Challenges on Materials Development For PEFC Applications

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Abstract

Current limitations related to the development of effective, durable and reliable MEA components for PEFC applications are addressed. Advancements made in the development of materials (catalysts, membranes, bipolar plates, etc.) for PEFC are shown. The effect of the catalyst on PEFC performances based on cells fed by hydrogen, direct methanol, direct propane, or direct acetal fuels are presented. The progress in cell performance and cathode research are discussed. Perspectives related to CO tolerance anodes are indicated. The effect of the membranes on the cell performance are shown and parameters which may help the development of appropriate membranes depending on the fuel are suggested. Openings for the future in materials processing and development for PEFC mass production are discussed.

Key words: Materials for PEFC; Direct Carbon Compound PEFC, prospects for new materials.

1) Introduction:

Due to the material issues, the development of PEFC technology is at its critical stage. Several issues are limiting PEFC products commercialisation :1) The first issue is the relatively poor electrochemical reactivity of oxygen at low temperatures. This is the greatest technology challenge confronting the use of oxygen in electrochemical processes like Polymer Electrolyte Fuel Cells (PEFC) because at least 60% of the cell potential loss at the cathode. Further, the porous air electrodes in PEFC requires optimised structure and very active catalyst for oxygen reduction. Efficient cathode electrodes must exhibit these two features at the same time. Since, platinum based electrode remain the best catalyst for the oxygen reduction in aqueous electrolyte like in PEFC, binary and ternary alloys of platinum show some promise. But the corrosion of these alloys in the operating conditions of Fuel Cell limits seriously there use. The second limitation is the anode CO poisoning. This limits PEFC performances if the cell operating temperatures are bellow 150 °C. The third difficulty is the critical choice of membranes for PEFC applications. This is related to the fact that the selection of the fuel is still straightforward and a number of fuels including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc.) are still in consideration for PEFC applications. Accordingly, cell temperature operation at temperature more than 150 °C is very interesting because at this range of temperatures, anode catalyst poisoning by CO is less. Per-fluorinated membranes cannot be used in PEFC operating in this range of temperature because they will loose their mechanical properties and their swelling properties will be lowered. They do not perform well in a light carbon compounds PEMFC and above 85 °C in hydrogen PEMFC. The fourth issue is the consideration for environmental friendliness processes of materials. This may limit the type of materials to be processed. This limitation may, for example favour the utilisation, of protonated rather than fluorinated membranes, in particular in the case of mass production of membranes. The fifth consideration is the material cost. This is a key issue for the technology because the current cost(at least 50 000 $ US/kW), the technology commercialisation will be limited. The reduction of materials cost related to mass production would not be enough to cut the current price to at least ten times for membranes and catalysts and twenty times for conventional graphite plates. As an example, with the current technology, the mass production would not be enough to cut the current price of the Nafion® (~ 650 $.m^{-2}) to at least one order of magnitude for PEFC application in electrical vehicles where at least 5 to 12 m^2 surface area of membrane is necessary to get 40 – 60 kW power for a middle size electrical car. To achieve this goal the development of New Materials is the key factor to meet those requirements. The aim of this paper is to present challenges related to the development of materials for PEFC applications and perspectives related to materials development are discussed.
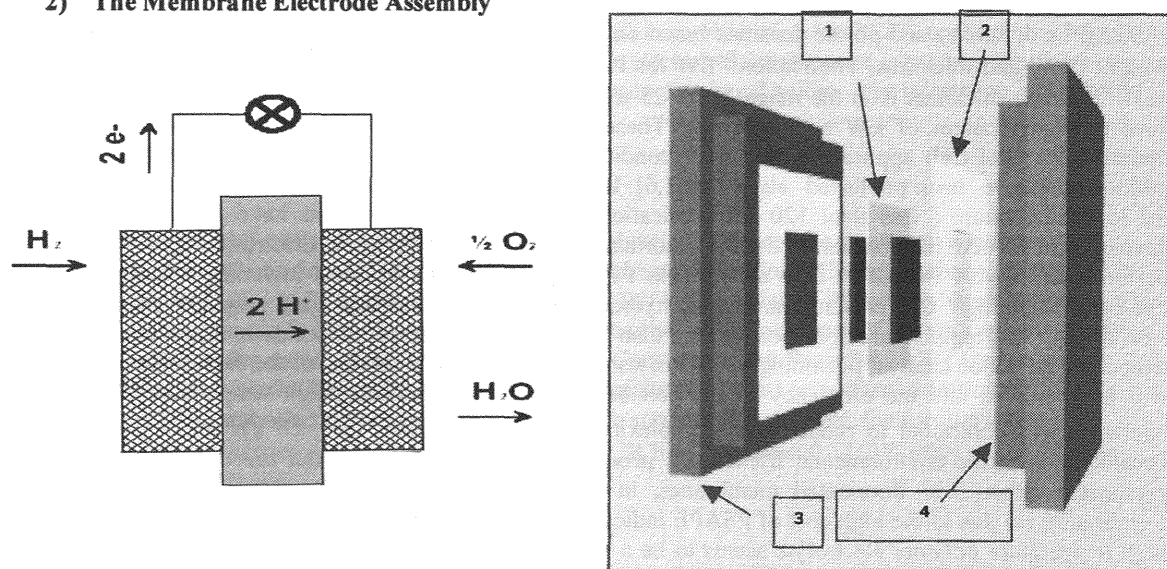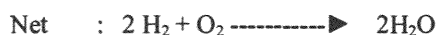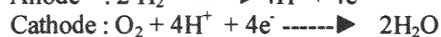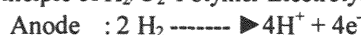
2)　The Membrane Electrode Assembly

