

Alternate Possibilities for Electrodes and Membranes for Direct Methanol Fuel Cells

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Abstract

Direct methanol fuel cells (DMFC) are one of the viable alternatives to the hydrogen oxygen fuel cells which can be easily adapted to the existing infrastructure of distribution and storage. Unlike the hydrogen oxygen fuel cells in its various forms, DMFC has not received considerable attention. However, like the hydrogen oxygen fuel cells, the commercialization of DMFC has also met with considerable barriers and two of the important aspects of DMFC are the electrodes for both fuel oxidation and also for oxygen reduction and the membrane. In the case of the membrane, the available Nafion® membranes allow the cross over of methanol from anode to cathode thus not only inhibiting the cathodic reduction of oxygen but also generate mixed potential which is affecting the efficiency of the resulting Fuel cell. The purpose of this presentation is to examine the alternate possibilities for these two applications in DMFC. However the alternatives considered are only meant to give one the direction for future research and they are not the end of the search itself. The alternatives proposed for the anodes are directed to functionalization of the support so as to sustain appropriate nanosize of the Pt clusters. The cathode selection is based on non noble metal cluster systems which possess similar properties like that of Pt. The search for alternate membranes based on hybrid systems though may not complete with Nafion® in the values of conductivity but can exhibit better 'selectivity' measure a compound property reflecting proton conductivity and methanol cross over.

Introduction

Fuel cells have been conceived to be possibly clean, efficient and silent energy conversion technology, which possibly can meet the various demands for energy even though not fully [1]. The anxiety and expectations with respect to their commercial introduction in transport sector and stationary applications have to be put off (from 2003 and 2001 respectively) since a viable and commonly adoptable technology has not yet evolved for this energy conversion device [2]. However, there are indications that this technology may become viable in the near future though the date of adaptation has been put off a number of times in the past and may possibly happen in the future too. There are a number of barriers for commercial adaptation of fuel cells. In this presentation, it is the intention to bring out two important aspects of Direct Methanol Fuel Cells (DMFC) that may be primarily contributing to the barrier for early commercialization.

Before one considers the two important aspects (considered in this presentation) namely development of cost effective, efficient and catalytically most active electrodes and viable membranes, it is necessary that some details of DMFC is considered. In Fig 1 a general schematic representation of a DMFC is shown.

The electrochemical reactions taking place in DMFC can be written [3] as:

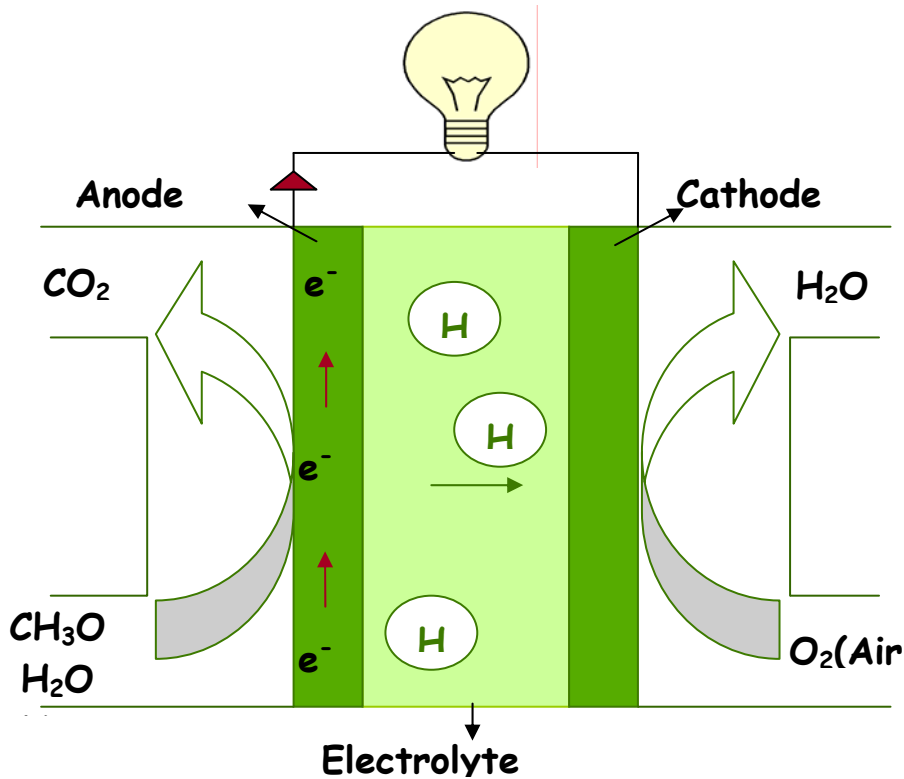
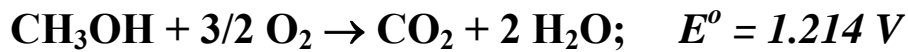
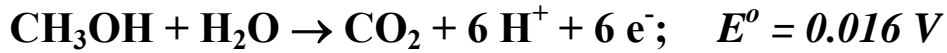


