NANOSTRUCTURED ELECTROLYTE MEMBRANES BASED ON POLYMER-IONIC LIQUIDS-ZEOLITE COMPOSITES FOR HIGH TEMPERATURE PEM FUEL CELL

Sprawozdania

Informacje na temat projektu

ZEOCELL

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Final Report Summary - ZEOCELL (Nanostructured electrolyte membranes based on polymer-ionic liquids-zeolite composites for high temperature PEM fuel cell)

Executive summary:

ZEOCELL (see http://ina.unizar.es/zeocell online) puts forward an innovative concept to overcome the current limitations of commercial available proton exchange membrane fuel cells (PEMFCs) based on the use of multifunctional nanostructured materials, capable to withstand temperatures in the range 130º - 200º C. Up to seven electrolyte membrane compositions have been studied. All of the electrolyte membranes comprise at least one of the following basic materials: poly-benzimidazole (PBI), protic ionic liquids and zeolites/zeotypes.

As the polymer membrane architecture plays the key role to ensure proton transport through heterogeneous media, dense and porous (random or straight pores) PBI films have been deployed as proton conductor supports. For proton conduction purposes, phosphoric acid doping and/or protic ionic liquid embedding have been mainly studied in the project. The incorporation of microporous materials either as inorganic fillers to the membrane casting solution or as thin film coatings onto pre-existing porous PBI membranes has been considered.

To gain insight the synergic effects provided by materials combination, different membrane categories, ranging from 1 component (i.e. Pure Polymeric Ionic Liquid Films), through binary (supported ionic liquid membranes in track-etched porous PBI substrates, supported ionic liquid membranes in randomly porous PBI substrates, reinforced polymeric ionic liquid membranes on porous PBI supports, acid doped track-etched porous PBI substrates), ternary composites (hybrid acid doped dense or porous PBI and hybrid dense or porous PBI embedding ionic liquid) to the final nanostructured electrolyte membranes based on four components (i.e. PBI, phosphoric acid, ionic liquid and microporous materials) have been deeply studied.

The best conduction performance of single component-membranes is exhibited by polymeric ionic liquid films prepared from ImSF0108b (350 mS/cm at 200ºC after 1000 h working). For 2 components-

membranes, it is clearly outstanding the conduction behaviour of poly[ImSF0108b] on randomly porous PBI supports (275 mS/cm at 200ºC after 1,000 h working). Thus, both membrane categories effectively accomplish with the durability and conductivity targets. Concerning 3 components-membranes, Hybrid Randomly Porous Doped PBI 75% in porosity prepared from TPP porogen including a 3% wt. of colloidal NaY type zeolite encapsulating 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide as inorganic filler shows 223 mS/cm at 150ºC as in-plane conductivity. The 4-components nanostructured electrolyte membrane based on phosphoric acid doped porous PBI (80% in porosity) embedding 1-H-3-vynilimidazolium bis(trifluoromethanesulfonyl)imide as proton conductor with ETS-10 titanosilicate type coatings as top layers allows attaining 100 mS/cm at 150ºC.

In addition to conduction requirements which have been successfully addressed, the hybrid doped PBI membranes and the nanostructured electrolyte membranes stand up as the most adequate in terms of methanol and hydrogen cross-over respectively. Overall, the most promising electrolyte membranes are those based on polymeric ionic liquids although further efforts to reduce fuel cross-over at temperatures above 120ºC are required. The cost assessment results clearly indicate that the aforementioned membranes would be competitive in the high temperature PEMFC stationary applications market. The business analysis of stacks based on ZEOCELL membranes in the Micro-Combined Heat and Power Systems and Backup/supplemental power for Telecom Applications has foreseen encouraging benefits in a hypothetical scenario with a 2% and 6% penetration in both markets respectively.

Project Context and Objectives:

The European Council in 2007 adopted ambitious energy and climate change objectives for 2020 including the reduction of greenhouse gas emissions by 20%, increasing the share of renewable energy to 20%, and making a 20% improvement in energy efficiency. The European Council has also given a long-term commitment to the decarbonisation path with a target for the EU and other industrialised countries of 80 to 95% cuts in emissions by 2050. Nevertheless, the existing strategy is currently unlikely to achieve all the 2020 targets, in particular those related to energy efficiency. EU energy and climate goals have been incorporated into the Europe 2020 Strategy for smart, sustainable and inclusive growth, adopted by the European Council in June 2010.

