of polypyrrole and secondly, by simultaneous deposition of polypyrrole and precipitation of Pt powder particles. Electrodes prepared by the former method proved to be electrocatalytically active for the oxidation of hydrogen in aqueous 0.5 M H_2SO_4 , with high current densities at low Pt loading and low over potential. The later method produced electrodes with Pt particles, mostly inactive for the oxidation of hydrogen. The ohmic resistance of the electrodes increased, on going from -0.2 to -0.3 V/SCE, due to the partial reduction of the polymer. Loading the polymer with Pt particles decreases the resistance at lower potentials (< -0.2 V/SCE), depending on the rate of Pt deposition.

Nappron *et al.*^{190j} studied the electrooxidation of C_1 molecules (MeOH, HCHO, HCOOH) on Pt based catalysts (Pt, Pt-Sn & Pt-Ru) dispersed into PANI matrix. Different electrodes were prepared in two main steps. First step was electro polymerization of aniline by potential cycling at a fixed scan rate (50 mV/sec) on a gold sheet (1cm² geometric area) in a solution of 0.1 H_2SO_4 and 0.1 M aniline. Second step was the insertion of metallic particles in the polymer matrix by electroreduction of metallic ions in aqueous solution of corresponding metallic salts at a constant potential (0.1 V/RHE). The conditions for dispersion were critical for co-deposition of Sn and Pt. The optimum concentration of Sn (IV) salt solution was found to be 6×10^{-4} M. Beyond this concentration the electrolytic solution containing Sn and Ru was found to be unstable. The observations of Nappron *et al.*^{192j} on electrooxidation of methanol on PANI for dispersed Pt based electrodes were as follows: The order of current density is: (mAcm⁻²): Pt-Sn (13.0) > Pt-Ru (8.65) > Pt-Ru-Sn @ Pt (7.3). The maximum peak potential (V/RHE) increases in

the order Pt-Ru (0.75) < Pt-Ru-Sn (0.8) < Pt-Sn (0.82) < Pt (0.85) and the starting potential (V/RHE) also varied and it was increasing in the order: Pt-Ru (0.375) < Pt-Sn (0.4) \cong Pt-Ru-Sn < Pt (0.5). It was stated that the method of preparing Pt-Sn electrodes might be a key point in determining the activity and this probably the reason for contrasting results often found in the literature concerning the behaviour of Sn as a promoter for the electrooxidation of small organic molecules on Pt.

Kelaidopourlou *et al.*¹⁹⁴ studied the morphology of Pt particles deposited in the poly (2-hydroxy-3-aminophenazine) (pHAPh) and PANI films prepared under similar deposition conditions using transmission electron microscopy. The mean diameter of the metallic particles was less than one micrometer. They have^{190j} incorporated binary catalyst particles into pHAPh matrix as described in the case of PANI. With this method, only Sn was codeposited with Pt in the pHAPh film, while (in contrast to PANI) Ru was not deposited. The codeposited Pt-Sn particles were similar in size (40-70 nm in diameter) to that of Pt alone. X-ray analysis of the pHAPh/Pt-Sn assembly showed that the amount of Sn was around 1.0%, whereas in the case of codeposition of Ru with Pt, Ru does not exist either as non-oxidized or oxidized particles in pHAPh/Pt assembly. The influence of Pb ad-atoms deposited at underpotential conditions towards the oxidation of methanol on Pt nanoparticles was also studied. According to the literature^{213a,b} smooth Pt modified by underpotential monolayers of Pb is a slightly better catalyst than pure Pt towards methanol electrooxidation in acid solutions. However, the underpotential deposition of Pb on Pt nanoparticles dispersed in pHAPh had no effect for methanol oxidation. Swathirajan *et al.*^{192a} reported the electrooxidation of methanol using poly (3-methyl) thiophene (PMT), the polymer was electrodeposited on a stationary graphite disk electrode from a solution of 0.05 M 3-MT and 0.1 M TBAF in acetonitrile. The polymer film was deposited by cycling the potential between 0.0 and +1.8 V/SCE at 200 mV/s. The electrodeposition of Pt-Sn was carried out either at constant potential or constant current.

Kulesza *et al.*¹⁹³ demonstrated the usefulness of poly-N-methyl pyrrole as a matrix for the fabrication of a composite film containing spatially dispersed Pt and highly reactive Ru oxo centres in a form of polynuclear ruthenium (III, IV) oxide/cyanoruthenates.

Fabrication of PMPy films was accomplished by potential cycling in the range -0.3 to 0.8 V in the solution of methyl pyrrole and H_2SO_4 . In this case, as the electropolymerization proceeds, anions of the supporting electrolyte were incorporated simultaneously into PMPy film on the electrode. Doping the anionic species of RuO/CNRu can neutralize the positive charge on the chain of PMPy. A general method of preparing electrodes covered with RuO/CNRu was described by Kulesza *et al.*²¹⁴. Variation in cycling time leads to different loadings of RuO/CNRu. Pt microcentres in the films were generated by electroreduction of chloroplatinic acid in H_2SO_4 by cycling the potential (0.8 to -0.3 V). It shall be noted that the electrochemical characteristics of RuO/CNRu resemble the behaviour of ruthenium oxide²¹⁵, except that, in the case of RuO/CNRu, Ru (III, IV) redox reactions are better defined and they appear at approximately 100 mV less positive potentials. This property makes RuO/CNRu more attractive, in comparison to Ru oxide, for electrocatalytic oxidation including that of methanol. Participation of the oxygen containing ruthenium species in the activation of Pt towards oxidation of methanol has been postulated for bimetallic Pt- Ru catalysts (alloys)²¹⁶. It is likely that the ruthenium oxo species, through 'cross-linked' by cyanoruthenates within RuO/CNRu, would also be able to induce activity of coexisting, dispersed platinum for methanol oxidation.

Laborde *et al.*¹⁹⁵ studied the electrocatalytic oxidation of methanol on the copolymer (pyrrole-dithiophene) electrodes modified with platinum. The copolymerization of pyrrole and thiophene was carried out electrochemically on a gold sheet under galvanostatic conditions from a solution containing pyrrole and dithiophene in acetonitrile with TBAP. Pt particles were then incorporated by electrodeposition from a solution of K_2PtCl_4 in KCl with pulses of potential. Later, Laborde *et al.*, studied the electrocatalytic oxidation of methanol on platinum dispersed in PANI matrix. PANI films were deposited on gold sheet by cycling the potential at a constant sweep rate in H_2SO_4 containing aniline. Pt particles were then incorporated by electrochemical deposition at constant potential from a solution of hexachloroplatinic acid in H_2SO_4 .

Swathirajan *et al.*^{192a} studied the electrooxidation of methanol using Pt-Sn particles dispersed on poly 3-methylthiophene (PMT). The polymer was prepared

by electropolymerization technique and the catalyst was electrodeposited using both potentiostatic and galvanostatic methods. The effect of catalyst deposition potential was studied by varying the potentials from 0.0 to -0.8 V/SCE and the alloy composition was determined using energy dispersive X- ray analysis. The tin composition was found to increase at less negative potentials and at -2.0 V/SCE a notable deviation was observed in the deposition characteristics especially in the morphology, surface area and catalyst activity. This observation was attributed to the co-adsorption of hydrogen at -2.0 V. The microscopic surface area and the apparent current densities (observed current / geometric area) for methanol oxidation were two fold higher compared to catalyst deposited at -0.8 V on PMT. Even though the apparent current density was higher, the real peak current density was only 0.1 mA/cm², which was 10% of the activity of smooth Pt. Also the increase in the width of methanol oxidation region to 0.55 V, which was about 100 mV higher than that observed for other Pt-Sn deposits and the onset potential was 0.1 V.

Adjustment of the deposition parameters, particularly, sweep rates and potential limits should allow this type of electrodes to be optimized. Another possible variable was the length of time the electrode was allowed to soak in H_2PtCl_6 solution prior to the reduction, as well as the composition of the solution. Following the observation of Vork and Barendrecht (1989), the current density during the metal deposition is also likely to be an important parameter²¹².

3.3.2 Influence of Metal Loadings and Film Thickness of Polymers

Swathirajan *et al.*^{192a} studied the effect of Pt loading towards electro oxidation of methanol on PMT film of 0.55 μm thickness which was prepared by potentiodynamic method. The Pt-Sn catalyst was electrodeposited at a constant current of 33 mA/cm² for periods between 20 and 120 sec., leading to Pt loadings in the range 20 - 120 $\mu\text{g}/\text{cm}^2$. Rutherford backscattering spectrometry (RBS) was employed to study the estimation of thickness and the distribution of the catalyst layer in the conducting polymer support. When the thickness of the catalyst film was plotted against the catalyst deposition charge, the peaks due to carbon and sulfur, and a shoulder due to Sn were all present at Pt loading of 20 $\mu\text{g}/\text{cm}^2$. As the loading was increased in the range 20 - 60 $\mu\text{g}/\text{cm}^2$ the carbon

and sulfur signals weaken considerably and the Sn signal was obscured by the Pt signal. The width of the Pt signal, a measure of catalyst film thickness remained constant. These observations showed that at low Pt loadings, when the catalyst film thickness was 100 nm, the pores of the polymer were not completely covered by the catalyst and the catalyst was deposited inside the polymer on its internal surface. For thicker catalyst films, there was a broadening of Pt signal and the signals due to other elements were completely disappeared. When the catalyst loading was beyond $80 \mu\text{g}/\text{cm}^2$, the catalyst film grew outside the polymer on its external surface even when the catalyst film thickness was less than the polymer thickness of $0.55 \mu\text{m}$. This behaviour was attributed to the negative potential (-0.6V) observed during the deposition of Pt-Sn catalyst. At that potential, the polymer film was in the reduced state and therefore unable to be doped by anions. Since Pt was present in solution in the form of anion complex, the ions were not allowed to enter in to the film due to electrostatic forces. At the lowest catalyst loading of $20 \mu\text{g}/\text{cm}^2$ the electrode showed no activity for methanol oxidation but the cathodic evolution of hydrogen and oxidation of hydrogen were both observed at these low loadings. Complete features of methanol oxidation were first observed at Pt loadings of $40 \mu\text{g}/\text{cm}^2$ and at Pt loadings of $120 \mu\text{g}/\text{cm}^2$ the CV curves resembled bulk Pt. The apparent increase in current densities with Pt loadings are attributed to the increase in microscopic surface area; but the current density was $< 50 \mu\text{A}/\text{cm}^2$, which was only 5% of that observed on smooth Pt.