Fig 1: Principle of H_2/O_2 Polymer Electrolyte Fuel Cell reactions and single cell components

Anode 　: $2 H_2$ ------- ▶ $4H^+ + 4e^-$

Cathode : $O_2 + 4H^+ + 4e^-$ ------▶ 　$2H_2O$

Net 　　: $2 H_2 + O_2$ ----------▶ 　$2H_2O$

The single cell components are: (1) Membrane Electrode Assembly (MEA); (2) Gasket; (3) Copper end plate and (4) graphite plate.

Membrane Electrode Assembly is the basic component of the single cell. It is located between two flow field plates which are designed to distribute the reactant the fuel (hydrogen) at the anode and the oxidant (oxygen or air) at the cathode. It collects also current produced from the reactions at the MEA interface. The MEA it self is a five layer structures: i)Proton Exchange Membrane (PEM) is the key element of this component which separates the two electrode structures to prevent reactant gas mixing and the formation of an electrical short. This makes its properties, functionality, cost and reliability very important for real cell operations; ii) each electrode structure consists of gas diffusion substrate and a catalyst (Pt-based) layer deposited on its surface. The catalyst can also be deposited on the membrane by screen printing, gravure printing, spraying, or rolling. In all the cases, catalyst layers must be thin as possible, e.g. 5 to 50 µm thick with the complete MEA around 500 µm or less. Challenges related to the MEA fabrications are: i) automation of its fabrication; ii) low-cost/high volume of materials processes; iii) reliable, durable and very effective characteristics; etc. With these requirements, each components must exhibit specific properties.

3)　Membrane Challenges

The main properties required for PEM to be used in Fuel Cell systems are[1]: i) good (over long periods) mechanical and chemical stability in strong oxidative environment; ii) high proton conductivity which can be obtained by increasing the proton exchange capacity, the water content and decreasing the membrane thickness; the proton conductivity may be due to the existence of ionic domains which swell in the presence of water; iii) high perm-selectivity for non-ionised molecules and anions; but conductivity decreases when selectivity increases and a comprise must be found. Most common potentially used membranes for low temperatures fuel cell applications are per-fluorinated sulfonic acid electrolyte (PSAE). The development of these membranes by DuPont [2,3] with continuous improvements until today; the development of Dow membrane[4], Flemion® from Asahi

Glass and Acilplex® from Asahi Chemicals[5] made significant contribution in the utilisation of theses membranes for Fuel Cell Applications (Fig.1). DuPont has achieved important work on improvement of PEMFCs durability and power densities based on their membranes by decreasing their Eqivalent Weight (EW) and thickness. The Nafion® EW for PEMFC application ranges from 1100 to 1000 or less!) and their thickness is in the range 175 – 25 μm. The Flemion® and Aciplex® membranes may have the same ranges of EW and thickness. These various membranes are the most studied in literature for Fuel Cell applications and their conditions of preparation, properties, and Fuel cell performance have been published elsewhere[1,6]. Until know, they seem to be the best membranes for low temperature (less than 120 °C) applications. However several reasons have induced the development of new membranes: i) the Per-fluorinated sulfonic acid Polymer Electrolyte (PSAPE) performance is very limited if they are used in PEFC fed by a number fuels including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc.); Accordingly, cell temperature operation at more than 150 °C is very interesting because at this range of temperatures, anode catalyst poisoning by CO is less important and the kinetics of the fuel oxidation will be improved and the efficiency of the cell be significantly enhanced. High temperature cell operation will contribute to reduce the complexity of the hydrocarbon fuel cell system; ii) the consideration of the environmental friendliness processes of materials may favour the utilisation of protonated rather than fluorinated membranes, in particular in the case of mass production of membranes; iv) due to the high cost of PSAPE indicated in the introduction, development of low cost high temperature polymer electrolyte seems to be a prerequisite for the creation of cost efficient and long time operating PEFC applications in both automotive and residential/stationary market; etc. Instead of per-fluorinated ionomer membranes, several approaches are currently used to develop new high temperatures Polymer Electrolytes: i) per-fluorinated inomer composite membrane[7,8]; ii) partially per-fluorinated ionomer membranes[9-11] ; iii) partially perfluorinated ionomer composite membranes; iv) non-per-fluorinated ionomer membrane and[1], v) non-per-fluorinated composite membranes[1]. As examples of current development, we have shown that: i) Nafion® can be modified with heteropolyacids(HPAs) to give effective composite membranes for Fuel Cell applications[7,12](Fig.2); ii) polybenzymidazole (PBI), a commercial polymer can be properly modified with sulfuric acid for PEFC application[13](Fig.3). Accordingly current commercial polymer can be modified to make new Polymer Electrolyte for PEFC applications.
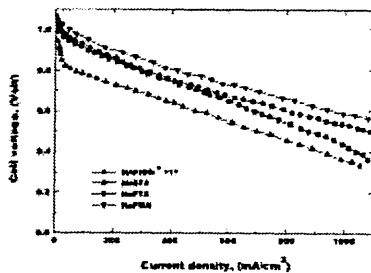