Fig.1: A schematic diagram of a Direct Methanol Fuel Cell. (Reproduced from B. Viswanathan, M. Helen and S. Srinivasa Murthy, 'Photo/ Electrochemistry & Photobiology for Environment, Energy & Fuel' (2005) 61.)

It is seen that DMFC provides similar voltage like that of hydrogen oxygen fuel cell and also has the flexibility that the existing infra structure for distribution and consumption can be easily adapted for the change over to methanol from the current liquid fuels[1].

Technically speaking DMFC is similar to Polymer Electrolyte Membrane Fuel Cells (PEMFC), though instead of hydrogen, one employs methanol and hence produces carbon dioxide. It is possible to develop DMFC for some portable applications in the range of 1-100W.

2. Seats of Electrochemical reactions in Fuel cells

In any electrochemical cells, the electron transfer reactions occur at the electrode/electrolyte interface. In the fuel cells the oxidation of the fuel occurs at the anode and the reduction of the oxidant (molecular oxygen) takes place at the cathode. It is generally perceived that the oxidation of the fuel is important and hence more attention is given for the development of suitable catalyst containing electrodes for the oxidation of methanol. The design and development of suitable anodes for methanol fuel cell had been one of the prime tasks of researchers. They have brought into application the concepts available in the catalytic oxidation of methanol for designing suitable anodes for DMFC. However there are various other limitations for the development of viable DMFC. In Table 1 these have been listed for convenience [4].

Table 1 Limitations in the development of a viable DMFC

- **Sluggish methanol oxidation (anode) kinetics:**
 - 6 electron transfer
 - formation of CO as an intermediate in the multi-step methanol oxidation mechanism – poisoning of catalyst
- **Large methanol crossover through the membrane:**
 - Linked to the electro osmotic drag
 - had detrimental effect on fuel efficiency
 - may poison the cathode
 - creates mass transport problems at cathode layer by wetting hydrophobic gas channels, leading to increased flooding
- **Cost of electro-catalysts**

Any fuel cell electrode development has to start with the development of suitable support for effectively dispersing the noble metal and also to functionalize them for subsequent interaction and activation of the fuel molecule. The conventional support in fuel cells is carbon. The desirable characteristics of carbon supports are summarized in Table 2.

Table 2 The Role and characteristics of Carbon support for fuel cell applications

- ❖ **High surface area (the desirable ranges are 1000s m²/g)**
- ❖ **High dispersion of noble metal particles to reduce the extent of noble metal loadings(in DMFC normally 1.5mg/cm² are employed)**
- ❖ **Avoid the agglomeration of the metal particles during operation, functionalize the noble metals so that they provide effective sites for activation of fuel molecules**

- ❖ **Good stability of electro-catalysts for long term use in fuel cells**
- ❖ **Improved activity of electro-catalysts through the metal support interaction**
- ❖ **Lower the resistance of mass transport – avoid any physical control of the electrochemical reaction**
- ❖ **Always superior to the respective unsupported systems**
- ❖ **Shorten the time of DMFC commercialization**
- ❖ **Electrochemical properties – carbon materials have a wide electrochemical potential window enabling a variety of substrates or fuels to be employed.**
- ❖ **Carbon supports have desirable chemical properties especially considerable corrosion resistance**
- ❖ **Appropriate electrical properties for use as electrodes - Good conductivity**
- ❖ **Mechanical properties - - Dimensional & mechanical stability and Light weight & adequate strength**

Among the various types of carbon materials available today carbon nanostructures have received considerable attention as electrochemical electrode support due to the desirable characteristics given in Table 3 [5].