Electrodeposition of Pt-Sn catalyst on PMT was found to have lower surface area compared to graphite substrate. The cathodic current density was lower on PMT than at graphite at all deposition potentials in the range 0.0 to $-0.8 \text{V}/\text{SCE}$. The higher resistivity of the polymer film led to higher polarization for the deposition process. The catalytic activity was higher on graphite support with a peak current density of $0.71 \text{mA}/\text{cm}^2$ compared to $0.55 \text{mA}/\text{cm}^2$ on PMT. The alloying of Pt with Sn led to a 150 mV catalytic shift (towards less positive region) for direct electrochemical oxidation of methanol.

Strike *et al.*^{191b} found that the thickness of PPY in the range (100-700 nm) has no effect on the behaviour of Au/PPY/Pt electrodes towards electrooxidation of methanol. It is known that the

counter ion could affect the film morphology and conductivity, the PPY films were deposited from solutions containing Cl^- , NO_3^- and TsO^- . After the Pt deposition and 12h polarization in neutral media, the current density supported by the films decreased in the order $\text{Cl}^- > \text{NO}_3^- > \text{TsO}^-$. The increase in current density with increase in Pt loading was greater for Au/PPY/Pt than Au/Pt electrodes. The percentage change in current between the 11th and 12th hour of 12h electrolysis as a function of Pt loading revealed that the Au/PPY/Pt electrodes deposited by the potentiostatic technique showed smaller rates of drift than the other electrodes at comparable Pt loadings. Pt dispersed in PPY films displayed electrocatalytic activity for methanol oxidation and some protective effect was also provided by the polymer against the poisoning reactions of methanol oxidation compared with Pt or platinized gold.

Kost *et al.*^{190d} reported current densities of about $1.0 \text{mA}/\text{cm}^2$ for 2-5 μm thick PANI films modified with $30 \mu\text{g}/\text{cm}^2$ of Pt; at 60 mV/Ag/AgCl in 1.0 M H_2SO_4 & 1.0 M MeOH. Whilst Aramata *et al.*²¹⁷ reported current densities of about $20 \mu\text{g}/\text{cm}^2$ (geometric area) for Nafion films about 20 μm thick loaded with 4.0 to 8.0 mg/cm^2 of Pt (1.0M H_3PO_4 , 1.0 M MeOH at 600 mV/RHE). In the reports of Strike *et al.*^{191b} current densities of $2.0 \text{mA}/\text{cm}^2$ were mentioned for 300 nm PPY film modified with about $200 \mu\text{g}/\text{cm}^2$ of Pt after running the electrodes for 12 h in 0.1 M H_2SO_4 or 1.0 M HClO_4 in 1.0 M MeOH at 500 mV/SCE and the electrodes were stable at elevated temperatures up to 333 K, where it supported current densities of the order of $30.0 \text{mA}/\text{cm}^2$. The hydrogen adsorption for the electrodes Au/PPY/Pt (pul) and Au/PPY/Pt (pot) is not well defined and therefore the estimation of effective surface area could not be made. The features of these electrodes were related to available surface area. The well-defined hydrogen adsorption waves were absent for Pt in copolymer of pyrrole and dithiophene and in polyaniline. In the former case, Pt being well dispersed, so no islands which could have the same adsorption properties like bulk Pt. The lifetime of Pt micro particles in anion or cation exchange membranes originated from an ability of the membranes to stabilize a surface mediator couple ($\text{Pt}^0/\text{Pt}^{2+}$).

The studies of Napporn *et al.*^{190h} on PANI containing $0.1 \text{mg}/\text{cm}^2$ of Pt, showed maximum apparent current density achieved was $7.3 \text{mA}/\text{cm}^2$

at 8.5 V/RHE and the oxidation started around 0.5 V/RHE. But in contrast to smooth Pt, poisoning effect was weak, confirming that the poisoning effect decreases as dispersion increases. Similar observations were made earlier from IR-*in situ* experiments with Pt of different roughness³⁵. When the electrode contains dispersed co-deposit of Pt and Ru, the current peak shifted to negative potentials (0.75 V/RHE) with an increase in current density (8.65 mA/cm²). Such an effect was observed previously and interpreted as bifunctional effect of the electrocatalyst.

Laborde *et al.*^{172f} reported that the electroactivity of Pt for methanol oxidation depend on the amount of deposited Pt on PANI matrix. The methanol oxidation starts at 0.55 V/RHE and the maximum current density was observed between 0.84 and 0.91 V/RHE for Pt amount varying from 0.0 to 110 $\mu\text{g}/\text{cm}^2$. The shift to more positive potentials of the current peak increased with the amount of deposited Pt. The current density was found to increase up to 70 $\mu\text{g}/\text{cm}^2$, and for further loading of Pt, the maximum current density becomes nearly constant and then slightly decreased. This slight decrease was attributed to the formation of Pt cluster, leading to a smaller dispersion. Electrochemically modulated infrared spectral studies (EMIRS) showed the absence of CO_{ads} signal in the region 1800-2200 cm⁻¹ with Pt modified PANI electrodes³⁸ compared with a bulk Pt electrode, confirming the low degree of poisoning observed on electro dispersed Pt. Also, there was a contribution from adsorbed CO₂ at 2350 cm⁻¹; CO₂ was formed during electro oxidation process. The increase in activity of dispersed Pt was attributed to an increase in available Pt area in the matrix. A comparison made for electrooxidation of methanol on pHAPh/GC/Pt and GC/Pt (same amount of deposited Pt = 0.12 mg cm⁻¹) revealed¹⁹⁴ that as on smooth Pt, the oxidation starts around 0.5 V/SHE, the maximum current density appeared at 0.85V. The maximum current density was @ 12 mA/cm² for GC/Pt and \cong 30 mA/cm² for GC/pHAPh/Pt. The maximum current density on smooth Pt under the same condition was \cong 5.0 mA/cm². The higher currents observed on GC/pHAPh/Pt was attributed to the large surface area of Pt particles and that Pt micro/nano particles were probably less sensitive to poisoning from adsorbed CO species. The current density of methanol oxidation depended on the amount of deposited Pt. The peak current density (j_p) increased with the mass of the metal incorporated and reached a maximum of 67 mA/cm² at Pt loading

of 0.48 mg/cm². Thereafter, the extra Pt added did not increase the active surface area but led to lower degree of dispersion. Comparison of variation in peak current density (j_p) with respect to Pt loading reported in this study (i.e., GC/pHAPh/Pt assembly) with that of earlier report^{190f} for PANI- modified GC (GC/PANI/Pt assembly) showed two main differences (i) The maximum value of j_p (\cong 67 mA/cm²) was observed for GC/pHAPh/Pt electrode, which was greater than the value of j_p \cong 12 mA/cm² reported for the GC/PANI/Pt electrode. (ii) The peak current density reached the maximum value on PANI/Pt at significantly lower Pt loading (0.07 mg/cm²) than on pHAPh/Pt. These differences were attributed to (a) thickness of the polymer film employed (since in the study of PANI/Pt, the film was thicker, 0.5 μm) and (b) to the low potential sweep rate employed (5 mV/s) in GC/PANI/Pt assembly.

To compare the activity of Pt particles deposited in pHAPh and PANI, Keladopoulou *et al.*¹⁹⁴ studied the electrooxidation of methanol on pHAPh/Pt and PANI/Pt electrodes of the same film thickness (0.3 μm), for the amount deposited (0.12 mg/cm² Pt) and potential sweep rate (5 mV/s). The peak current density on GC/PANI/Pt was 13 mAcm⁻² which was comparable to the previous report^{190f}, while on GC/pHAPh/Pt showed higher catalytic activity (30.0 mAcm⁻²). The morphology of Pt particles in both the polymers (TEM results) showed that in PANI the Pt nano - particles aggregate in larger groups, leading to lower degree of dispersion; whereas in pHAPh, Pt yielded spherical catalyst particles of 40-70 nm in diameter and surround the polymer fibrils in a uniform manner thereby the penetration and diffusion of methanol through the film had been a slow process. Under rotating conditions, the intercept of the plot j_p^{-1} vs $\omega^{-1/2}$ (ω = rotation rate) was proportional to the film thickness, showing that the transfer of methanol is also one of the factors. This behaviour further confirmed that Pt particles were distributed in 3D manner and not concentrated on polymer-solution interface. The oxidation of methanol on GC/pHAPh/Pt-Sn assembly exhibited lower onset currents as well as higher currents at less positive potentials (130 mV), indicating the enhanced electrocatalytic activity compared to pure dispersed Pt. Underpotential deposition of Pb on Pt nano particles dispersed in pHAPh had no effect for methanol oxidation.

The data on the role of polymer towards the metal loading as well as on the methanol oxidation activity

are given in Table IV. Assuming that the thickness of the polymer is not playing a major role, the comparison is made between the maximum loading, activity and the mass specific activity. It appears that polyaniline shows the maximum mass specific activity, but it is not true because the maximum loading on polyaniline is only 0.07 mg/cm^2 without any appreciable agglomeration, so even if the loading is increased further, the activity will not vary much. But in the case of the ladder polymer ploy (2 – hydroxy – 3-aminophenazine), since the amount of heteroatoms present in the polymer backbone is more, it can accommodate more amount of platinum without any appreciable agglomeration. So the mass specific activity will not give the true picture of the actual performance of the electrode material in these cases.

It is concluded from the studies of micro particulate electrodes that the catalytic activity of such electrodes is a function of not only of the amount of electrodeposited catalyst but also size of particles and transport conditions outside and inside of the film.

