

# Platinum based Anode Catalyst Systems for Direct Methanol Fuel Cells

B. Viswanathan

National Centre for Catalysis Research

Indian Institute of Technology, Madras, Chennai 600 036

## 1. Introduction

The development of efficient energy conversion devices has been one of the motivations for scientific research for over a century. Among the various devices so far developed, Fuel cells assume an important position since the efficiency of these devices can exceed even at times the Carnot limitation. Among the various types of fuel cells, the Proton Exchange Membrane Fuel Cells (PEMFC) have been advocated for a variety of stationary and mobile applications because of its efficiency [1]. The obtained efficiency in the energy conversion process of these devices is due to low operating temperature employed, low pollution emission, easy transportation feasibility and high-power density. Though conventional PEMFC devices employ hydrogen as fuel at the anode and oxygen/air as reductant in the cathode and Pt as the most active metal electrodes for fuel cell reactions [2,3], alternate catalyst systems have also been examined at various times [4,5]. Among the various versions of the PEMFC, Direct Methanol Fuel cells (DMFC) have been receiving extensive attention as promising energy conversion devices due to the fact that they employ renewable liquid methanol as fuel which is safe for storage and transportation [6]. In addition, DMFCs exhibit considerable anodic reaction rates since methanol oxidation does not involve the C-C bond breakage and also methanol has a high energy density ( $6100 \text{ Wh kg}^{-1}$ ). In spite of all these developments, the current level of technology of catalysts is insufficient to support large-scale commercialization of these devices. The basic challenges involve addressing the sluggish kinetic rates of methanol oxidation (anodic reaction) and the cathodic oxygen reduction reaction (ORR) [7]. There is a phenomenon called methanol cross over from anode to the cathode and thus affect adversely the cathodic reaction. The anodic electrodes employed in DMFC are most often poisoned or susceptible to the partial oxidation products like CO of methanol and it has become necessary to eliminate or promote the complete combustion of these partially combusted intermediates by adding another metallic component to the mostly employed platinum electrodes. This has led to development of many multi-metallic catalyst systems in which the added component normally promotes the oxidation of partial combusted products like CO which otherwise blocks the Pt sites required for the oxidative adsorption of methanol [8, 9]. The factors that are considered for the selection of another metal to be added to Pt are the adsorption enthalpy and the electrode potential [9]. Since the energy required to form CO is less than that for  $\text{CO}_2$ , the indirect reaction is favoured and in order to avoid the formation of CO on Pt electrodes binary or hybrid alloys of Pt are employed as electrocatalytic materials on DMFC anodes [10-15]. It is known that addition of Ru to Pt prevents the adsorption of CO by decreasing the oxidation over potential of the anode [16]. It has become mandatory that the extent of loading of Pt must be considerably reduced ( the total catalyst loading desirable in DMFC application is in the range of

0.2 to 0.5 mg/cm<sup>2</sup>) if these devices were to be affordable, thus it means that the existing electrode material based on Pt should be combined with another less costlier element ( since the cost of Pt is higher than \$ 1600 per Oz). These efforts have led to a number of studies concerning the fabrication of the Pt based electrodes, since the catalytic activity is dependent on the particle shape, size and size distribution.[17]. However, the conventional methods of preparation of wet impregnation and chemical reduction of the metal precursors do not always yield desired particle shape and size [17]. Alternate synthesis methods have been developed based on microemulsion [18], sonochemistry [19.20], and microwave irradiation [[21-25]. These methods can generate controlled colloids and clusters on the nanoscale and with greater uniformity [26]. In addition to these methods, other methods like surface functionalization of the carbon support, electrochemical deposition, electroless deposition and other physical methods have also been resorted to control the particle size of the metal anodes for DMFC application [27,28].

Though Pt has been the most effective catalyst system so far studied for Methanol Oxidation Reaction (MOR), addition of another metal like Fe, Co, Ni, Ru, Rh and Sn to Pt Is considered desirable to overcome the poisoning effect arising due to adsorbed CO [7]. Generally, the bifunctional mechanism and ligand effect (electronic factor) are proposed to account for the increased electrocatalytic activity of Pt-Me systems for MOR. It is conceived that methanol adsorption and oxidation take place on Pt sites and the added metal facilitates the dissociation of water at lower potential and thus promote the oxidation of adsorbed CO. In terms of the ligand effect, the added metal alters the electronic property of Pt and lowers the adsorption energy of adsorbed CO thus promoting the oxidation of adsorbed CO at a lower electrode potential. This means that the d and sp band structures of metallic Pt or in other words the Density of States (DOS) in these two bands constituted by the frontier orbitals of the metal is the critical factor. The density of states of d and sp band for Pt is shown in Fig.1. It is seen that the orbital character at the Fermi surface is composed of mainly sp orbital character with the d level participation is below the Fermi level. This type of directional character of the filled and unfilled orbitals at the Fermi surface may be responsible for the observed poisoning by adsorbed CO.

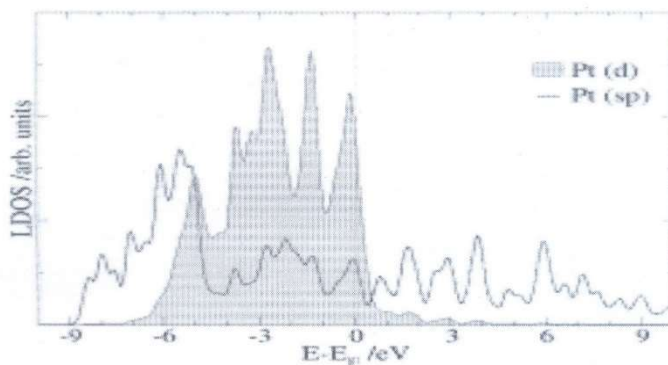
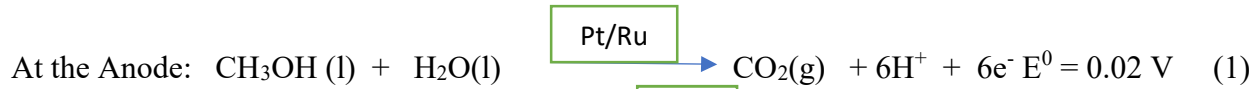


Fig 1 The density of states of d and sp orbitals of Pt. Note that at the Fermi level the shape of d and sp bands [Figure reproduced from web and also adopted from ref.29]

## 2. DMFC Reactions

The reactions that take place in a DMFC can be represented by the following equations



It is essential to comprehend the working of a practical DMFC. The components and reactions taking in the respective electrodes are shown in Fig.2.

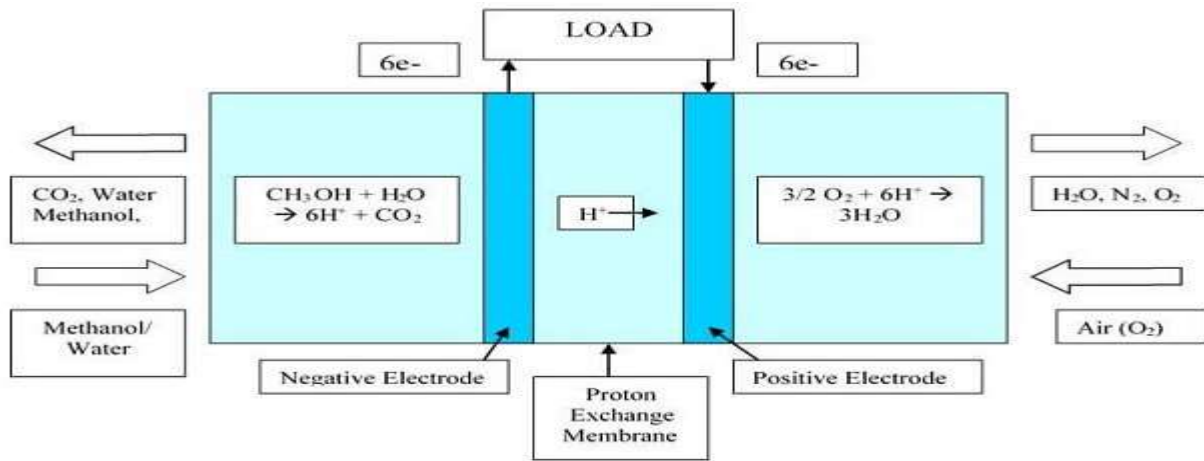


Fig.2. Schematic and reactions taking place in the respective electrodes in DMFC [adopted and reproduced from ref [30]].

