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Critical review of fuel cell's membranes and identification of alternative types for automotive applications

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ABSTRACT

Hydrogen is considered one of the most important energy vector of the future and fuel in transport sector. The Fuel Cells (FCs) Traction System present some advantages respect to the traditional traction engine, consisting in lower emissions and noise. The more suitable Fuel Cells in automotive applications are those that use Polymer Electrolyte Membrane (PEM). The main obstacles to the commercialization of PEM fuel cells are largely concerning the cost, mechanical weakness and low durability of the membranes with increasing temperature. This latter aspect in particular referring to the fact that water is present in the membranes, thereby limiting the operating temperature of a fuel cell, which on average is about 80 °C. This in turn results in lower performance of the fuel cells due to a slower kinetics of electrodes and essentially no CO tolerance. It can be improved to improve the performance of a PEM increasing the temperature above 100 °C, changing the membrane type making it resistant to the natural increase in temperature of the system so as to improve the electrodes kinetics. The present work has the purpose of highlighting the orientation of the current research towards the development of specific types of membrane for the FC performance improvement.

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Introduction

The main difficulties to the PEM fuel cells commercialization are the membrane cost and the membrane mechanical weakness at high temperatures. To improve the performance

of a PEM by increasing the temperature (above 100 °C), it could be necessary to change the type of membrane in a way that it could become resistant to the natural temperature increase of the system so as to improve the kinetics on the electrode surface, and to manage more efficiently the heat and the water formed. Another problem with temperatures exceeding

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100 °C, is the reduction of the electrochemical surface of the electrodes due to the narrowing of the electrolyte (Nafion phase) within the catalytic layers.

CO tolerance grows with the operating temperature of the cell at above 100 °C. This was demonstrated by Yang and coworkers [1] highlighting as the CO coverage of the catalyst surface is reduced by increasing the temperature. An higher operating temperatures ensures a more efficient cooling process because there is a greater pushing force of the cooling flow, and then it is possible to reduce the auxiliary equipment. Moreover, operating at higher temperatures, fuels can be preheated through the exhaust heat. The current cost of polymer membranes are prohibitive, especially for fluorinated membranes. The objectives and parameters directly influence the direction of research for the development of such membranes. The following are the targets for the development of polymeric materials capable of operating at higher temperature [2]:

- I. A conductivity of about $\sigma = 0.1$ S/cm.
- II. A good performance at 120 °C, without pressurizing, with a relative humidity (RH) $\leq 40\%$. At this temperature about 50 ppm CO may be tolerated.
- III. A chemical stability similar or higher than Nafion, i.e. a life of approximately 40,000 h.
- IV. A hydrogen–oxygen gas permeability which is not more than the current Nafion-type membrane: $\leq 10\text{--}12$ (mol cm)/(cm² s kPa).
- V. A low electro-osmotic drag of the water in the membrane.
- VI. A circumscribed swelling (water absorption $\leq 100\%$ when boiled in water).

The design factors that influence the performance of the polymer membrane are [2–5] its very nature, the nature of the side chain, the equivalent weight, the nature and strength of the acid group, the thermo–mechanical properties, and the degree of cross-linking of the membranes [6–14]. In the present work the orientation of the current research towards the development of specific types of membrane for the FC performance improvement has been examined.

Strategy for alternative conductive membrane development: high temperature membranes

Malhotra and Datta [15] suggested that a hydrophilic inorganic additive can be inserted in the perfluorated membranes to enhance the binding energy with H₂O molecules retaining water at higher temperatures and to increase and number of acid sites enhancing the acidity. The effectiveness of this procedure has been confirmed by the introduction of heteropolyacids in the Nafion [15]. It is also possible to include other inorganic additives such as: zirconia sulfate, zirconium phosphate, and silica gel. Up to now, the interaction between the inorganic phase and the proton conductor is a phenomenon that is not sufficiently clear and understood; the stability of the material in the polymer is also uncertain, indeed some materials (such as heteropolyacids) can be dissolved in the water produced in the fuel cells and can be also leached out.

Therefore, despite this approach seems to be promising, positive results, so far, has appeared limited.

Current research is therefore focused on the development of nanocomposite proton exchange membranes (NCPM) that are chemically and mechanically more stable at higher temperatures. They are composite materials with nanoparticles of inorganic acids embedded within a polymer membrane such as Nafion. The target of the operation of this type of fuel cell is a temperature higher than 100 °C with relative humidity at around 30–40%. The development of Nafion – MO₂ (M = Zr, Si, Ti) nanocomposite membranes allows to enhance the H₂O retention and the proton conductivity at lower relative humidity and higher temperatures (40% RH, 120 °C), improving also the thermo-mechanical properties. The possibility of raising the working temperature of the cells PEMFCs to a value higher than 80 °C is of great interest. As a matter of fact, with temperature, the functioning of the cells improve because the electrochemical kinetics increases, CO tolerance improves, the management of heat and water becomes easier [1,16–26]. There have been numerous membranes developed for the operation of fuel cells at a higher temperature, either by modifying those based on Nafion, that dominate the market, or through the development of new membranes. Various types of polymer membranes have been the focus of scientific research: aromatic-sulfonated polymers membranes (for example polyetherketonesulfonate, SPEEK [27] and polyetherketone, PEEK), and Polybenzimidazole membranes: PBI [28–31]. Generally speaking, in aromatic-sulfonated polymers membranes there is an extremely structural hydrophobic phase which gives morphological stability and a phase with extremely functional hydrophilic groups. These functional groups, aggregated to form the hydrophilic nano-domains, act as water reservoirs. Therefore the conductivity of the aromatic sulfonated polymers also depends on the degree of sulfonation. At low aromatic polymers sulfonation levels, we have a lower water content and much lower conductivity of 10⁻² S/cm by limiting its use in fuel cells. However, if the degree of sulfonation increases, the conductivity improves, but the mechanical properties of the membrane deteriorate. It is necessary to reach a compromise with certain and controlled mechanical and chemical properties. In literature, also, the guidelines have been defined to reach the objectives of high temperature membranes development [2–5].

Normally water is used as solvent, but other non-aqueous solvents could replace it, having the same function as the water [4]. The logic is that other liquid solvents, with better physical characteristics are able to perform the function of water in the proton conduction. Two prominent examples of water substitution are phosphoric acid and imidazole. In order to replace water, the solvent must have a high dielectric constant, a low volatility and the capability to behave as a Brønsted base to solubilize the protons. Unfortunately, these solvents are generally soluble in the produced water and can leak. When another solvent, that is not water, is used, the challenge is the complete immobilization of the liquid to ensure stable performance for longer periods and when the water is the solvent, the challenge is to retain water within the inner part of the membrane in conditions of high temperature and low humidity because of its high volatility.

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