Fig.2[7, 12]
Potential-current polarisation curves of H2/O2 fuel cells using NafionÒ 117 (thickness = 180 μm. and water uptake of 30%), NaSTA (thickness = 175 μm and water uptake of 60%), NaPTA (thickness = 165 μm. and water uptake of 70%) and NaPMA (thickness = 160 μm. and water uptake of 95%).

I - V characteristics of H₂/O₂ SPEFCs based on PBI doped with H₂SO₄ and dried.
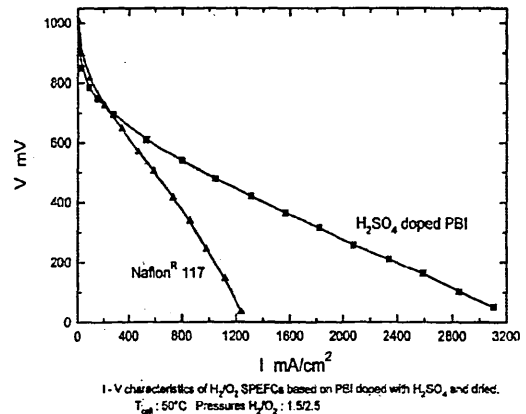T_cell : 50°C   Pressures H₂/O₂ : 1.5/2.5

Fig.3.V-I curves of H₂/O₂ PEFC[13]

The critical choice of membranes for PEFC is related to the fact that the selection of the fuel is still straightforward and a number fuels including reformed hydrogen with high CO content and light hydrocarbons (alcohol, natural gas, propane, etc) are still in consideration for PEFC application. The most important challenge related to high temperature polymer electrolyte development is to search for new electrolytes based on new ionomers which have never been developed before. The interesting issue should be to look for composite membranes.

5) Catalyst issues

Until now, Pt-based catalysts are the best for PEFC application. They are the most active in operating conditions for O_2 reduction; H_2 Oxidation and they are the stable against PEFC corrosive environment In commercial H_2/O_2 PEFC systems, carbon supported Pt (high loading of $Pt.cm^{-2}$) is used at the cathode and carbon supported Pt-Ru($< 1mgPt$-Ru cm^{-2}) is at the anode. Various types of carbon supports can be used for catalyst dispersion: i)Vulcan XC 72 R (cabot Corp.); ii) Black Peals BP 2000 (Cabot Corp.) iii)Ketjen carbon black (Ketjen Back Inter.); iv) Shawinigan (Chevron) or v) Denko carbon black (Denkon). The catalyst activity depends, of course of the support. For example, the specific activity $(mA.cm^{-2}.Pt)$ for oxygen reduction at 900 mV vs NHE, iR free, increases: 0.34(BP2000) < 0.48(Vulcan XC72R) < 0.94(Shawinigan) <1.85(Pt-black) [14].

5.1) The oxygen problem
The oxygen reduction reaction(ORR) over-voltage is the most important contribution in cell voltage losses in operating conditions of PEFC(Fig. 4) [see paper of Professor Ota Group in this proceedings].
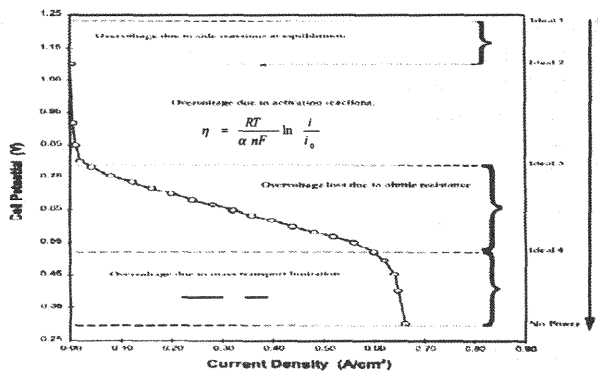

Fig. 4: Various contributions of potential loss: The loss of potential related to cathode luck of activity is from ideal 1 to ideal 3, e.g. at least 60% of the cell potential.