It is known that the widespread application of these cells employs mostly Pt or Pt based electrodes. However, most of these tried alternative electrode materials perform at low levels and hence immediately cannot replace the use of platinum. In addition, as stated above, the formation and accumulation of the surface intermediate species of the oxidation of methanol such as  $\text{CO}_{\text{ad}}$  and  $\text{CHO}_{\text{ad}}$  are adsorbed on Pt surfaces and hence limit the efficiency of the electrode reactions due to the poisoning of the active Pt sites. In order to develop electrodes with greater tolerance to CO, a second metal which will promote the oxidation of CO is usually associated with Pt, the choice of the second metal is based on the fact that the added metal lowers both the adsorption energy for  $\text{CO}_{\text{ad}}$  as well as promotes the oxidation of CO at lower potential possibly by adsorbed OH species. This has to be associated with the electronic structure or more precisely the density of states at or near the Fermi surface of the added second metal and that of Pt. Therefore, it seems that the modification or optimization based on monometallic Pt catalyst may be a feasible option than to search an altogether alternative non-noble metal-based electrode. This strategy is schematically shown in Fig.3.

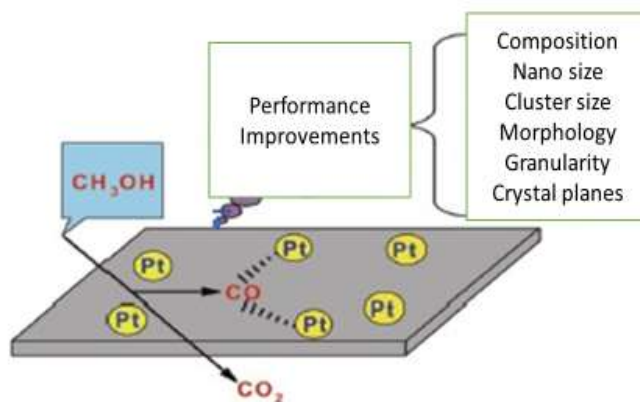


Fig.3. Schematic representation of the modification of monometallic Pt catalyst for efficient DMFC application.

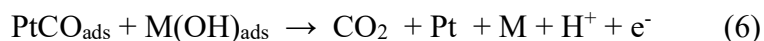
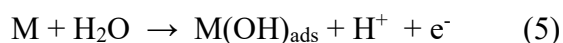
The poisoning effect of CO on Pt surfaces is due to shift of the d orbital DOS to lower energies as a result of by hybridization of the orbitals of CO and the d states of Pt. The most probable configuration for adsorbed CO is on top the surface Pt cluster and hence the adsorption bond is strong due to occupancy of the hybridized orbital. This aspect has recently been probed simultaneously by two techniques namely Resonant Inelastic X-ray scattering (RIXS) and Ultraviolet Photoelectron Spectroscopy (UPS) [31]. These two techniques probe selectively the occupancy of Pt DOS (RIXS) while UPS indicates the occupancy of the s and p DOS states of the adsorbed species. This shift to lower energy side favours the strong bond between surface cluster and adsorbed CO. This adsorption is most pronounced in the atop configuration.

### 3. Pt as electrodes (catalysts) in DMFC

Poisoning by reaction intermediates, low kinetic rates of MOR and the cost are the three factors which limit the use of pure Pt as anode in DMFC. To overcome these limitations, attempts have been consistently made to examine as electrodes with two or three component systems by partially introducing another metal to platinum thus lowering the usage of Pt [32-34]. The average particle sizes of the Pt employed in DMFC applications are in the range 2-5 nm as revealed by high resolution microscopic techniques [35]. Among the various bimetallic systems studied for DMFC applications, the PtRu (1:1 though other proportions are reported [36]) is the most active system which is supposed to be operating by the bifunctional mechanism but the toxicological effect of

the addition of Ru metal still remains uncertain [37]. Among the binary alloys consisting of Pt with Ru, Rh, Au, Sn, Ni, Co, Fe, the systems containing Ru, Rh or Sn are considered to exhibit higher catalytic activity.

The addition of Ni to Pt promotes some structural and electronic modification which is responsible for better reaction performance of the resulting system. Similarly, the addition of Au into Pt enhanced the electrocatalytic activity, this enhancement effect has been accounted for in terms of the changed electronic structure and alterations in the electrochemically active area (ECSA) [38]. The enhancement effect observed is attributed to control of poisoning of Pt sites by adsorbed CO which is considered to be facilitated by the extent of donation from the  $5\sigma$  orbital of CO and backdonation to  $1\pi^*$  orbital due to alterations in the Fermi energy level of Pt alloying with another metal [39]. Though this picture is the accepted proposal, the alteration of the internuclear distance in CO may also have contributed to the weak bonding of CO on alloyed surfaces. The enhancement of the effect of addition of second metal like Sn or Co to Pt has also been attributed to the activation of water creating  $-OH$  ions and other  $O_2$  containing species to oxidize CO-intermediate species on Pt site [40]. The reaction mechanism which may also be applicable to other transition metal addition to Pt for MOR can be conceived in terms of the following reaction sequence.



As a consequence of this exercise, ternary and quaternary metallic systems with Pt like PtRuSn [41], PtRuNi [42], PtRuMo [43], PtRuOsIr [44], PtRuIrSn [45] have also been tried for MOR and also for effective removal of adsorbed CO intermediate. Though it has been reported that addition of a third or a fourth component to Pt system enhances MOR activity, the optimization of the catalyst composition and morphology are still not yet established [35]. Alternate synthesis approaches have also been adopted to generate various architectures of the nano states like core-shell, mesoporous nanospheres, nano-onions in the case of binary bimetallic systems (PtM). The nano-state systems generated have shown better catalytic activity for MOR [46]. In addition, the generation of the metallic catalyst systems involves a reduction reaction and this step can be achieved in a number of ways (using a chemical reducing agent like  $NaBH_4$ , or employing gaseous Hydrogen) and the systems generated showed improved performance in some cases [47].

It is still an interesting exercise to find a substitute for noble metals like Pt, Pd, Rh and Ru for certain chemical and electrochemical reactions like oxidation of hydrogen, CO, and alcohol and the reduction of oxygen. Transition metal carbides (TMC) especially tungsten carbide (WC) have been shown to have better tolerance to CO poisoning in methanol electrooxidation [48]. WC is also known to be a more active for the formation of methoxy group ( $CH_3O^-$ ) as compared to Pt [49]. In recent times, researchers are exploring the potential of Pt supported on WC as ideal electrode catalyst for DMFC [50].