The development of economically feasible more efficient energy conversion systems, is one of the most important technological challenges for the XXI century. The European Strategic Energy Technology (SET) Plan has identified fuel cells and hydrogen among the technologies needed for Europe to achieve the 2020 targets. Much of the research on new materials for PEMFC membranes, while promising, may be too far away from commercialization to meet this timeframe, and could be the next generation technology. Certainly, fuel cells and hydrogen are medium and long-term energy technology options and, therefore, their contribution to meet the 2020 EU targets on greenhouse gas emissions, renewable energy and energy efficiency will be limited. However, they are expected to play an important role in achieving the EU vision of reducing greenhouse gas emissions by 60-80% by 2050. By that time it is expected that the critical barriers preventing commercialisation of these technologies (i.e. cost and durability of fuel cells, availability of large amounts of emissions-free, affordable hydrogen, development of a long term stable regulatory framework) will be overcome and their full socio-economic and environmental benefits realized.

Among FCs, proton exchange membrane fuel cells (PEMFC) are favourably identified in three out of four priorities (i.e. Transport & Refuelling Infrastructure, Stationary Power Generation & Combined Heat and Power (CHP) and Early Markets) settled in the Multi-annual Implementation Plan 2008-2013 adopted by FCH JU. However, cost reduction seems to be the main challenge to a widespread PEM Fuel Cell commercialization.

The low temperature proton exchange membranes present some disadvantages that may reduce their effectiveness in fuel cell applications. These disadvantages can be overcome by adopting high temperature operation of the membrane. The advantages of high temperature Polymer Electrolyte Membrane (PEM) fuel cells include the simplifications of the balance of plant, the generation of more useful high-grade waste heat and improvements in the catalyst activity. With respect to the balance of plant, a membrane not dependent on water to maintain fast-ion transport processes would allow significant simplification of the system. The energy-cost associated with humidifying hydrogen and air would be reduced, resulting in a net efficiency gain. The waste heat produced in the stack would be more easily collected and removed and could provide useful heat (CHP applications) or more straight forward removal to the environment with smaller forced-convective radiators and air blowers (demanding less energy from the system). Operation at higher temperatures would also enhance the properties of the catalysts within the fuel cell stack.

For the anode, fuelling options would become more flexible as the anode catalyst becomes more tolerant to impurities present in primary reforming streams. This leads to reductions in cost, complexity of the system balance of plant and improvements in the net efficiency. The cathode performance will also be enhanced. Provided the level of water within the stack remains low, improvements in electro-kinetic performance are expected at elevated temperatures. The term 'high temperature' refers to the temperature range, 100º-200ºC (150º-200ºC for some authors) which does not appear to be high from an engineering point of view. However, in the current state of the art, development of high temperature PEM for fuel cells is very important in the field of materials science and engineering.

Over the past decade, several basic research projects supported by the EU have been focused on the High-Temperature PEMFC topic. FURIM project funded by FP6 developed new high temperature polymer electrolyte membrane fuel cells based on acid-base blend membranes (30% SFS and 70%PBI) with H3PO4 imbibed. Conductivity values up to 87.5 mS/cm (180ºC/ 5% RH) were attained. However, durability tests revealed the MEA performance decayed after 300 hours for operation at 200ºC/1000 hours at 180 ºC/ 5000 hours at 150ºC. CARISMA network was focused on MEAs development for high temperature applications (100ºC, 110ºC and 120ºC) while maintaining reasonable performance at lower temperatures (80ºC and 60ºC). Thus, a new perfluorosulfonic acid membrane (PFSA) called E79-03S developed by Solvay Solexis were successfully incorporated into MEAs showing significant performance improvements (0.5 W cm-2 at 0.65 V, 500 hours steady state durability at 110ºC with stable performance in presence of 17% RH). Polysulfone membranes were also tested (polysulfone-graft-poly(vinylphosphonic acid) with proton conductivities of 10 mS/cm at dry conditions and 100 mS/cm at 100% RH and 120ºC by doping with 2-5% sulfonated polymer (Nafion N11) at the expense of lower durability. PFSA membranes were also developed as Hyflon Ion E87 from Solvay Solexis with similar performance to Nafion 117. However, long time test at dry conditions results in a loss of performance (30% decay at 100ºC/700h; 50% decay at 120ºC/375h).

The incorporation of ZrO2 with phosphotungstic acid imbibed to Nafion was also studied without any significant improvements. Funded by FCH JU, the objective of MAESTRO (2010-2012) (see http://www.maestro-fuelcells.eu/ online) is to improve the mechanical properties of state of the art perfluorosulfonic acid membranes by using chemical and thermal processing and filler reinforcement methodologies, since due the most relevant failure mode in extended life time operation is associated with membrane mechanical failure. More recently (2011-2013), STAYERS project (see http://www.stayers.eu online) pursues stationary PEMFCs with lifetime beyond 5 years. To reach the high goals of the project, basic material research is given maximum attention.