The loss of performance(due to catalyst activity), at operating conditions, of a pure H_2/O_2 PEMFC from a MEA based on Pt catalyst is: i) at least 300 mV from V^{eq} for O_2 reduction and; ii) few tens of mV for H_2 oxidation. This is due to very poor kinetics of O_2 reduction. The O_2 reduction exchange current density (i_o) is in the range $10^{-12} - 10^{-10}$ $A.cm^{-2}$ at room temperature. Increasing the temperature from 25 to 120 °C, will improve he current density from 10^{-10} to 10^{-6} $A.cm^{-2}$. Fundamental factors contributing to lowering the catalytic activity of O_2 reduction on Pt are:i) Break a strong O - O bond early in 4-electron reduction:

$O_2 +4e^- +4$ $H^+ = 2H_2O$; V^{eq} (20 °C) =1.23 V vs NHE .
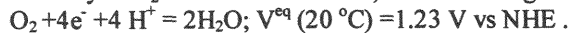
This is notable for the catalyst; ii) Open circuit potential(V_{oc}) is lowered from thermodynamic value (V^{eq}) due to the production of hydrogen peroxide according to:

$O_2 + 2H^+ + 2e^- = H_2O_2$; V^{eq} (20 °C) =0.68 V vs NHE;
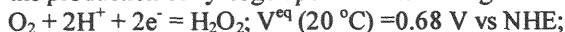
And; iii) formation of platinum oxides at high cell potential according to :

$Pt + H_2O = Pt$-O $+2$ $H^+ + 2e^-$;　V^{eq} (20 °C) =0.88 V vs NHE;
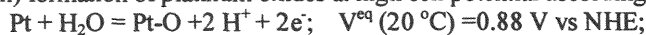
Materials which have been successfully considered as oxygen cathode and which exhibited interesting intrinsic activity are Pt Alloys: Pt-Fe; Pt-Mn; Pt-Ni; Pt-Cr; Pt-Zr; Pt-Ti; etc. In PEFC operating conditions,

they exhibited a 25 mV more improved over-voltage than the corresponding pure Pt cathode which results in a 2% increase in cell electrical efficiency. But if we consider stability and cost effective issues their development for commercial systems should be limited. Approaches on the development of cathodes based on non-noble catalysts have been also introduced. They include lighted ruthenium based chalcogenides [15] and pyrolysed Fe porphyrins [16], metal carbides [17]. These catalysts are less active than Pt-alloy for O_2 reduction. Some mixed catalysts based on Pt-metal oxide are also under active development[18-23]. These types of cathodes are interesting because they may contain five to ten times less noble metal catalysts and their activities for ORR are better than either Pt or each metal oxide.

　Development of effective catalysts for ORR is one of the key element which must pay particular attention if we want to move PEFC technology forward. Challenges are to look for catalysts which may have the following characteristics: i) allow O_2 adsorption better than Pt due to modified anion and water adsorption; ii) sensitive to electronic effect; iii) exhibit a more favourable inter-atomic distance than Pt-Pt; iv) have a preferential crystal orientation; v)exhibit improvement in the stability to sintering; vi) exhibit increase of catalyst surface area due to surface roughening after removal of some base atoms; vii) exhibit catalyst crystallites (2-4 nm) smaller than in pure Pt (more than 6 nm). Accordingly fundamentally different approaches are required if we want to recover the maximum of the 300 –400 mV available at the cathode. One of the new approaches could be the development synergetic catalysts which will allow the elaboration of composite catalyst which more active than each components of the composite material. As an example, specific activity ($\mu A.cm^{-2}$) e.g. the current density at 900 mV of O_2 reduction in acid medium is i_{Pt}= 50 $\mu A.cm^{-2}$; i_{H2WO4}= 1 $\mu A.cm^{-2}$ and $i_{Pt-H2WO4}$ = 1200 $\mu A.cm^{-2}$[19-25]. These results indicate that the composite electrode Pt-H_2WO_4, is better catalyst for ORR than Pt or H_2WO_4. This concept can be supported by quantum-chemical calculations of oxygen reduction energies on catalysts surface using ab initio simulation based on density functional theory and solid state physics. This is important because it is now well now that the oxygen adsorption process, and the first proton transfer step to the adsorbed oxygen are the determining step for ORR. The sequence succession are not know but it has been suggested that the oxygen adsorption structure on the catalyst surface is the key factor for the reactivity of ORR. Accordingly simulation on the oxygen adsorption may help to understand the oxygen behaviour on catalyst surface. For example simulations show that materials (Fe, Ni, Pd, Pt) can have similar oxygen adsorption mechanism but they can display differences in adsorption energy which decreases in the order: Fe > Ni > Pd > Pt[26] Another approach is to work on the catalyst utilisation by improving catalyst fabrication and dispersion. Improvement of catalyst utilisation leads to improved cell performance at the lower electrode platinum loading.
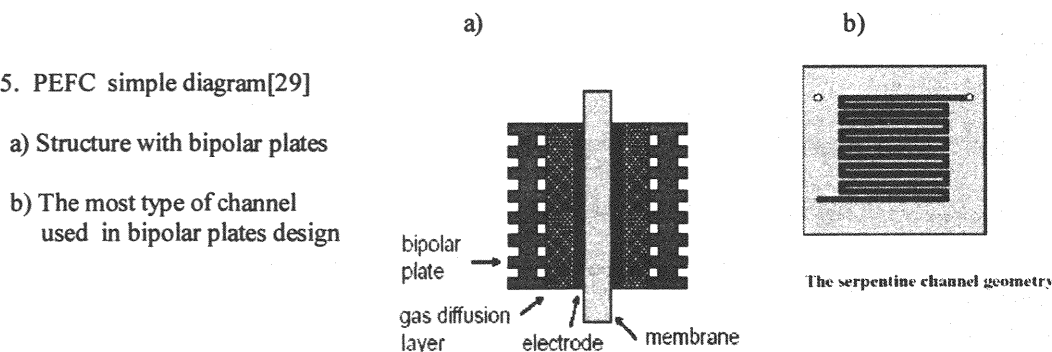
5.2) Anode catalyst