Table 3 Characteristics of Carbon nanotubes as an electrode support in fuel cells

- **Mesoporosity (2-50nm)**
- **Improved mass transfer**
- **Better dispersion**
- **Surface bound groups**
- **High accessible surface area**
- **High purity → avoids self-poisoning**
- **Good electronic conductivity**

3. Alternate Anodes for DMFC

Having decided on the nature of the carbon support for fuel cell applications a synthetic strategy has been evolved for the development of anodes for DMFC which consisted of preparing the functionalized carbon nanotubes and loading the noble and other active species on them. Four different kinds of nitrogen containing carbon precursors are chosen to make nitrogen containing carbon nanotubes [6]. The details of the synthesis strategy adapted are given elsewhere [4, 7, and 8]. The results obtained using in the oxidation of methanol on these materials as supports for Pt are given in Table 4.

It is seen that the Pt loaded on nitrogen containing carbon nanotubes shows higher activity for methanol oxidation as compared to PT loaded on commercial carbons and also there is an optimum amount of nitrogen where the dispersion of Pt (in terms of size and activity) is best suited for methanol oxidation.

Table 4 Electro-catalytic activity of the Pt/N-CNT electrodes in comparison with commercial catalysts for methanol oxidation [7, 8]

Electrode	Nitrogen content	Activity Ip (mA/cm ²)
Pt	-	0.076
GC/ETek 20% Pt/C Naf	-	1.3
GC/CNT-Pt PPP-Naf	0.0	12.4
GC/CNT-Pt PVP -Naf	6.63	16.2
GC/CNT-Pt PPY -Naf	10.5	21.4
GC/CNT-Pt PVI-Naf	16.7	18.6

PPP - poly (paraphenylene); PVP- Poly (vinylpyrrolidone); PPY – Polypyrrole; PVI - Poly (vinylimidazole).

When normally alloy system is employed as anodes like Pt-Ru, the main focus appears to exploit the bifunctional mechanism so that the formed CO could be removed and oxidized at the alternate metallic sites. However, it is also possible to use unconventional supports like metal oxide nanotubes like TiO₂ or WO₃ which will facilitate the spillover route (both hydrogen and oxygen) and thus can be expected to exhibit enhanced anodic oxidation activity. In order to test this hypothesis, titanium oxide nanotubes were preformed in the pores of alumina membrane and then subsequently loaded with Pt using H₂PtCl₆. Similar strategies were adapted for the preparation of other oxide nanotubes. The results obtained on these types of systems are given in Tables 5 and 6 [4].

Table 5 The activity of Pt/TiO₂ nanotube for electrochemical oxidation of methanol

Electro-catalyst	Anodic scan peak potential (V) vs. Ag/AgCl	Anodic peak current density (mA cm ⁻²)
Bulk Pt	Bulk Pt	0.16
20 % Pt/C	0.762	1.3
Pt/TiO ₂ nanotube	0.680	13.2

Table 6 Electro-catalytic activity of Pt/WO₃ nanorods and Pt/C for methanol Oxidation

Electro-catalyst	Pt loading µg/cm ²	Specific activity mA/cm ²
Pt/C	20	29.5
Pt/WO ₃ nanorods	20	62.0

The promotion effect of TiO₂ nanotubes in the methanol oxidation can be rationalized on the basis of Strong Metal Support Interaction (SMSI) as well as the OH adsorption on Ti

ion site facilitating the oxidation of CO on Pt sites which are otherwise poisons the metallic sites and thus renders these metallic sites unsuitable for methanol oxidation. A pictorial model of these postulates is given in Fig.2.

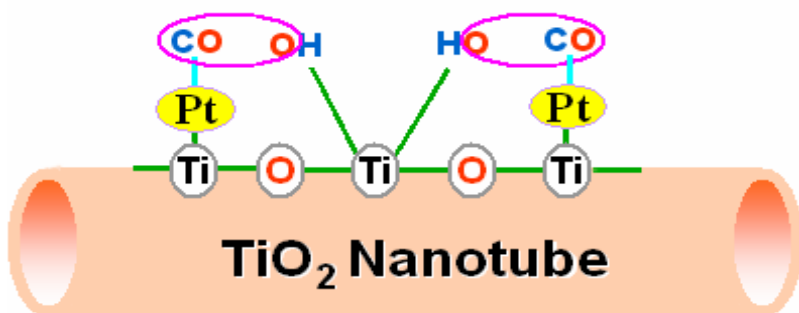


Fig. 2. A possible mechanism for the removal of CO poisoning intermediates during methanol oxidation over TiO₂ nanotube supported Pt catalysts. The step envisaged is: Pt-CO + OH(ads) → Pt··CO₂ + H⁺ + e⁻

OH (ads) forms on TiO₂ surface and oxidizes Pt-CO by a combination of metal support interaction (SMSI) and OH adsorption on TiO₂.

