FUEL CELLS AND ETHANOL: A TECHNOLOGICAL ADVANTAGE

ABSTRACT 151/2003

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ABSTRACT

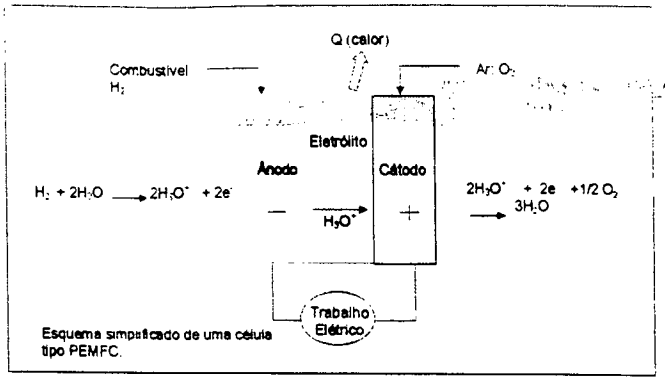
A new technological concept of electric energy ...ation appeared in the last years. The concept of ...ergy generation via "fuel cell" is becoming more and more important for energetic planning, due to its sole characteristics. This paper aims to relate and discuss the energetic fuel cell using ethanol, directly or indirectly, as a renewable fuel and show its importance and advantages within the field of alternative energies. The advantages of utilizing ethanol are very big. However for the commercial utilization, in both cases, of these technologies, it is necessary to implement a lot of work on R&D&I. In the short range period, the catalytic reform seems to be the best technological option. It is point out the importance of this alternative to be considered by the Brazilian Government, which would allow our sustainable entry for the so called "Hydrogen Economy".

INTRODUCTION

Ethanol is a primary renewable fuel which has performed important and growing role in the control of air quality in big urban Brazilian centers. Similarly, fuel cells represent, even in the medium range term, a clean, efficient and promiser technology for electricity generation for automotive vehicles, houses, industry and commercial buildings. Today, the markets for ethanol and fuel cells are being contemplated with big investments in technology and production. However, little attention is being paid to the combination of these two technologies, in our country and abroad. Many advantages can be obtained from this combination, as we will show in this paper, utilizing ethanol as a fuel, directly or indirectly, for fuel cells.

FUEL CELLS: As shown in the simplified sketch of Figure 1 fuel cells are, in principle, batteries of continuous operation, producing continuous current by the cold electrochemical combustion of a liquid or gaseous fuel, generally hydrogen.

Figure 1: A schematic acid fuel cell.



So, hydrogen is oxidized to protons in a gaseous diffusion electrode, releasing electrons, according to the equation 1 [1]:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (1)$$

In the opposite electrode, also a gaseous diffusion electrode, and considering the proton exchange membrane fuel cell (acid medium) the reaction is:

$$2e^- + \tfrac{1}{2} O_2 \rightarrow H_2O \qquad (2)$$

The global reaction, followed by heat releasing, could be written as:

$$H_2 + 1/2\, O_2 \rightarrow H_2O \qquad (3)$$

Cell work potential for the system hydrogen/oxygen between 0,5 and 0,7 V could be obtained. Open circuit potentials result between 1 and 1,2 V. Due to its high reactivity, hydrogen is, today, the best choice for the fuel. The different types of fuel cells are classified, generally, by the type of electrolyte employed and the operation temperature [1]. To gain proper work potentials, of course, it is necessary to stack some unities in series.

Actually, in the development of the fuel cells, it is avoided its dependence of pure gases as primary fuel and are preferred gases like natural gas, methane, gasoline and ethanol, reformed. Besides, for oxidant agent it is preferred atmospheric air instead of pure oxygen [1,2].

The energetic fuel cell has unique properties, like its environment character and high efficiency. It is proper to different uses like mobiles (autotraction), portables (laptops, mobiles, and so on) and stationary (distributed generation of electric energy).

PEM FUEL CELLS: The so called PEMFC (Proton exchange membrane fuel cell) are the most promissory for the mobile electric energy generation due to its high power density, easy on/off operations, flexibility in the build up of the unity, strength and other advantages like high efficiency with low pollutant emissions. Due to the low temperature operation, there are almost no NOx emissions, even employing air as cathode feeder. Low temperatures fuel cells apply also to stationary units. Platinum based electrocatalysts are to be employed in the PEM fuel cells for operations at temperature range of 70 °C to 90 °C in order to speed up the electrode kinetic and produce higher current densities. In PEM cells the particles of the electrocatalyst are in the range of nanometric size (2 nm), dispersed, generally, in particles of carbon black [3,4].