The durability of all components of a stack of PEM fuel cells, especially that of the Membrane Electrode Assembly (MEA) supplied by Solvay Solexis, rims and seals, cell (bipolar) plates, and flow field is of paramount importance for a stationary power generator. APOLLON-B project (2006-2009) aimed to develop new materials for high-temperature PEMFCs (130º-200 °C). Novel polymers comprising aromatic polyethers with pyridine units were synthesised and evaluated. A new polymer from Advent, now commercially available ADVENT TPS, revealed exceptional continuous operating stability, with no decay in performance for over 2,000 hours at 180 °C under H2/air feed. Funded by FCH JU, the objective of DEMDEA (2010-2012) (see http://demmea.iceht.forth.gr online) is to understand the functional operation and degradation mechanisms operating in high temperature PEMs based on H3PO4 imbibed PBI, and its electrochemical interfaces; and advanced state of the art MEAs based on aromatic polyethers bearing pyridine units.

Similarly, the U.S. Department of Energy between 2003 and 2007 funded the project 'Development of Polybenzimidazole-Based High-Temperature Membrane and Electrode Assemblies for Stationary and Automotive Applications' managed by Plug Power Inc. The investigation was focused on the high-temperature polybenzimidazole (PBI) membrane optimization supplied by BASF to meet the performance, durability and cost targets required for stationary fuel cell applications. Conductivity values up to 270 mS/cm (160ºC/ 70% RH) were attained. The long time durability studies gave a loss of performance in 400 hours of 2.77% at 160ºC, which made impossible to achieve the durability goal for the project (20000 hours). BASF longer tests exhibited a loss performance >16% in 12000 hours.

In this context, the purpose of ZEOCELL project was the development of nanostructured electrolyte membranes based on the synergic combination of zeolites, ionic liquids and polymers able to operate at 130º-200ºC with the following features:
- High ionic conductivity: higher or equal than 100 mS/cm at 150ºC.
- Suitability for operating at temperatures between 130-200ºC (the membrane materials are expected to be thermally stable up to 200ºC. Membrane performance will be validated on single cells at temperatures of at least 150ºC).
- Good chemical, mechanical and thermal stability up to 200ºC.
- Durable (<1% of performance degradation during the first 1000 working hours).
- Low fuel cross-over (- Reduced manufacturing costs (< 400 EUR/m2).

For such promising candidates, their manufacturing process has been evaluated from an industrial point of view in an attempt to identify the next steps for the final implementation and industrial exploitation of the developed technologies. PEM fuel cells are commonly applied in transportation, stationary applications, and portable power generation. The integration of HT-PEMFC technology in the mentioned sectors is considered highly interesting because it reduces drastically the overall system complexity. Within the ZEOCELL framework, the exploitation plans for high temperature PEMFCs have been mostly focused on two stationary markets: Backups and micro or domestic combined heat and power (micro-CHP or dCHP) systems.

According to the Multiannual Implementation Plan Targets of the FCH JU, both of them are included within the RTD priorities. With the rapid expansion of wireless communication systems worldwide, and the increasing socioeconomic benefits of mobile technology, the need for dependable and economical backup power is critical. Electric grid loss throughout the year, whether from severe weather, natural disasters, or limited grid capacity, is an ongoing challenge for network operators. Traditional telecom backup power solutions include batteries for short duration backup and diesel and propane generators for longer duration backup. Batteries are relatively inexpensive for one to two hours of backup power. However, batteries are not ideal for longer duration backup power applications because they can be expensive to maintain, unreliable after aging, temperature sensitive and hazardous to the environment after disposal. Diesel and propane generators are capable of longer duration backup power. However, generators are unreliable, maintenance intensive, and environmentally unfriendly. Thus, clean fuel cell technology is the clean solution with minimal environmental impact. Fuel cells are reliable, with fewer moving parts and a wider operating temperature range than a battery. In addition, a fuel cell system has a lower lifetime cost than a generator.

Combined heat and power (CHP) systems based on fuel cells offer high efficiency, low emission, and decentralized power and heat supply for buildings and industries. They can operate from the existing natural gas distribution network, using a reformer to convert methane gas to hydrogen thus minimizing infrastructure requirements. There is considerable interest in installing CHP systems in domestic environments, and also for large scale applications such as community heating or industries. It is expected that by 2050 combined heat and power (CHP) generation and dCHP will become increasingly important as smart grids integrate a large number of distributed power generation units in 'virtual plants'. Ultimately, stationary fuel cells will establish themselves as the reference technology for on-demand power generation in the residential and industrial sector. Globally, pre-commercial projects have already been initiated for the implementation of dCHP systems on the larger scale. A combination of low-temperature reforming with a high-temperature PEMFC (120°C - 180ºC) opens a unique perspective in thermal management for both domestic (up to 10kW) and industrial (up to 150kW) CHP systems, with a total efficiency yield of primary energy above 80%. The high temperature operation of the PEMFCs tolerates higher impurity levels in the fuel, and thereby simplifies the reforming system (fuel cell and reformer synergy).