Transition metal nitrides are also considered as ideal support for Pt due to its excellent electrical conductivity (metallic), hardness and good electrochemical stability in fuel cell operating

conditions. Pt supported on titanium cobalt nitride showed excellent electrochemical activity towards Oxygen Reduction Reaction (ORR) due to greatly improved ECSA. A high performance and durable electrocatalyst in the DMFC application is obtained using large surface area Pt(Ru)/TiN system. This system showed electrochemical activity toward MOR with nearly 52% improvement of catalytic activity and good stability/durability compared to commercial JM-Pt(Ru). In nitride supported systems, the particle size of Pt appears to be optimum for MOR and is also well dispersed. Possibly the electronic coupling may be the reason for the observed good synergistic effect of the system. Similarly, the non-carbon TiN nanotubes supported Pt catalyst showed enhanced activity for MOR compared to the commercial Pt/V catalyst [35].

Another set of Pt electrocatalysts supported on nano-state transition metal oxides have been examined for MOR since these systems can promote the oxidation of the intermediate  $\text{CO}_{\text{ads}}$  as well as prevent the agglomeration and corrosion of Pt [35]. Though in principle, any oxide that can be fabricated in nano state (nanotubes, hollow mesoporous or microporous oxides) can be used for loading Pt,  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$  and many other oxides are being extensively employed with Pt as DMFC anodes. From the catalytic activity point of view, it can be stated that the addition of these metal oxides enhances the electrocatalytic activity of DMFC. The incorporation of these conducting metal oxides together with Pt catalyst could also facilitate the oxidation process of CO intermediates. In a recent study, PtRu/ $\text{TiO}_2$ -CNF system has been examined for single cell performance and it has been found to be 5.5 times higher than the commercial electrocatalyst. The higher activity is due to the nanofiber architecture of  $\text{TiO}_2$  and also due to strong metal support interaction (SMSI) which may be responsible for reducing the poisoning aspect of adsorbed intermediate  $\text{CO}_{\text{ads}}$  [51]. Hence, these types of metal oxides supported Pt systems have high potential to be used as anode electrodes in the near future.

#### **4. Carbon supports for Pt electrocatalysts**

In order to effectively utilize the maximum amount of the noble metals in electrochemical reaction, it is customary to support the metal on a conducting material like carbon. The choice of carbon for these applications stems from the high surface area offered by carbon materials and their stability in both acidic and basic media. It is believed that carbon materials can influence the electrocatalytic properties such as metal particle size, morphology, metal dispersion, alloyed degree, and stability. Carbon supports can also affect the performance of supported catalysts in fuel cells, such as mass transport and catalyst layer electronic conductivity, electrochemical active area (ECSA), and metal nanoparticle stability during the operation in the fuel cell.

In recent times, a great effort is focused on the development of a variety of carbon materials with greater stability and also to function as conducting support for noble metals. Supported materials of nanoparticles are considered to be the promising materials for catalytic activity in fuel cells, including the DMFC systems. As stated above, mostly Pt has been traditionally used as the noble catalysts for many fuel cells application. However, the high cost and low reserve are in the way for commercialization of this technology. This has driven the researchers to make the effective use of the catalyst. So the major effort has been expanded towards nano-scaling of the catalyst nanoparticles to form more active sites per mass unit. The morphology, structure, and activity of the catalyst, and correspondingly the whole lifetime of a cell, thus strongly depend on the catalyst

support. Various morphologies of carbon materials like graphene, single and multi-wall nanotubes, and nanofibers have been employed as support for anode electrodes in fuel cell applications.

The reduced graphene oxide (rGO), graphene and modified graphene have been employed as support for Pt and these systems exhibited high electrocatalytic activity toward methanol electrooxidation (MOR) process. In these supported- systems the particle size distribution and size, morphologies are optimum and catalytic activities of Pt and Pt alloys using graphene (surface area in the order of  $2600 \text{ m}^2 \text{ g}^{-1}$ ) as supporting material showed improvement in fuel cell performance. It has also been reported that nitrogen substitution in graphene carbon layer facilitates the dispersion of Pt at the appropriate size on anchoring sites of the support. In addition to increased electrochemical activity (nearly 3 times current density as compared to commercial Pt/C), the onset potential for MOR is shifted negatively by about 150 mV and showed better Co tolerance [35].

The Pt particles supported on SWNT/MWCNT showed closer contact in spherical geometry of Pt particles. The benefits of the SWCNT support are due to its greater electrochemical surface-active area (ECSA) and easier charge transfer at the electrode/electrolyte interface because of the graphitic crystallinity, high amount of oxygen-containing surface functional groups, and highly mesoporous structure of SWNT. The electrodeposition technique used contributed to higher utilization and more uniform dispersion of Pt particles on nanotube carbon support.

The use of single/multiple walled carbons as supports provides altered structural, surface, and electrochemical properties of supported Pt and thus exhibit better performance in catalysis of methanol oxidation (MOR) process [52]. However, as a comparison, SWCNT possess a high degree of graphitization, highly mesoporous structure, and contain more oxygen-containing functional groups at its surface sites. In relation with these properties, the SWCNT exhibits a higher electrochemically accessible surface area and faster charge transfer rate at the electrode/electrolyte interface [35].

Carbon nanotubes (CNTs) support also improves fuel cell performance; for example, Pt can be fixed to the inner wall and the outer wall of CNTs and may cause improvement in the electrocatalytic properties of platinum-CNTs [53]. It has been proposed that fuel cells using CNTs as the catalyst support showed higher current densities. It has been [54] proposed that the high catalytic performance of Pt-Ru/CNT for MOR can be due to the presence of CNT as the support because of the following factors: (i) the as-synthesized Pt-Ru/CNT electrocatalyst retains the nanosized particles and composition, (ii) the presence of functional group on the CNT surface increasing the hydrophilicity of CNT, which facilitates electrochemical reaction on the electrode, and (iii) the high electronic conductivity of the CNT support lowers the resistance in MOR. The attributes of carbon nanotubes namely good electric conductivity, high surface area, good chemical and electrochemical stability, quasi one-dimensional architecture and the morphology make them as appropriate support for active Pt-based catalyst systems. In addition, the supports contribute for high dispersion of the active noble metals and thus aid in achieving high catalytic activity in methanol oxidation (MOR) reaction.

Another support material which can sustain high dispersion of noble metals at the same prevent the agglomeration of metal particles is carbon nanofibers. Nearly 50% increase in electrochemical activity was reported for PtRu supported on carbon nanofiber as compared to PtRu Colloid anode electrocatalyst [55].

It was reported that Pt/CNF nanocomposites obtained by the reduction of hexachloroplatinic acid precursor with formic acid in aqueous solution of electrospun CNFs at room temperature showed higher current density than systems like Pt/CNFs and was approximately 3.5 times greater than that of the E-TEK Pt/C electrocatalyst [56]. There are also other similar reports on PtAu/CNF systems and also on PtRu/CNF system prepared using reducing agents like sodium borohydride, methanol and formate species [57,58].

Mesoporous carbon (MPC) support is another ideal candidate as an electrocatalyst support material for DMFC and fuel cell applications. Mesoporous carbons are of two classes namely ordered mesoporous carbons (OMCs), with uniform pore size and, nonordered mesoporous carbons with irregular pores. A well-dispersed and ultralow Pt catalyst (PtFe) supported on ordered mesoporous carbon (OMC) was prepared and showed superior catalytic activity. Kuppan and Selvam [59] synthesized four types of Pt/ mesoporous carbon by using different reducing agents like NaBH<sub>4</sub>, ethylene glycol (EG), hydrogen, and paraformaldehyde. Among these, one of the systems namely Pt/mesoporous carbon synthesized using paraformaldehyde as reducing agent showed highest current density due to small Pt particle size of ~5 nm and also large ECSA. These systems will be useful when mass transfer limitations were encountered while using large molecules.