It is possible that a variety of other exotic anode electro-catalyst may be developed with increased activity and also considerably reducing the noble metal loading (say in sub-milligram scale without sacrificing the activity and long term stability of the electrodes.

4. Recent Developments in Cathode for DMFC

As pointed out, it is the oxygen reduction reaction that is sluggish and requires development of most efficient catalysts. Designing catalysts that can operate efficiently and last a long time is a barrier to making fuel cell technology commercially viable. Though Precious metal Platinum is the natural choice its cost and also its life time are the two limiting factors. In spite of all the developments, nearly upto 40% of the fuel cell's efficiency is lost in the cathode. Hence, according to Shouheng Sun (Professor at Brown University) the cathode reaction [9] "is a crucial step in making fuel cells a more competitive technology with respect to internal combustion engines and batteries". The group at Brown University has designed an exotic catalyst system based on the core shell model where in the core is generated from iron pentacarbonyl and shell of platinum was obtained by the decomposition of platinum acetylacetonate, thus effectively reducing the extent of use of platinum to the extent of 30%. These authors have claimed that the catalyst system that they have developed is 12 times more active and is stable over 10,000 cycles which are remarkable considering the current status of the possible oxygen reduction electrodes available today. In fact as early as 2000, Jens Rostrup-Nielsen has pointed out that the designing of effective catalyst for the oxygen reduction reaction is a dream for the researchers for over past five decades. Numerous reports have dealt with the preparation and functioning of noble and non-noble metal based catalysts (especially the control of the size of the metal particles) for oxygen reduction reaction. Among them Pt-Ir showed the highest voltage of 1.75 V (at 80 °C /1 mg/cm² loading) [10]. Materials with physical and chemical properties approximating to those of noble metals and whose electronic configuration is related to the noble metals are being explored. So far the general criteria for choosing the materials for ORR include high electronic conductivity,

thermal stability and also the chemical stability in acidic environment. The suitability of the noble metal based catalysts has been evaluated by several research groups. All these studies based on noble metal catalysts could only improve and enhance the output voltage by only 0.2 V. However, the aimed improvements in the fuel cell output is overshadowed by the attendant increase in cost as a result of the complex methods of preparation and also the instability of the catalyst to the unfavourable environment of the reaction. Non noble metal based materials are abundant in nature and also are cost effective than the noble metal based materials. The search for the non noble metal based materials is important due to the fact that they do not lose their reactivity and the productivity when they are employed in the methanol based fuel cells. Venkateswara Rao [11] has carried out ORR on various sizes of Pt particles supported on carbon [2.0, 2.5, 3.5, 4.0, 5.0 and 6.0 nm]. The Pt/C catalysts were synthesized and their reactivity was measured. The highest ORR activity (4.3 mAcm^{-2} at 0.7 V NHE) was exhibited by Pt with a particle size of 3.5 nm. In addition some complexes of Pt have also been studied for more than two decades. According to Yang *et al.*, [12] ORR has been carried out on Pt and Pt Ni complexes. The observed results indicated that the output voltage is only 0.9 V which is numerically greater than the reports of Stamenkovic *et al* [13], and Mukerjee and Srinivasan. [14]. The bi-functional mechanism of Pt/Ru catalyst has been studied extensively. According to these studies a Pt/Ru ratio 90:10 is the most effective stoichiometry for methanol electro-oxidation. Two effects were considered for the superior activity of binary Pt-Ru catalysts: the ligand effect and the bifunctional mechanism. Chalcogens appear to have most of the features expected for ORR catalyst. Since the complex Pt-Ru-chalcogen showed enhancement in the ORR activity, several research groups have worked on similar materials and the variation in composition of the constituents and preparation methods have been documented [11]. In spite of all these efforts, there are still some aspects of oxygen reduction reaction that have to be fully understood.

Recently, taking clue from biological systems, various nitrogen containing complexes have been tried as catalysts for ORR [15]. The tetramethoxyphenylporphyrin and phthalocyanine complexes of iron and cobalt have been examined as ORR electrodes, especially the heat treated samples which could generate the metal nitrogen clusters which exhibited considerable ORR activity.

Typical results obtained for ORR activity of iron and cobalt tetramethoxyphenylporphyrin complexes are given in Table.7. The point that emerges from the results given in this table is that the heat treated tetramethoxyphenylporphyrin complexes of iron and cobalt show ORR activity comparable to that commercial Pt catalyst thus showing that it is possible to generate appropriate non noble catalyst systems for oxygen reduction reaction in Fuel cells. It is also to be noted that the activation barrier may be reduced on non-noble metal catalyst systems as compared to the commercial Pt catalysts.

