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## Reformed Methanol Fuel Cells: Proposed Plant for Vehicular Applications

Kliton Bylykbashi

*University for Business and Technology - UBT*, [kliton.bylykbashi@ubt-uni.net](mailto:kliton.bylykbashi@ubt-uni.net)

Roberto Capata

*University of Rome La Sapienza*, [roberto.capata@uniroma1.it](mailto:roberto.capata@uniroma1.it)

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As shown in Figure 1, the PEM membrane, anode and cathode and GDL are combined into the Electrode Assembly (MEA) membrane. The latter is compressed between two bipolar plates that

serve as conductors for electrons, so that they can flow between contiguous cells, but also as a field flow that distributes the reagents on the GDL. Usually the bipolar plates are graphite-polymer composite made. The assembly of the various parts of the cell in a single component allows reducing the space occupied and maximizing the efficiency. There are two types of PEM fuel cells:

- high temperature PEFC (HTPEFC);
- low temperature PEFC (LTPEFC).

The main difference is that LTPEFC operate at temperatures below 100°C and their membranes, in Nafion, need to be constantly humidified by water. HTPEFC operate at temperatures above 100°C and the membrane is Polybenzimidazole (PBI) made, doped with phosphoric acid. As they do not require cooling or dehumidification, the main advantage is the high tolerance to impurities such as CO. The CO is a poison for catalysts, due to the high selectivity of the membrane against the H<sub>2</sub>. The disadvantage is that they need to be heated up to the operating temperature before they can be considered "enabled" and, generally, their efficiency is lower than the LTPEFC.

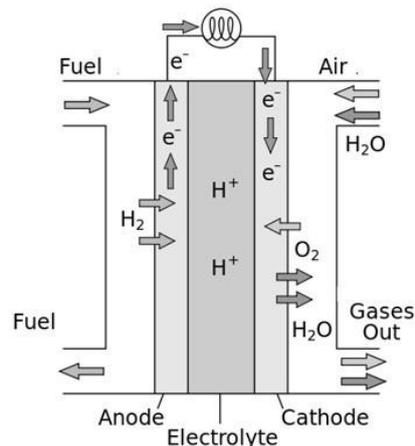


Fig. 1. Hydrogen fuel cells structure

A fuel cell typically has a maximum voltage of about 1V in open circuit conditions. However, the voltage decreases as the cell current density increases (see figure 2). In the case where the cell is used in applications where the electric load is not constant, for example in the automobile field, it requires intervention to mitigate this problem. In fact, a load increase would lead to a current increase, necessary to maintain the voltage at nominal rate. Excessive load leads to a voltage drop that stops the cathodes reaction and, then, blocking the operation of the cell. Considering that is not possible to increase the cell surface too much, to produce more current, the energy efficiency is increased by placing more fuel cells in series. In addition, to avoid any energy demand peaks, the cell works in parallel with a DC battery, that is recharged at low level and discharged at high power demand.

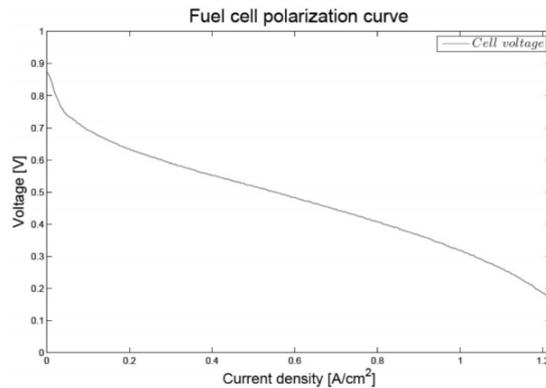


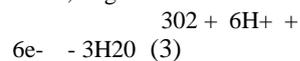
Fig. 2. Polarization curve Hydrogen

## Direct Methanol Fuel Cells DMFC

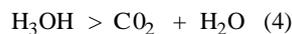
Continuous research into alternative energy generation methods has led to the development of other types of fuel cells which. These devices use a different fuel or ion exchange systems, but, do not differ from the PEMFC for the operating principles. In this scenario, the fuel cells with direct methanol can be considered. A DMFC (Direct Methanol Fuel Cell) operates at temperatures between 70 and 100°C and is directly powered by CH<sub>3</sub>OH, oxidized electro-chemically to the anode [6.7.8]. The possibility to use, as fuel, directly in the cell, makes DMFC particularly suitable as portable generators. In this case, the methanol is not pure, but it is present in a mixture containing water. The water is necessary to initiate and develop the anodic oxidation reaction. The methanol/water mixture can be used as refrigerant of cell stack too. Moreover, the accumulation of methanol, liquid at temperature and ambient pressure, is of considerable practical simplicity compared to hydrogen (it has to be compressed at very high pressures). The global reaction is the following ones. The methanol is supplied to the anode where ionic catalyzed splitting occurs:



Hydrogen protons and electrons, migrated to the cathode, reacts with oxygen:



The final reaction will be:



The process produces water, electric current and CO<sub>2</sub>. For these reasons, the reaction is not completely "clean" as in the case of hydrogen. Such a cell has efficiencies of 25%. The efficiency reduction is due to the strong heat dissipation correlated to the reaction (of about 75% energy loss) and the so-called "crossover" phenomena of methanol. This efficiency decreases is due to the methanol leakage, through the membrane (not very selective), that reaches the cathode, directly reacting with oxygen. The crossover is characterized by two main disadvantages:

- Reduction of the production of H<sup>+</sup> ions and consequent reduction of transported electrons to the cathode;
- Increase of the electrochemical potential to the cathode due to the reaction of CH<sub>3</sub>OH with oxygen, resulting in a decrease in the potential difference

between anode and cathode and, consequently, a lower electron transport gradient.

The solutions focus on new, more selective membranes. These membranes almost completely screen methanol, optimizing the ratio  $\text{CH}_3\text{OH}/\text{H}_2$  and generating a complete methanol consumption. Consequently, a higher efficiency is achieved. However, DMFC are very attractive if is applied to small portable electronic devices and in the case of backup power generation plants, where battery storing is insufficient. The strong point of DMFC is the high methanol energy density, about

30-40 times higher than lithium ion (Li-ion) batteries. In fact, even considering their low efficiency, it is experimentally obtained an energy density 10 times more. Low efficiency is not necessarily a problem if the project goal is the extension of the device/object/vehicle operative life. In fact, the DMFC are widely used in military applications, in the remote energy generation for computers, satellite phones and emergency kits.

## The proposed Reformed Methanol Fuel Cell Plant

The proposed technology bases its operation on the use of reformed methanol to provide hydrogen to be used in a fuel cell. A small practical plant is proposed to ensure a wider use in different applications. This type of cell compared to DMFC has several advantages. First, the highest energy efficiency due to the non-direct use of methanol thus avoiding the problems associated with it. The efficiency of the proposed system is strictly dependent on the temperature in each stage. For this reason, it is necessary to ensure a precise control of the operating conditions. Then, the liquid fuel must be vaporized before entering into the reforming reactor. This particular need leads to the coupling of the two phenomena. The liquid fuel controls the plant operating temperature. In this manner, a preheating and vaporization of the reactor supply current is obtained.

The methanol supplied to the plant is not pure but in mixture with water. This is necessary for the steam reforming reaction development and is supplied in a slightly higher stoichiometric ratio ( $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1.2:1.5 \text{ mol}/1 \text{ mol}$ ). The methanol quantity is higher than necessary for the reaction, but an almost complete conversion of methanol can be obtained. The steam reforming reactions are:

In the WGS reaction, water is necessary. The water is already present in the plant thanks to the excess water flow rate supplied at the reformer inlet. There are several possibilities of the reformer-fuel cell plant configuration:

- ATR (Auto Thermal Reforming) reactor. In the reactor both reactions (steam reforming and the methanol partial oxidation) occur. The total energy balance is positive. The system needs a strong control over the temperatures generated by the partial oxidation. In fact, a sudden increase of the temperature improves the reaction of methanol decomposition and a consequent greater production of carbon monoxide. From eqt. (6) the total hydrogen production is lower;
- Reactor where only the steam reforming reaction takes place, avoiding the partial oxidation by a reduction of oxygen quantity in the vacuum system. The heat needed to the reaction is provided through an electrical resistance that wraps the catalytic bed, guaranteeing optimum distribution of heat flows. The production of hydrogen is higher and temperature sensors can control the bed temperature.

To limit the adverse effects of CO production, different solutions can be used:

- Use a high-temperature (HTPEFC) fuel cell, more tolerant of carbon monoxide poisoning. On the other hand, higher operating temperatures and lower

efficiencies characterize this system. This choice allows removing the water gas shift treatment from the system, decreasing the initial dimensions and costs. It should be recalled that, however these cells are more tolerant to poisoning; they require scheduled maintenance in the short/medium term. Not recommended in long-term applications.

- Insert a catalytic functioning WGS (water-gas shift reactor) reactor for the reduction of carbon monoxide using a lower temperature fuel cell (in this case a PEFC). The disadvantage is due to the presence of an additional system parts that also require constant temperature controls.