It is known that carbon black is used in many commercial fuel cell applications. There are a few types of carbon black like Vulcan XC-72, Black Peral 2000, Ketjen EC-3001 (the most used in commercial devices) and a few others, because of their porosity properties and stability in the medium of operation. The effect of several carbon black supports on the performance of DMFCs has been investigated [60] and it has been shown that Ketjen Black EC-3001 is the most successful support material by increasing ECSA. As is well-known that new varieties of carbon materials are being introduced in recent times. As the new varieties of carbon materials are being developed they will be examined as supports for fuel cell applications and the performance will be evaluated in comparison to the normal carbon black materials as supports for noble metal catalyst systems in fuel cells.

## **5. Conducting Polymer Supports**

Conducting polymers like poly (N-vinyl carbazole), Poly (9-(4-vinyl phenyl) carbazole), polyaniline (PANi), Polypyrrole and other systems have been employed as support for Pt based electrodes in DMFC applications. The performance of Pt based systems supported on conducting polymers is due to (i) the high electrical conductivity of the polymer support (ii) the increase of electrochemical surface area of the fabricated electrocatalyst (iii) the higher diffusion behavior of the electrolyte (iv) increased CO tolerance [61]. The electrocatalytic performance of Pt/PANi/WC/C electrocatalyst for methanol electrooxidation (MOR) and oxygen electro-reduction (ORR), were studied and was shown to exhibit higher MOR activity, high CO resistance, and improved stability compared to Pt/C electrocatalyst in the presence of methanol [62]. The investigations on polymer supported noble metal materials is not as extensive as that on carbon supported materials. In addition, the performance of polymer supported electrodes were not good as carbon supported noble metal electrodes. Future studies may improve the performance of conducting polymer supported noble metal electrodes.

## **6. Evaluation of Pt based electrodes for DMFC applications**

The major issues in the development of Pt based electrodes for DMFC applications is the slow kinetics of MOR reaction, stability of the electrodes due to poisoning by partially oxidized



products cross over of methanol which decreases the cell efficiency and also the high cost of the Pt based materials. It is known that Pt is at present the most effective catalyst in spite of these limitations, but the high cost of this material has promoted the search for alternate material for Pt. In this direction, one of the approaches pursued is to look for materials which will have similar electronic band structure and density of states of Pt. In this direction, carbide materials like WC and possibly MoC have been tried as alternate to Pt or in combination with Pt in order to reduce the amount of costly Pt in the electrode material [63,64]. A second approach is to add another metallic component like in PtRu which will facilitate the oxidation of partial oxidized products like CO and  $\text{CHO}_{\text{ads}}$ . Though the overall reaction sequence in DMFC can be represented in terms of equations 1-3, the actual steps may be more complex.

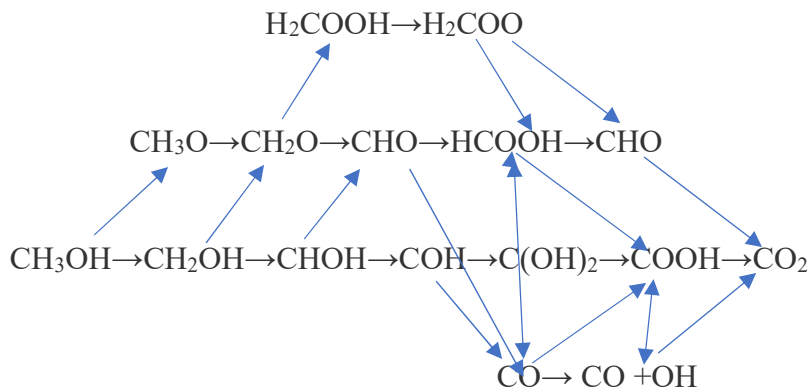


Fig. 4. Possible reaction net-work in the electrochemical oxidation of methanol [adopted from Ref.35].

In Fig 4 the possible schematic representation of the reaction network in the electrochemical oxidation of methanol is shown. CO is formed in a indirect route and is responsible for the poisoning of the Pt sites. In order to facilitate the oxidation of adsorbed CO by the OH species formed hybrid systems like PtRu, PtSn, PtMo, PtPb, PtCo, PtNi, PtRuMo, PtRuSn and PtRuNi are employed as electrocatalytic material for DMFC applications. Essentially the addition of another metal to Pt is to decrease the adsorption of CO on Pt by reducing the oxidation over potential of the anode catalyst.

## 7. Degradation processes in DMFC

There are three main degradation processes namely carbon corrosion, Ru dissolution and cross over and methanol cross over that need to be considered in the development of electrodes for DMFC.

### 7.1. Carbon Corrosion.

In operating fuel cells, among the various electrochemical reactions, the Pt promoted carbon corrosion (the potential for carbon-self oxidation is around 1.1 V vs RHE) is an issue and takes place at a lower potential. New carbon materials like SWNT and others are more resistant to

corrosion as compared to carbon black and hence new architectures of carbon materials are employed as support for Pt as stated in this presentation.

Graphitization of the supports with small specific surface areas and chemical inertness is generally adopted to effectively disperse Pt nanoparticles on such support materials and reduce the extent of carbon corrosion. Functionalization of supports especially nitrogen-incorporated carbon materials is known to enhance the support-metal (SMSI) chemical binding and modify the electronic structure of the metal particles. These effects are considered to contribute to better dispersion and stabilization of metal nanoparticles, thus leading to improved activity and durability of the catalysts. Importantly, nitrogen doped carbon materials are shown to possess high electrocatalytic activity for ORR, better than that of Pt/C, in alkaline medium. Alternatives to carbon materials, including diamonds, oxides, carbides and nonconductive whiskers have also been examined as supports for noble metals and are known to give better stability to the electrodes [7]. In addition to carbon supports, TiO<sub>2</sub> has also received attention because of its inherent stability in an electrochemical environment and beneficial interaction with metal catalysts. It is known that carbon corrosion can be affected by agglomeration and coalescence of noble metal particles. Two-dimensional (2-D) carbon material namely Graphene has been extensively employed as support because of its unique structure, high surface area, and high electrical conductivity and possibly less carbon corrosion. From the device point of view, it is desirable to have improved durability without sacrificing mass activity.

### **7.2. Ru Dissolution and Crossover**

Ru is added to Pt in order to effectively reduce the poisoning effect due to CO<sub>ads</sub>. The Ru sites dissociate at low potentials and the adsorbed OH groups facilitate the oxidation of CO. However, it is generally known that Ru is prone to dissolution under the DMFC environment. This dissolved Ru from the anode will be transported through the membrane and gets redeposited at the cathode thus accounting for the efficiency loss of the fuel cell [65]. It is still a concern the process by which Ru is transported through the membrane and the type of species deposited at the cathode. In addition to the demonstration of loss of activity for MOR and the reduction in CO tolerance, efforts have been focused to stabilize Ru on the anode by adopting suitable fabrication processes like hot pressing or addition of another element like Au or TiO<sub>2</sub> can possibly increase the oxidation potential of Ru thereby reducing the Ru dissolution.