Table.7 Estimated metal and nitrogen content, on set potential for oxygen reduction and ORR activity of catalysts generated from Fe- and Co- TMPP systems and that of commercial Pt Catalyst.

	Metal loading (%)	Nitrogen content (%)	Onset Potential in mV versus NHE	ORR activity at 700 mV versus NHE in mAcm ⁻²
CDX1-FeTMPPcl (UT)	2.01	2.0	+810	0.2
CDX2-FeTMPPCl(UT)	2.03	2.0	+830	0.4
CDX1-FETMPP (HT)	1.96	1.9	+840	4.2
CDX2-FeTMPP (HT)	1.97	1.9	+870	4.9
CDX1-CoTMPP (UT)	1.98	2.0	+740	0.2
CDX2-CoTMPP (UT)	1.97	2.0	+760	0.3
CDX1-CoTMPP (HT)	1.89	1.9	+795	3.2
CDX2-Co(TMPP (HT)	1.93	1.8	+860	4.5
Pt/Vulcan XC72R (E-TEK)	2.07	---	+915	4.9

UT – un treated HT – heat treated

The diffusion limited plateau polarization curves for carbon supported catalysts are shown in Fig.3. The model proposed by Jiang and Anson[16] shows that the plateau is inclined when the distribution of active sites is less uniform and the reaction is slower. A steep reduction wave similar to that observed on Pt catalysts is seen on these catalysts systems which have been supported on HNO₃ treated oxidized carbon. It has been deduced that the presence of quinine type species with well dispersion of MN₄ species may be responsible for the observed ORR activity. The surface oxygen functionalities generated by the nitric acid treatment may be facilitating the dispersion of MN₄ type species without much agglomeration of the active species.

It is therefore possible that alternate Oxygen Reduction electrodes without the use of noble metals can be successfully developed and exploited in DMFC.

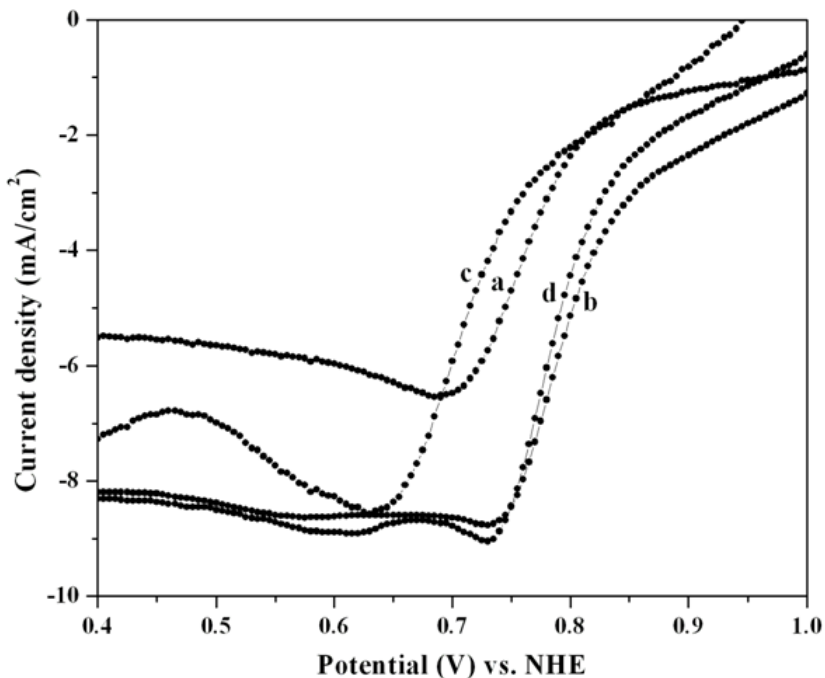


Fig.3. Polarization curve of heat-treated MTMPP (M = Fe and Co) supported on as-received and oxidized carbon catalysts: (a) CDX1-FeTMPPCl(HT), (b) CDX2-FeTMPPCl(HT), (c) CDX1-CoTMPP(HT) and (d) CDX2-CoTMPP(HT) in O₂- saturated 0.5 M H₂SO₄; Scan rate – 10 mV s⁻¹

5. Studies for Membrane Development

In order to avoid the complete monopoly of Nafion membranes, the concept of hybrid membrane has been introduced. The conceptual framework for this development is shown in Fig.4.