## Methanol Reforming

The methanol reforming is realized through selective catalysis for the production of hydrogen alone. The objective is to achieve a reactor where both the oxidative methanol steam reforming for H<sub>2</sub> production and the CO concentration reduction (< 30ppm CO). Several studies have demonstrated the efficacy of Cu ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts for the selective production of H<sub>2</sub> and of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for the conversion of CO. Combinations of different types of catalysts lead to better efficiencies in terms of conversion of methanol, hydrogen production, lower production of carbon monoxide or higher consumption through its catalytic conversion. The reaction takes place in a fixed down-flow bed reactor. Moreover, the methanol reforming requires the lowest temperature for the reaction (operating temperature between 180 and 275 °C). The most interesting aspect is that the CO-formation varies depending on the temperature. With the temperature decrease from 275°C to 180°C, its production decreases from 1.5% to 0.05%. This is due to two reasons, the low reaction temperature can suppress the methanol decomposition reaction (that produces CO), and the WGS, at low temperatures, converts CO into CO<sub>2</sub> and H<sub>2</sub>.

Experimental evidence has shown that all Cu ZnO-based commercial catalysts have high conversions compared to methanol. At 275°C All Cu ZnO-based catalysts lead to 100% conversions, but significant traces of carbon monoxide can be found within the product. At 230°C, catalysts reach conversions between 93 and 98% with lower CO production. For the methanol oxidative reforming, for portable applications, air can be used as an oxidizing. The variation of molar ratio O<sub>2</sub>/CH<sub>3</sub>OH influences on the progress of the methanol reaction and conversion, on carbon monoxide and hydrogen production.

Table 1. The variation of molar ratio O<sub>2</sub>/CH<sub>3</sub>OH

Ratio O <sub>2</sub> /CH <sub>3</sub> OH	Conversion CH <sub>3</sub> OH	Production CO (ppm)	Production H <sub>2</sub> (mol%)
0	60.8	848	70.4
0.1	74.6	2602	66.6
0.2	86.9	3125	69.2
0.3	97.4	3371	54.4
0.5	98.4	3642	49.4

With the ratio increase, the conversion of methanol increases. This increase is apparently related to the partial oxidation reaction that generates a decrease of relative hydrogen production and an increase of carbon monoxide production. Note also that lower values of the O<sub>2</sub>/CH<sub>3</sub>OH ratio cause a reduction of the transport gas (inert N<sub>2</sub>) and a consequent worsening of the thermal transport conditions. These conditions changes generate strong thermal gradients due to the different natures of steam reforming (endothermic) and partial oxidation (strongly exothermic) reaction. It is necessary to find a compromise. Always respecting the constraint of the smallest possible overall dimensions (for onboard applications), it can try to unite two catalysts with base copper-zinc and with platinum base. The aim is to simultaneously initiate

the two reactions (SR and WGS). Several experiments have been carried out and the obtained results are based on two main specifications:

- Hybrid Catalyst with 1% Pt/Al<sub>2</sub>O<sub>3</sub> in mechanical mixture with a catalyst CuZnO/Al<sub>2</sub>O<sub>3</sub> with weight ratio between the two catalysts equal to 1:3;
- Two-layer catalytic bed of which in one is present only 1% Pt/Al<sub>2</sub>O<sub>3</sub> and in the only response Cu-ZnO/Al<sub>2</sub>O<sub>3</sub>, always in relation in weight 1:3.

To initiate the reaction, air is used with a ratio of O<sub>2</sub>/CH<sub>3</sub>OH equal to 0.3 at a temperature of 230°C. The process path follows the direction of CuZnO > Hybrid > Two layers catalysts.

These results led to the development of series reactors systems. A first reactor, where steam reforming and methanol partial oxidation take place, is based on a catalyst copper-zinc, maintained at 230 °c with a molar ratio H<sub>2</sub>O/CH<sub>3</sub>OH = 1.4 and molar ratio O<sub>2</sub>/CH<sub>3</sub>OH = 0.3

In the second reactor takes place the preferential oxidation of carbon monoxide through a 1% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, maintained at a temperature of 150 °C with an extra air supply between the first and the second reactor within 11 and 53% of air delivered to the first reactor.

