

Quantum jumps in the PEMFC science and technology from the 1960s to the year 2000

Part I. Fundamental scientific aspects[☆]

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Abstract

Proton exchange membrane fuel cells are at present in the forefront of all types of fuel cells because of the ‘quantum jumps’ in its technology since its application in the 1960s in NASAs Gemini space flights as an auxiliary power source. PEMFC technology since the 1960s highlights the ‘quantum jumps’ both in the fundamental areas of research (Part I) and in the engineering and technology and developmental (Part II), which are leading to the era of promising applications. This part of the review is on the ‘quantum jumps’ in the fundamental areas of research, which have enabled the rapid advances in the technology development, i.e. (i) transition from polystyrene sulfonic acid to perfluorosulfonic acid membranes; (ii) a 10- to 100-fold reduction in the platinum loading in electrode by using nanosize electrocatalyst particles supported on high surface area carbon and impregnation of the proton conducting electrolyte into the active layer of the electrode; (iii) optimization of structure of electrode and of membrane and electrode assembly to enhance power densities to 0.5–0.7 W cm⁻² at desirable efficiencies; (iv) using perfluorosulfonic acid membranes for DMFCs instead of liquid electrolytes to attain reasonably good efficiencies and power densities. The vital scientific challenges needing resolution for further advances in the technology are also summarized. © 2001 Elsevier Science B.V. All rights reserved.

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1. Evolution of PEMFC technology and essential features of PEMFCs

Proton exchange membrane fuel cells (PEMFCs) have reached the stage of being in the forefront among the different types of fuel cells. The PEMFC (originally referred to as the solid polymer electrolyte fuel cell) was the first type of fuel cell to find an application — power source for NASA’s Gemini space flights in the 1960s [1,2]. Though this technology was dormant for about 20 years thereafter, the California Environmental Legislations and the USA Partnership for a New Generation of Vehicles program (PNGV), which was initiated in 1993 and sponsored by the US government and the big three US automobile

manufacturers, stimulated its worldwide renaissance for the transportation application; this renaissance, in turn, gave birth to the R&D programs for the portable power and power generation applications.

Fig. 1 illustrates the main components of a PEMFC power source: (i) the single cell containing the porous gas diffusion electrodes (anode and cathode), the proton conducting electrolyte, anodic and cathodic catalyst layers, mostly deposited on the electrode (but more recently in some work on the proton conducting membrane) and current collectors with the reactant flow fields; (ii) a stack of cells in series, with the current collectors also serving as the bipolar plates; (iii) cell stacks (modules) connected in series or parallel, depending on the voltage and current requirements for specific applications; and (iv) needed auxiliaries for thermal and water management and for compression of gases. The unique feature of the PEMFC, as compared with other types of fuel cells (except for the solid oxide fuel cell) is that it has a solid proton conducting electrolyte. PEMFCs operate at low temperature (below 100°C) and generate a specific power (W kg⁻¹) and power density (W cm⁻²) higher than any other type of fuel cell. It is for this reason that the PEMFC has

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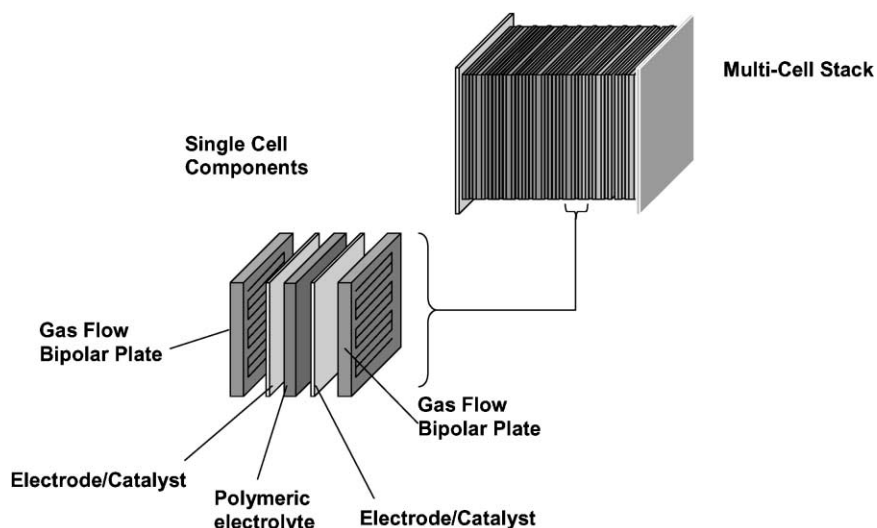


Fig. 1. Schematic of fuel cell and stack.

captured attention and is the leading fuel cell candidate as power sources for transportation, small-scale power generation and portable power. To reach this stage, there have been several ‘quantum jumps’ in fundamental science and engineering research and in the technology development of PEMFCs. Part I of this review focuses on the ‘quantum jumps’ in the fundamental scientific areas made to date, as well as on the challenges for reaching the era of applications and commercialization in the 21st century. Part II deals with the strides in the engineering and technology development, the technical and economic challenges still faced with for reaching the era of applications and commercialization in the 21st century.

2. Quantum jumps in PEMFC science enabling rapid performance improvement

2.1. Proton conducting membranes

The proton conducting membrane is the vital component of a PEMFC, which makes it possible to attain high power densities. The biggest ‘quantum jump’ in the PEMFC technology, was when the polystyrene sulfonic acid membrane (the electrolyte in the general electric 1 kW solid polymer electrolyte fuel cell (SPEFC), used as an auxiliary power source in every one of NASA’s Gemini flights in the

1960s), was replaced by Du Pont’s perfluorosulfonic acid membrane (Nafion[®]) in the 1970s [3]. Prior to the use of polystyrene sulfonic acid in GE’s SPEFC, other similar membranes were proposed, i.e. (i) phenolic membranes, prepared by polymerization of phenol–sulfonic acid with formaldehyde — this membrane had low mechanical strength; (ii) partially sulfonated polystyrene sulfonic acid, prepared by dissolving polystyrene sulfonic acid in ethanol-stabilized chloroform and sulfonated at room temperature — this membrane was brittle in the dry state; and (iii) inter-polymer of cross-linked polystyrene–divinylbenzene sulfonic acid in an inert matrix (polyvinylidene fluoride films impregnated with monostyrene, divinyl benzene and peroxides) — this membrane had very good physical properties. The polystyrene sulfonic acid membrane had a better water uptake and thus a higher proton conductivity than all the above-mentioned membranes. However, the main problems with all those types of membranes were that (i) the proton conductivities were not sufficiently high to reach a power density even as low as 100 mW cm^{-2} ; and (ii) oxidation of the C–H bonds occurred in the membrane due to the high potential of the PEMFC cathode, as well as by hydrogen peroxide, often formed at the anode by small amounts of cross-over from the cathode to the anode in the PEMFC. The ‘quantum jump’ in PEMFC performance, due to the transition from phenol sulfonic acid and polystyrene sulfonic acid membranes to Nafion (Table 1), were due to two