The theoretical efficiency η of a electrochemical energy production process, like those existing in PEM fuel cells is calculated by the quotient:

$$\eta = \Delta G/\Delta H \qquad (4)$$

Therefore fuel cells have much higher theoretical efficiency than the Carnot machines, mainly at low temperatures.

AUTOMOBILES DRIVEN BY PEM FUEL CELLS: the experiment to produce an automobile driven by a fuel cell is not new. Kordesch [5] was the first to build a car of this type in the final of the 60's. In the beginning of the 70's, in Dresden, Schwab et alli erected a cycle motor with cells using hydrazine and furthermore a microbus VW, which was successful until middle of the 90's. All these vehicles utilized alkaline cells.

Ballard, a Canadian company was the first to develop, successfully, a block of cells type 275 HP, electric power 200 kW , for the electrotraction of busses. The main difference for the conventional busses is the elevated roof, where are the pressure tanks (200 bar) for hydrogen [1,6]. The companies Ballard Automotive and Daimler-Chrysler developed not only a bus driven by a PEMFC as well as performing various stages for the development of a feasible passenger automobile driven by a PEM fuel cell. The base for this decision was the positive answer for the question of the future economic feasibility of the automotive traction by PEMFC, compared to internal combustion engines. As a result of the efforts, this company showed to the public some automobiles driven by hydrogen and other by methanol, as those of the NECAR series [1,6].

Actually almost all the great passenger automobile producers of the world are interested in the development of electrical vehicles driven by fuel cell. Various development of prototypes are in process, like those of Toyota, RAV4-FCEV, an sport utility; Opel (General Motors), zafira, a minivan built in the platform of Astra; Ford P2000, also a sport utility built in the platform of Mondeo. Others programs are in development by Honda, Jeep, VW, etc. For more detailed information on these projects see reference [7].

The utilization of hydrogen as a fuel for electrotraction, for substitution of the internal combustion

engines (Otto) is not a simples task since hydrogen requires for its handling complex techniques like high pressure cylinders. Even in the liquid form or in the form of a metallic hydride severe safety measures must be taken. Besides up to now there is neither a distribution net nor production capacity enough for the demand of a fleet of this type of vehicle. Methanol is, then, other candidate to a energy reservoir. Has also the advantage that its reform and conversion on board are simpler than those for gasoline and methane, since it has higher relative reactivity [1]. The reform of methanol is possible at 200°C (equation 5) whereas that of methane proceeds at 1000°C.

$$CH_3OH + H_2O \rightarrow CO_2 + 3\,H_2 \qquad (5)$$

Obviously it would be very interesting the development of a PEM which performed the direct inversion of methanol electrochemically, avoiding all intermediate stages of reform and purification. In fact, this is possible only in experiments of short duration, with significant densities of currents and powers, with low platinum charges. After some minutes occurs the poisoning of the catalyst, since the active surface of the catalyst is occupied by CO. In this case, there is the called DMFC (direct methanol fuel cell). However the amount of catalyst to be employed (noble metals) is ten times greater then the necessary for the direct conversion of hydrogen, to attain equivalent power density. This fact is not allowed economically for automotive electrotraction. Another problem is the high permeability of the membrane (electrolyte) to methanol producing the poisoning of the cathode catalyst, thus appearing an effect similar to a "short circuit" of the cell.

On the other hand it is known that an increase in the operation temperature of the cell from the actual 90 °C to, roughly, 200 °C would reduce considerably the problems of the electrode kinetics present in the direct anodic oxidation of the of methanol. The reason for that is the weakening of the adsorption bond of the CO on platinum at high temperature and the considerable acceleration of all chemical stages of the methanol anodic oxidation. But at 200°C one could no more utilize the membrane NAFION® as electrolyte, since its mechanics of conduction requires that the membrane be humidified and at this temperature of operation (200°C) it would be dry and could loose its ionic conductivity. The key for the direct conversion of methanol or ethanol would be not only the development of new catalytic systems but also in the introduction of acid ionic exchange membranes, which, even at high temperatures have important ionic conductivity.

ETHANOL AS FUEL: as the methanol, ethanol could be utilized in type PEM cells, since it is a liquid fuel easily produced with a relatively low cost, presenting some advantages over methanol as a fuel: it is less toxic, renewable, relatively cheap and with a good infra-structure in Brazil and the existence of technical standards for production, storage and distribution.

Ethanol has a relatively high energy density, 8kWh/kg (gasoline 11kWh/kg) and shows other advantages in relation to other conventional fuel such as gasoline or natural gas, like it does not contain sulphur, can be added to gasoline producing a mixed fuel of good performance, generates less toxic gases by burning, see Table 1, since it contains 35 % of oxygen and is much less toxic [9].