Kulesza *et al.*¹⁹³ used PMPY-RuO/CNRu-Pt electrodes with Pt loading of $3.0 \text{ } \mu\text{g/cm}^2$ and Pt diameter of 20-30 nm. Determination of Ru was difficult due to high reactivity of Ru(IV) oxo centers and their higher surface concentration relative to Pt. Several order of increase in methanol oxidation peak at 1.1 V than at 0.7 V was attributed to the fact that PMPY matrix becomes more conductive at more positive potentials enhancing the system's mediation capabilities and supported the overall catalytic process at 1.1 V. The methanol oxidation current was enhanced three times at higher temperatures, showing the physicochemical stability of PMPY film at 333 K and the inhibiting effect of methanolic residues such as (CO_{ads}) was decreasing at higher temperatures. It was speculated that 'synergistic' effect of RuO/CNRu on Pt increases the activity of Pt towards methanol oxidation. However, in this study, there was no mention about the thickness of the polymer film and there are no reports on systematic variations in film thickness as well as the extent of Pt loadings.

Laborde *et al.*¹⁹⁵ studied the electrooxidation of methanol on dispersed Pt (loading: 0.1 mg/cm^2) on a co-polymer (pyrrole-dithiophene) of thickness $2.0 \text{ } \mu\text{m}$. The methanol oxidation starts at 0.55 V/RHE and the maximum current density was found to be 1.0 mA/cm^2 at 0.9 V/RHE. The current densities were smaller than those obtained with a Pt modified PANI electrode for the same amount of Pt. However, the poisoning was very weak in this case.

This survey unequivocally demonstrates that a small change in a single experimental variable may influence the properties of the resulting polymer enormously and therefore the results obtained under widely varying conditions cannot be uncritically used to draw universal conclusions. More studies based on the variation of polymer film thickness, morphology and substrate are necessary to investigate the various interdependent phenomena to develop fuel cell applications.

The electronically conducting polymers, with π -conjugated systems, show interesting redox properties and due to their amorphous nature these polymers show good permeability to electrolytes in different solvents when used as electrodes. In principle, this should allow direct contact between the electrolyte solutions with the bulk of the polymers at molecular scale, not only at the interface. However, the compatibility of these organic conducting polymers with solvents and particularly with ionic groups, is low, resulting in low ionic mobility in such materials. Hence, the charge transfer in short time scale is restricted by the slow ion exchange in the systems. The network of electron-conducting polymer and ion-conducting polymers might offer solution to this problem.

Lefebvre *et al.*²¹⁸ prepared a variety of Pt and Pt-Ru supported catalysts by chemical deposition on chemically prepared poly (3,4-ethylenedioxythiophene)/ poly (styrene-4-sulfonate)(PEDOT/PSS) and PEDOT/polyvinylsulfate (PVS) composites. They show high electron and proton conductivities, facilitate rapid electrochemical reaction

Table IV
Role polymer towards metal loading in methanol oxidation

Electrode	Maximum loading (mg/cm^2)	Activity (mA/cm^2)	Thickness of polymer film (mm)	Mass Specific Activity (mA/mg)
GC/PANI/Pt	0.07	12.5	0.5	178.5
GC/pHaPh/Pt	0.6	65.0	0.3	108.3

rates of thick layer of catalyst. The methanol electrooxidation using these polymers are under investigation. Ghosh *et al.*²¹⁹ have prepared PEDOT-PSS, an electronically conductive electroactive polymer blends with an ion conducting polymer, polyethylene oxide (PEO), to increase ionic mobility in the material. As super capacitor electrodes, the blends gave much higher energy densities at high power densities compared to the pure PEDOT-PSS and this enhancement in electrochemical properties was attributed to both intrinsic ionic conductivity of the PEO and the swelling of the former in liquid electrolyte solution, creating space for ionic movement. By suitably fabricating mixed electronic and ionic conducting polymers as supports for catalytic particulates, the utilization of catalytic particulates may be enhanced.

In this context of discussions on ion conducting polymers, it is worth mentioning the role of Nafion, a perfluorinated sulfonic acid polymer with excellent chemical, mechanical and thermal stability. In DMFC membrane electrode assemblies (MEA), the catalytic particles were coated with Nafion, which acts as polymer electrolyte and the catalyst binder. Shimazu *et al.*²²⁰ described the enhancement of catalytic activity of Pt micro particles for the oxidation of methanol by dispersing them in to Nafion film and by the subsequent RF-plasma treatment. The time-course of current density at 0.3 V/SSCE for 30 min duration showed that the initial activity was larger by a factor of 1.5 on Pt-Nafion/GC (Nafion film thickness = 500 nm) than Pt/GC. The oxidation current decayed with the polarization time on both electrodes, but faster on Pt/GC. Thus, the activity at Pt-Nafion /GC was larger by a factor of 2.1 than Pt/GC at 30 min. The current density at 30 min for Pt-Nafion/GC is dependent on film thickness. For thin Nafion film (<100 nm), a part of the individual Pt particles with a diameter of 100-200 nm was exposed directly to the bulk solution out of polymeric film, and hence no activity enhancement was found. But when film thickness was increased from 250-500 nm the activity increased by a factor of 1.5-2.0 at 30 min. This increase was approximately same as that (2 times) for the Pt chemically plated to Nafion membrane (Pt-SPE) as reported by Aramata and Ohnishi²¹⁷. It is worth noting that the present electrode carries only 20 $\mu\text{g}/\text{cm}^2$ of Pt, which was two order of magnitude less than that of Pt/SPE. The activity enhancement by Nafion film is attributed to the interaction between

the particles and film, and/or an environment change of the Pt particles in the Nafion matrix. Further, RF-plasma treatment makes a Nafion film structurally more compact due to the cross-linking, so that the film becomes more hydrophobic.

The data on mass specific activity (mA/mg) given in the Table V are particularly interesting since, it provides a means for a priori selection of support (conducting polymers) as well as active metal combination for possible use in methanol oxidation. General systems which exhibit activity of the order of 100 or high mA/mg will be suitable candidate for exploitation.

4 Status of Polymer Based Electrodes – A Perception

Critical evaluation of studies on electrooxidation of methanol using catalysts in/on conducting polymers leads one to arrive at the following points.

Most of the polymers that have been successfully employed as conducting films for studies on electrooxidation of methanol possess several basic characteristics. First, they are aromatic and can be oxidized at relatively low anodic potentials.

Polymer films are produced by an oxidative process, it is important that the electrode does not oxidize concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a Pt or Au electrodes. However, films have also been prepared using a variety of semiconducting materials and graphite.

Polymers can be prepared by electrochemical methods. Of the electrochemical techniques, the potential cycling method is a good choice, since this technique provides various parameters related to the degree of growth. This allows one to have maximum control over the quality of the films produced. A slight shift in the switching potential can cause a tremendous change in the reaction rate. Monomer concentration, temperature and potential can be used interchangeably to reach a defined reaction rate. Higher potentials are needed for a lower monomer concentration. Likewise, a higher potential is needed for the sustainable formation of polymer at lower temperatures. As the solid films are concerned, the specific nature of the solid state, such as the electrical resistivity, capacitive effect, lattice relaxation, swelling properties and the relative permeability to ions and solvent etc.,

Table V
Methanol oxidation performance on noble metal(s) supported on conducting polymer electrodes

S.No	Electrode	Metal(s)/oxide	Thickness of polymer (μm)	Performance		Reference
				Pot (V/NHE)	Mass Sp. Activity (mA/mg)	
1	Au/PANI	Pt	0.5	0.85	73.0	190h
		Pt-Ru		0.75	86.5	
		Pt-Sn		0.82	130.0	
		Pt-Ru-Sn		0.80	73.0	
2a	Au/PANI	Pt	0.5	0.86	80	190f
2b	Au/PANI	Pt-Ru	0.5	0.75	141.2	190 1
3	GC/PANI	Pt-Ru	-	0.23	24.0	190k
		Pt-Sn		0.23	16.0	
4	Au/PANI	Pt	-	0.38	33.33	190d
5	Au/PPy	Pt	0.3	0.26	10.0	191b
6	Gc/PPY	Pt	0.8	0.48	1006.7	191d
7	Au/PPy	Pt(3D)	0.3	0.36	212.1	191e
8	GC/PMpy	RuO/CNRu-Pt	-	0.96	2063.0	193
9	GC/PMT	Pt-Sn	0.8	0.4	194.1	192
	GC	Pt		0.45	333.3	
10	Au/copolymer (Pyrrole-dithiophene)	Pt	2.0	0.90	10.0	195
11	-	Pt	-	0.844	100	194
	GC/pHAPh	Pt	0.3	0.860	180	
		Pt-Sn	0.3	0.860	250	
12	VulcanXC-72/PEDOT/PSSI	28% Pt-Ru-MB	-	0.76	68.75	218
		24% Pt-Ru/MB		0.31	46.25	
		21% Pt-Ru/PEDOT/PVS		0.51	25.00	
		29% PT/MB		0.51	62.50	
		Commercial Pt-Ru		0.51	18.75	
13	Nafion	Pt	-	0.6	0.0263	217
		Platinised Platinum		0.6	0.00114	

* Current density (mA/cm^2); # Current (mA); At 333K; # chemical preparation

PANI-Polyaniline; PPy-Polypyrrole; PMT-Poly(3methyl)thiophene;

PHAPh-poly (2 hydroxy-3'aminophenazine); PEDOT-poly(3,4-ethelenedioxythiophene)

PSS-poly(styrene-4-sulfonate); PVS-polyvinylsulfate; MB-PEDOT_{1.5}(NO₃)_{0.15}Fe_{0.14}PSS.1.5 H₂O

must be taken in to consideration in the interpretation of voltametrical behaviour of conducting polymers. These properties depend not only on the polymeric chain structure (chain-length, chain-branching, cross-linking), but also to a great extent, on the tertiary structure. The properties of polymers formed in different reaction environments may differ from one another. Although the potential determines the charging

levels of oligomer radical cations and accordingly, influences the chain-length of the resulting polymer, it does not necessarily follow that changing the potential in a certain range can always bring about the expected change in polymer structure. The change of chemical environment due to different reaction rate may have a profound effect on the properties of resulting polymer.

High degree of π -electron conjugation constitutes a necessary criterion for obtaining high-energy donor polymer bands and/or low energy acceptor polymer bands. Typically, ionization potentials smaller than 6.5 eV and electron affinities larger than 2.0 eV appear to be necessary in order to form highly conducting charge transfer complexes. Polymers with hetero atom in their backbone were extensively used as matrices to disperse metal particulates in the studies of electrooxidation of methanol. The presence of lone pair of electrons on electronegative atoms such as N, S or O might be utilized to form bonds with the dispersed metal particulates. This metal-polymer interaction contributes to effective spatial distribution of metal atoms in the matrix. The available wave functions of metallic sites are suitably altered in symmetry and energy with the incoming reactant molecules for interaction.