Table 1
Quantum jumps in the development of proton conducting membranes

Time	Membrane	Power density (kW m^{-2})	Lifetime (thousand of hours)
1959–1961	Phenol sulfonic	0.05–0.1	0.3–1
1962–1965	Polystyrene sulfonic	0.4–0.6	0.3–2
1966–1967	Polytrifluorostyrene sulfonic	0.75–0.8	1–10
1968–1970	Nafion experimental	0.8–1	1–100
1971–1980	Nafion production	6–8	10–100

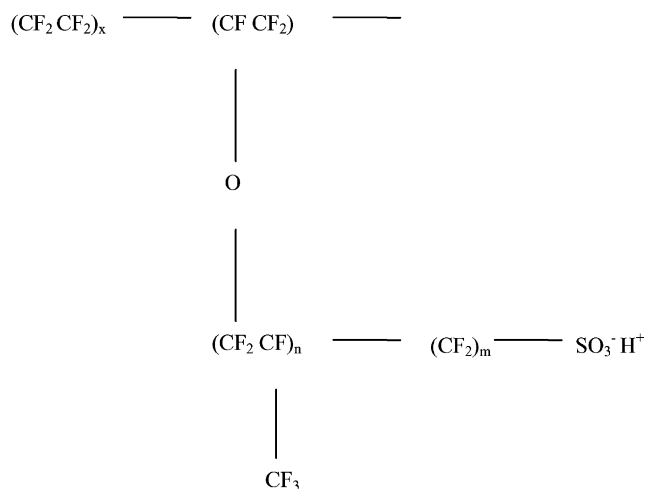


Fig. 2. Structure of Nafion.

reasons: (i) Nafion is a perfluorosulfonic acid, with a structure similar to that of Teflon, except that it has side chains with ether linkages, followed by CF_2 groups prior to the sulfonic acid (Fig. 2). The high electronegativity (i.e. electron affinity) of the fluorine atom, bonded to the same carbon atom as the SO_3H group, makes the sulfonic acid a superacid (e.g. like the trifluoromethane sulfonic acid). Thus, there was at least a two-fold increase in the specific conductivity of this membrane, as compared with the polystyrene sulfonic acids (Table 1); and (ii) the CF_2 groups are highly stable at the potential of the oxygen cathode and also at the anode, which may contain small amounts of hydrogen peroxide, as stated above. The most dramatic result by using Nafion, was that it extended the lifetime of PEMFCs at least by four orders of magnitude (Table 1). The Dow Chemical Company and Asahi Chemical Company synthesized advanced perfluorosulfonic acid membranes with shorter side chains and a higher ratio of SO_3H to CF_2 groups [4]. The lower equivalent weights of these membranes compared to Nafion account for their higher specific conductivities, which enabled significant improvements in PEMFC performance [4] (Fig. 3), i.e. about 50–100 mV increase in cell potential at $1 A cm^{-2}$ over that on the control Nafion[®] 115, with about the same thickness ($\sim 100 \mu m$).

Since the ohmic overpotential is predominant in PEMFCs in the intermediate to high current density range (0.3 – $1 A cm^{-2}$), one logical method of enhancing power densities is to use membranes thinner than Nafion[®] 115. Experiments have shown that H_2/O_2 PEMFCs with Nafion[®] 112 membranes ($50 \mu m$ thick) exhibit a cell potential of about 0.75 V at a current density of $1 A cm^{-2}$. However, there have been problems of (i) small amount of cross-over of the reactant gases, which reduced the open circuit potential of the cell by about 0.1 V and (ii) mechanical stability of the thin membranes, which have created hot-spots and cell failure. W.L. Gore and Associates were able to partially overcome the first problem and significantly the second problem by using supported Nafion[®] membranes [5]. In these membranes,

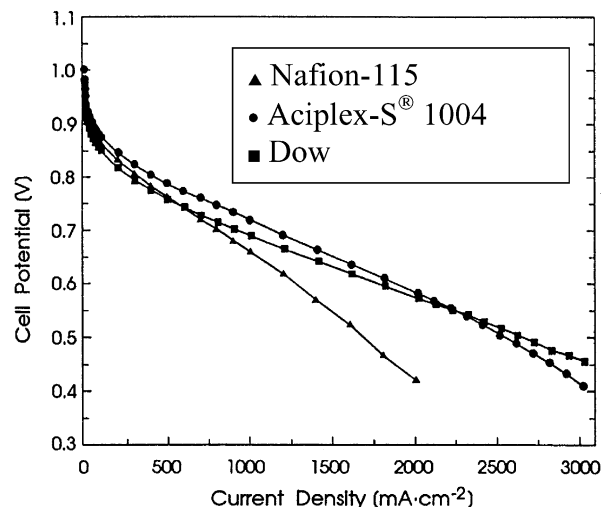


Fig. 3. Effect of different proton conducting membranes on PEMFC performance: H_2/O_2 reactants (E-TEK electrodes, 20% Pt/C, $0.4 mg Pt cm^{-2}$); $95^\circ C$; $P = 5 atm$. From [4], with permission.

solubilized Nafion is incorporated in a fine-mesh Teflon support. These membranes have a high mechanical strength, even when the thickness is as low as $10 \mu m$. Furthermore, even though the active proton conductor (Nafion) occupies only a fraction of the overall volume of the supported membrane, there is a compensation because the recast Nafion[®] in the membrane probably has a lower equivalent weight, and hence a higher proton conductivity than the conventional Nafion film. To date, the Gore membrane and electrode assemblies [6] (MEAs) exhibit the best performance in PEMFCs (e.g. as shown in Fig. 4) and several of the fuel cell developers (IFC, energy partners, plug power) are using these MEAs in their stacks.