The advantage of the anode reaction ($H_2=2H^+ +2e^-$); V^{eq} = 0.00 Vvs NHE) compared to ORR for PEFC application is the high activity of Pt-based catalysts for H_2 oxidation ($i_o \geq 10^{-3} A.cm^{-2}$) and their low activity for O_2 reduction ($i_o<10^{-7} A.cm^{-2}$). At 80 °C of MEA operation, it may have significant poisoning issues at the anodes. Efficient catalyst anode operate at potential less than 0.20 V vs RSH. At those potentials, the effective alloy element to Pt weakens the Pt-CO bond. The exact mechanism is not proposed here. Several Pt-alloys including PtRu PtMo, PtSn, PtW, PtWo$_x$ etc. have been investigated, but except PtRu, no stable anodes has been identified for real PEFC. The best tolerant anode for hydrogen containing CO is PtRu[14]. The most current approach on the anode development is on the improvement of catalyst of catalyst composition and preparation. Accordingly, it has been shown that: i) PtRu at the composition from $Pt_{0.5}Ru_{0.5}$ to $Pt_{0.3}Ru_{0.7}$ is the best anode to solve CO poisoning effect without any lost of activity because there is sufficient Ru incorporated in Pt lattice and, ii) the preparation of thin catalysts layers (5-20 μm) allow higher tolerance to CO. They can be made by using either catalyst loading of 40 wt% Pt and 20 wt % Ru or high Electrode Pt surface area with PtRu ink preparations. There is still a big challenge related to the development of low loading of catalysts and high efficient anode for reformed hydrogen fuel containing more than 100 ppm of CO and for direct carbon compound Fuel Cells. The approach of synergetic materials could be an interesting concept for the development of effective catalysts PEFC anode. This concept can be supported by quantum-chemical calculations of CO, H and OH adsorption energies on catalysts surface using ab initio simulation based on density functional theory and solid state physics[27]. We have shown that PtSn and PtMo systems are better CO oxidation systems than Pt-Ru system[28].For Pt-Ru systems, a Pt over-layer enhances the Pt-Ru tolerance to CO oxidation. But attention may be paid relative to results based on simulation, because simulations involve a lot of

parameters on intrinsic properties of materials in quantum chemistry and particle interactions; but they do not take into account the catalyst fabrication procedure and the PEFC operating conditions. Consequently quantum chemistry calculations may help in selecting interesting materials.But it may be possible that they cannot be used in pratical systems. This is the case for example of PtSn systems which is not used in DMFC because it is unstable at elevated temperatures.

6) Bipolar plate issues

In a cell stack, bipolar plates serve several purposes: i) rigidity for the MEA; ii) distribution and separation of the fuel and oxidant; iii) electron flow through the stack; iv) good electrical contact with micro-diffuser Characteristics required for bipolar plates: i)high electrical conductivity and thermal compatibility with other component; ii) high corrosion resistance; iii) high mechanical strength; iv) low gas permeation ; v) low mass and volume for FC stack; vi) easy to manufacturer in low cost/high volume by automation; vii) low cost material. State-of-the-art stacks contain graphite machined or moulded bipolar plates. Graphite is the most common materials used because of its following interesting properties: i) good electronic conductor; ii) high corrosion rate; iii) low weight when compared to most of the metal. But graphite is limited for bipolar plate application due to its following week points: ; iv) low mechanical strength; v) high gas permeation if not treated with polymer resin to fill the pores; vi) high cost material for machined plates(70-120 $ US/kW) compared for example to aluminium coated with nickel by chemical bath

a)　　　　　　　　　　　　　　b)

Fig. 5. PEFC simple diagram[29]

　　a) Structure with bipolar plates

　　b) The most type of channel
　　　　used in bipolar plates design

bipolar plate

gas diffusion layer

electrode

membrane

The serpentine channel geometry

deposition (less than 5 $ US/kW).Conversely, metal plates (aluminium, steels, etc.) exhibit high strength, but corrosion passive oxide reduce their electronic conductivity. To increase structure strength and minimise gas permeation, graphite plates are usually thick. This allows gas channels on both sides. To ensure high rigidity to the system and collect the current from the bipolar plates, some copper end plates(Fig.1) are added to the structure. This can be very heavy and can be decrease if metals plates are used because they can be more thin and can act at the same time as bipolar and end plates. For example for a 60-cell stack, the mass distribution for its 33 kW PEFC stack is respectively[30]: i) 40 kg with graphite plates and they represent 88% of the stack weight; ii) 24 kg with coated aluminium plates and 81 % of the stack weight. Even graphite machined or moulded is the material for reference for bipolar plates applications in PEFC, its high cost (in particular for graphite machined) and its high mass and volume (more than 75% of stack mass and volume); other materials must be considered . Potential materials which are currently studied are: stainless steels; titanium; aluminium coated with gold; electroless nickel on aluminium; composite materials; plastics coated metals; other coated metals; etc. The main challenge for the bipolar issues is to develop light and low-cost materials which can act as bipolar and end plates in PEFC. Research on light metal alloys and composite materials could be interesting approaches for suitable bipolar plates development.