Structurally simple polymers such as polyacetylene and polypyrrole are more efficient than corresponding substituted systems or copolymers. The presence of substituents like methyl groups can (a) lower the symmetry and as a result decrease the band widths (b) promote the departure from planarity (c) lead to chemical reactions with dopants as in poly methyl acetylene. In case of polyacetylene, the complex it forms with platinum is the one, which is responsible for its resulting activity. PPY is not used in the studies of electrooxidation of methanol since, its electroactive domain is not of methanol oxidation region.

In general, all polymers due to their porous texture capable of accommodating the incorporated metal particles; however, not all metal particles present in the matrix are completely utilized for catalytic activity, in spite of increase in geometrical surface area due to dispersion. We presume that: (i) The metal is dispersed throughout the polymer either in 2D or 3D manner according to the preparation method adopted for deposition. (ii) The morphology of the polymer is an important criterion for spatial distribution of metal particles. However the percentage utilization of (catalytic activity) metal depends on 'where does exactly the metal get anchored in the polymer backbone'. That is, the molecular level interaction (specific site) of polymer with the metal decides the percentage utilization and individual reactivity. The intrinsic activity of catalytic particle present in the metallic foil is different from that of dispersed metal particulates on the support. Further the net charge density on

the metal particulates depends on the surface structure of the support. In the case of conducting polymers as supports, the deposition leads to uniform distribution of catalytic particles throughout the polymer. But, the intrinsic activity of metal present on the sites of heteroatoms of the polymer will be different from that present on other constituent of polymer bone. The electrons present on heteroatoms will facilitate bond formation with the metal particulate thereby changing its electronic environment, and thus oxidation state. As this bonding between the heteroatoms and the catalytic particulate is stronger, there is a weakening of M-CO bond and this facilitates to the easy walk of poison (CO) on metallic terraces.

The 'good catalytic activity' of metal incorporated in the polymer matrix is reflected in either or both of the following factors: (a) The shift in potential towards less positive region and/or increase in current density. (It is worth noting that in many reports the current density was calculated only from the geometrical area of the electrode and not from the active surface area). (b) Lower poisoning effect from methanol oxidation residues. In the first case, the shift in potential depends on the conductivity of polymer as well as its morphology. The second factor depends on whether the polymer is shielding or deshielding the electrons of metal. The extent of perturbation of oxidation state of metal decides the weakening/strengthening of metal-CO bond.

Electrooxidation of CO and/or poisoning by CO on Pt alloys have been extensively investigated. The coverage of adlayer at the electrode was evaluated on the basis of the electric charges at the hydrogen adsorption-desorption region. The electronic property of the metal was modified when they were dispersed on polymer matrix. In XPS studies, photoelectron peaks for dispersed Pt was positive shifted from that of pure Pt. This suggests that the density of valence electrons (5d) of the dispersed Pt is lower than that of pure Pt. To understand the trends fully, it is necessary to have the detailed quantum mechanical information about the bonding mechanism between dispersed Pt and bulk Pt. Such information is not available at present. However, the lower electronic density of the d-band in the dispersed Pt can be easily understood in terms of the orbital mixing. Hybridization of the occupied state of an electron rich metal (Pt) with the unoccupied levels of an hetero atom in the polymer chain leads to a loss of Pt character in the occupied

states and hence the reduction in the electron density on the dispersed Pt. On the basis of this assumption, we propose a mechanism for CO tolerance; i.e., the lowered electron density of the 5d orbital of Pt decreases the electron back donation from the Pt 5d orbital to the $2\pi^*$ orbital of CO, and consequently suppresses CO-Pt bonding, resulting in the lowered CO coverage. Further, the CO on dispersed Pt expected to have a higher mobility by the weakened Pt-C bonding than the pure Pt. We presume that the CO tolerance on dispersed Pt particulates was brought about by the lowering of the CO coverage and bonding strength to the Pt, but not via by facilitating oxidation.

The electronically conductive polymers must switch rapidly between the conductive and the insulating states. This switching process requires that counter ions be incorporated into (insulator-to-conductor transition) and subsequently expelled from (conductor-to-insulator transition) the polymer film. The rate of counter ion diffusion within the polymer limits the overall rate of the switching process. If higher switching rates are to be achieved, electronically conductive polymers, which are also fast ion-conductors must be developed.

Morphology determines the facility of ion-transport and there are number of evidences suggesting that a fibrillar/microporous morphology is optimal for electronically conductive polymers. Polyacetylene has fibrillar/microporous morphology but the fibril diameter is too large to allow for rapid, quantitative switching. Thus polyacetylene does not possess ideal version of this morphology. Polypyrrole has a dense, amorphous morphology and should exhibit even slower switching rates than polyacetylene. An appealing method for forcing electronically conductive polymers is based on the electronically conductive composite polymer membrane concept, in which an electronically conductive polymer is grown within the pore structure of a host membrane. The diameter of these fibrils is determined by the pores in the host. Furthermore, a large fraction of the polymer sites are electrochemically active in the fibrillar/microporous membranes than conventional homogeneous films.

Large surface area and catalytic activity were found for electrodes with dispersed Pt^0 (3D) nano particles in the polymer matrix than electrodes with electrodeposited Pt^0 on the surface (2D) of the conducting polymer. The mechanistic approach for

the electroactive metal particles in carbon is different from that on conducting polymer films. This allows us to venture the supposition that nature of electrochemical activity of composites is connected with electronic transitions between redox centres of the components of nano/micro particles.

5 Directions for Further Studies

A key concern in the development of DMFC is to evaluate whether there are any better catalysts than PtRu and to find whether PtRu electrodes are capable of further improvement or there is a natural limit. The best strategy for this search is a combined approach of theoretical and fundamental electrochemical studies and a modern screening method such as combinatorial analysis in order to achieve meaningful results under realistic conditions. The use of alkaline solutions is very attractive as far as the organic fuel reactions are concerned, but the problem of carbonation must be circumvented in some manner. It seems worthwhile to undertake studies of the various fuels in saturated bicarbonate solutions since these cannot carbonate any further. An added advantage of bicarbonate solutions is their buffering capacity, which will serve to maintain the pH at well-defined levels, despite load variations.

Determination of the electrochemically active surface area is a key component for a reliable and meaningful comparison of different catalysts. Mass normalization has a limited value since it does not take into account the area in contact with the electrolyte. Another approach is coulometric analysis of hydrogen desorption waves and applying it to the normalization of methanol oxidation current. By combining this later technique with mass normalization Liu *et al.*²²¹ estimated the catalyst utilization. Another approach is measurement of double layer capacitance since it is generally proportional to the active surface area. These methods are useful in unsupported catalysts, but both methods are not likely to be successful in the case of supported catalysts since: hydrogen desorption may be masked by the redox currents of the carbon support, and double layer capacitance measurements cannot distinguish between the metal and carbon in contact with the electrolyte. In such cases, it was proposed that a combination of particle size analysis by TEM and double layer capacitance measurements by impedance spectroscopy might be a workable proposition. The total area in

contact with the electrolyte can be derived from the double layer capacitance and the portion due to metal can be derived from particle size analysis. Recently, Easton *et al.*²²² provide another approach in that chemical modification of fuel cell electrodes with electro active probes has the potential to improve the diagnostic value of data obtained by cyclic voltammetry (CV) and impedance spectroscopy. Since using CV, the areas of the peaks for electrochemical hydrogen adsorption/desorption provide the measure of the active Pt area. However, the use of this parameter has number of limitations including the fact that it can not be measured while the fuel cell is actually operating and the full Pt area that is active for hydrogen adsorption is unlikely to be active for the fuel cell reaction because insufficient reactant gas access and resistance losses at high current densities.

In the case of chemical modification of electrodes with electro active probes, the quantity of the probe present can be accurately controlled, so that the percentage that is active can be determined and it can be placed in the desired regions (macroscopic/microscopic) of the catalyst layer to monitor local properties. Electro active probes can offer better accuracy and precision in active area determination and simplify the analysis of impedance data. Chemical modification methods may be used to improve the characteristics of the electrode such as proton conductivity and hydrophilicity/hydrophobicity. They can also be used to immobilize the transition metal complexes as catalysts.

The polymerization of aniline, pyrrole and thiophene and their derivatives in layered systems like $V_2O_5 \cdot nH_2O$ xerogels yield a conducting polymer / oxide bronze, a layered molecular composite^{223,224}. Though, V_2O_5 can be used as the co-catalyst like WO_3 , the significant leaching of V_2O_5 under operating condition limits the use of V_2O_5 as the co-catalyst, the intercalation of conducting polymer inside the layered lattice not only alters the redox potentials of the individual components, but also increase the stability during the operating condition. So, the catalytic particles can be supported on the intercalated material and can be used as the fuel cell anodes.

Another approach to improve the redox properties of conducting polymers is the use of heteropolyanion-doped polymers and this also improve the thermal stability (523 K) of such systems. Since, conjugated

polymers with entrapped heteropolyanions (examples include 12-molybdophosphoric acid, 12-tungstophosphoric acid, 12-tungstosilicic acid etc.,) represent interesting electrochemical systems²²⁵ whose electrochemical activity combines two types of redox processes: those associated with conjugated polymer backbone and those connected with several possible redox states of the entrapped hetero poly anions. Supports obtained by doping ion conducting polymers with electron conducting polymers can be exploited for better catalyst utilization.

The phenomenon of spillover involves the 'transport of an active species sorbed or formed on a active phase on to another phase that does not under the same condition sorb or form the species. The result may be the reaction of this species on the second phase with other sorbing moieties or the activation of the second phase²²⁶. Thus, methanol oxidation mechanism on multimetallic supported/ unsupported systems may be viewed from the concept spillover of hydrogen, oxygen and carbon monoxide. Limited literature is available on oxygen surface mobility²²⁷ and on CO spillover²²⁸. However, they are not exploited to methanol oxidation studies. In order to achieve rapid methanol electro oxidation, one has to find suitable multicomponent system, which will facilitate oxygen and/ or CO spillover.