One of the major problems with the perfluorosulfonic acid membranes has been and still is their high cost ($\sim US\$ 700 m^{-2}$). Thus, for a PEMFC operating at the

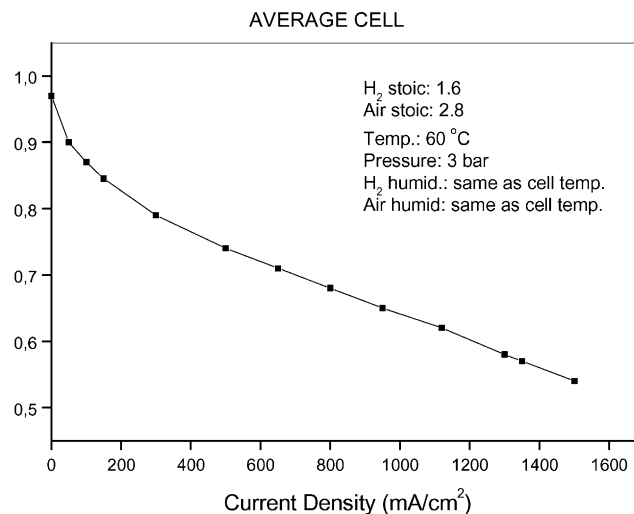


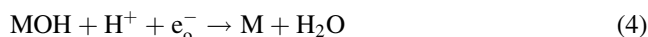
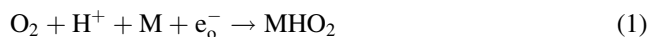
Fig. 4. Example of performance with a Gore membrane-electrode assembly.

desired power density of about 0.6 W cm^{-2} , the cost of only the membrane will be about $\text{US\$ } 120 \text{ kW}^{-1}$. This is at least 10 times too high to meet the projected cost ($\text{US\$ } 30 \text{ kW}^{-1}$) of the cell stack in the PNGV program. According to Du Pont and Asahi Chemical, increasing the production of perfluorosulfonic acid membranes to that required for at least a million vehicles per year, could make it possible to reduce the cost of the membrane by a factor of 10. The cost problem has created an incentive for developing other types of proton conductor membranes. The high cost of perfluorosulfonic acid membranes is due to the expensive fluorination step: thus partially-fluorinated and non-fluorinated ionomer membranes are currently under study [7]. The most promising membranes synthesized so far are based on: (i) sulfonated trifluorostyrene, (ii) sulfonated copolymers based on α , β , β -trifluorostyrene monomer, and (iii) radiation-grafted membranes. Among the non-fluorinated membranes, the following ones have been proposed recently: (i) sulfonated poly(phenylquinoxalines), poly(2,6-diphenyl-4-phenylene oxide), poly(arylether sulphone) or poly(2,6-diphenylol)-based membranes; (ii) acid doped polybenimidazole; (iii) sulfonated polyimides membranes; (iv) styrene/ethylene-butadiene/styrene triblock copolymers; (v) partially sulfonated poly(arylene ether sulphone); (vi) partially sulfonated polyether ether ketone (PEEK); (vii) poly(benzyl sulfonic acid) siloxane (PBSS) based membranes; and (viii) protonic electrolytes based on hydrogels. However, due to the low dissociation enthalpy of the C–H bond, the lifetime of the partially-fluorinated and non-fluorinated membranes is much shorter than that of Nafion, which is still the state-of-the-art membrane for PEMFCs.

2.2. Electrodes and electrocatalysis

In a PEMFC, as in the case of other low or intermediate temperature fuel cells (PAFC, AFC), Pt and Pt alloys are the best electrocatalysts, to date, for both hydrogen oxidation and oxygen reduction. In these types of fuel cells, the overpotential for the former reaction is considerably lower than that for the latter one — for example, in a PEMFC operating at current densities of 1 A cm^{-2} , the overpotential at the hydrogen electrode is about 20 mV and at the oxygen electrode is about 400 mV. About one half of the overpotential at the oxygen electrode is due to its loss at open circuit. The departure of the potential of the PEMFC from the reversible value is due to the extremely low exchange current density (i_0) for oxygen reduction (about $10^{-9} \text{ A cm}^{-2}$, very low if compared to that for the electro-oxidation of hydrogen, $10^{-9} \text{ A cm}^{-2}$ versus $10^{-3} \text{ A cm}^{-2}$) on smooth platinum electrodes. Because of such a low i_0 value, competing anodic reactions (oxide formation, oxidation of organic impurities) are responsible for setting up a mixed potential of about 1.00 V for the oxygen electrode at open circuit. Oxygen reduction is considerably more complex than hydrogen oxidation because of (i) the strong O–O bond and the formation of highly stable Pt–O or Pt–OH

species; and (ii) it being a four electron transfer reaction, and (iii) the possible formation of a partially oxidized species (H_2O_2). Being a four electron transfer reaction, there are at least four intermediate steps, as for example:



Even after over 50 years of research, we have still not reached a conclusive mechanism for the intermediate and the rate determining steps for this reaction on different types of electrocatalysts. This is unlike in the case of the two electron transfer hydrogen oxidation reaction, where there is definitive evidence for the reaction pathway:



with the first step being rate determining on platinum.

One of the major problems with the Pt electrocatalysis for hydrogen electrode is its low tolerance to CO in H_2 from reformed fuels (see sub-section 2.4 for approaches to increase the CO tolerance). Furthermore, according to the US Department of Energy, an increase of the cell potential to about 0.75–0.8 V is necessary for PEMFCs to compete with compression injection direct ignition (CIDI) engines in order to meet the goal of an efficiency of 45% for fuel consumption in the PNGV program. The improvement can only be possible by reduction of oxygen overpotential by 50–100 mV. A recent investigation has demonstrated that such an improvement is possible by using intermetallic electrocatalysts of platinum with a transition metal [8,9], as used in the state-of-the-art PAFCs. Fig. 5 shows that,