### **7.3, Methanol Crossover**

Limited studies are reported on methanol crossover in the long-term performance of catalysts however methanol crossover gives rise to substantial detriment in short-term performance of DMFCs. This aspect has been attended to in multiple directions namely (i) developing alternate ionomeric membranes or modifying the Poly[perfluorosulphonic acid (PFSA) and other membranes (ii) adopting alternate ways for the fabrication of membrane electrode assembly (MEA) the design of the cell and changing the operating parameters and (iii) introducing methanol tolerant cathodes [7]. The strategy adopted is to increase the proton conductivity ( $\sigma$ ) and the control of methanol diffusion coefficient ( $D$ ) and thus the ratio  $\sigma/D$  can be suitably adjusted with the use of alternative ionomeric membranes, thus improving the performance. Altering the ion exchange capacity (IEC) of the membrane or adjusting the concentration of methanol in the anode are the two ways the methanol crossover can be reduced.

## 8. Conclusion

In this presentation, it has been attempted to account why Pt is the highly active catalyst system for methanol oxidation (MOR). Catalyst selection is usually based on a volcano type relationship between the structural parameter and activity. One such relationship is shown in Fig.5 wherein (ORR) the activity for oxygen reduction reaction is plotted against oxygen binding energy on typical noble metal surfaces and it is seen that Pt surfaces shows highest activity among the noble metals and the same may hold good for methanol oxidation catalysis. Similar type of volcano type plots has been frequently utilized in literature for catalyst/material selection for a given application. The volcano type relationship has also been shown to exist on Pt-M systems between the intrinsic activity for ORR and d-band centre of these systems as shown in Fig 6.

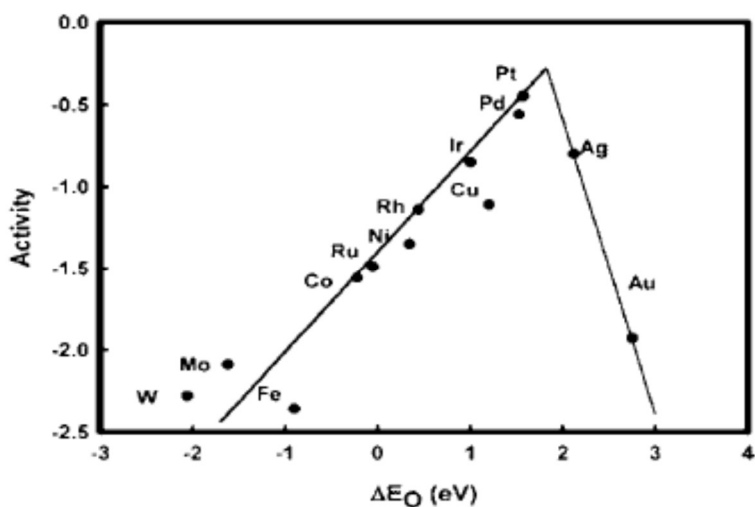


Fig.5. The relationship between the catalytic activity for ORR reaction and oxygen binding energy [reproduced with permission from Ref.66].

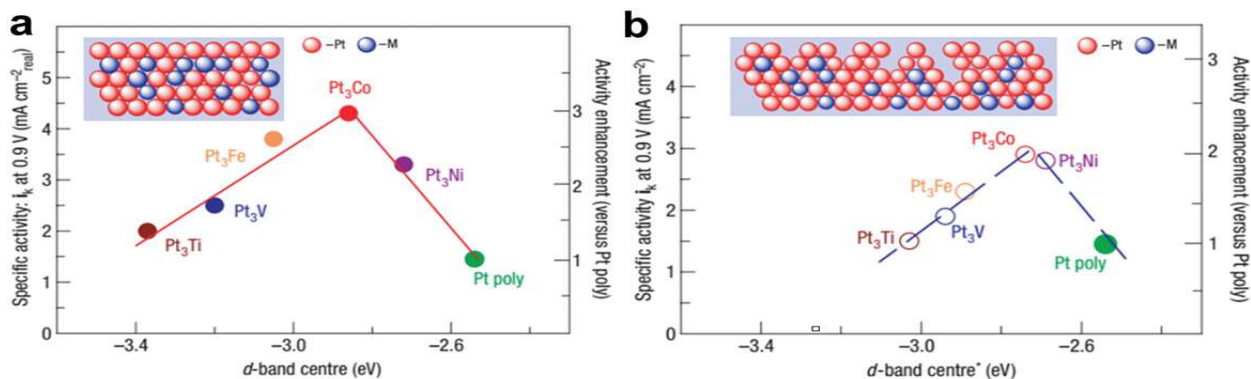


Fig.6 Volcano relationship between the measured activity for ORR and d band centre in alloys of Pt with other metals {reproduced from Ref.66}

Considerable advances have been made in recent time in the development and optimization of Pt-based catalysts mostly supported on a variety of carbons (nano and meso-structured) and conducting polymers for DMFC anode electrode. although their applications face challenges in terms of synthesis, metal loading, and electrode preparation. The limitations on the use of Pt namely the cost and CO poison effect have been addressed already adequately in literature. The solutions proposed in literature are using high surface area supports (varieties of carbon both SWNT MWNT and other meso porous carbon support and conducting polymer support) and increased dispersion of the noble metal and also alloying Pt with metals like Fe, Co, Ni, Ir, Ru, Rh and Pd decreased the CO poison effect on bare Pt. It has been recently shown that the Platinum nano-clusters (limited number of atoms single or multiple) [67] and also heteroatom anchored platinum sites are effective for MOR reaction due to morphological [68,69], structural, durable control of the electroactive sites on the electrode. It can be predicated that the modification of the carbon surfaces (increasing hydrophobicity by surface functionalization) can be in future used as effective support for Pt in DMFC applications.

## 9. Prospects and outlook

There are many issues in which clarity have to evolve. The possible prospects of this technology are listed as points below:

1. The poisoning effect of partially oxidized product namely CO is rationalized in terms of reaction to the reactive species OH formed from water on Ru sites. This reaction may take place by spillover mechanism of the adsorbed species. However, the molecular level. Mechanistic details have yet to evolve.
2. In order to alter the binding energy (mostly decrease) of oxygen (for ORR or MOR) on the active Pt systems, d-band centre needs to be shifted downwards. It should be established the extent of this shift by the addition of the second metal to Pt
3. Another aspect is that the bi- or multi-metallic systems should have morphological specificity like equi-distribution of the components at least skin depth or other architectures like core-shell morphology of the multi-component systems. It has to be established how the morphological specificity accounts for the increased activity and durability.
4. The optimum composition of bi- or multi-component systems and structures should be established such that the oxidation potential of the active component namely Pt is improved.
5. The self-stability of the support and the modifications taking place in the active component in the electrochemical environment should be established.
6. The extent of interaction and also the alterations that are possible in this interaction and the operation of SMSI effect should be clearly understood.
7. It must be ensured that the improved durability of catalysts is taking place without the loss in catalytic activity.
8. One must ensure that the ratio of performance to cost is a respectable number, so that the marketability of DMFC technology is feasible.

9. The positive advantages of the special morphology of the metal loaded systems have to be established [70, 71].

10. The appropriate functionalization of the support and geometrically controlling the texture of the support and the interaction with the metal nanoparticles have to be rationalized.

11. The rationalization of the optimum compositions (atomic ratio) of bi- and multi-metallic systems for MOR has to be possible for predicting future anode electrodes [72-74].

12. There are a variety of techniques like electroless and electrodeposition, chemical reduction methods have been adopted for metal loading, it is necessary that these techniques have to be properly evaluated and appropriate one has to be formulated [75].