6 Conclusion

In this article, the available literature on the various types of anode materials for DMFC applications is reviewed, keeping in mind, to bring out the rationale for the selection of these materials as well as to examine the limitations experienced in these systems. There are various kinds of supports like, conducting polymers, carbon materials, on which the active noble metals like Pt, Pt-Ru, etc., are loaded. The available information on these supported systems have not yet reached the level of maturity required for a priori / prediction and designing of the optimum material composition for anode applications in DMFC. The purpose of this presentation is therefore to critically evaluate the available information on these materials and assimilate them from the points of view of evaluation of the active surface, their geometry, size, the support effect as well as to provide directions for future studies which will enable the a priori formulation of active systems for DMFC applications.

The available data do not permit their evaluation and comparison on a normalized scale, since the variables employed and the information reported grossly in a decade for evolving such a global pattern. However, it is hoped that this presentation will pave the pathway for the evolution of such a pattern, which will be useful for selection of anodes for DMFC applications.

References

- 1 K V Kordesch and J C T Oliveira *Fuel Cells Ullmann Encyclopedia of Industrial Chemistry* VCH Weinheim Germany A12 55
- 2 J O' M Bockris and S Srinivasan *Fuel Cells: Their Electrochemistry* McGraw Hill U S A (1969)
- 3 R Narayan and B Viswanathan *Chemical and Electrochemical Energy System* University Press India (1998)
- 4 K Metkemeijer and P Achard *Int J Hydrogen Energy* **19** (1994) 535
- 5 A J Bard, R Parsons and J Jordan *Standard Potentials in Aqueous Solution* Marcel Dekker Inc New York (1985)
- 6 K V Kordesch and G Simader *Fuel Cells and Their Applications* VCH Weinheim (1996)
- 7 S Birkle, R Kircher, C Nolscher, H Voigt, B Ganser and B Hohlein *Energiewirtschaftliche Tagesfragen* **44** (1994) 441
- 8 R Parsons and T Vander Noot *J Electroanal Chem* **257** (1988) 9
- 9 NA Hampson, MJ Willars and B D McNicol *J Power Sources* **4** (1979) 191
- 10 T Iwasita, W Vielstich, C Tobias and H Gerischer *Advances in Electrochemical Science and Engineering* VCH Weinheim **1** (1990) 127
- 11 DS Cameron, GA Hards and D Thompsett *Proc Electrochem Soc* (1992) 10
- 12 W Vielstich, T Iwasita (Ed. G Ertl H Knozinger and J Weitkamp) *Handbook of Heterogeneous Catalysis* Wiley Chichester **4** (1997)
- 13 K Kordesch and G Simader *Fuel Cells and Their Applications* VCH Weinheim (1996)
- 14 G Horanyi and A Wieckowski *Proc Electrochem Soc* (1992) 192; *Proc Workshop Direct Methanol-Air Fuel Cell* (1990) 70
- 15 T Iwasita and F C Nart *J Electroanal Chem* **317** (1991) 291
- 16 S Wilhelm, T Iwasita and W Vielstich *J Electroanal Chem* **238** (1987) 383
- 17 A Papoutsis, J M Leger and C Lamy *J Electroanal Chem* **359** (1993) 141
- 18 K I Ota, Y Nakagawa and M Takahashi *J Electroanal Chem* **179** (1984) 179
- 19 K Kunimatsu *Ber Bunsenges Phys Chem* **94** (1990) 1025
- 20 P A Christensen, A Hamnett and G L Troughton *J Electroanal Chem* **362** (1993) 207
- 21 D Pletcher and V Solis *Electrochim Acta* **27** (1982) 775
- 22 K Itaya, S Sugawara, K Sashikata and N Furuya *J Vac Sci Technol A* **8** (1990) 515
- 23 (a) B J Kennedy and A Hamnett *J Electroanal Chem* **283** (1990) 271; (b) L D Burke and J K Casey *Ber Bunsenges Phys Chem* **94** (1990) 931
- 24 (a) O M Magnussen, J Hagebock, J Hotlos and B J Behm *Faraday Disc Chem Soc* **94** (1992) 329
- (b) E Herrero, K Franaszczuk and A Wieckowski *J Phys Chem* **98** (1994) 5074
- 25 J Sobkowski and A Wieckowski *J Electroanal Chem* **41** (1973) 373
- 26 (a) J Sobkowski, K Franaszczuk and K Dobrowolska *J Electroanal Chem* **330** (1992) 529; (b) G Horanyi and G Inzelt *J Electroanal Chem* **86** (1978) 215
- 27 DN Upadhyay, Y Yegnaraman and G Prabhakara Rao *J Power Sources* **36** (1991) 11
- 28 H Kita, Y Gao, T Nakato and H Hattori *J Electroanal Chem* **373** (1994) 177
- 29 S G Sun and J Clavilier *J Electroanal Chem* **236** (1987) 95
- 30 (a) V S Bagotzky and Yu B Vasil'ev *Electrochim Acta* **12** (1967) 1323; (b) R Inada K Shimazu and H Kita *J Electroanal Chem* **277** (1990) 315; (c) A K Aramata, M Masuda and T Kodera *J Electrochem Soc* **136** (1989) 3288
- 31 P A Christensen, A Hamnett and S A Weeks *J Electroanal Chem* **250** (1988) 127
- 32 A Heinzel, R Holze, C H Hamann and J K Blum *Electrochim Acta* **34** (1989) 657
- 33 (a) P A Attwood, B D McNicol, R T Short and J A Van Amstel *J Chem Soc Farad Trans* **176** (1980) 2310; (b) B D McNicol, P A Attwood and R T Short *J Chem Soc Farad Trans* **177** (1981) 2017
- 34 M Watanabe, S Saegusa and P Stonehart *J Electroanal Chem* **271** (1989) 213
- 35 B Beden, F Hahn, J M Leger, C Lamy, C L Perdriel, N R De Tacconi, R O Lezna and A J Arvia *J Electroanal Chem* **307** (1991) 129
- 36 P A Christensen, A Hamnett, J Munk and G L Troughton *J Electroanal Chem* **370** (1994) 251
- 37 H A Gasteiger, N M Markovic, P N Ross and E J Cairns *J Phys Chem* **97** (1993) 12020
- 38 H A Gasteiger, N M Markovic, P N Ross and E J Cairns *J Electrochem Soc* **141** (1994) 1795

7 Acknowledgement

The authors gratefully acknowledge the award of Research Associateship by Council of Scientific and Industrial Research (CSIR), New Delhi to the first author (MAS) and the research grant by the Ministry of Non-conventional Energy Sources (MNES), Government of India, New Delhi.