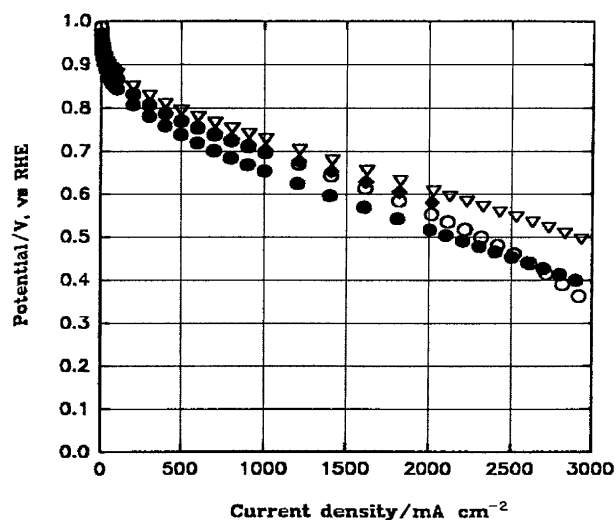


Fig. 5. Effect of Pt and Pt alloy electrocatalysts on PEMFC performance: H_2/O_2 reactants; 95°C ; 5 atm. Pt (●); Pt + Ni (○); Pt + Co (◆); and Pt + Cr (▽). From [8], with permission.

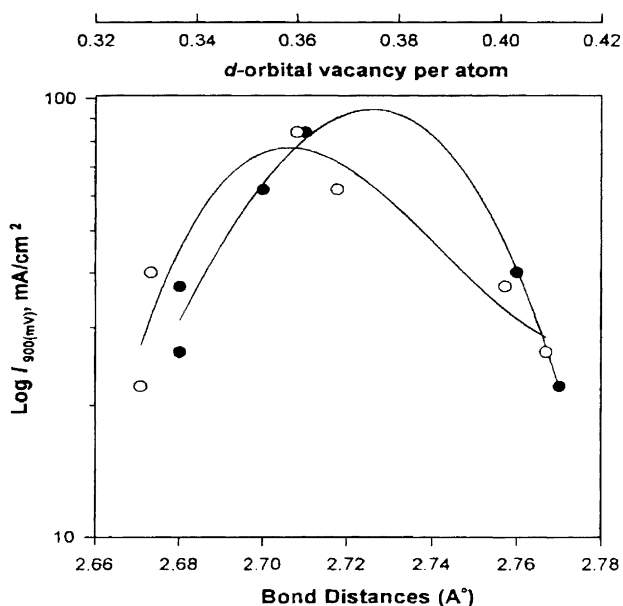


Fig. 6. Correlation of oxygen electrode performance ($\text{Log } i_{900mV}$, mA cm^{-2}) of Pt and Pt alloy electrocatalysts in PEMFC with Pt–Pt bond distance (●); and the d-orbital vacancy of Pt (○) obtained from in situ XAS. From [10], with permission.

with a Pt–Cr electrocatalyst, it is possible to meet the aforementioned goal for reduction of the overpotential for the electroreduction of oxygen. In this study, which also used an in situ electrochemical X-ray absorption spectroscopy technique, it was shown that there is a parabolic type of behavior for the dependence of the electrocatalytic activity on both the Pt–Pt interatomic distance and the d-band vacancy (Fig. 6) for the tested Pt–intermetallics [10]. These plots provide an explanation for Pt–Cr intermetallic having the most profound effect on the electrocatalytic activity.

One of the challenges in acid and alkaline fuel cells research has been to find non-platinum containing electrocatalysts for the fuel cell reaction. Platinum and/or platinum alloys are still the best electrocatalysts and are used in the state-of-the-art fuel cells. Significant progress was made in the late 1970s and early 1980s with a heat-treated metal–organic macrocyclic (e.g. cobalt tetraphenyl porphyrin) as the electrocatalyst for the oxygen electrode reaction in alkaline media. The electrocatalytic activity was close to that on Pt or Pt alloys. Due to the low corrosion rate of this transition metal, as well as of other transition metals such as iron or nickel which were tested as similar type metal–organic macrocyclics [11,12], in the perfluorosulfonic acid polymer electrolyte, there was a considerable degradation in performance. In the 1990s, studies on ruthenium-oxide pyrochlore ($\text{Pb}_2\text{Ru}_{2-x}\text{Pb}_x\text{O}_{7-x}$) [13] and on pyrolyzed Fe^{II} acetate adsorbed on 3,4,9,10-perylenetetra-carboxylic dianhydride [14], showed reasonable activities for the oxygen reduction reaction in acidic media, but these electrocatalytic activities were less than that of platinum.

2.3. Optimization of composition and structure of membrane and electrode assembly

The membrane and electrode assembly (MEA) is the ‘heart’ of the PEMFC. Its structure and composition are of vital importance: (i) to minimize all forms of overpotential and maximize the power density; (ii) to minimize the noble metal loading (and thus, the cost per kW of the PEMFC) in the gas diffusion electrodes by high utilization of the surface areas of nano-sized particles of the electrocatalyst; (iii) for effective thermal and water management (the latter including operation at the PEMFC without external humidification); and (iv) to attain lifetimes of PEMFCs, as necessary for the power generation, transportation and portable power applications. It is in this area of science and technology that major ‘quantum jumps’ have been made in the late 1980s and in the early 1990s.

The breakthrough to make a 10-fold reduction in platinum loading from about 4 mg cm^{-2} (as used in the Gemini space flights) to 0.4 mg cm^{-2} or less (in the PEMFC developed in the 1980s and 1990s, arose out of an invention [15] from Los Alamos National Laboratory, LANL). This was made possible by using platinum supported on high surface area carbon (e.g. Vulcan XC72R) as electrocatalysts (rather than pure Pt black crystallites, as in the Gemini fuel cells) and impregnation of a proton conductor (e.g. Nafion) into the active layer of the porous gas diffusion electrode. The main reasons for making it possible to reduce the platinum loading from more than $4\text{--}0.4 \text{ mg cm}^{-2}$ are: (i) the considerably higher BET surface area of the carbon supported electrocatalysts (particle size about 30 \AA) than that of the unsupported previously developed PEMFCs electrocatalyst (particle size about $100\text{--}200 \text{ \AA}$); and (ii) extension of the three dimensional zone in the electrode by the impregnation of the proton conductor so that the utilization of the electrocatalyst is similar to that in a fuel cell with a liquid electrolyte (e.g. phosphoric acid, potassium hydroxide).