The challenges that one has to face in the commercialization of this technology are:

1. Heat and water management in the cell – The reaction between methanol and oxygen produce heat and this heat facilitates the methanol crossover. This will lead to a concept of mixed potential and this situation lowers the efficiency of the cell. This has to be optimized through appropriate design of the cell.
2. Water transport restrictions – This limitation imposes on the concentration of methanol to be used in the cell. The flooding in the methanol fuel cell in terms of oxygen supply in the cathode side has to be addressed.[76]

The DMFC technology will meet the commercialization opportunities in the coming years due to various factors like the possibility of utilizing the existing infra-structure for outlets, favourable situation with respect to supply-demand, price fluctuations, regulations [77] investor confidence, with regional market dynamics. The analysis of important questions regarding the market value in region-wise is given in ref.78. Alternate electrode materials like oxides [79] and other materials similar to the electronic structure like platinum namely carbides have been tried and till date they have not yet attained the efficiency of Pt anode based DMFC technology.

In essence, all these studies indicate that the penetration in the energy conversion market by DMFC technology is not only feasible but it will take place in the near future.

**Acknowledgment:** The Department of Science and Technology, Government of India is gratefully acknowledged for supporting NCCR at IITM.

## References

[1] S.J. Peighambardoust, S. Rowshanzamir, and N. Amjadi, Review of the Proton Exchange Membrane for fuel cell applications, *Int. J. Hydrogen Energy*,17(35),9349-9384 (2010).

[2] T.R.Ralph, and M.P.Hogarth, Catalysts for Low Temperature Fuel cells, *Platinum Met.Rev.*,4(46)146-164 (2002).

[3] Wang Zonghua, Shi Guoyua, Xia Jianfei, Zhang, Feifei, Xia Yanzhi, Li Yanhui and Xia Linhua, , Research Progress on Pt-Based anode catalysts in the direct Methanol Fuel cell, *Acta Chim. Sinica* , 71, 1225—1238 (2013).

- [4] M.A. Scibioh and B. Viswanathan, The status of catalysts in PEMFC technology, in *Catalysis for Alternative Energy Generation*, L. Gucci and A. Erdohelyi (eds) Springer pp.329-368 (2012)
- [5] Nitul Kakati, Jatindranath Maiti, Seok Hee Lee, Seung Hyun Jee, Balasubramanian Viswanathan and Young Soo Yoon, Anode Catalysts for Direct Methanol Fuel Cells in Acidic Media: Do We Have Any Alternative for Pt or Pt–Ru? *Chem. Rev.*, 114, 12397-12429 (2014).
- [6] H. S. Liu and J. J. Zhang, (ed)., *Electrocatalysis of Direct Methanol Fuel Cells: From Fundamentals to Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009.
- 7] Xiao Zhao, Min Yin, Liang Ma, Liang Liang, Changpeng Liu, Jianhui Liao, Tianhong Lu and Wei Xing, Recent advances in catalysts for direct methanol fuel cells, *Energy Environ. Sci.*, 4,2736-2753(2011)
- 8] S.Basri, S.K.Kamarudin, W.R.W.Daud and Z.Yaakub, Nano-catalyst for direct methanol fuel cell (DMFC), *International Journal of hydrogen energy*, 35,7957-7970 (2010).
- [9] S.Basri, S.K.Kamarudin, W.R.W.Daud, Z.Yaakub and A.A.H.Kadhum, Novel anode catalyst for Direct Methanol Fuel Cells, *The Scientific world Journal*, Volume 2014, Article ID 547604.
- 10] A. Sandoval-González, E. Borja-Arco, J. Escalante, O. Jiménez-Sandoval, and S. A. Gamboa, “Methanol oxidation reaction on PtSnO<sub>2</sub> obtained by microwave-assisted chemical reduction,” *International Journal of Hydrogen Energy*, vol. 37, no. 2, pp. 1752–1759, 2012.
- 11] V. Baglio, A. Stassi, A. di Blasi, C. D'Urso, V. Antonucci, and A. S. Aricò, Investigation of bimetallic Pt-M/C as DMFC cathode catalysts, *Electrochimica Acta*, vol. 53, no. 3, pp. 1360–1364, 2007.
- [12] M. V. Martínez-Huerta, N. Tsiouvaras, M. A. Peña, J. L. G. Fierro, J. L. Rodríguez, and E. Pastor, “Electrochemical activation of nanostructured carbon-supported PtRuMo electrocatalyst for methanol oxidation,” *Electrochimica Acta*, vol. 55, no. 26, pp. 7634–7642, 2010.
- [13] Y. Huang, J. Cai, and Y. Guo, “Roles of Pb and MnO<sub>x</sub> in PtPb/MnO<sub>x</sub>-CNTs catalyst for methanol electro-oxidation,” *International Journal of Hydrogen Energy*, vol. 37, no. 2, pp. 1263–1271, 2012
- [14] C. Xu, J. Hou, X. Pang, X. Li, M. Zhu, and B. Tang, “Nano-porous PtCo and PtNi alloy ribbons for methanol electrooxidation,” *International Journal of Hydrogen Energy*, vol. 37, pp. 10489–10498, 2012.
- [15] B. P. Vinayan, R. I. Jafri, R. Nagar, N. Rajalakshmi, K. Sethupathi, and S. Ramaprabhu, “Catalytic activity of platinum-cobalt alloy nanoparticles decorated functionalized multiwalled carbon nanotubes for oxygen reduction reaction in PEMFC,” *International Journal of Hydrogen Energy*, vol. 37, no. 1, pp. 412–421, 2012.

- [16] V. A. Ribeiro, O. V. Correa, A. O. Neto, M. Linardi, and E. V. Spinacé, "Preparation of PtRuNi/C electrocatalysts by an alcohol-reduction process for electro-oxidation of methanol," *Applied Catalysis A: General*, vol. 372, no. 2, pp. 162–166, 2010.
- [17] I.S.Armadi, Z.L. Wang, T.C. Green, A. Henglein, and M.A. El-Sayed, Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles, ***Science* 1996, 272, 1924.**
- [18] Z.L.Liu, J.Y. Lee, M. Han, W.X. Chen, and L.M. Gan, Synthesis and characterization of PtRu/C catalysts from microemulsions and emulsions, *J. Mater. Chem.*, 12,2453 (2002).
- [19] K.Okitsu, A.Yue, S.Tanabe, and H. Matsumoto, Sono-chemical preparation and catalytic behavior of highly dispersed Palladium nanoparticles on Alumina, *Chem. Mater.*, 12,3006 (2000).
- [20] T. Fujimoto, S.Teraushi, H. Umehara, I. Kojima and W.Henderson, Sono-chemical preparation of single dispersion metal nanoparticles from Metal salts, *Chem. Mater.*, 13,1057 (2001).
- [21] W.Y.Yu, W.X. Tu, and H.F. Liu, Synthesis of nanoscale Platinum colloids by microwave dielectric heating, *Langmuir*, 15,6-9 (1999).
- [22] W.X.Tu, and H.F. Liu, Continuous synthesis of colloidal metal nanoclusters by microwave irradiation, *Chem. Mater.* 2000, 12, 564-567.
- [23] S.Komarneni, D.S. Li, B. Newalkar, H. Katsuki, and A.S. Bhalla, Microwave polyol process for Pt and Ag nano-particles. *Langmuir* 18, 5959-5962 (2002).
- [24] W.X.Chen, J.Y. Lee and J.L. Liu, Microwave assisted synthesis of carbon supported Pt nanoparticles for fuel cell applications, *Chem. Commun.* 2002, 2588-2589.
- [25] Z.L.Liu, J.Y. Lee, W.X.Chen, M. Han and L.M. Gan, Physical and electrochemical characterizations of microwave-assisted polyol preparation of carbon-supported PtRu nanoparticles, *Langmuir* 20, 181-187 (2004).
- [26] Zhaolin Liu., Xing Yi Ling, Xiaodi Su, and Jim Yang Lee, Carbon-Supported Pt and PtRu Nanoparticles as Catalysts for a Direct Methanol Fuel Cell, *J. Phys. ., B*, 108, 8234-8240 (2004).
- [27] Huajie and Xin Wang, Recent progress on carbon-based support materials for electrocatalysts of direct methanol fuel cells, *J. Material Chemistry A* 2,6266-6291 (2014).
- [28] Hanan Teller, Diwakar Kashyap, Shani Ohanuona Danino, and Alex Schechter, Ultra-Low Loading of Highly Active Pt and PtSn Catalysts on Hierarchical Tin as Anodes in Direct Methanol Fuel Cells, *Journal of The Electrochemical Society*, 165 (14) F1242-F1248 (2018).
- [29] M.C..Leandro, . Pinto Paola Quaino, D.Mauricio, Arce, Elizabeth Santos, and Wolfgang Schmickler, Electrochemical Adsorption of OH on Pt(111) in Alkaline Solutions: Combining DFT and Molecular Dynamics, *ChemPhysChem* 15, 2003 – 2009. (2014).
- [30] <https://www.fuelcellstore.com/blog-section/direct-methanol-fuel-cell-improvements>.

