1. Summary

Polymer electrolyte fuel cells have become a subject of energy research with great impact. They convert the reaction energy involved in the electrochemical reaction of gaseous and liquid energy sources with oxygen or air, directly into electricity. They are characterised by high efficiencies and low emission of pollutants. When using natural gas and carbon-containing energy sources, water and carbon dioxide result as by-product. Further advantages consist in their modular building method, their noiseless operation and fast reactivity on load changes. Thus, this electrochemical energy transformation offers important solutions to the problem of a rational and pollution free power supply and traffic engineering. The operational areas of fuel cells are in the traction and stationary current generation as well as for central and decentralised applications. Most of the work is related to hydrogen fuel cells; however membrane development for direct methanol fuel cell (DMFC) applications has gained much interest over the last decade. The DMFC using liquid feed is seen as a potential power source especially for portable applications, due to its inherent simplicity of operation, not requiring reformers to convert the fuel in hydrogen to feed the cell. Currently significant power performance has been achieved, however still lower than hydrogen fuel cells. Still relatively low concentrations of methanol are used. At concentrations higher than approximately 2M, the cell voltage declines significantly due to permeation of methanol through the membrane, i.e. methanol crossover. This permeation results in a mixed potential at the cathode with a significant loss in oxygen reduction performance and also poor fuel utilisation. In order to be competitive, the DMFC must be reasonably cheap and capable of delivering high power densities. At present, there are some challenging problems for the development of such systems. These mainly consist of finding:

- Electrolyte membranes which have high ionic conductivity and low-methanol cross-over,
- methanol-tolerant electro catalysts with high activity for oxygen reduction,
- electrocatalysts which can effectively enhance the electrode-kinetics of methanol oxidation,
- optimal operation conditions.

For that reason, all aspects related to fuel cell stack development are of particular relevance, in particular, materials and design of cell housing, bipolar plates, gaskets and stack auxiliaries. At present, the cost of the entire system is mainly determined by the presence of noble metals in the catalyst and the use of Nafion membranes. Although perfluorinated ion-exchange polymers, such as Nafion from DuPont [1,2], Flemion from Asahi Glass, Aciplex from Asahi Chemical [3], Neosepta from Tokuyama Soda, Gore-Select from Gore and the perfluorosulfonic acid from Dow [4] are very suitable as polymer electrolyte membrane (PEM) in hydrogen fuel cells, they are not suitable for DMFC applications due to the high methanol permeability. Nowadays much research is focused on the development of new materials to be used as interface between anode and cathode in DMFC applications. There is a real need for new and better materials for DMFC based on good barrier properties for methanol, high proton conductivity and thermal and chemical resistance.

The purpose of this research was the development of membrane materials alternative to Nafion for the DMFC from polymers such as sulfonated polyether ketone (s-PEK) and sulfonated polyether ether ketone (s-PEEK), containing heteropolyacids in order to improve the proton conductivity of the material, and an oxide phase in order to reduce the methanol and water permeability through the membrane.

Heteropolyacids have been described in the literature as good proton conductors when they are in crystalline forms with determined numbers of water molecules in their structure [5-7]. They are under investigation for hydrogen fuel cell, but the main disadvantage is its high solubility in water [5, 8, 9]. To overcome this problem, two different approaches [10] were followed in the first step of this work to fix the heteropolyacid into the membrane and make it suitable for applications in DMFC: a) the *in situ* generation of an oxide network by the sol-gel process from a metal alkoxide and b) the modification of the anion structure of the heteropolyacid. Therefore membranes have been developed using s-PEK as organic polymer matrix and different heteropolyacids with an inorganic network of ZrO_2 or $RSiO_{3/2}$. The inorganic oxide network had the function of decreasing the methanol and water permeability through the membrane (Table 1-1), as well as decreasing the bleeding out of the heteropolyacid from 152 mS/cm for s-PEK·WPA (60·40) to 52 mS/cm for s-PEK·ZrO_2·WPA (64·8·28) and from almost 100 % for s-PEK·MoPA (60·40) to 27% for s-PEK·ZrO_2·MoPA (64·8·28) in NMP. An increase in the proton conductivity was also observed, from 54 mS/cm for s-PEK to 112 mS/cm for s-PEK·WPA (60·40).

Table 1-1. Methanol and Water permeability for hybrid membranes from s-PEK

Composition		**Thickness (μm)**	$P \times 10^{18}$ **($m^2 s^{-1} Pa^{-1}$)**	
			MeOH	**H_2O**
s-PEK	100	70	10	70
s-PEK · ZrO_2 · WPA	64 · 8 · 28	108	2	20
s-PEK · ZrO_2 · MoPA	64 · 8 · 28	92	2	20

The same behavior was observed for similar hybrid membranes from s-PEEK; methanol and water permeability across the membrane was decreased (Table 1-2), as well as the bleeding out of the heteropolyacid decreased from almost 100% for s-PEEK·WPA (60·40) to 69% for s-PEEK·ZrO_2·WPA (57·9·34) and to 68 % for s-PEEK·ZrO_2·MoPA (64·8·28).