Table 1: Emissions of ethanol compared to the emissions of gasoline [10].

ETHANOL
15% Reduction of organic volatiles compounds.
40% Reduction of CO.
20% Reduction of particles.
10% Reduction of NO_x.
80% Reduction of sulphates.
Low emissions of hydrocarbons.
High emissions of ethanal and acetaldehyde.

The availability of ethanol is very satisfactory as it can be produced by the fermenting and distilling of sugar of different vegetables, as sugar-cane, crop, wood, wheat, and every other vegetable containing sugar, amido or cellulose.

Ethanol is particularly attractive as alternative fuel for countries like Brazil, with well established technologies of production and distribution, supplying the automotive industry (mixture with gasoline). Brazil produces and consumes about 4 billions of gallons per year [10]. The introduction of the so called DEFC (direct ethanol fuel cell) for the automotive electrotraction could be immediate, without great changes in the infra-structure already operating. One should consider, also, the aspect of being a renewable source of energy supported by ethanol production in great amounts from the fermentation of sugar-cane, easily cultivated in our country due to the climate and availability of agricultural areas.

However there are challenges to exploit this area of utilization. To get significant efficiencies with this fuel, in this type of system, the cell must be operated at higher temperatures, as already said, for methanol. At the moment, there is no polymeric material with all required characteristics to operate such a cell, it would be reasonable, for a limited time, the utilization of new polymeric materials with good ionic conductivity at 200°C, to perform electrocatalytic studies. A polymeric electrolyte of this type was suggested by Savinell et alli

[11.12.13.14] for applications in DEFC. poly-benzylmidazol. doped with acid (PBI).

Recent papers of these authors relate that they searched in the United States the direct oxidation of alcohols. in fuel cells utilizing membranes of PBI. doped with H_3PO_4. as electrolyte. Thus. it is suggested the following oxidation process of ethanol. involving 2 electrons. forming acetaldehyde:

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \quad (6)$$

Acetaldehyde diethylacetal pode ser formado por catálise ácida segundo a reação:

$$CH_3CHO + 2CH_3CH_2OH \leftrightarrow CH_3CH(OCH_2CH_3)_2 + H_2O \quad (7)$$

In presence of water the reaction (7) is strongly placed to the left, remaining only traces of acetal acetaldehyde for a anode feeding containing ethanol. The relative distribution of CO_2 is very low due to the oxidation of methanol (90 to 100 %). The global reaction for the oxidation of methanol to CO_2 can be written:

$$CH_3CH_2OH + 3\,H_2O \rightarrow 2\,CO_2 + 12H^+ + 12e^- \quad (8)$$

The water supplies the oxygen required for the reaction (8). Comparing the percentage of CO_2 produced by the oxidation of methanol with that of ethanol. one conclude that the break of the bond C-C, in the case of ethanol. plays an important role in the formation of CO_2. For the maximum utilization of the fuel it is required the total oxidation of ethanol to CO_2. However. from the environment standpoint. the formation of ethanal is preferable. since it is significantly less toxic compared to CO2 and formaldehyde. Besides it does not accumulate neither in live specimens nor in the environment. since it can be degrade biologically. However. before the utilization of ethanol as an alternative fuel be feasible. the yield of CO_2 during the direct oxidation of ethanol shall be considerably increased in order to increase the converting efficiency of the chemical energy to electrical in this type of fuel cell. The most proper way to be followed. aiming this goal. is the searching for more selective electrocatalysts for this system.

The option of indirect utilization of ethanol for hydrogen production can also be considered. in an intermediate step. until the technological problems with DEFC be satisfactorily solved [15.16.17]. As starting point we have the opposite catalytic reaction of the formation of ethanol. by 350°C:

$$CH_3CH_2OH + H_2O \leftrightarrow 2\,CO + 4\,H_2 \quad (9)$$

followed by the displacement conversion reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (10)$$

Besides. we should add a step of catalytic oxidation of CO not reacted. in order to reduce its concentration to figures less than 100 ppm. allowed by a PEM cell. and preferably 10 ppm. All these chemical steps should be processed catalytically and we should consider that the conditions of the process for the opposite reaction as well as the choose catalysts are not necessarily the same utilized for the reaction of the ethanol synthesis.

In Table 2 one can see a comparison between the characteristics of the two ways of ethanol utilization as fuel. the direct with DEFC and the indirect with reform processes.

Table 2 Comparison between direct ethanol utilization DEFC and the indirect utilization with reform processes.