- 39 X H Xia, T Iwasita, F Ge and W Vielstich *Electrochim Acta* **41** (1996) 711
- 40 T Iwasita, W Vielstich and E Santos *J Electroanal Chem* **229** (1989) 367
- 41 B Bittins-Cattaneo, E Santos, W Vielstich and V Linke *Electrochim Acta* **33** (1988) 1499
- 42 K Wang, H A Gasteiger, N M Markovic and P N Ross *Electrochim Acta* **41** (1996) 2587
- 43 H A Gasteiger, N M Markovic and P N Ross Jr *Catal Lett* **36** (1996) 1
- 44 N M Markovic, H A Gasteiger, P N Ross, X Jiang, I Villegas and M J Weaver *Electrochim Acta* **40** (1995) 91
- 45 H A Gasteiger, N M Markovic, P N Ross and E J Cairns *Electrochim Acta* **39** (1994) 1825
- 46 K Franaszczuk, E Herrero, P Zelenay, A Wieckowski, J Wang and R I Masep *J Phys Chem* **96** (1992) 8509
- 47 R Ortiz, O P Marquez, J Marquez and C Gutierrez *J Phys Chem* **100** (1996) 8389
- 48 M M Hefny and S Abdel-Wanees *Electrochim Acta* **41** (1996) 1419
- 49 B Bittins-Cattaneo and T Iwasita *J Electroanal Chem* **238** (1987) 15
- 50 M M Janssen and J Moolhuysen *Electrochim Acta* **21** (1976) 869
- 51 T D Jarvi, S Sriramula and E M Stuve *J Phys Chem B* **101** (1997) 3649
- 52 M Watanabe, Y Genjima and K Tarumi *J Electrochem Soc* **144** (1997) 423
- 53 H Matsui and A Kunugi *J Electroanal Chem* **292** (1990) 103
- 54 K -I Machida, A Fukuoka, M Ichikawa and M Enyo *J Electrochem Soc* **138** (1991) 1958
- 55 E Ticianelli, J G Berry, M T Paffett and S Gottesfeld *J Electroanal Chem* **258** (1989) 61
- 56 J Sobkowski, K Franaszczuk and A Piasecki *J Electroanal Chem* **196** (1985) 145
- 57 H Ogasawara and M Ito *Chem Phys Lett* **245** (1995) 304
- 58 T Iwasita, F C Nart, B Lopez and W Vielstich *Electrochim Acta* **37** (1992) 2361
- 59 R Lanniello, V M Schmidt, U Stimming, J Stumper and A Wallau *Electrochim Acta* **39** (1994) 1863
- 60 E P M Leiva and M C Giordano *J Electrochem Soc* **130** (1983) 1305
- 61 M Cstroluna, M C Giordano and A J Arvia *J Electroanal Chem* **259** (1989) 173
- 62 A V Tripkovic and K D J Popovic *Electrochim Acta* **41** (1996) 2385
- 63 N M Markovic and P N Ross *J Electroanal Chem* **330** (1992) 499
- 64 B D McNicol *J Electroanal Chem* **118** (1981) 71
- 65 S Srinivasan *J Electroanal Chem* **118** (1981) 51
- 66 A J Appleby *J Electroanal Chem* **118** (1981) 31
- 67 J O M Bockris, B E Conway, E Yeager and R E White *Comprehensive Treatise of Electrochemistry* Plenum Press New York **3** 1981
- 68 B D McNicol (Ed. W E O'Grady, S Srinivasan and R F Dudley) *Proc Workshop on the Electrocatalysis of Fuel Cell Reactions* The Electrochemical Society Pennington 1978 p 93
- 69 O Lindstrom and C Sylwan *J Electrochem Soc* **126** (1979) C 109
- 70 N A Hampson, M J Willars and B D McNicol *J Power Sources* **4** (1979) 191
- 71 V S Bagotskii and A M Skundin *Chemical Power Sources* Academic Press New York (1980)
- 72 A Capon and R Parsons *J Electroanal Chem* **45** (1973) 205
- 73 A Capon and R Parsons *J Electroanal Chem* **44** (1973) 239
- 74 A Hamnett *Catalysis Today* **38** (1997) 445
- 75 S Wasmus and A Kuver *J Electroanal Chem* **461** (1999) 14
- 76 (a) K J Cathro *Electrochem Tech* **5** (1967) 441; (b) K J Cathro *J Electrochem Soc* **116** (1969) 1609
- 77 (a) J Wang, H Nakajima and H Kita *J Electroanal Chem* **250** (1988) 213; (b) H Nakajima *J Chem Tech Biotechnol* **50** (1991) 555
- 78 G L Troughton and A Hamnett *Bull Electrochem* **7** (1991) 488
- 79 (a) A S Arico, P Creti, N Giordano, V Antonucci, P L Antonucci and A Chuvilin *J Appl Electrochem* **26** (1996) 959; (b) A S Arico, Z Poltarzewski, H Kim, A Morana, H Giordano and V Antonucci *J Power Sources* **55** (1999) 159
- 80 A Hamnett, B J Kennedy and S A Weeks *J Electroanal Chem* **240** (1988) 355
- 81 A Hamnett, P Stevens and G L Troughton *Catalysis Today* **7** (1990) 219
- 82 (a) P K Shen and A C C Tseung *Proc 186th Meeting of Electrochem Soc Ext Abstr* 576 Hawaii 16-21 May 1993; (b) A K Shukla, M K Ravikumar, A S. Arico, G Candiano, V Antonucci, N Giordano and A Hamnett *J Appl Electrochem* **25** (1995) 528; (c) K I Machida, M Enyo, G Y Adachi and J Shiokawa *J Electrochem Soc* **135** (1988) 1955; (d) T Ohmari, Y Nodasaka and M Enyo *J Electroanal Chem* **281** (1990) 331; (e) P C Biswass, T Ohmari and M Enyo *J Electroanal Chem* **305** (1991) 205; (f) A C C Tseung and K Y Chen *Catalysis Today* **38** (1997) 439; (g) K Lasch, L Jorissen and J Garche *J Power Sources* **84** (1999) 225
- 83 (a) J H White and A F Sammells *J Electrochem Soc* **140** (1993) 2167; (b) K L Machida, M Enyo, G Y Adachi and J Shiokawa *Bull Chem Soc Jap* **60** (1987) 411
- 84 (a) R Ya Shaidullin, A P Semenova, G D Vovchenko and Yu B Vasiliev *Zh Fiz Khim* **57** (1983) 1019; M S U-Zanartu, P Bravo and J Zagal *J Electroanal Chem* **337** (1992) 241; (b) H Okamoto, G Kawamura, A Ishikawa and E Kudo *J Electrochem Soc* **134** (1987) 1645; (c) S Ya Vasina, S A Stuken, O A Petrii, I L Gogichadz and V A Mukhin *Elektrokhimiya* **23** (1987) 1127; C C Hays, R Manoharan and J B Goodenough *J Power Source* **45** (1993) 291; (d) A Kawahima, T Kanda and K Rashimoto *Mat Sci Eng* **99** (1988) 521
- 85 (a) O A Petrii, B I Podlovchenko, A N Frumkin and Hiralal *J Electroanal Chem* **10** (1965) 253; (b) R Binder, A Kohling and G Sandstede (Ed. B S Baker) *Hydrocarbon Fuel Cell Technology* (1965) Academic Press New York 91; (c) V S Entina and O A Petrii *Elektrokhimiya* **4** (1968) 678

- 86 (a) M Watanabe, T Suzuki and S Motoo *Denki Kagaku* **38** (1970) 927; (b) M Watanabe, T Suzuki and S Motoo *Denki Kagaku* **39** (1971) 394; (c) M Watanabe, T Suzuki and S Motoo *Denki Kagaku* **40** (1972) 205 & 210; (d) M Watanabe and S Motoo *Denki Kagaku* **41** (1973) 190; (e) M Watanabe and S Motoo *J Electroanal Chem* **60** (1975) 267
- 87 M Watanabe, M Uchida and S Motoo *J Electroanal Chem* **229** (1987) 395
- 88 T Iwasita, F C Nart and W Vielstich *Ber Bunsenges Phys Chem* **94** (1990) 1030
- 89 P A Christensen, A Hamnett, J Munk and E Skou *J Appl Electrochem* **401** (1996) 215
- 90 M Krausa and W Vielstich *J Electroanal Chem* **279** (1994) 307
- 91 B J Kennedy and A Hamnett *J Electroanal Chem* **283** (1990) 271; J B Goodenough, A Hamnett, B J Kennedy and S A Weeks *Electrochim Acta* **32** (1987) 1233; L D Bruke and J K Casey *Ber Bunsenges Phys Chem* **94** (1990) 931
- 92 (a) J B Goodenough, A Hamnett, B J Kennedy, R Manoharan and S A Weeks *J Electroanal Chem* **240** (1988) 133; (b) K Franasczuk and J Sobkowski *J Electroanal Chem* **327** (1992) 235
- 93 B J Wagner, B J Kennedy and F E Wagner *J Catal* **124** (1990) 30
- 94 A Hamnett, S A Weeks, B J Kennedy, G Troughton and P A Christensen *Ber Bunsenges Phys Chem* **94** (1990) 1014
- 95 (a) R A Gasteiger, N M Markovic, P N Ross and E J Cairns *J Electrochem Soc* **141** (1994) 1795; (b) P N Ross and R A Gasteiger *Proc First Inter Symp on New Mater for Fuel Cell Systems* Montreal July 9-13 1995; (c) K Wang, R A Gasteiger, N M Markovic and P N Ross *Electrochim Acta* **41** (1996) 2587; (d) N M Markovic, R A Gasteiger, P N Ross, X Jiang, I Villegas and M J Weaver *Electrochim Acta* **40** (1995) 91; (e) R A Gasteiger, N M Markovic, P N Ross and E J Cairns *Electrochim Acta* **39** (1994) 1825
- 96 H A Gasteiger *Interface* **3** (1994) 49
- 97 W Chrzanowski, R Kim, G T Filho, A Wieckowski, B Grzybowska and Kulesza *J New Mat Electrochem Systems* **1** (1998) 31
- 98 D R Rolison, P L Ragans, K E Swider and J W Long *Langmuir* **15** (1999) 774
- 99 T Iwasita, R Roster, A J Anacker, W F Lin and W Vielstich *Langmuir* **16** (2000) 522
- 100 D S Cameron, G A Havds and D Thompsett *Proc Electrochemical Societies* (1992) 92-14 *Proc Workshop Direct Methanol-Air Fuel Cell* (1990) 10
- 101 A B Anderson, E Grantscharora and P Shiller *J Electrochem Soc* **142** (1995) 1880
- 102 (a) B Bittins-Cattaneo and T Iwasita *J Electroanal Chem* **238** (1987) 151; (b) J Sobkowski, K Franasczuk and A Piasecki *J Electroanal Chem* **196** (1985) 145; (c) T Frelink, W Visscher and J A R van Veen *Electrochim Acta* **39** (1994) 1871; (d) M Watanabe, Y Furuuchi and S Motoo *J Electroanal Chem* **191** (1985) 367
- 103 Z Wei, H Guo and Z Tang *J Power Sources* **58** (1996) 239
- 104 K L Ley, R Liu, C Pu, Q Fan, N Leyarovska, C Segre and E S Smotkin *J Electrochem Soc* **144** (1997) 1543
- 105 E Reddington, A Sapienza, B Gurau, R Viswanathan, S Sarangapani, E S Smotkin, T E Mallouk *Science* **280** (1998) 1735
- 106 R Moss *Catalysis* **4** (1981) 131
- 107 P J Kulesza and L R Faulkner *J Electrochem Soc* **136** (1989) 707
- 108 J Hanika, V Macheck, V Nemeč, V Ruzicka and J Kunz *J Catal* **77** (1982) 248
- 109 V Macheck, V Ruzicka, M Souvkova, J Kunz and L Janacek *Collect Czech Chem Commun* **48** (1983) 517
- 110 P Ehrburger, O P Mahajan and P L Walker Jr *J Catal* **43** (1976) 61
- 111 A Linares-Solano, F R Reinoso, C S Martinez Delecea, O P Mahajan and P L Walker *Carbon* **201** (1982) 177
- 112 F R Reinoso, F R Ramos, C M Castilla, A G Ruiz and J D Lo-Gonzalez *J Catal* **99** (1986) 171
- 113 P Ehrburger, A Mongilardi and J Lahaye *J Colloid Interface Sci* **91** (1983) 151
- 114 P Ehrburger *Adv Colloid Interface Sci* **21** (1984) 275
- 115 K Kinoshita *Carbon: Electrochemical and Physicochemical Properties* John Wiley & Sons Inc New York (1987)
- 116 K Kinoshita and P Stonehart *Modern Aspects of Electrochemistry* 12 (Eds. J O'M Bockris and B E Conway) Plenum Press **12** New York (1997)
- 117 M B Palmer and M A Varulice *J Chem Tech Biotechnol* **30** (1980) 205
- 118 D Richard and P Gallezot *Preparation of Catalysts* (Eds. B Delmon, P Grange, P T Jacobs and G Poncelet) Elsevier Amsterdam (1987)
- 119 J Hanika, V Macheck, V Nemeč, V Ruzicka and J Kunz *J Catal* **77** (1982) 248
- 120 D Jannakoudakis and E Theodoridou *Synth Met* **10** (1984/1985) 131
- 121 K F Blurton *Carbon* **10** (1972) 305
- 122 H G Petrow and R J Allen *Catalytic Platinum Metal Particles on a Substrate* U S Patent 3992331 (November 16 1976)
- 123 H G Petrow and R J Allen *Finely Particulated Colloidal Platinum Compound and Sol for Producing It* U S Patent 3 992 512 (November 16 1976)
- 124 F G Ciapetta and C J Plank *Catalysis Fundamental Principles* (part I) vol I (Ed P.H Emmett) Reinhold New York 315
- 125 S C Davis and K J Klabunde *Chem Rev* **82** (1982) 153
- 126 N M Kagen, G F Muchnik, Y N Pisarev, Y A Kaller and V A Panchenko *Elektrokhimiya* **9** (1973) 1498
- 127 A Stoyanova, V Naidenov, K Petrov, I Nikolov, T Vitanov and K Budevski *J Appl Electrochem* **29** (1999) 1197
- 128 K Jakikozawa, J Fujii, J Matsuda, K Nishimura and J Takasu *Electrochim Acta* **36** (1991) 973
- 129 J B Goodenough, A Hamnett, B J Kennedy and S A Weeks *Electrochim Acta* **32** (1987) 1233
- 130 (a) A Katayama *J Phys Chem* **84** (1980) 376; (b) A Katayama and R Ohnishi *J Electroanal Chem* **162** (1984) 153
- 131 R Van Hardeveld and A Von Montfoort *Surf Sci* **4** (1966) 396
- 132 H E Vandam and H Van Bekkum *J Catal* **131** (1991) 335