The above-mentioned invention led to the demonstration of high power density PEMFCs with electrodes containing a platinum loading of 0.4 mg cm^{-2} or less by an optimization of not only the structure of the electrode, but also by that of the MEA [16]. The performance level of these PEMFCs were as good as or even better than PEMFCs developed with high platinum loading electrodes (Fig. 7). The spade-work to attain the ‘quantum jumps’ in the PEMFC performance at LANL, were followed first by investigations at Texas A&M University, and thereafter at a multitude of organizations—universities, industries and national laboratories [17,18]. The ‘quantum jumps’ at these laboratories were achieved by: (i) the above mentioned impregnation of the proton conductor into the active layers of electrodes (containing a low platinum loading), followed by hot-pressing of the electrodes to the perfluorosulfonic acid membrane, under the desired conditions of temperature ($130\text{--}140^\circ\text{C}$ for Nafion), pressure (2000 psi) and time (about 1 min). This procedure resulted in MEAs which exhibited a 10-fold increase in

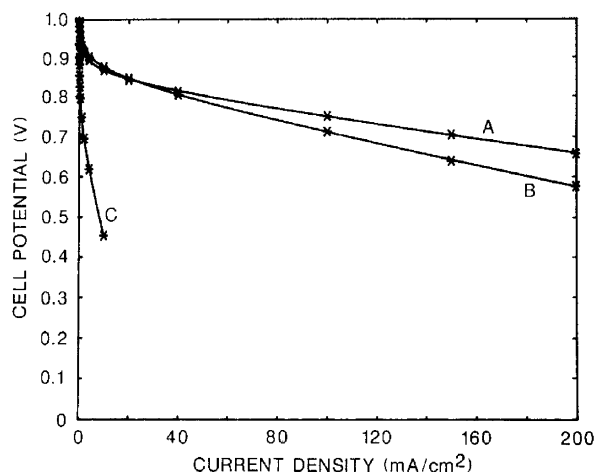


Fig. 7. Effect of platinum loading and electrode impregnation on PEMFC performance: H_2/O_2 reactants; $50^\circ C$; 1 atm. A and C cells with Nafion-impregnated and as-received Prototech electrodes ($0.35 \text{ mg Pt cm}^{-2}$), respectively; B cell with GE/HS-UTC membrane and electrode assembly (4 mg Pt cm^{-2}). From [16], with permission.

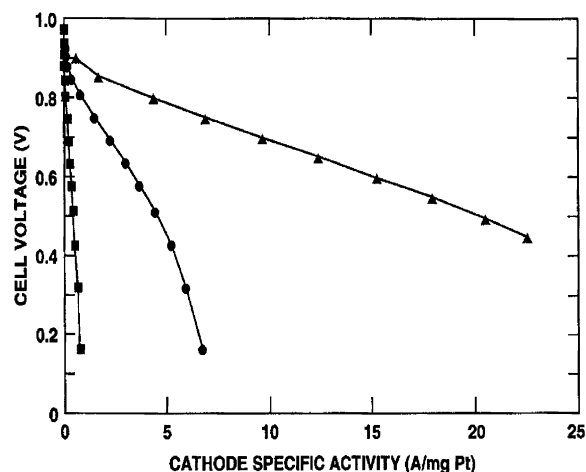


Fig. 8. Utilization of different types of catalyst layers in contact with ionomeric membranes (H_2 /air reactants): Pt black/PTFE (4 mg cm^{-2}) (■); ionomer-impregnated gas-diffusion electrodes ($0.45 \text{ mg Pt cm}^{-2}$) (●); thin film of Pt/C/ionomer composite ($0.13 \text{ mg Pt cm}^{-2}$) (▲). From [18], with permission.

performance, as compared with control samples, and about the same level of performance as an MEA with 10 times the Pt loading (Fig. 7); (ii) reduction in the thickness of the active layer of the electrode from 100 to $50 \mu\text{m}$, by using carbon supported platinum electrocatalysts with a Pt content of 20% instead of 10% as in conventional porous gas diffusion electrodes in order that PEMFCs could have (a) a better utilization of platinum, (b) lower activation, mass transport and Ohmic overpotentials, and (c) higher power densities; (iii) by using perfluorosulfonic acid membranes with a lower equivalent weight (i.e. higher ratio of SO_3H to CF_2 content), the specific conductivity and water retention characteristics in the membrane were increased, thus again making it possible to attain high power densities in PEMFCs ($0.5\text{--}1 \text{ W cm}^{-2}$ at over 50% efficiencies, Fig. 3).

In the late 1990s, other significant increases in power densities, with even further reduction in platinum loading (to a level of about 0.05 mg cm^{-2} for the hydrogen electrode and 0.1 mg cm^{-2} for the oxygen electrode) were achieved by deposition of thin active layers of the supported electrocatalyst and proton conductor on an uncatalyzed electrode [19,20] or on the proton conducting membrane [18] (Fig. 8). These active layers are only about $10\text{--}20 \mu\text{m}$ and contain no Teflon as in conventional electrodes. Because the active layers are considerably thinner than the conventional electrodes ($10 \mu\text{m}$ versus $50 \mu\text{m}$), the ohmic and mass transport overpotentials in the electrodes, (generally predominant at intermediate and high current densities) are greatly minimized. An equally important advantage of such types of electrodes is the increase in platinum utilization from about 20–25 to 50–60%. The high utilization of platinum is essential from the point of view of reducing the platinum loading and hence the cost of platinum in the electrode.

It is worthwhile stressing at this point that minimizing ohmic overpotentials is vital for attaining high power densities; and the most recent ‘quantum jump’ in performance of PEMFCs was made possible by using supported membranes (prepared by impregnation of Nafion into microporous Teflon mesh, see Chapter 2.1) invented by W.L. Gore and associates, and by deposition of very thin active layers (about $10 \mu\text{m}$), containing only the carbon supported platinum nanocrystallite and Nafion, directly on the supported membrane. The recast film of Nafion in the supported membrane has a higher specific conductivity and better mechanical strength than these of the commercial Nafion film with the same thickness. By deposition of the active layer on the supported membrane, the contact resistance between the two is greatly minimized. Thus, this MEA has shown the best PEMFC performance to date (Fig. 4) and is being widely used by fuel cell developers in the USA and Japan.