7) Issues Related to Direct light Carbon-compound PEFC Development

The selection of the fuel is still straightforward and a number of fuels including reformed hydrogen with high CO content and light carbon-compounds (acetals, alcohol, natural gas, polyhydric alcools, propane, etc.) are still in consideration for PEFC application. If pure hydrogen used as a fuel from reforming

process, the reformed fuel must be passed through a shift reactor and a catalytic preferential oxidation (CPOX) reactor. This reduces CO content in hydrogen at less than 100 ppm in which must feed the stack. Accordingly, significant additional cost and complexity of the stack must be considered due to reformer shift reactor and CPOX reactor. This complexity and cost can be avoided by feeding directly the stack with light crabon-compounds. Among the light carbon-compounds, methanol is the most studied for fuel Cell application. Very recent results[30] have shown that power density of 200 mW can be obtained at 120 °C, using 0.5 M CH_3OH, catalyst loading of $3mg.Pt.cm^{-2}$ at the cathode with a 50% reduction of methanol cross-over through Nafion 115 compared to 1M of CH_3OH; but the cross-over still exists. Even with this performance, methanol fuel still exhibited week points which should be taken into account before mass production of commercial Direct Methanol PEFC products. Some of the methanol limitations are: i) handling related to toxicity ; ii) anode poisoning related to the CO intermediates formed during its oxidation path (see problem of CO poisoning catalysts in section 5.2); iii) cross-over through membranes which creates the cathode depolarisation. Some other light carbon-compound should be deeply investigated because they have more strong interesting points than metahnol for PEFC applications. Few of them are listed in table 1.

Table 1: Some light carbon compound fuels for Direct PEFC and some properties

Type of Fuel	Formula	Solubility in water(25°C, g/l)	Vapour pressure (20 °C), bar	Melting point (m. p.)or boiling point(b.p.),°C	n^*
Methanol	CH_3OH	∞	0.13	65 (b. p)	6
Dimethylether (DME)	$(CH_3)_2O$	78	5.2	-23 (b. p)	12
Methylal	$((CH_3O)_2CH_2)$	33	0.44	42 (b. p)	16
Ethylal	$(CH_3O)_2(CH_2)_3$	90	0.78	88 (b. p)	28
1,3-dioxolane	$C_3H_6O_2$	∞	-	75 (b. p)	18
Trimethoxymet-hane (TMM)	$(CH_3O)_3CH_2$	∞	-	101 (b. p)	20
Trioxane	$CH_2O)_3$	∞	-	64 (b. p)	12
Ethanol	CH_3CH_2OH	∞	0.056	79 (b. p)	12

* n is the number of electrons transferred by complete electro-oxidation of one molecule

Dimethylether $(DME)(CH_3)_2O$) is an interesting fuel because: i) it is less toxic than Methanol; ii) it has no C-C bonding and its complete oxidation to CO uses 12 electrons instead of 6 electrons for methanol complete oxidation to CO_2; iii) it mass production seems to be more possible; iv) it is possible candidate to replace diesel fuel for compression- ignited engine and; v) the technology of handling and storage is already available even its vapour pressure is higher than methanol. Recent preliminary studies done on the Direct DME PEFC[32, 33] have shown that: i) the cell power density is similar to methanol; ii) the cell total efficiency is better than methanol and; iii) no oxidation of DME was observed at the cathode.
The acetals are methylal, ethylal and 1,3-dioxolane. The molecular formula of methylal is $(CH_3O)_2CH_2$ and its other synonyms are dimethyl orthoformate, dimethoxymethane or methylene dimethylether. The molecular formular of ethylal is $(CH_3O)_2(CH_2)_3$ and its other synonyms are diethoxymethane or diethylformal. The molecular formular of 1,3-dioxolane is $(C_3H_6O_2)$ and its other synonyms are dihydro-1,3-dioxole, dioxacyclopentane, ethylene glycol formaline, or formal glycol. Some other related fuels like trimethyl orthoformate($(CH_3O)_3CH_2$)), synonym of trimethoxymethane and trioxane $((CH_2O)_3)$ are also interesting due to the same raisons indicated above for DME.
We have established a programme of research on the development of direct acetals PEFC (DAPEFC) for portable application. The aim of this programme is to look for catalysts and membrane which may be very suitable for efficient DAPEFC. We studied the electro-oxidation of acetals in a half-cell on various anode catalysts [34]. The electro-oxidation of acetals exhibited higher current density than methanol oxidation (Fig.6). Electro-oxidation of methal, ethylal and 1,3-dioxolane has been performed on various composite electrodes and the comparison of their current density at 0.7 volt is shown in Fig. 7. As shown, the highest
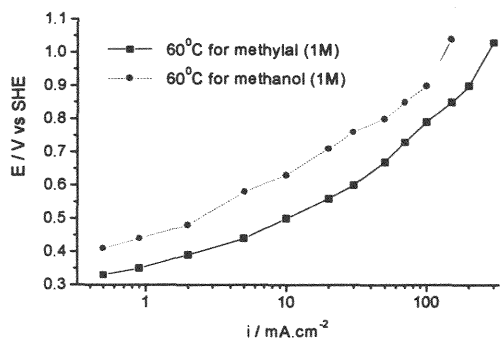
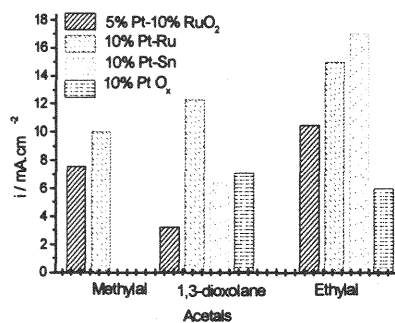Fig 6:Quasi-steady-state polarisation curves for the direct electro-oxidation of methylal (60°C) and methanol (60°C) in 1 M H$_2$SO$_4$.