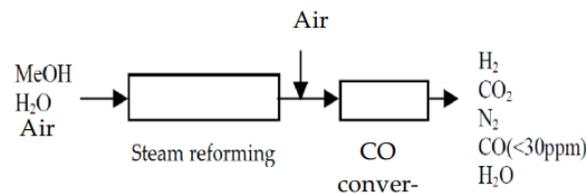


Figure 3. Example of an integrated reactor for the production of hydrogen from methanol

## The proposed plant

The system is composed by an ATR reactor system with WGS bottoming purification systems. A LTPEM type fuel cell is considered. Initially, the methanol/water mixture is stored into a reservoir. Successively, a pump (P) delivers the mixture to the system. From the tank, the mixture enters a vaporizer, where it reaches the necessary conditions to start the reforming. The vaporizer must reach a temperature of 80°C for the considered H<sub>2</sub>O/CH<sub>3</sub>OH mixture. This vaporization can be implemented in three (3) ways:

- Through the heat produced by the combustion of part of the mixture in a dedicated component;
- The heat produced by the combustion of the unreacted gas inside the fuel cell;
- By exchanging heat with the hot parts of the system, exploiting the dual function of temperature control.

In our case, it is considered more efficient, to "compose" the vaporizer with all these three modules. When the system is switched on, due to the absence of heat in the system and unreacted gases, it is necessary to use the methanol combustion to vaporize the mixture, and achieve the operative temperature (230 °C). Once the system reaches the stability conditions, the vaporization is obtained by thermal exchanges with the plant parts and by the combustion of the not-reacted H<sub>2</sub>.

Once entered the reactor, the charge follows the reactions described in the previous section by transforming into synthetic gas ready to be sent to the fuel cell. The reactor is realized by placing the two chambers, OXSR and WGS, in close contact, concentrating the hot parts of the system in a single point. Some blowers supply the air to these hot parts. The reaction chambers are built by inserting flow breakers inside them. On the walls, it is positioned the specific catalyst, forcing the charge to enter into contact with them. This system

guarantees a good mixing and an easier limitation of the reactor overall dimensions. The produced synthesis gas, with a low carbon monoxide concentration, is delivered to the anode of the LT-PEFC. In combination, the air is sent to the cathode. So, the reactions can be initiated. At anode outlet, the retention valve will be opened very frequently (it was also considered the option of not inserting it at all). The procedure is necessary to avoid the large accumulation of carbon dioxide and oxide that do not participate to the reaction, preventing the entrance of the synthesis gas. The purged gas presumably contains unreacted hydrogen that can be burnt to provide necessary heat for the mixture vaporization. The exhausted gases are delivered into the atmosphere or, in a green scenario, to a CO<sub>2</sub> storage system for its reuse in the sustainable production of methanol. The fuel cell outgoing water is vaporized and released into the atmosphere or stored.

## Onboard RMFC plant

Currently, the interest of many manufacturers is to optimize the use of fuel cells in the automotive sector. In our case, the considered fuel cell and the plant studied could be a good compromise solution. There are reformed methanol fuel cell with reduced dimensions and weights, compared to a commercial ICE. The downside is the start-up period, about 30 minutes, which are incompatible with the automotive application. For these reasons, the opportunity to use a low temperature cell has been investigated. In addition the reformer can be warmed by the methanol combustion, decreasing the time of initialization. During this period, necessary for the start-up of the entire device, the vehicle is moved by a battery package. The battery nominal power is lower than the currently used on the hybrid vehicles. The purpose of the package is to compensate the energy peaks required by providing energy, and to store the excess energy produced by the cell.

In the case of an onboard application, modifying commercial vehicles, the following results could be achieved:

- Complete integration and sustainability of the vehicle
- Increase in vehicle range
- Use of excess heat for the heating of the vehicle
- No particulate production.

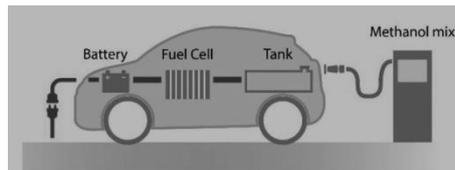


Figure 5. A RMFC on board plant

## Conclusions

The RMFC have, therefore, several advantages and different aspects that require further development and research. They are to be considered a viable alternative to the traditional generation systems. The use of methanol is interesting because it is considered to be "liquid electricity", since it is a hydrogen carrier among the best on the market with the possibility of being used in energy generation at low cost. In addition, the malleability of methanol

production, i.e. the possibility of being produced by both traditional and innovative methods, greatly facilitates the energy transition. This factor could entice fuel companies to invest in its use.

In addition, methanol compared to fossil fuels is a green alternative in many respects, whether they are productive or emission-related. As far as the proposed plant is concerned, a further study and optimization of the components, necessary for the assembly of the system, is necessary. In addition, an economic feasibility analysis is needed to make this solution competitive. Once the technical and economic feasibility has been demonstrated, a careful analysis of the system security will be mandatory.

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