2.4. Tolerance to impurities in reformed fuels

Hydrogen is the ideal fuel for PEMFCs, generating the highest level of electrochemical performance. Many routes for hydrogen production have been developed; these include water electrolysis and reforming or partial oxidation of organic fuels such as natural gas, methanol and gasoline. Of all these processes, water electrolysis is the only one that produces ultra-high purity hydrogen; on the other hand, the level of CO impurities in the hydrogen produced via the steam-reforming or partial oxidation route is too high for PEMFC applications. The performance behavior of a PEMFC in the presence of CO in the fuel stream has been analyzed since the 1980s [21,22], and it has been observed that concentrations as low as 10 ppm lead to a decrease of

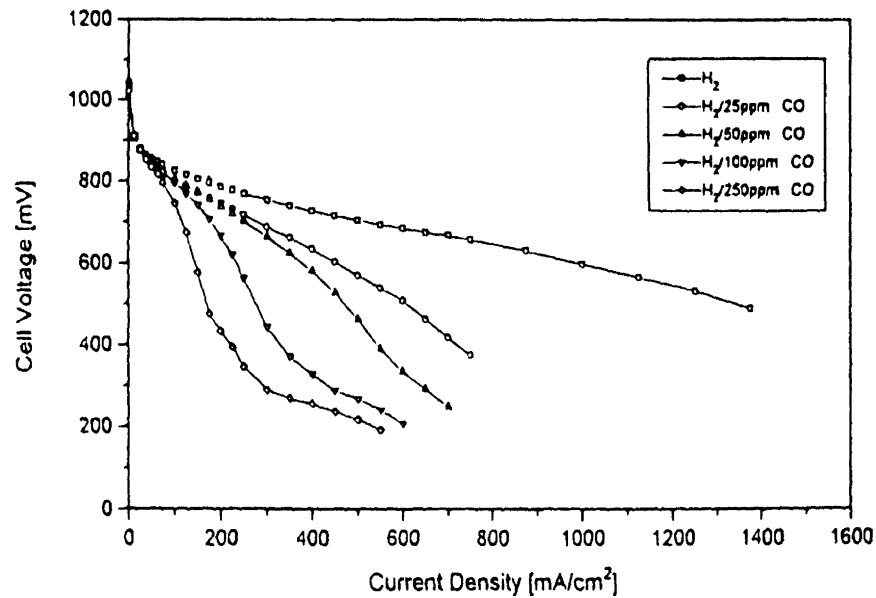


Fig. 9. Performance of H_2/O_2 PEMFC in presence of CO in the fuel stream. Electrodes: 30 wt.% Pt on Vulcan XC 72, 80°C , $P(H_2) = 0.22$ MPa, $P(O_2) = 0.24$ MPa. From [22], with permission.

performance by about $0.2\text{--}0.3$ V at 0.8 A cm^{-2} ; the dramatic loss of performance for CO contents of $25\text{--}250$ ppm in the hydrogen fuel stream is shown in Fig. 9. This is due to the fact that CO is preferentially adsorbed by the Pt electrocatalyst (e.g. the strength of the Pt–CO bond is higher than the Pt–H bond [23,24]), thus hindering the dissociative adsorption of hydrogen on platinum and its subsequent ionization. ‘Quantum jumps’ towards the goal of realizing a CO tolerant PEMFC have been made in the 1980s and 1990s, by: (i) the use of binary Pt–Ru catalysts and (ii) the

technique of oxygen bleeding in the fuel. The use of Pt–Ru alloy catalysts for PEMFCs was first proposed in the 1980s [25], and recent results [26] show that the cell potential is 0.4 V at 1 A cm^{-2} with an electrocatalyst loading of 1 mg cm^{-2} of $\text{Pt}_{0.5}\text{Ru}_{0.5}$ when 250 ppm of CO are present in the hydrogen fuel (Fig. 10); the same cell exhibits a potential of 0.68 V at 1 A cm^{-2} when operated with pure hydrogen. One explanation for the enhanced electrocatalytic activity of Pt–Ru is related to the changes in the lattice structure and in the surface properties due to alloying, which

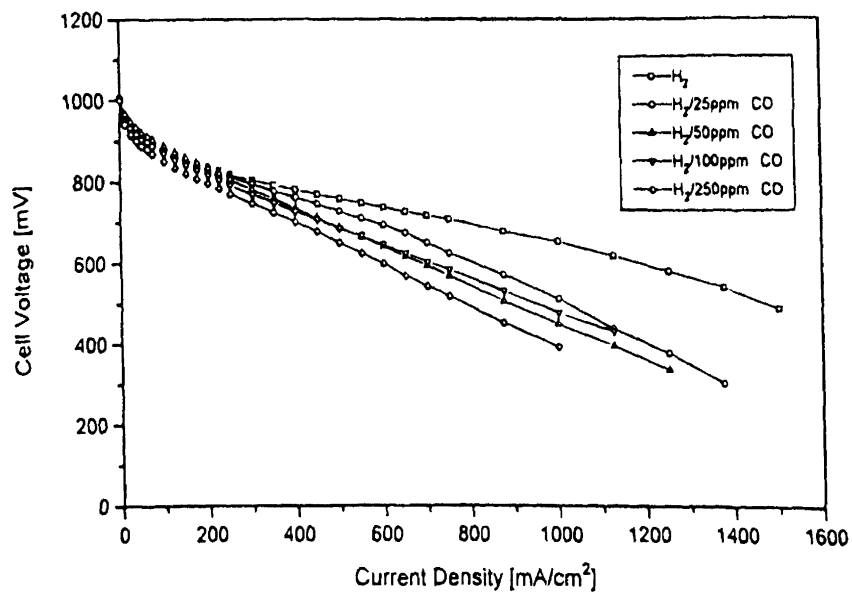


Fig. 10. Performance of H_2/O_2 PEMFC in presence of CO in the fuel stream, with 30 wt.% $\text{Pt}_{0.5}\text{Ru}_{0.5}$ on Vulcan XC 72 at the anode. Cathode: 30 wt.% Pt on Vulcan XC 72; 80°C , $P(H_2) = 0.22$ MPa, $P(O_2) = 0.24$ MPa. From [22], with permission.