To evaluate their potential share in the market, the cost evaluation for the 2kW HT-PEMFC based stack has been compared with the current manufacturing processes considering different aspects: cost (EUR/kW), number of membranes manufactured and necessary equipment. In general terms, fuel cell systems integrating the membranes developed in ZEOCELL would be cost-competitive by the implementation of a mass manufacturing process; although further efforts on endurance properties are required. Economical use of PEM fuel cell power for stationary applications demands a lifetime of the fuel cells of at least 5 years, or more than 40,000 hours of continuous operation. For the stationary use, especially in the chemical industry and in remote areas, robustness, reliability, and longevity are often more important than the cost of the initial investment. For stationary generators the yearly cost of maintenance and overhaul are expected to be much larger than for intermittent applications such as automotive- and back-up power. Currently, most fuel cells exhibit major performance decay after around a thousand hours of operation. The DOE targets pursue a life time of 40,000 h by 2011 with 40% efficiency for distributed power and $1500/kW for stationary applications. According to ZEOCELL estimations, the costs for high temperature PEMFC stack (2 kW) are estimated at 214 EUR/kW for automated manufacturing process on a 500.000 units/year basis. The foreseen total units sold globally by 2015 for both applications, could reach 360,000 and 43,000 for micro-CHP and back-ups respectively, considering from the micro-map study 'mini and micro CHP market assessment and development plan' (supported by the European Commission SAVE Programme) and Ballard Power System reports and assuming a high temperature PEMFC technology share in the market of 10% and 20% respectively. Within this scenario, and considering the ZEOCELL membranes cost and the manufacturing process layouts; it is worthwhile to reconsider the business opportunities in the medium term (2015-2025).

Project Results:

Background

The PEMFC technology represents one of the most promising opportunities in the field of the alternative fuels for an environmentally friendly energy production. However, fuel cells and hydrogen are definitely medium and long-term energy technology options. During the past few years, many advances have been made but there are still technical and economic obstacles in the commercialization of fuel cell. In this regard, many efforts have been made to develop membranes for PEMFC's with excellent performance and durability and low cost. Particularly, good ionic conductivies at high temperatures and low humidity, low gas permeability, low electro osmotic drag coefficient, good chemical/thermal stability and mechanical properties, excellent fuel cell performance are being pursued by scientific-industrial partnerships. As already stated ZEOCELL aims to put forward an innovative concept based on the use of multifunctional nanostructured materials to overcome the existing drawbacks of PEMFCs. Particularly, a synergic combination of microporous zeolite type materials, protic ionic liquids (PILs) and porous polymers is proposed to develop improved and mass manufacturable electrolyte membrane materials capable to withstand temperatures in the range of 130-200ºC. Operation at this temperature is desirable since at temperatures over 120ºC most of the functional problems currently associated with PEMFCs such as catalyst CO poisoning, water management, efficiency (polarization effects and electrochemical reaction rates), and cogeneration possibilities can be overcome.

In this 'new' high temperature scenario, the most important challenges are related to the electrolyte performance and durability, and also to the fuel utility (cross-over phenomena). Apart from sulfonated aromatic hydrocarbon polymers, organic-inorganic composite membranes (mostly based on Nafion and Silica) and polymer blends; acid-base Polybenzimidazole membranes are among the most studied for HT-PEMFCs. PBI membranes impregnated with phosphoric acid have been studied as electrolytes in high temperature PEMFCs 5-9 for more than a decade. PBI polymer is commercially available at a relative low cost (150-220 EUR/kg), exhibits excellent stability in both reducing and oxidizing environments and its glass transition and decomposition temperature values are between 425-435ºC and above 600ºC respectively. Being a basic polymer (pK equals approximately 6.0) it easily captures oxo- acids (phosphoric or sulphuric acid), which helps stabilization and provides with proton conductivity.

The first patent related to phosphoric acid doped PBI membranes for high temperature PEMFCs belongs to Savinell & Litt and dates back to 1996; since then, numerous patents have emerged from this group. A high acid concentration provokes a drastic worsening in the membrane mechanical resistance due to the soaking process that takes place provoking separation among the polymer chains and reduction of intermolecular interactions. Therefore, an optimal doping of the membrane implies an improvement in conductivity without affecting the mechanical properties. Moreover, phosphoric acid autodehydration at temperatures above 140ºC is a serious limitation due to the formation of lower conductivity oligomers like pyrophosphoric acid (H4P2O7).

ZEOCELL: A basic research project on multifunctional materials

Starting from the well-known PBI polymer, ZEOCELL pushes the 'state of the art' with the development of nanostructured electrolyte membranes based on the synergic combination of porous PBI, protic ionic liquids and microporous inorganic nanocrystals. The final aim is to use the advantages of each primary building block by choosing a proper electrolyte membrane configuration. Up to seven electrolyte membrane compositions have been studied.