- 133 J Wang, G M Swain, T Tachibana and K Kobashi *Electrochem Soc Solid State Lett* **3** (2000) 286
- 134 H Guo and A R Guadalupe *Langmuir* **15** (1999) 759
- 135 T J Schmidt, H A Gasteiger and R J Behm *Electrochem Comm* **1** (1998) 1
- 136 K Y Chen, P K Shen and A C C Tseung *J Electrochem Soc* **142** (1995) L185
- 137 P K Shen and A C C Tseung *J Electrochem Soc* **141** (1994) 3082
- 138 K Y Chen, Z Sun and A C C Tseung *Electrochem Soc Solid State Lett* **3** (2000) 10
- 139 M C R Martinez, D C Amoros, H Yamashita, S Demiguel and O A Scelza *Langmuir* **16** (2000) 1123
- 140 K F Blurton, P Greenberg, H G Oswin and D R Rutt *J Electrochem Soc* (1972) 559
- 141 P Stonehart *Electrochim Acta* **18** (1973) 343 349 907; **20** (1975) 101; **23** (1977) 45
- 142 P Stonehart, J A Bett and K Kinoshita (Ed. M W Breiter) *Proc Symp Electrocatalysis San Francisco The Electrochem Soc Princeton NJ* (1974) p 275
- 143 O M Poltorak and V S Boronin *Intern Chem Eng* **7** (1967) 452
- 144 C S Nicolau, H G Thorn and E Pobitschka *Trans Faraday Soc* **55** (1959) 1430
- 145 L J Hillenbrand and J W Lacksonen *J Electrochem Soc* **112** (1965) 245
- 146 L J Hillenbrand and J W Lacksonen *J Electrochem Soc* **112** (1965) 249
- 147 Y Takasu, J Fujii and Y Matsuda *Bull Chem Soc Jpn* **59** (1986) 3937
- 148 L J Bregoli *Electrochim Acta* **23** (1978) 489
- 149 P N Ross (Ed. U V Rao *Precious Metals* (1986) *International Precious Metal Institute Allentown PA* 1986 355 M L Sattler and P N Ross *Ultramicroscopy* **20** (1986) 21
- 150 K Kinoshita (Ed. J O M. Bockris, B E Conway and R E White) *Modern Aspects of Electrochemistry* Plenum Press New York **4** (1982) p 557
- 151 (a) M Watanabe, S Saegusa and P Stonehart *Chem Lett* (1988) 1487; (b) M Watanabe H Sei and P Stonehart *J Electroanal Chem* **261** (1989) 375
- 152 N Giordano, E Passalacqua, L Pino, A S Aric, V Antonucci, M Vivaldi, K Kinoshita *Electrochim Acta* **36** (1991) 1979
- 153 F Parmigiani, E Kay and P S Bagus *J Electron Spectrosc Relat Phenom* **50** (1990) 39
- 154 Y Takasu, J Fujii, K Yasuda, Y Iwanaga and Y Matsuda *Electrochim Acta* **34** (1989) 453
- 155 P A Attwood, B D McNicol and R T Short *J Appl Electrochem* **10** (1980) 213
- 156 P L Antonucci, V Alderucci, N Giordano, D L Cooke and H Kim *J Appl Electrochem* **24** (1994) 944
- 157 M Enyo, K Machida, A Fukuoka and M Ichikawa (Ed. O J Murphy) *Electrochemistry in Transition* Plenum Press New York p 359
- 158 K Yahikozawa, J Fujii, Y Matsuda, K Nishimura and Y Takasu *Electrochim Acta* **36** (1991) 973
- 159 T Frelink, W Visscher and J A R Vanveen *J Electroanal Chem* **382** (1995) 65
- 160 (a) H P Boehm, E Diehl, W Heck and R Sappok *Angewandte Chem (Engl Ed)* **3** (1964) 669; (b) J B Donnet *Carbon* **6** (1968) 161; (c) M L Deriney *Adv Coll Interface Sci* **2** (1969) 237; (d) B R Puri *Chemistry and Physics of Carbon 6* (Ed. P I Walker) Decker New York (1970) 191; (e) J B Donnet *Carbon* **20** (1982) 267
- 161 J B Donnet and A Voet *Carbon Black- Physics Chemistry and Elastomer Reinforcement* Marcel Decker Inc New York (1976)
- 162 (a) P L Antonucci, V Alderucci, N Giordano, D L Cocke and H Kim *J Appl Electrochem* **24** (1994) 58; (b) A K Shukla, A Hamnett, A Roy, S R Barman, D D Sarma, V Alderucci, L Pino and N Giordano *J Electroanal Chem* **352** (1993) 337; (c) C P Burguete, A L Solano, F R Reinoso and C S Martinez de Lecea *J Catal* **115** (1989) 98; (d) F C Pasual, A S Escibano, J L G Fierro and F R Reinoso *Langmuir* **10** (1994) 750; (e) H E van Dam and H van Bekkum *J Catal* **131** (1991) 335
- 163 J S Mattson and H B Mark *Activated Carbon: Surface Chemistry and Adsorption from Solution* Decker New York 1971
- 164 H P Boehm *Advances in Catalysis* (Ed. D D Eley, H Pines and P B Weisz) Academic Press New York **16** (1966) 179
- 165 F R Reinoso, J D L Gon Zalez and C Berenguer *Carbon* **22** (1984) 13
- 166 (a) J Hanika, V Macheck, V Nemeck, V Ruzicka and J Kunz *J Catal* **77** (1982) 248; (b) V Macheck, V Ruzicka, M Sourkova, J Kunz and L Janacek *Collect Czech Chem Commun* **48** (1983) 517
- 167 C Flynn and S E Wanke *J Catal* **37** (1975) 423
- 168 S C Roy, A W Harding, A E Russell and K M Thomas *J Electrochem Soc* **144** (1997) 2323
- 169 (a) S C Roy, P A Christensen, A Hamnett, K M Thomas and V Trapp *J Electrochem Soc* **143** (1986) 3073; (b) C W Hills, M S Nashinov, A I Frenkel, J R Shapley and R G Nuzzo *Langmuir* **15** (1999) 690; (c) K E Swider and D R Rolison *J Electrochem Soc* **143** (1996) 813
- 170 K E Swider and D R Rolison *Electrochem Solid State Lett* **3** (2000) 4
- 171 T E Fischer and S R Keleman *J Catal* **53** (1978) 24
- 172 (a) J Oudar *Catal Rev-Sci Eng* **22** (1980) 171; (b) G C Bond *Catalysis by Metals* Academic Press New York (1962)
- 173 K E Swider and D R Rolison *Langmuir* **15** (1999) 3302
- 174 B J Kennedy and A Hamnett *J Electroanal Chem* **283** (1990) 271
- 175 V Radmilovic, H A Gasteiger and P N Ross *J Catal* **154** (1995) 98
- 176 M Morita, Y Iwanaga and Y Matsuda *Electrochim Acta* **36** (1991) 947
- 177 R S A Babu, S S Murthy and B Viswanathan *Stud Surf Sci Catal* **131C** (1998) 787
- 178 H Zhang, Y Wang, E R Fachini and C R Cabrera *Electrochem Solid State Lett* **2** (1999) 437
- 179 C W Hills *Langmuir* **15** (1999) 690