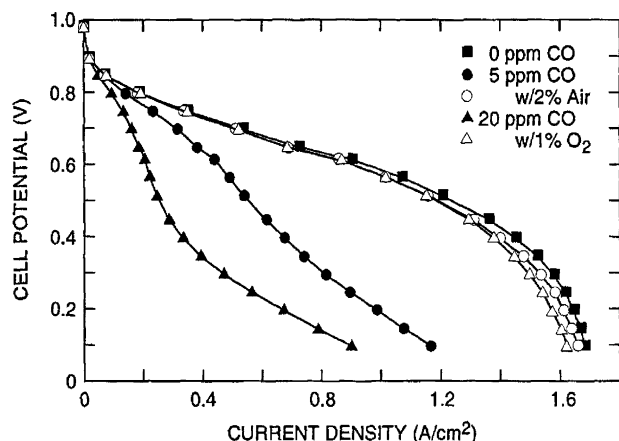


Fig. 11. Cleansing by oxygen bleeding of a platinum anode catalyst in presence of CO in the oxygen fuel. Results obtained with a Pt/C/ionomer thin film bonded to the membrane, $0.14 \text{ mg Pt cm}^{-2}$. From [27], with permission.

decrease the strength of the CO adsorption without increasing the overpotential for electroreduction of hydrogen; another is that the ruthenium in the electrocatalyst is in a partially oxidized state and provides the radical for the oxidative removal of CO adsorbed on neighboring platinum sites. Oxygen bleeding, the second technique proposed in the 1990s to solve the CO poisoning problem, involves injection of 0.4–2% O_2 into a CO contaminated hydrogen stream to rapidly oxidize CO adsorbed on the platinum electrocatalyst. The performance of a PEMFC with only the Pt electrocatalyst operating with up to 100 ppm of CO in hydrogen was found to be identical with that using pure hydrogen [21,27] (Fig. 11). However, a drawback of this method is that it cannot be used for higher concentrations of CO in the fuel stream, because higher concentrations of oxygen will be needed for its removal, and the limit in O_2 concentration is about 4–5%, which is close to the threshold value for causing an explosion. Further, oxygen bleeding could create hot-spots and the subsequent development of pin-holes in the membrane. Another drawback is that the oxygen remaining after the reaction with CO (e.g. most of the oxygen added) reacts with the hydrogen in the fuel, causing a loss in coulombic efficiency of the fuel cells. A related technique which was tested was to add small amounts (1–5%) of hydrogen peroxide to the humidification system; this led to the oxidative removal of CO by nascent oxygen [28]; the PEMFC tolerance level was about 100 ppm of CO on a pure Pt electrocatalyst.

A high percentage of CO_2 in the fuel stream can lead to a higher anodic overpotential than that expected from hydrogen dilution effects [29]. The reason is that the water gas shift reaction causes the electroreduction of CO_2 to CO in the PEMFC, and hence electrode poisoning. Oxygen bleeding and the use of Pt–Ru catalysts have been demonstrated to be efficacious in removing the adsorbed CO.

Another ‘quantum jump’ in increasing the CO tolerance of PEMFCs could be made by operating the cell at high

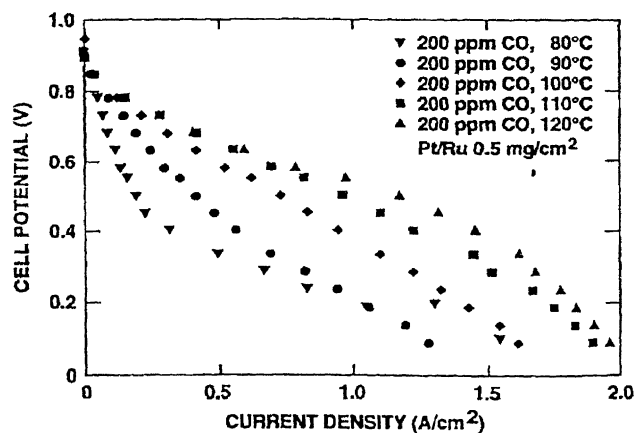


Fig. 12. Effect of temperature on a H_2/O_2 PEMFC fed with CO contaminated fuel stream. From [30], with permission.

temperature [30] (Fig. 12). This is because the strength of the CO adsorption on the Pt electrocatalyst at above 150°C is considerably decreased as compared with that of hydrogen adsorption; as a consequence the CO tolerance of the PEMFC increases. In fact, it has been well demonstrated that the level of CO tolerance in PAFCs is about 1% at 200°C . However, the possibility of operating PEMFCs at such a high temperature would need another ‘quantum jump’; the state-of-the-art PEMFCs cannot work above 100°C without increasing the pressure above the desired technical and economical limits for stationary and mobile plant applications. This limitation of operating temperature is due to the intrinsic characteristics of the perfluorosulfonic acid membranes, whose proton conduction mechanism requires complete hydration; research efforts are in progress at the present time to find new or modified proton conducting membranes for PEMFC operation in the temperature range $120\text{--}200^\circ\text{C}$.

2.5. Direct methanol fuel cells — electrocatalysis and methanol cross-over

Since the 1960s [31], the development of DMFCs has been a ‘Fuel Cell Researcher Dream’. The main reasons for this great interest were and still are: (i) methanol is a liquid fuel with a gravimetric and volumetric energy density of about half that of gasoline, thus a DMFC powered automobile, with about twice the efficiency of an internal engine powered automobile, will have the same range as an IC engine powered vehicle; (ii) successful development of a DMFC will eliminate the fuel-processor sub-system to produce hydrogen on board the vehicle. Since the weight and the volume of the fuel-processor sub-system are about the same as that of the electrochemical stack sub-system, this elimination will have the effect of significantly increasing the gravimetric and volumetric power and energy densities of the power plant; (iii) a DMFC is an ideal portable