For proton conduction purposes, mainly phosphoric acid doping and/or protic ionic liquid embedding have been studied in the project. Since phosphoric acid autodehydration is a serious limitation for operation above 140ºC, when less conductive oligomers are formed, the deployment of Protic Ionic Liquids as proton carriers has been demonstrated as clearly beneficial due to its physical and chemical properties. The synthesized Protic Ionic Liquids exhibiting decomposition temperatures above 300ºC have revealed highly attractive possibilities, not only as embedded proton carriers in porous PBI due to its conductive properties, but also as guest molecules inside large pore zeolites to eventually improve the proton conduction properties of these microporous inorganic materials.

Molecular dynamics simulations show that the protic ionic liquids fit energetically inside the faujasite cells and their ions are mobile within the zeolite framework. The protic ionic liquid entrapped in large pore zeolites shows a gradual increase of conductivity up to a maximum followed by a decrease with temperature. Thus, synergic-inhibition effects between both proton conductors (i.e. protic ionic liquids and H2O molecules) coupled to protic ionic liquid dragging by water desorption, explain the observed behaviour. The temperature, at which the conductivity of the composite starts to decrease, depends on the hydrophilicy of not only the zeolitic host but also of the ionic liquid itself . Furthermore, polymeric ionic liquid based membranes with excellent proton conduction properties have been fabricated to address durability and lifetime requirements.

As it has already been pointed out, one of the strategies to improve the performance of acid doped PBI membranes relies on the addition of inorganic fillers (zirconium phosphates, phosphotungstenic acid, silicotungstenic acid, zirconium tricarboxilphosphate, polyoxometals, sulfonic silica nanoparticles) followed by phosphoric acid doping. Following a similar approach, the ZEOCELL contingency plans involve the addition of zeolites and titanosilicates nanocrystals to the PBI casting solution.

However, the addition of inorganic particles to a polymer results in a greater rigidity of the final polymeric membrane and eventually provokes the appearance of undesired voids at the organic-inorganic interface. Therefore, adequate surface properties coupled to small particle sizes are two of the main requirements for the inorganic fillers when preparing electrolyte membranes with suitable transport selectivity and mechanical properties.

The most widely studied chemical interactions between zeolites and polymer surfaces are those involving covalent linkages. For such reason in this project, the external surface of zeolites and titanosilicates has been modified by means of reaction with organosilanes to:
i. Promote their ionic conductivity,
ii. Facilitate chemical interactions with PBI chains,
iii. Improve the compatibility at the organic-inorganic interface; and,
iv. Enhance the mechanical strength of the composite membranes.

Specific functionalization protocols of the microporous materials have been established by grafting and filming techniques in order to ensure an adequate degree of surface coverage.

Because the polymer membrane architecture plays the key role to ensure proton transport through heterogeneous media, dense and porous PBI films (prepared from Fumion powder) have been systematically deployed as proton conductor supports. Randomly porous PBI membranes have been prepared by leaching out a porogen (CIDETEC route) and also by delayed demixing (UTWENTE route). In the former approach, PBI membranes are obtained by casting from a polymer solution (5 wt% in DMAc) containing the porogen (dibutylphthalate or triphenylphosphate) in %wt. ranging from 30% to 75% on a glass plate support. After peeling and solvent removal, the leaching of the porogen was induced by immersion in ethanol for 3 h at 50º C rendering in porous membranes with controlled thickness between 45 and 100 µm.

In the second approach, randomly porous PBI membranes were prepared by the inverse-phase method (UTWENTE route). For such purposes, a 12 wt % Fumion solution was prepared at 160 ° C under reflux in NMP. The inclusion of additives (PVP K30 and PVP K90) to the casting solution as weak solvents is demonstrated to promote pore interconnectivity and to suppress macro-void formation during the phase separation process. The membrane casting was performed at 20 ° C over the surface of glass plates previously cleaned by using a 0.1 nanometres casting knife, and immediately placed in the coagulation bath. First, the cast polymer solution was immersed in NMP / Water (50/50) mixture during 30 minutes. Subsequently, the membrane formation was completed in a second coagulation bath containing DD water for 1 h. Finally the membrane was immersed in DD water to rinse out the last traces of solvent and stored in pure water. The most remarkable feature is that no macrovoids are identified along and across the membrane confirming the viability of both preparation procedures

The application of the as prepared randomly porous PBI is potentially attractive in the field of gas separations at high temperature and pressure conditions. In addition, by taking advantage of the asymmetric porous structures exhibited by porous PBI membranes prepared by chemical routes, liquid phase separations are also feasible. In both cases, the porous PBI membrane could play the role of a material separation agent capable to separate selectively the components in the feed mixture thanks to a driving force. One of the project side results in this respect was the ability of the porous PBI membranes (prepared by leaching out a porogen) with a short non-porous PBI skin to successfully separate H2 / CO2 mixtures at temperatures up to 200ºC with permselectivity values around 25. Indeed, the separation of H2/CO2 at high temperatures is extremely important because it opens the potential of developing membrane reactors for the Water Gas Shift Reaction.