- 180 C L Chiders, H Huang and C Korzeniewski *Langumir* **15** (1999) 786
- 181 P K Guha, A Bhattacharya and K K Kundu *Indian J Chem* **28A** (1989) 267
- 182 (a) P K Guha, A Bhattacharya and K K Kundu *Indian J Chem* **28A** (1989) 825; (b) T Frelink, W Visscher and J A R van Veen *J Electronal Chem* **382** (1995) 65
- 183 P K Guha, A Bhattacharya and K K Kundu *Indian J Chem* **28A** (1989) 735
- 184 (a) S Iijima *Nature* **354** (1991) 56; (b) M S Dresselhaus, G Dresselhaus and P C Eklund *Science of Fullerenes and Carbon Nanotubes* Academic Press New York 1996; (c) T W Ebbesen *Carbon Nanotubes: Preparation and Properties* CRC Press Boca Raton FL (1997) 225; (d) A C Dillon, K M Jones, T A Bekkedahl, C H Kiang, D S Bethune and M J Heben *Nature* **386** (1997) 377; (e) V Z Mordkovich, M Bazendale, R P H Chang and S Yoshimera *Synth Met* **86** (1997) 2049; (f) C Niu, E K Sichel, R Hoch, D Moy and H Tennet *Appl Phys Lett* **70** (1997) 1480; (g) J M Planeix, N Coustel, B Coq, V Brotons, P S Kumbhar, R Dutartre, P Geneste, P Bemier and P M Ajayan *J Am Chem Soc* **116** (1994) 7935; (h) P J Britto, K S V Santhanam and P M Ajayan *Bioelectrochem Bioenerg* **41** (1996) 121 (i) J J Davis, R J Coles and A O H Allen *J Electroanal Chem* **440** (1997) 270
- 185 (a) C R Martin *Science* **226** (1994) 1961; (b) C R Martin *Acc Chem Res* **28** (1995) 61; (c) C R Martin *Chem Mater* **8** (1996) 1739
- 186 G L Che, B B Lakshmi, C R Martin, E R Fisher and R S Ruoff *Chem Mater* **10** (1998) 260
- 187 (a) T Kyotani, L F Tsai and A Tomita *Chem Commun* (1997) 701; (b) T Kyotani, L F Tsai and A Tomita *Chem Mater* **7** (1995) 1427; (c) T Kyotani, L F Tsai and A Tomita *Chem Mater* **8** (1996) 2109
- 188 (a) B Rajesh, K R Thampi, J M Bonard and B Viswanathan *J Mater Chem* **10** (2000) 1757; (b) B Rajesh, K R Thampi, J M Bonard and B Viswanathan *Bull Mater Sci* **23** (2000) 341; (c) C A Bessel, K Laubernds, N M Rodriguez and R T K Baker *J Phys Chem* **105** (2001) 1115
- 189 C Beard and P N Ross *J Electrochem Soc* **133** (1986) 1839
- 190 (a) F T A Vork, L J Janseen and E Barendrecht *Electrochim Acta* **31** (1986) 1569; (b) M Gholamian and A Q Contractor *J Electronal Chem* **289** (1990) 69; (c) M Gholamian, J Sundaram and A Q Contractor *Langmuir* **3** (1987) 741; (d) K M Kost, D E Bartak, B Kazee and T Kuwana *Anal Chem* **60** (1988) 2379; (e) P O Esteban, J M Leger, C Lamy and E Genies *J Appl Electrochem* **19** (1989) 462; (f) H Laborde, J M Leger and C Lamy *J Appl Electrochem* **24** (1994) 219; (g) K Shimazu, R Inada and H Kita *J Electroanal Chem* **284** (1996) 523; (h) W T Napporn, H Laborde, J M Leger and C Lamy *J Electroanal Chem* **404** (1996) 153; (i) F Ficiocioglu and F Kadirgan *J Electroanal Chem* **430** (1997) 179; (j) W T Napporn, H Laborde, J M Leger and C Lamy *J Electroanal Chem* **404** (1996) 153; (k) C T Hable and M S Wrighton *Langmuir* **9** (1993) 3284; (i) H Laborde, J M Leger and C Lamy *J Appl Electrochem* **24** (1994) 1019
- 191 (a) E M Genies and C Tsintavis *J Electroanal Chem* **195** (1985) 109; (b) D J Strike, N F De Rooij, M K Hep, M Ulmann and J Augustynski *J Appl Electrochem* **22** (1992) 922.; (c) M Ulmann, R Kostecki, J Augustynski, D J Strike and M K Hep *Chimia* **46** (1992) 138; (d) H Yang, T Lu, K Xue, S Sun, C Lu and S Chen *J Electrochem Soc* **144** (1997) 230; (e) M Hepel *J Electrochem Soc* **145** (1998) 124
- 192 S Swathirajan and Y M Mikhail *J Electrochem Soc* **139** (1992) 2105
- 193 P J Kulesza, M Matezak, A Wolkiewicz, B Grzybowska, M Galkowski, M A Malik and A Wieckowski *Electrochim Acta* **44** (1999) 2131
- 194 A Kelaidopoulou, E Abelidou and G Kokknidis *J Appl Electrochem* **29** (1999) 1255
- 195 H Laborde, J M Leger, C Lamy, F Gamier and A Yassar *J Appl Electrochem* **20** (1990) 524
- 196 H Naarman and H J Sterzel *Ger Offen* DE 3912735 (1990)
- 197 (a) T A Skotheim *Handbook of Conducting Polymers* Marcel Dekkar New York (1986); (b) E M Genies, A Boyle, M Lapkowski and C Tsintavis *Synth Met* **36** (1990) 139; (c) W S Huang, B D Humphrey and A G MacDiarmid *J Chem Soc Faraday Trans* **52** (1986) 2385; (d) E M Genies and C Tsintavis *J Electroanal Chem* **195** (1985) 109
- 198 S U Byun and S S Irn *J Appl Polym Sci* **56** (1995) 425
- 199 (a) R DeSurrille, M Jozefowicz, L T Yu, J Perichon and R Buvet *Electrochim Acta* **13** (1968) 1451; (b) A MacDiarmid, J C Chiang, M Halpern, W S Huang, J R Krawczyk, R J Mammone, S L Mu, N I Somasiri and W Wu *Polym Prepr Am Chem Soc Div Polym Chem* **25** (1984) 248; (c) A G Green and A E Woodhead *J Chem Soc (Trans)* **97** (1910) 2388; (d) A G Green and A E Woodhead *J Chem Soc (Trans)* **107** (1912) 1117
- 200 (a) A Kitani, M Kaya and K Sasaki *J Electrochem Soc* **133** (1986) 1069; (b) N Noufi, A J Nozik, J White and L F Warren *J Electrochem Soc* **129** (1982) 2261; (c) A Volkov, G Tourillon, P C Lacaze and J E Dubois *J Electroanal Chem* **115** (1980) 279; (d) A F Diaz and J A Logan *J Electroanal Chem* **111** (1980) 111; (e) A Kitani, J Izumi, J Yano, Y Hiromoto and K Sasaki *Bull Chem Soc Jpn* **57** (1984) 2254; (f) C Carlin, L J Kepley and A J Bard *J Electrochem Soc* **132** (1985) 353; (g) S H Glarum and J H Marshall *J Electrochem Soc* **134** (1987) 142
- 201 D E Stilwell and S M Park *J Electrochem Soc* **135** (1988) 2497
- 202 A F Diaz, K K Kanazawa and G P Gardini *J Chem Soc Comm* (1979) 635
- 203 G K Chandler and D Pletcher *Specialist Periodical Report on Electrochemistry* Royal Society of Chemistry London **101** (1985) 115
- 204 G K Chandler and D Pletcher *J Appl Electrochem* **16** (1986) 62
- 205 J Y Lee and T C Tan *J Electrochem Soc* **137** (1990) 1402
- 206 S Holdcroft and B L Funi *J Electroanal Chem* **240** (1988) 89
- 207 M Zhou and J Heinze *Electrochim Acta* **44** (1999) 1733
- 208 (a) T Ohsaka, S Kunimura and N Oyama *Electrochim Acta* **33** (1988) 894; (b) C Barbero, J J Silber and L Sereno *J Electroanal Chem* **291** (1990) 81; (c) C Barbero, J J Silber and L Sereno *J Electroanal Chem* **263** (1989) 333; (d) S

- Kunimura, T Ohsaka and N Oyama *Macromolecules* **21** (1988) 894
- 209 P J Peerce and A J Bard *J Electroanal Chem* **112** (1980) 97
- 210 G Kokkinidis, A Papoutsis and I Poulis *J Electroanal Chem* **379** (1994) 379
- 211 (a) K Chiba, T Ohsaka and N Oyama *J Electroanal Chem* **219** (1987) 117; (b) J Yano, A Shimoyama and K Ogura *J Chem Soc Faraday Trans* **88** (1992) 2523; (c) D Sazou, I Poulis and G Kokkinidis *Synth Met* **32** (1989) 113
- 212 E Vork and E Barendrecht *Synth Met* **28** (1989) C121
- 213 (a) B Beden, F Kadirgan, C Lamy and J M Leger *J Electroanal Chem* **127** (1981) 75 & 142 (1982) 171; (b) G Kokkinidis and D Jannakoudakis *J Electroanal Chem* **153** (1983) 185
- 214 (a) P J Kulesza and M Bandoch *J Electroanal Chem* **323** (1992) 131; (b) P J Kulesza *J Electroanal Chem* **220** (1987) 295
- 215 L D Burke, J K Muleahy and S Venkatesan *J Electroanal Chem* **73** (1976) 207; **81** (1977) 339
- 216 (a) H A Gasteiger, N M Markovic, P N Ross and E J Cairns *J Electrochem Soc* **141** (1994) 1795; (b) B N Grgur, C Zhuang, N M Markovic and P N Ross *J Phys Chem B* **101** (1997) 3910; (c) X Ren, M S Wilson and S Gottesfeld *J Electrochem Soc* **143** (1996) L12
- 217 A K Aramata and R Ohnishi *J Am Chem Soc* **105** (1983) 658
- 218 M C Lefebvre, Z Qi and P G Pickup *J Electrochem Soc* **146** (1999) 2054
- 219 S Ghosh and O Inganas *Electrochem Solid State Lett* **3** (2000) 213
- 220 K Shivazu, R Inada and H Kita *J Electroanal Chem* **284** (1990) 523
- 221 R X Liu, K Triantafillou, L Liu, C Pu, C Smith and E S Smotkin *J Electrochem Soc* **144** (1997) 148
- 222 E B Easton and P G Pickup *Electrochem Solid State Lett* **3** (2000) 23
- 223 V D Pokhodenko, V A Krylov and Y I Kurys *Theor Expt Chem* **31** (1995) 301
- 224 M G Kanatzidis and C G Wu *J Am Chem Soc* **111** (1989) 4139
- 225 K Pielichowski and M Hasik *Synth Met* **89** (1997) 199
- 226 W C Conner, G M Pajonk and S J Teichner *Adv Catal* **34** (1986) 1
- 227 (a) B Delmon *Stud Surf Sci Catal* **112** (1997) 1; (b) B Delmon *Stud Surf Sci Catal* **112** (1997) 179; (c) B Zhou, E Sham, T Machej, P Bertrand, P Ruiz and B Delmon *J Catal* **132** (1991) 157; (d) F M Faus, B Zhou, H Matrails and B Delmon *J Catal* **132** (1991) 200; (e) L T Weng and B Delmon *Appl Catal A* **81** (1992) 141; (f) E M Gaigneaux, P Tsiakaras, D Herla, L Gahenne, P Ruiz and B Delmon *Catal Today* **33** (1997) 151; (g) L T Weng, L Cadus, P Ruiz and B Delmon *Catal Today* **11** (1992) 455
- 228 (a) T Inui, Y Ono, Y Takagi and J B Kim *Appl Catal A* **202** (2000) 212; (b) S R Samms, S Wasmus, R F Savinell *J Electrochem Soc* **143** (1996) 1498