Fig.7: Bar chart representation of direct electro-oxidation current density for methylal, 1,3-dioxolane and ethylal in 1 M H$_2$SO$_4$ at 25°C and 0.6 Volt vs SHE on various electrode materials

current densities are obtained with ethylal electro-oxidation. The value of the current density varies, of course, with the anode catalyst material. The highest current density is obtained with Pt-Sn, and Pt-Ru for ethylal and 1,3-dioxolane respectively. This is an indication of the selectivity of the anode reactions. Plotting the current densities at 0.70 V vs SHE vs the atomic radius of their respective metal. Volcano behaviour is obtained. The highest current density was obtained with platinum and rhodium and the lowest was obtained with palladium and ruthenium. Binary-alloy-based catalysts show an interesting correlation

between the current density at 0.70 V vs SHE with $\Delta R = R_{metal} - R_{Pt}$ as shown in Fig. 8. The lowest current density is obtained when ΔR is close to zero and catalytic activity of the binary catalyst increases with $|\Delta R|$. Accordingly, the highest values of current density are obtained for Pt-Sn and Pt-Ru.

We have obtained the same results with methanol electro-oxidation. This may explain why the Pt-Sn and Pt-Ru alloys are considered, up to now, the best binary platinum catalyst for the methanol fuel cell anode [34-38]and references therein]. This also explain why Pt-Ru and Pt-Sn have shown to be the efficien catalysts for the electro-oxidation of dimethoxymethane, trimethoxymethane and 1, 3, 5-trioxane [39]. Polarisation curves of Direct Acetal PEM fuel cells based on these anodes are in agreement with the relationship between the results obtained in Fig. 8 and the performances of fuel cells based on these electrodes (Fig. 9). This might help in the selection of alloys for the electro-oxidation of acetals from a combination of catalytic binary alloys having particular value of ΔR. Consequently, new binary alloys could be designed for direct acetal fuel cells.

Low-temperature Direct Propane Polymer Electrolyte Membrane Fuel Cell (DPFC) based on low-cost modified membranes was demonstrated for the first time[40]. . The propane was fed into the fuel cell directly without the need for reforming. A PBI membrane doped with acid and a Nafion® 117 membrane modified or non-modified with silicotungstic acid were used as the polymer membranes. The anode was based on Pt, Pt-Ru or Pt/CrO$_3$ electro-catalysts and the cathode was based on a Pt electrocatalyst. For non-optimised fuel cells based on H$_2$SO$_4$ doped PBI membranes and Pt/CrO$_3$ anode, the open circuit potential
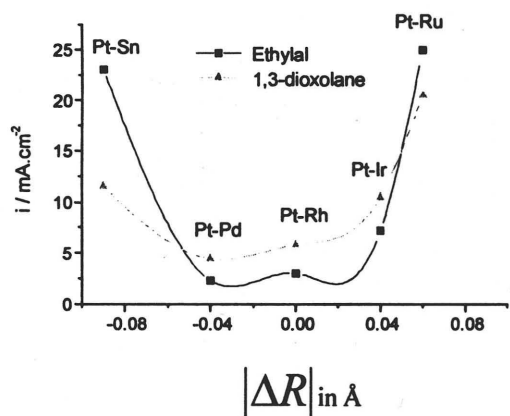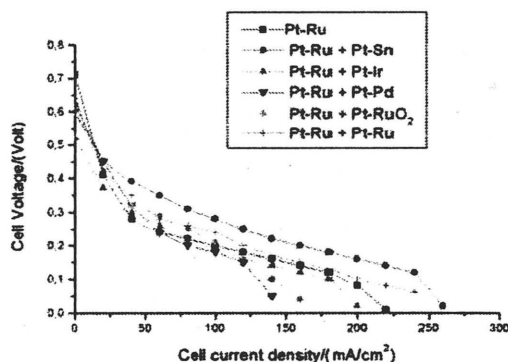
Fig.8: Variation of i with $|\Delta R|$