On the other hand, straight porous PBI supports have been prepared either by track-etching technology (CRF-FIAT route) or micro-transfer moulding (INA route). Herein, it is worthwhile to underline that both methods have been applied for the first time to PBI films within the framework of this project. Ion track technology is widely used for the industrial production of filters (Whatman, Trackpore), printed circuit boards (IST), and other devices. It opens a low-cost route to micro and nanotechnology as a vertically cutting tool, enabling high aspect ratio structures, distributed at arbitrary number density. In this field, the main outcome of ZEOCELL has been the possibility to track-etch PBI films with thickness below 30 microns to obtain nano-porous (30-50 nm in pore size) membranes. The application of APA masks has proved to be not feasible due to the angular divergence of the incident beam and to charging and damaging phenomena on the alumina support. Thus, the pore distribution in the plane parallel to the polymeric layer is disordered, but the pore shape is straight and the aspect ratio of the channels is about 1000. Ion-track technology on PBI polymer could also be explored for the production of Li-ion batteries separators. In fact, advanced separators, able to block the thermal runaway of the lithium ion batteries are of extreme importance for the safety of the device itself.

2D ordered porous PBI structures have been successfully prepared by soft lithography techniques. In particular, the application of microtransfer moulding technique has allowed developing replicas by using a relief pattern of a flexible mould (PDMS). By this fabrication route, porous PBI membranes with 25% of porosity, 15 micron in pore diameter and 30 micron in pitch have been successfully prepared. Among the potentialities of this new type of micro-patterned PBI films, it is noteworthy the use as structural layer for applications demanding harsh conditions (high temperature, extreme pH or oxidant-reducing conditions) thanks to the intrinsic properties of PBI polymer. A new research path emerges on micro-patterned PBI films to fill the existing gap in lab on chip applications, mainly dealing with biomedical applications.

More specifically, Lab on chip, Micro Total Analytical Systems, Flexible Structured Micro Reactor and Micro fuel cells based on microstructured PBI films are envisioned in the short term. Holdcroft and co-workers were the first to propose the concept of making PEMs from curable liquid precursors and pointed out that such a liquid-to-PEM approach may enable the formation of PEMs conformable by injection molding, formed as microchannels and unique shapes, or strongly adhering to the catalyst layer without hot pressing. The fabrication of MEAs from these PEMs resulted in fuel cells outperforming those based on commercial materials. The patterned membranes provided a larger interfacial area between the membrane and catalyst layer than standard flat counterparts and demonstrated higher power densities without an increase in the macroscopic area of the fuel cells.

ZEOCELL goal: Development of nanostructured electrolyte membranes for high temperature PEMFCs

Nearly all samples prepared comprise PBI as base polymer. Different membrane structures have been obtained: dense PBI membranes, randomly porous PBI membranes prepared by delayed demixing and also by leaching out a porogen, track-etched porous PBI membranes and micropatterned PBI membranes. For proton conduction purposes, phosphoric acid doping and/or 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Im0008b) ionic liquid embedding have been mainly studied in the project. The phosphoric acid autodehydration is a serious limitation for operation above 140ºC, where lower conductivity oligomers like pyrophosphoric acid are generated. Thus, the deployment of protic ionic liquids as proton carriers has been demonstrated as clearly beneficial due to its physical and chemical properties.

In a further step, in an attempt to improve endurance properties, and considering the successful UV assisted polymerization of monomers prepared from Im008b ionic liquid, polymeric ionic liquid (PIL) based membranes have also been developed. In particular, pure dense PIL-membranes, and reinforced PIL on porous PBI supports have revealed enormous possibilities as proton conductors. The incorporation of microporous materials either as inorganic fillers to the membrane casting solution (contingency plan) or as thin film coatings onto preexisiting porous PBI membranes has been considered. In the first case, conduction/durability issues of acid doped PBI membranes were pursued. On the other hand, the role of microporous top layers was mainly related to fuel cross-over and ionic liquid leakage with time on stream.

To gain insight on the synergic effects provided by materials combination, different membrane categories, ranging from 1 component (i.e. Pure Polymeric Ionic Liquid Films), through binary (supported ionic liquid membranes in track-etched porous PBI substrates, supported ionic liquid membranes in randomly porous PBI substrates, reinforced polymeric ionic liquid membranes on porous PBI supports, acid doped track-etched porous PBI substrates), ternary composites (hybrid acid doped dense or porous PBI and hybrid dense or porous PBI embedding ionic liquid) to the final nanostructured electrolyte membranes based on four components (i.e. PBI, phosphoric acid, ionic liquid and microporous materials) have been studied in detail in most cases, morphological (SEM), physicochemical (TGA-DSC, H2 and methanol permeabilities), mechanical (DMA) and electrochemical (in plane and through-plane proton conductivity and durability) properties have been evaluated.