Table 1-2. Methanol and Water permeability for hybrid membranes from s-PEEK

Composition		**Thickness (μm)**	**$P \times 10^{18}$ ($m^2 s^{-1} Pa^{-1}$)**	
			MeOH	**H_2O**
s-PEEK	100	70	Membrane dissolved	
s-PEEK · ZrO_2 · WPA	64 · 8 · 28	70	1	20
s-PEEK · ZrO_2 · MoPA	64 · 8 · 28	87	8	90

However all the hybrid membranes prepared with s-PEEK shown lower proton conductivity than the plain polymer, explained by interactions between $–SO_3H$ groups in the polymer matrix, with the ≡Zr-OH surface groups of the oxo-polymer network as well with protons in the heteropolyacid, as was found in the FTIR spectra of the hybrid membranes in comparison to that of the plain polymer and confirmed with SAXS and ASAXS studies.

In order to decrease the bleeding out of the heteropolyacid into the polymer matrix, another step was done: the synthesis of new heteropolyacids. For instance, hybrid membranes from s-PEK, ZrO_2 or $RSiO_{1,5}$ and with $H_5NiMo_{11}PO_{39}$.aq or $H_3(RSi)_2OPMo_{11}O_{39}$.aq were less susceptible to bleeding out than those obtained with commercial molybdophosphoric acid (9 and 7%, respectively), but the proton conductivity of these composites were still lower than the plain polymer for the same reason above mentioned.

In a third step [11] a further more effective method was investigated in order to avoid the bleeding out of the heteropolyacid and the lower proton conductivity: the modification of the anion structure of the heteropolyacid and their covalent bonding to an insoluble inorganic phase dispersed in a polymer matrix, without affecting its acidity. Once again, the inorganic phase has the role of decreasing the water and methanol crossover, besides fixing the heteropolyacid to the membrane. Organosilyl derivatives of the divacant tungstosilicate $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ were prepared using GPTS (3-glycidoxypropyltrimethoxysilane). The introduction of GPTS in the anion structure of a lacunary heteropolyacid enable its attachment to a host material, by an epoxy ring opening reaction with appropriate functional groups present in the surface of the host material, without involving the protons and therefore without affecting the proton transport. The ring opening reaction between the epoxy group, contained in the anion structure of the heteropolyacid and the amino group attached to the insoluble oxide phase was successful to fix the heteropolyacid in the membrane, a bleeding out of 45% was determined for s-PEEK ·H_4 [γ-Si(2)] (62.38), 35% for s-PEEK ·H_4 [γ-Si(4)] (62.38) and around 15% for s-PEEK·H_4[γ-Si(4)]·Aerosil-NH_2 (54.8.38) and s-PEEK·$RSiO_{1,5}$·H_4 [γ-Si(2)] (59.5.36). The acidic groups were kept free, i.e. were not affected during the fixation of the heteropolyacid; that was reflected in the proton conductivity of these organic-inorganic materials, which is in the same order of magnitude of that of the plain polymer (Table 1-3).

Table 1-3. Proton conductivity for hybrid membranes from s-PEEK and Organosilyl derivatives of the divacant tungstosilicate

Composition		**Proton conductivity (mS/cm)**		
		50°C	70°C	90°C
s-PEEK	100	8	12	20
s-PEEK · H_4 [γ-Si(2)]	62 · 38	16	18	19
s-PEEK · Aerosil-NH_2 · H_4 [γ-Si(2)]	54 · 8 · 38	11	15	18

The stability in methanol solution was considerably higher for the organic-inorganic membranes with heteropolyacid bonded to oxides than that of the plain membrane. Methanol and water permeability of these hybrid membranes was considerably lower than that of the plain membrane (Table 1-4).

Table 1-4. Methanol and Water permeability for hybrid membranes from s-PEEK and Organosilyl derivatives of the divacant tungstosilicate

Composition		**Thickness (μm)**	**$P \times 10^{18}$ ($m^2 s^{-1} Pa^{-1}$)**	
			MeOH	**H_2O**
s-PEEK	100	70	Membrane dissolved	
s-PEEK · Aerosil-NH_2	91 · 9	70	3	30
s-PEEK · H_4 [γ-Si(2)]	62 · 38	100	20	150
s-PEEK · Aerosil-NH_2 · H_4 [γ-Si(2)]	54 · 8 · 38	85	10	100

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