Fig.9:V-I curves of Direct Acetals/O₂ PEFC

was 1.0 Volt and the current density at 0.40 Volt was 118 mA.cm⁻² at 95°C. For fuel cells based on Nafion® 117 membranes modified with silicotungstic acid and on Pt/CrO₃, the open-circuit voltage was 0.98 Volt and the current density at 0.40 Volt was 108 mA.cm⁻² while fuel cells based on non-modified Nafion® 117 membranes exhibited an open-circuit voltage of 0.8 Volt and the current density at 0.40 Volt was 42 mA.cm⁻²(Fig.10). It was also shown that propane fuel cells using anodes based on Pt-Ru/C anode (42 mW.cm⁻²) exhibit a similar maximum power density to that exhibited by fuel cells based on Pt-CrO₃/C-anode (46 mW.cm⁻²), while DPFC using a Pt/C-based anode exhibited lower maximum power density (18 mW.cm⁻²) than fuel cells based on the Pt-CrO₃/C anode (46 mW.cm⁻²)(fig.11).
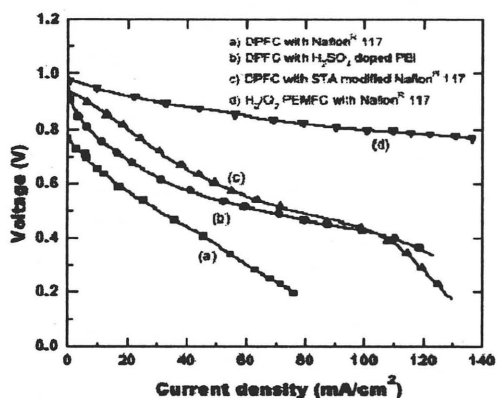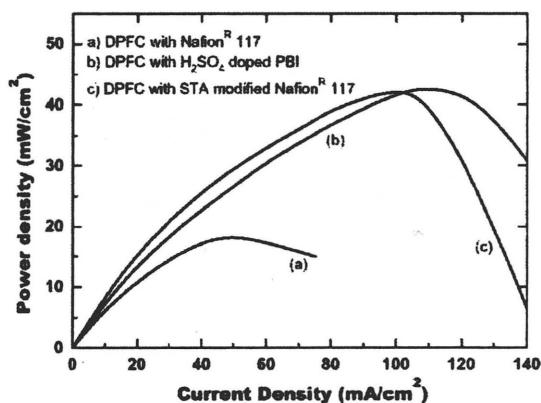

Fig. 10: V-I curves of Direct Propane/oxygen PEFC

Fig. 11: Power density vs current density plots derived from Fig. 10

8) Conclusion

 The current cost (at 50 000 $ US/kW) of PEFC stack technology for stationary or electrical vehicle application is not favourable for commercialisation. Several issues are responsible for this high cost. The first consideration is the materials cost (catalysts, membranes, bipolar plates). It seems that the Pt loading used in the state-of-the-art technology does not allow significant reduction of the catalyst cost in the stack. With about 10 g of Pt per kW, the problems of platinum for PEFC applications seem to be related to: i) the intrinsic cost and/or availability of the platinum metal; ii) the limited performance of Pt for oxygen reduction and/or iii) the non-optimisation of the catalyst utilisation. This optimisation can be achieved by making very thin catalyst layer (less than 50 μm) on the catalyst support. Even with this further optimisation, new catalyst development is one of the key element for performance enhancement and cost cut. High temperatures new low cost ionomer polymer electrolyte and/or composite polymer electrolyte are the key factors for breakthrough in membrane cost and increase stack performances. Even with moulded method of fabrication, graphite bipolar plate would not allow significant breakthrough in the cost reduction of the plates. Accordingly, development of new bipolar plates (light metal alloys, metal or coated metals, composite, etc.) is necessary. The second issue is the absence of automation of components and stack fabrication. Cost reduction related to mass production will be achieved if appropriate automation system for the components and stack are developed. The third issue is related to the improvement of the stack performance (new oxygen catalysts, high temperature electrolytes, etc.) durability, reliability, while maintaining high power density and specific energy density. These issues are the key parameters to be improved for low cost mass production PEFC stacks. We may have some dreams: i) Find an available and low-cost non-noble metal catalyst which is very efficient for oxygen and hydrogen reactions in PEFC operating conditions at temperatures higher than 150 °C.; ii) Find a low cost high temperatures proton electrolyte which may perform well in such conditions; iii) Find a conducting, low cost and light material for bipolar and end plates applications. These dreams may keep us very active because if we want to achieve mass production of market PEFC products, we must reduce the stack cost and improve its performance, durability and reliability. To achieve this goal the development of New Materials is the key factor to meet those requirements. Furthermore, the development of PEFC components based on thin films and surface modification technologies should also be our objective.

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