For a better understanding, the most outstanding features in relation to the defined technical targets, the MEA performance and the estimated manufacturing costs (if available) for a future exploitation are separately discussed for each membrane type in the subsequent sections below. Although the core of the project is focused on high temperature applications, the performance of porous polyimide membranes developed within the framework of the project and capable to withstand temperatures up to 120ºC, is firstly reviewed due to the considerable improvement of performance obtained in comparison with Nafion 212.

1) Porous sPEI based membranes for low-medium temperature applications

Porous sulfonated naphthalenic copolyimides (sPEI) films (15%-60% nominal porosity) with controlled thickness between 60 and 100 µm have been prepared by casting from a polymer solution containing DBP porogen-type molecules. Series of tough sulfonated polyimide films are obtained with controlled thickness between 45 and 50 µm. Previous to characterization, the membranes are acid-treated with 0.1 M H2SO4 solution at room temperature for 14 h and then rinsed with DDW. As can be observed, the behaviour is clearly outperforming Nafion. However, at temperatures higher than 90 ºC the membranes become fragile, and for this reason, they have rejected as solid electrolyte for high temperature PEMFC. In spite of this result, these membranes are really promising as electrolyte for low temperature PEMFCs, since their conductivity values at 60 ºC are considerably higher than available commercial membranes (up to 1.6 times the Nafion 212 values). The polarization curves at 70ºC of the as prepared sPEI membranes on commercial electrodes and GDLs are quite similar to Nafion212 used as benchmark. Despite the potential applications of porous polyimides membranes (fluorine free) are in the medium temperature (80-120ºC) range, i.e. outside the scope of this project, these co-lateral results are highly promising and we consider them as exploitable foreground.

2) Electrolyte Membranes from single materials: Polymeric Ionic Liquid (PIL) Membranes

This electrolyte membrane category has been the result of a modified work-programme in accordance to the periodic risk assessment carried out by the project steering committee. Finally, the preparation of highly proton conducting polymeric ionic liquid membranes based on the selected protic ionic liquid Im0008b has been successfully achieved. In general, the proton conductivity decreases with increases in the cross-linker percentage (i.e. 1000 mS/cm to 0.64 mS/cm at 150 ºC). On the other hand, higher CL degree increases the rigidity/fragility of the membrane. Therefore, an optimization of the cross-linker content was performed.

The evaluation in H2-FC performance (with 2.5cm*2.5cm of electroactive area) has been compared with commercial MEAs from Advent at 120ºC. Comparing with pure PBI MEAs and commercial Advent MEAs, the PILs based MEAs performance seems quite encouraging. Thus, the 'proof of concept' has been successfully demonstrated even better results can be expected by electrode optimization and improvements in fuel-cell components (i.e. bipolar plates). As the power density obtainable increased as a function of temperature, the deposition of PBI dense thin layers by spin coating over the top surfaces of PILs based membranes is being pursued to minimize H2 cross over.

3) Electrolyte Membranes from two components: Reinforced Polymeric Ionic Liquid onto Porous PBI Membranes (PIL-PBI)

This electrolyte membrane category has been conceived as a consequence of the experimentation carried out with pure polymer protic ionic liquid membranes. More specifically, the main purpose of reinforced polymer ionic liquids is to enhance not only the chemical stability of pure PIL in presence of solvents, but also the mechanical properties and at the same time to take advantage of the conduction performance of pure polymer ionic liquid. The use of PBI as support is justified by the existence of commercial membranes and MEAs based on this high temperature resin type polymer. For such reasons, the eventual implementation of PIL-PBI membranes into the standard MEA procedures already developed at industrial scale for PBI will be facilitated.

As expected, the conduction-temperature dependence is similar to the observed for pure PIL without CL. For reinforced PIL-PBI membranes conductivity values up to 250 mS/cm and 340 mS/cm at 150 ºC and 200 ºC respectively, are achieved in presence of 5% of water partial pressure. Similarly, reinforced PIL membranes on track-etched APA supports from Anodisc® (35% in porosity, 100 - 200 nm in pore size) have also been prepared. However, the expected conductivity values through straight APA pores are somewhat hindered due to poor APA wetability. In spite of this, conductivity values as high as 25 mS/cm has been attained at 200ºC. For reinforced PIL onto porous PBI supports the activation energy is twice that evaluated for pure PIL membranes indicating that the length of percolating pathways is higher for the former. On the other hand, for straight APA pores, the limited number of percolating pathways increases five-fold the activation energy required for proton hopping.