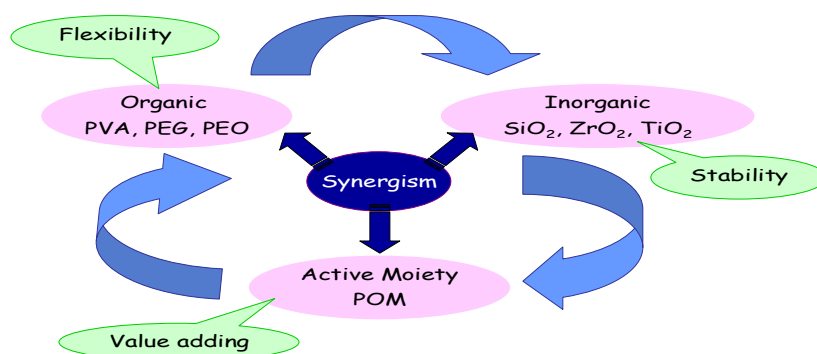


Fig.4. The synthetic strategy employed for the preparation of hybrid membranes (Adopted from S. Shanmugam, *Some device applications of (embedded) metal oxygen cluster compounds*. PhD thesis, Indian Institute of Technology, Madras (2004).

The development of hybrid membranes with inorganic organic components with active moiety has gone through a step wise process as shown in Fig.5 in order to eliminate the drawbacks normally found in the developed membranes. In this exercise, the methanol cross over from anode to cathode has to be considerably reduced as compared to what is achieved in commercial Nafion[®] 115 membranes.

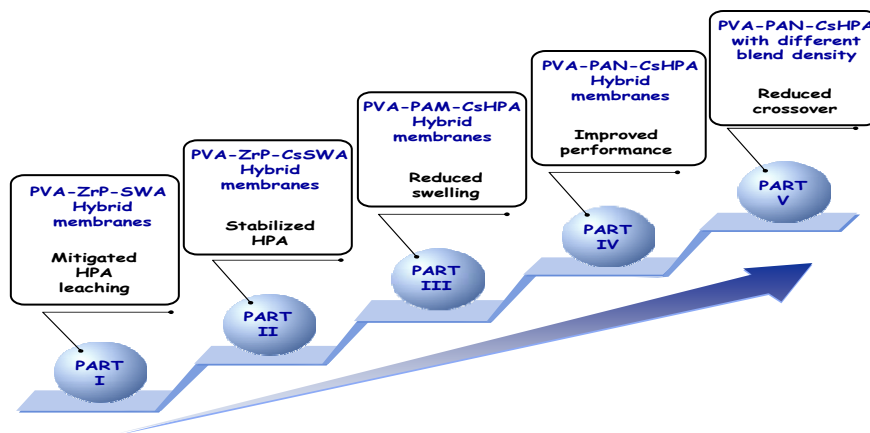


Fig. .5. The five step process for the development of hybrid membrane.

Various types of membranes have been developed for deployment in DMFC. Poly (vinyl alcohol) (PVA) based [17] have been tried but the strong hydrophilic characteristics and the swelling behaviour in aqueous solutions have been the main drawbacks for their direct use in DMFC. A set of hybrid membranes with different blend ratio of PVA and polyacrylonitrile with proton conductors based on heteropoly acids has been designed and prepared. The properties of the developed membranes are given in Table.8 together with the values for Nafion.

Table.8. Water uptake, Methanol uptake, Swelling and Ion-Exchange Capacity (IEC) values for different hybrid membranes compared with that of Nafion[®]115

Membrane	Water uptake (%)	Methanol uptake (%)	Swelling (%)	IEC meq.g ⁻¹
Nafion [®] 115	22	80	12	0.9
PVA(90)-PAN(10)-CsPMA-Glu	46	5.7	4	0.61
PVA(80)-PAN(20)-CsPMA-Glu	30	4.2	2.4	0.59
PVA(70)-PAN(30)-CsPMA-Glu	21	2.2	2	0.55
PVA(90)-PAN(10)-CsPWA-Glu	34	6.5	3.6	0.7
PVA(80)-PAN(20)-CsPWA-Glu	27	4.9	2.2	0.65
PVA(70)-PAN(30)-CsPWA-Glu	18	3	1.7	0.62
PVA(90)-PAN(10)-CsSWA-Glu	30	8	2.4	0.74
PVA(80)-PAN(20)-CsSWA-Glu	25	6.5	2	0.7
PVA(70)-PAN(30)-CsSWA-Glu	16	4.6	1.3	0.7