DIRECT OXIDATION	CATALYTIC REFORM
Feasibility proved by R. F. Savinell em 1997. Refs 11-14.	Viabilidade comprovada por A. D. Little em 1998. http://www.ethanolmarketplace.com/102902news.asp
Formation rate of aldehyde is faster than the degradation to CO_2 and H_2O.	Process and catalysts are not well developed.
New electrocatalysts should be done: R&D	The broke of C-C bond catalyzed by Rh, Co and La, expensive metals.
New electrolytes that could work at 200°C.	

The comparison of the results of the ethanol reform and the methanol reform using a multi-fuel reformer developed by Ahmed [18, 19] are shown in Table 3.

Table 3 – Hydrogen concentration in the reformate gas from different fuels.

Fuel	Theorical% of H_2	Experimental% of H_2	Selectivity of H_2	Temp(°C)
Methanol	70	64	91	450
Ethanol	71	62	88	580
Isooctane	68	60	88	630
2-Pentane	67	58	88	670

In Table 4 one can see the emissions relate to different fuels.

Tabela 4 – Emissões relativas a vários combustíveis.

	N° of Buses	HC (g/mile)	CO (g/mile)	NOx (g/mile)	PM (g/mile)
Diesel	8	0.13	4.9	30.1	0.28
Natural Gas	10	15.8	9	20.8	0.02
Ethanol	5	8.9	37.1	13.4	0.63
Methanol	5	37.5	25.1	11.6	0.39
Fuel Cell	1	0.23	7.32	0.01	<0.01

ipen - Instituto de Pesquisas Energeticas e Nucleares, in São Paulo/Brazil, performs activities of research, development and formation of human resources in the field of new sources of alternative energies utilizing fuel cells as source of efficient and low aggression to environment energy. The IPEN program, in course since 1998, covers the study and development of systems associated to the technology of PEM cells and encompass the study of the production of hydrogen by the catalytic reform (cracking) of ethanol, strategic for Brazil and considered to have zero emission, since the CO_2 produced in the reform is absorbed by the biomass during the growing of the sugar-cane (carbon kidnapping).

The integration of the technology of the fuel cells and the use of ethanol as primary fuel have some challenges. First, to call the attention of the government and of the companies to the completely settled infra-structure of production and distribution of the fuel. Second, to establish the operational conditions of systems and sub-systems involved in the union of the technologies. Some items of this future development are:

- Response time of the power transients during operation and in the start-up conditions;
- Time balance of the response time of the fuel cell systems and ethanol reform;
  Physical constraints of the fuel cells systems and ethanol reform (weight, dimensions, etc.);
- Environment constrains of the production of the systems;
- Analysis of the emissions of the complete system in operation, specially the NOx emissions, since the emissions of CO/CO_2 are kidnapped of the atmosphere by the growing of the biomass.

Some extra benefits can be emphasized. From the social-economic standpoint this association would be beneficial, reducing the need for petroleum and increasing the job generation, since the supply-chain of ethanol production is a strong job generator, opposite to that of petroleum.

The development of the supply-chain formed by the ethanol production and the fuel cells technology could be supported by the Kyoto protocol and the developed countries responsible for a sustainable development.

CONCLUSIONS

Fuel cells require a hydrogen source to generate electricity. Hydrogen, however, is difficult to produce and storage. Applications requiring great amounts of fuel and the supply in a lot of positions distributed in a great area, as in the automotive industry, have as an ideal fuel the one that is liquid, of easy production, renewable, of low cost, non-toxic, and non aggressive to environment. Ethanol is the only one that fulfills theses requirements. It is a liquid rich in hydrogen, with production, storage and distribution technologies well settled. Production, storage and distribution are a big challenge for a fuel for fuel cell systems.

Two ways of application of ethanol in PEM fuel cells can be considered: the direct oxidation and the catalytic reform. The advantages of the utilization of ethanol are enormous. However, in both ways, there are complex tasks to be performed in the field of R&D&I, up to the commercial maturity of the technology. New ionic conductor polymeric membranes and new electrocatalysts systems should be developed.

In the short range the catalytic reform appears to be the best technological option, since ethanol is simpler to reform than gasoline and other alternative fuels, because of the simplicity of its molecular structure.

Brazilian government should give more attention to this alternative. Due to its fertile land extension and good climate for plantation, Brazil is in a peculiar position to produce ethanol. Besides, it has good infra-structure of production, storage and distribution of this fuel. The association of ethanol to the technology of fuel cells would contribute positively for the national energetic matrix. This would require great effort of industry, government, agencies for environment protection, research institutes, universities and technologies companies, together.

We foresee that this will be the best way to be followed in order that Brazil enters, in a sustained way, the so called "hydrogen economy".

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