power source for civilian and defense applications — laptop computers, cellular phones, portable power. The DMFC will have a considerably higher energy density than even the most advanced rechargeable batteries (e.g. nickel–metal hydride and lithium ion) currently used for such applications. Several organizations (e.g., Exxon, Shell, Allis Chalmers, Hitachi) were actively involved in DMFC R&D in the 1960s. Sulfuric acid was mostly used as the electrolyte. Two problems, which were and are still encountered are: (i) the low electrocatalytic activity of noble metals or their alloys, even at a high loading, for the electro-oxidation of methanol; and (ii) the cross-over of methanol from the anode to the cathode, which results in a significant loss in coulombic efficiency of a DMFC and in the depolarization of the oxygen electrode reaction at the cathode. Both these problems are the main causes of losses in cell potential and efficiency of the DMFC. There were also other problems such as degradation performance due to adsorption by intermediates and partial oxidation of methanol to formaldehyde and formic acid. However, in the 1960s and early 1970s, prototype fuel cells power sources were developed and demonstrated. R&D activities in this technology were dormant in the 1970s and 1980s. There was a renewed activity in the 1990s, mainly because of the rapid advance in the PEMFC technology. ‘Quantum jumps’ in the performances of DMFCs, with Nafion membrane as the electrolyte, were made at JPL in cooperation with Giner Inc. [32] and at LANL [33] (Fig. 13). A 50% Pt–50% Ru alloy electrocatalyst at a noble metal loading of $2\text{--}4\text{ mg cm}^{-2}$ yielded the best performance. Short stacks (a few hundred watts) developed by JPL/Giner Inc. and LANL have exhibited performance levels of about 300 mA cm^{-2} at 0.5 V . The researchers at JPL and LANL have shown that by operating at a current density of about 300 mA cm^{-2} , using at most a

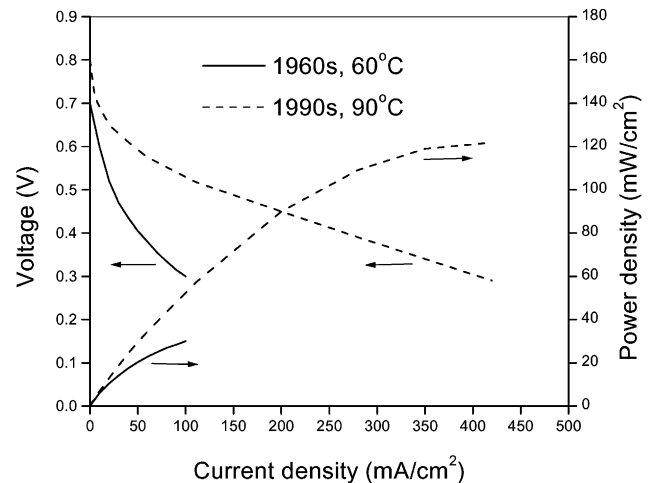


Fig. 13. DMFC performance in the 1960s and 1990s.

methanol concentration of $1\text{--}2\text{ M}$ in the fuel and a Nafion 117 membrane, the cross-over current can be greatly reduced, but this means operating the DMFC close to the limiting current density. Another approach to enhance the electrocatalytic activity for methanol oxidation, and reduce the cross-over current in DMFCs was discovered by researchers at CNR-TAE, Messina [34]. In this case, a composite membrane consisting of Nafion and silicon oxide was used as the electrolyte to operate the DMFC at a temperature of 140°C , rather than at $60\text{--}80^\circ\text{C}$, as in the above mention investigations. The electrocatalytic activity was enhanced and the methanol cross-over diminished to low values at current densities of about 300 mA cm^{-2} . The performance of the DMFC illustrated in Fig. 14 reveals the advance made using this approach. In this type of a fuel cell,

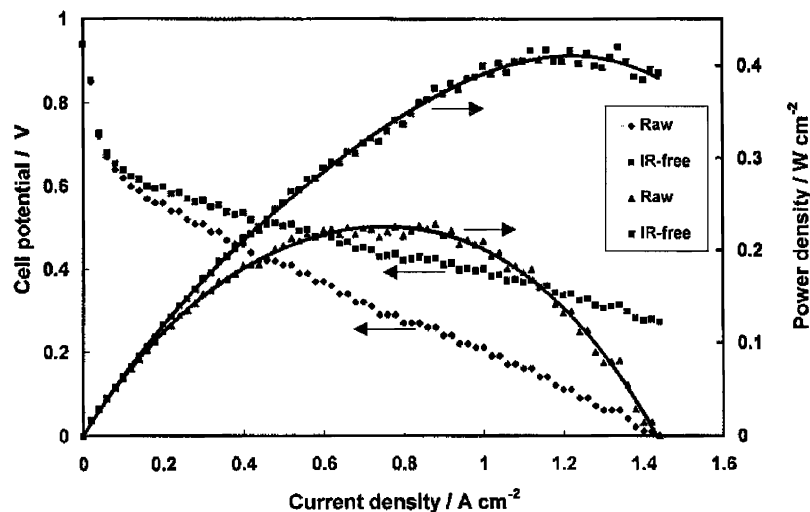


Fig. 14. DMFC performance with Nafion/silicon oxide composite membrane (electrolyte), 40% Pt–20%Ru/Vulcan XC 72, 2 mg Pt cm^{-2} (anode) and 20% Pt/Vulcan XC 72, 2 mg Pt cm^{-2} (cathode). $T = 140^\circ\text{C}$; anode $2\text{ M CH}_3\text{OH}$, 4.5 atm , cathode O_2 , 5.5 atm . From [34], with permission.

it was also shown that ethanol could also be used as the fuel, with a 95% coulombic efficiency.

3. Vital scientific challenges needing resolution for further advances in technology

Even though the research efforts, made so far, have led to successful solutions of many scientific and technological problems, bringing the PEMFC technology close to the era of commercialization, there are still some scientific challenges: (i) finding anodic electrocatalysts tolerant to CO at levels of 100 ppm (with noble metal loading lower than 0.1 mg cm^{-2} or less); (ii) inventing a cathodic electrocatalyst, to reduce the overpotential encountered at open circuit and to significantly enhance the exchange current density; (iii) finding alternative proton conducting membranes with lower cost but about the same proton conductivity of the state-of-the-art perfluorosulfonic acid membranes; (iv) developing new proton conducting membranes not depending on water for high temperature operation between 150 and 200°C ; and (v) discovering new materials for electrocatalysts and proton conducting membranes in order to advance DMFC technology to significantly increase the exchange current density for methanol oxidation, inhibit poisoning of the anode electrocatalyst by intermediates formed during methanol oxidation and minimize cross-over of methanol from the anode to the cathode. The achievement of the above mentioned goals (and of the technological challenges described in Part II of this work) is vital in order to speed up the process of manufacturing and commercializing PEMFCs and DMFCs. From a positive point of view, the rapid R&D advances in the last two decades has raised the hopes for commercialization of PEMFCs within the first two decades of the 21st century.

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