- [31] Pieter Gratzel, Jagdeep Singh, Kristina O.Kvashnina and John A.van Bokhoven, In situ Characterization of the 5d Density of States of Pt Nanoparticles upon adsorption of CO, *J.Am.Chem.Soc.*,132,2555-2557 (2010).
- [32] C.Coutanceau, R.K. Koffi , J-M. Léger, K.Marestin, R.Mercier, C. Nayoze C and P. Capron Development of materials for mini DMFC working at room temperature for portable applications. *J Power Sources* 160, 334–339 (2006).
- [33] R.Baronia, J.Goel, S.Tiwari, P.Singh, D.Singh, S.P. Singh and S.K. Singhal SK, Efficient electro-oxidation of methanol using PtCo nano-catalysts supported reduced graphene oxide matrix as anode for DMFC. *Int J Hydrogen Energy* 42,10238–10247 (2017)
- [34] J. Yao and Y. Yao Y, Experimental study of characteristics of bimetallic Pt–Fe nano-particle fuel cell electrocatalyst. *Renew Energy* 81:182–196(2015).
- [35] Z.A.C. Ramli and S.K. Kamarudin, Platinum-based catalysts on various carbon supports and conducting polymers for Direct Methanol Fuel Cell Applications: A review, *Nanoscale Research Letters*, 13, 410-435 (2018).
- [36] M. Shi, W. Zhang, D. Zhao, Y. Chu and C. Ma, Reduced graphene oxide-supported tungsten carbide modified with ultralow-platinum and ruthenium-loading for methanol oxidation. *Electrochim. Acta.* 143,222–231(2014).
- [37] X-W. Zhou, R-H. Zhang, Z-Y. Zhou and S-G. Sun, Preparation of PtNi hollow nanospheres for the electrocatalytic oxidation of methanol. *J Power Sources.* 196:5844–5848 (2011).
- [38] G. Chang, Z. Cai, H. Jia, Z. Zhang, X. Liu, Z. Liu R. Zhu and Y. He, High electrocatalytic performance of a graphene-supported PtAu nanoalloy for methanol oxidation. *Int J Hydrogen Energy.*43,12803–12810 (2018).
- [39] Yan Feng, Jinhua Yang, Hui Liu, Feng Ye and Jun Yang, Selective electrocatalysts toward a prototype of the membrane less direct methanol fuel cell, *Scientific Reports*, 4, 3813-3819 (2014).
- [40] S. Sharma, A. Ganguly, P. Papakonstantinou, X. Miao, M. Li, J.L .Hutchison, M. Delichatsios and S. Ukleja, Rapid microwave synthesis of CO tolerant reduced graphene oxide-supported platinum Electrocatalysts for oxidation of methanol. *J Phys Chem C.* 114, 19459–19466 (2010).
- [41] C. Pan, Y. Li, Y. Ma, X. Zhao and Q. Zhang, Platinum–antimony doped tin oxide nanoparticles supported on carbon black as anode catalysts for direct methanol fuel cells. *J Power Sources.*196, 6228–6231(2011).
- [42] Y. Zhou, X. Hu, Y.Xiao and Q. Shu, Platinum nanoparticles supported on hollow mesoporous tungsten trioxide microsphere as electrocatalyst for methanol oxidation. *Electrochim Acta.* 111, 588–592(2013).



- [43] G.R. Salazar-Banda, K.I.B. Eguiluz, M.M.S. Pupo, H.B. Suffredini, M.L. Calegaro and L.A. Avaca, The influence of different co-catalysts in Pt-based ternary and quaternary electro-catalysts on the electro-oxidation of methanol and ethanol in acid media. *J. Electroanal. Chem.*,668, 13–25 (2012).
- [44] Y.M. Alyousef, M.K Datta, K. Kadakia, S.C. Yao and P.N. Kumta, Sol–gel synthesis of Pt-Ru-Os-Ir based anode electro-catalysts for direct methanol fuel cells. *J Alloys Compd.*,506, 698–702(2010).
- [45] T. Huang, R. Jiang, J. Liu, J. Zhuang, W-B. Cai and A.Yu, Synthesis of well-dispersed PtRuSnO<sub>x</sub> by ultrasonic-assisted chemical reduction and its property for methanol electrooxidation. *Electrochim. Acta.* 254, 4436–4440, (2009).
- [46] Y. Hu, Q. Shao, P. Wu, H. Zhang and C. Cai, Electrochemistry communications synthesis of hollow mesoporous Pt – Ni nanosphere for highly active electrocatalysis toward the methanol oxidation reaction. *Electrochem. Commun.* 18,96–99 (2012).
- [47] N. Tsiouvaras, M.V. Martínez-Huerta, O. Paschos, U. Stimming, J.L.G. Fierro and M.A. Peña, PtRuMo/C catalysts for direct methanol fuel cells: effect of the pretreatment on the structural characteristics and methanol electrooxidation. *Int J Hydrogen Energy*, 35,11478–11488 (2010).
- [48] Y. Liang, L. Chen and C. Ma, Kinetics and thermodynamics of H<sub>2</sub>O dissociation and CO oxidation on the Pt/WC (0001) surface: a density functional theory study. *Surf Sci.*, 656,7–16(2017).
- [49] M.M.O. Thotiyl, T. Ravikumar, and S. Sampath, Platinum particles supported on titanium nitride: an efficient electrode material for the oxidation of methanol in alkaline media. *J Mater Chem.* 20,10643–10651 (2010).
- [50] C. Ma, W. Liu, M. Shi, X. Lang, Y. Chu, Z. Chen, D. Zhao, W. Lin and C. Hardacre, Low loading platinum nanoparticles on reduced graphene oxide-supported tungsten carbide crystallites as a highly active electrocatalyst for methanol oxidation. *Electrochim. Acta*, 114, 133–141(2013).
- [51] N. Abdullah, S.K. Kamarudin and L.K.Shyuan, Novel anodic catalyst support for Direct Methanol Fuel cell: Characterizations and single-cell performances, *Nanoscale Research Letters*,13, 90-102 (2018).
- [52] Z. Zhao, X. Fang, Y. Li, Y. Wang, P.K. Shen, F. Xie and X. Zhang X , The origin of the high performance of tungsten carbides/carbon nanotubes supported Pt catalysts for methanol electrooxidation. *Electrochem. Commun.*, 11,290–293(2009).
- [53] L.Zhao, Z-B. Wang, J-L. Li, J-J. Zhang, X-L.Sui and L-M. Zhang, Hybrid of carbon-supported Pt nanoparticles and three dimensional graphene aerogel as high stable electrocatalyst for methanol electrooxidation. *Electrochim. Acta*, 189:175–183 (2016).