CsPMA; CSPWA and CsSWA – Cesium salt of phosphomolybdic acid; phosphotungstic acid and silicotungstic acid respectively. Glu - glutaraldehyde

Using these hybrid membranes, methanol cross over studies have been carried and the results obtained are shown in Fig.6. and follows the order PVA-PAN--CsSWA-Glu < PVA-PAN--CsPWA-Glu< PVA-PAN--CsPMA-Glu << Nafion® 115. The selectivity defined as the ratio of conductance and the methanol cross over is also another parameter for selecting membranes for DMFC application. The data for the hybrid membranes are shown in Fig.7. All the designed membranes outperformed Nafion® 115. The high selectivity of the hybrid membranes is attributed to the dense interpenetrating network that is formed, leading to low methanol permeability.

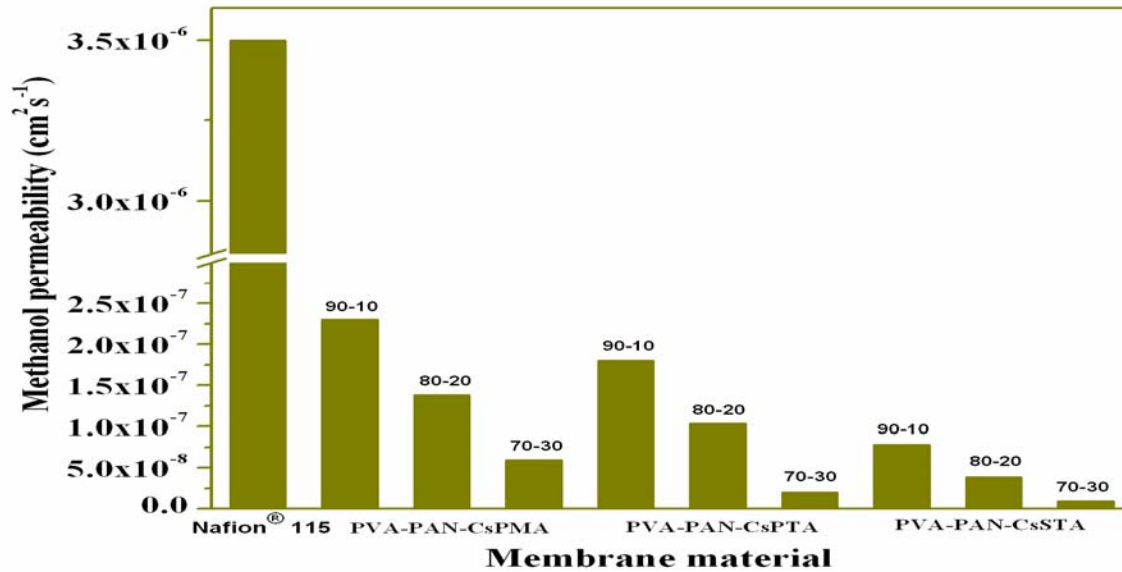


Fig.6. Methanol permeability of hybrid membranes with different blend density compared with that of Nafion® 115.

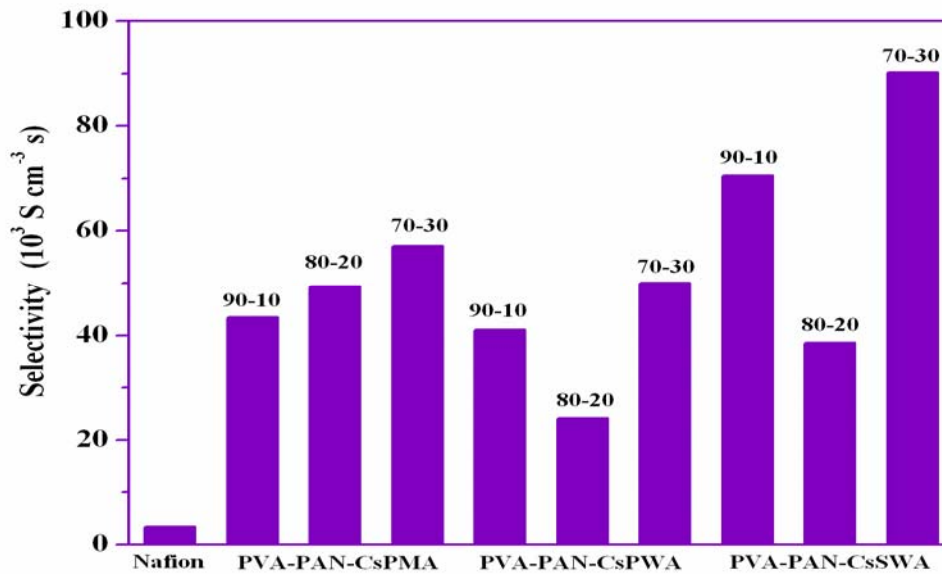


Fig.7. Selectivity of hybrid membranes compare with that of Nafion® 115.