- [54] J. M. Sieben, A. Anson-Casaos, M Martínez and E. Morallón, Single-walled carbon nanotube buckypapers as electrocatalyst supports for methanol oxidation. *J Power Sources* 242,7–14 (2013).
- [55] E.S. Steigerwalt, G.A. Deluga, D.E. Cliffel and C.M.Lukehart, A Pt - Ru / graphitic carbon nanofiber nanocomposite exhibiting high relative performance as a direct-methanol fuel cell anode catalyst. *J. Phys. Chem* 105,8097-810192001).
- [56] D.Wang, Y. Liu, J. Huang and T You, In situ synthesis of Pt/carbon nanofiber nanocomposites with enhanced electrocatalytic activity toward methanol oxidation. *J Colloid Interface Sci* 367,199–203(2012).
- [57] L.Giorgi, E. Salernitano, T. Dikonimos Makris, S. Gagliardi, V. Contini and M. De Francesco, (2014) Innovative electrodes for direct methanol fuel cells based on carbon nanofibers and bimetallic PtAu nano-catalysts. *Int. J. Hydrogen Energy* 39, 21601–21612 (2014).
- [58] J.G. Calderón, G. García, L. Calvillo, J.L. Rodríguez, M.J. Lázaro and E. Pastor, Electrochemical oxidation of CO and methanol on Pt–Ru catalysts supported on carbon nanofibers: the influence of synthesis method. *Appl. Catal. B Environ*, 165,676–686 (2015).
- [59] B. Kuppan, and P. Selvam, Platinum-supported mesoporous carbon (Pt / CMK-3) as anodic catalyst for direct methanol fuel cell applications: the effect of preparation and deposition methods. *Prog Nat Sci Mater Int* 22, 616–623 (2013).
- [60] G. Wang, G. Sun, Q. Wang, S. Wang, H. Sun and Q. Xin, Effect of carbon black additive in Pt black cathode catalyst layer on direct methanol fuel cell performance. *Int J Hydrogen Energy*, 35,11245–11253 (2010).
- [61] S. Kim and S-J. Park, Electroactivity of Pt–Ru/polyaniline composite catalyst-electrodes prepared by electrochemical deposition methods. *Solid State Ionics* 178:1915–1921(2008).
- [62] M. Yaldagard, M. Jahanshahi and N. Seghatoleslami, Pt catalysts on PANI coated WC/C nanocomposites for methanol electro-oxidation and oxygen electro-reduction in DMFC. *Appl Surf Sci* 317,496–504 (2014).
- [63] H.H. Hwu, J.G. Chen, K. Kourtakis and J.G. Lavin, Potential application of tungsten carbides as Electrocatalysts. 1. Decomposition of methanol over carbide-modified W(111). *J. Phys. Chem B* 105:10037–10044 (2001).
- [64] V.Venkatasubramanian, M Sankaran B. Viswanathan and V R Subramanian, Tungsten carbide as possible support for Pt in electrochemical Reactions, *Bulletin of the Catalysis Society of India*, 7,146-152(2008).
- [65] P.Piela, C.Eickes, E.Broscha, F.Garzon and P.Zelenay, Ruthenium Crossover in Direct Methanol Fuel Cell with Pt-Ru Black Anode BATTERIES, FUEL CELLS, AND ENERGY CONVERSION *J.Electrochem.Soc.*, 151, A2053-A2509 (2004)

[66] J.K.Norskov, J.Rossmeisl, A.Logadottir, L.Lindqvist, J.R.Kitchin, T.Bligaard and H.Jonsson, *J. Phys. Chem.*, 108,17886-17892 (2004).

[67] J.Liu, M.Jiao, L.Lu, H.M. Barkholtz, Y..Li Y.Wang, L.Jiang, Z.Wu, D..Liu, L.Zhuang, C.Ma, J..Zeng, B..Zhang, D. Su and P.Song, *Electrocatalyst for oxygen reduction reaction*, *Nature communications*,8,1-9 (2017).

[68] M. Li, M. Li, Z. Zhao, T. Cheng, A. Fortunelli, C.Chen, R. Yu, L. Gu, B.Merinov, Z.Lin, E.Zhu, T.Yu,,Q. Jia, J. Guo, L/ Zhang, I. WAG, Y. Huang and X. Duan, *Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction*, 9050. *Science* 354:1414–1419(2016).

[69] L. Bu, N. Zhang, S.Guo, X. Zhang, J. Li, J. Yao T.Wu, G. Lu, D. Su, and X. Huang *Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis*. *Science* 354:1410–1414 (2016).

[70] B Rajesh, K Ravindranathan Thampi, J.M. Bonard, N. Xanthopoulos, *Carbon nanotubes generated from template carbonization of Polyphenyl acetylene as the support for electrooxidation of methanol*, *The Journal of Physical Chemistry B* 107 (12), 2701-2708(2003).

[71] Y.Tsukagoshi, H.Ishitobi and N.Nakagawa, *Improved performance of direct methanol fuel cells with the porous catalyst layer using highly-active nanofiber catalyst*, *Carbon resources Conversion*, 1,61-72 (2018).

[72] E.Antolini, T.Lopes and E.R.Gonzalez, *An overview of Platinum-based catalysts as methanol resistant oxygen reduction materials for direct methanol fuel cells*, *Journal of Alloys and Compounds*, 461, 253-262 (2008).

[73] C.Suo, W.Zhang, X.Shi and C.Ma, *Investigation of nano Pt and Pt-based alloys electrocatalysts for direct methanol fuel cells and their properties*, *AIP Advances*, 4,031340 (2014).

[74] A.Hassan and E.D.Ticianelli, *Activity and stability of dispersed multimetallic Pt-based catalysts for CO tolerance in Proton Exchange Membrane Fuel cell anodes*, *Annals of the Brazilian Academy of Sciences*, 90 (suppl.1) 697-718 (2018).

[75] H.Teller, D.Kashyap, S.Ohanuona Danino and A.Schechter, *Ultra-low loading of highly active Pt and PtSn catalysts on Hierarchical tin as anodes in direct methanol fuel cells*, *Journal Electrochemical Soc.*, 165,F1242-F1248(2018).

[76][https://www.zsw-bw.de/fileadmin/user\\_upload/PDFs/Vorlesungen/est3/WS\\_2017/Seminar-Notes/DMFC.pdf](https://www.zsw-bw.de/fileadmin/user_upload/PDFs/Vorlesungen/est3/WS_2017/Seminar-Notes/DMFC.pdf).

[77] *Future of Direct Methanol Fuel Cells (DMFC) Market Outlook to 2025 - Growth Opportunities, Competition and Outlook of Portable, Fixed, Transportation Direct Methanol Fuel Cells Market across Different Applications and Regions Report*,

<https://www.researchandmarkets.com/reports/4759113/2018-future-of-direct-methanol-fuel-cells-dmfc>.

[78] <http://news.decresearch.com/direct-methanol-fuel-cells-market-global-briefing-future-outlook-2018-2023/>.

[79] V Raghuvier, K Ravindranathan Thampi, N. Xanthopoulos, HJ Mathieu, B Viswanathan, Rare earth cuprates as electrocatalysts for methanol oxidation, *Solid State Ionics* 140 (3-4), 263-274 (2001).