6. Epilogue: The purpose of this presentation is to provoke alternative thinking for the conventional Pt based electrodes and nafion® membranes for DMFC. The postulates and principles enumerated in this presentation are only indicative conceptual possibilities and certainly not the exhaustive listing. It is clear that alternative most active, efficient, cost effective electrodes and membranes may be developed in the future and the DMFC will become a viable alternative energy source.

References

1. B.Viswanathan and M Aulice Scibioh, Fuel Cells: Principles and Applications, CRC press, January 2008.
2. Frank de Bruijn, The current status of fuel cell Technology for mobile and stationary applications, Green Chem., &, 132 (2005).
3. Heinzl, C. Hebling, M. Müller, M. Zedda, C. Müller, Fuel cells for low power applicaitons, J Power Sources, 105, 250 (2002).
4. T, Maiyalagan, *Electro-catalytic supports for noble metals for exploitation as electrodes for fuel cells*. PhD thesis, Department of Chemistry, Indian Institute of Technology, Madras.(2007)
5. Man-Yin Lo, I-Husan Liao, Chun-Chieh Huang, Key issues in the preparation DMFC electro-catalysts, Int. J. Hydrogen energy 32, 731 (2007)
6. Roy,S.C., A.W. Harding, A.E.Russell, and K.M. Thomas, Spectroelectrochemical study of the role played by carbon functionality in fuel cell electrodes, J Electrochem.soc., 144, 2323 (1997)
7. Maiyalagan, T. and B. Viswanathan, Template Synthesis and Characterization of Nitrogen Containing Carbon Nanotubes. *Mater. Chem.Phys.*, 93, 291-295 (2005).
8. Maiyalagan,T., B. Viswanathan and U.V. Varadaraju , Nitrogen containing carbon nanotubes as supports for Pt – Alternate anodes for fuel cell applications. *Electrochem. Commun.*, 7, 905-912. (2005).
9. <http://www.physorg.com/news193937033.html>; C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, "Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction", J. Am. Chem. Soc. 2007, 129, 6974; C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, "A General Approach to Size and Shape Controlled Synthesis of Pt Nanoparticles and Their Catalysis for Oxygen Reduction Reaction", Angew. Chem. Int. Ed. 2008, 47, 3588.
10. Millet, P., R. Durand and M. Pineri (1990) Preparation of new solid polymer electrolyte composites for water electrolysis. *Int. J. Hydrogen Energy*, 15 (4) 245. 10. 1 .
11. Venkateswara Rao, Ch., On the search for efficient catalysts for oxygen reduction reaction, Ph. D., thesis, IIT Madras (2008).
12. Yang, H., W. Vogel, C. Lamy, and N. A. Vante (2004) Structure and Electrocatalytic Activity of Carbon-Supported Pt–Ni Alloy Nanoparticles Toward the Oxygen Reduction Reaction. *J. Phys. Chem. B*, 108 (30), 11024.
13. Stamenkovic,V., T. J. Schmidt, P. N. Ross, and N. M. Markovic., (2002) Surface Composition Effects in Electrocatalysis: Kinetics of Oxygen Reduction on Well-defined Pt₃Ni and Pt₃Co Alloy Surface. *J. Phys. Chem. B*, 106 (46), 11970.

14. Mukerjee, S., and Supramaniam Srinivasan, Enhanced electro catalysis of oxygen reduction on platinum alloys in proton exchange membrane fuel cells, *Journal of Electroanalytical Chemistry*, 357, (1-2), 201. (1993).
15. Venkateswara Rao, Ch., and B. Viswanathan, Oxygen reduction by FeN₄ - a DFT study, *Indian J Chem., Sec A* 43A, 2333 (2004).
16. Jiang, R., and F C Anson, The origin of inclined plateau currents in steady state voltammograms for electrode processes involving electrocatalysis, *J. Electrochem. Soc.*, 147, 4605 (1991).
17. Helen, M., Development of Hybrid Membranes for Application in Direct Methanol Fuel Cells, Ph D Thesis submitted to the Indian Institute of Technology, Madras April 2009