Methanol cross-over through reinforced PIL membranes has been notably improved in comparison with pure PIL membranes. The most outstanding feature for these membranes was the decrease of methanol permeability with temperature. This pattern strongly suggests:
i. The absence of non-selective free voids; and
ii. A permeation process mainly controlled by diffusion-solution mechanism.

These hypotheses are also in agreement with the lower permeation rates exhibited in comparison with the porous PBI support at temperatures above 50ºC.

The H2-FC performance (with 2.5cm*2.5cm of electroactive area) has been evaluated at 120ºC. Thus, the 'proof of concept' has been deemed successful by comparison with commercial counterparts (Advent); and, even better results can be expected by electrode optimization and improvements in fuel-cell components (i.e. bipolar plates).

4) Electrolyte Membranes from two components: Supported Protic Ionic Liquid Membranes onto Porous PBI supports

The conduction properties of bulky protic ionic liquids coupled to their physical and chemical properties have been the main factors that motivated the study of supported liquid membranes on porous PBI as supports. The development of experimental procedures (assisted by vacuum and/or temperature) to achieve a complete filling of the porous supports by protic ionic liquids and avoids its leakage, is one of the main challenges for this dual system.

In addition, proton conduction over Im008b Protic Liquid Supported Membranes, unlike phosphoric acid doped porous PBI membranes, primarily depends not only on support porosity but also on pore connectivity (coordination number) as revealed by modelling studies. In general, the conductivity values of heterogeneous media increase markedly with porosity for values above the percolation threshold. Therefore, the conduction performance of the supported Protic Ionic Liquid Membranes has been somewhat limited due to the availability of adequate PBI porous supports.

Conductivity values up to 20 mS/cm at 150ºC have been achieved for the imbibed on 80% porous PBI membranes and 100 nm in pore size. This behaviour is in agreement with the pore architecture attained by delayed-demixing membrane process. Nevertheless, the conductivity decreases with time on stream (below 6 mS/cm at 150ºC after 150 h) for all samples prepared due to Im008b leakage and/or water dragging effect during testing in presence of 0.05 water molar fraction. The 80% porous support provides better performance than the track-etched membranes with 1% porosity (almost 10 times higher). However the amount of ionic liquid encapsulated is not comparable at all due to porosity differences.

As expected, higher values are attained by using track-etched supports due to the shorter proton diffusion pathways. In addition, the endurance properties of the supported liquid membrane on 50 nm track-etched pores, are notably improved. Thus, the proton conductivity at 150ºC remains nearly constant after 150h at about 0.6 mS/cm (membrane support with 1% in porosity). Thus, supports with low pore diameters are clearly preferred for durability at the expense of a lower porosity and conductivity. In this region, only track-etched technology is feasible although up to now it has been scarcely explored for PBI type polymers. Acid doped track-etched porous PBI membranes have also been studied. A clear improvement was observed when compared with doped dense PBI membranes prepared under identical conditions. Thus, 1 % of porosity allows up to 25-fold enhancement of through-plane conductivity at 180 ºC. This fact is related to proton transport kinetics aided by wetted wall straight cavities with H3PO4 molecules.

Theoretical conductivity calculations have been carried out over straight porous PBI membranes with 25% of porosity and 15 nanometres in pore diameter prepared by micro-moulding. Thus, 45 mS/cm and 64 mS/cm are calculated for Im008b supported on patterned PBI at 170ºC and 200ºC respectively. In addition, the porosity value required to fulfil ZEOCELL technical targets in term of conductivity is technologically feasible. Acid doped micro-moulded PBI membranes have also been studied. A clear improvement was observed when compared with doped randomly porous PBI membranes with similar porosity values. Thus, 25% porosity allows up to 2-fold enhancement of through plane conductivity at 180ºC. This field constitutes one of the main exploitable foregrounds not only for FC applications but also in the 'Smart Microsystems' field.

5) Electrolyte Membranes from three main components: Phosphoric Acid Doped Hybrid PBI Membranes

Hybrid membranes based on acid doped PBI and microporous materials have been successfully developed as a result of the contingency plan for HT PEMFCs applications. In fact, this electrolyte concept has been intellectually protected (PCT/EP2010/064857; priority date 05/10/2010). Basically two fillers have been mainly studied: ETS-10 titanosilicate type material externally functionalized with sulfonic groups and NaY type zeolite embedded in Im008b. Thus, the organic functionalization of the external surface of microporous ETS-10 crystals (circa 4%wt loading), has allowed to improve the intrinsic conductivity of the inorganic loading attaining proton conductivity values as high as 30 mS/cm at 150ºC under saturated conditions. This fact is due to the coexistence of the two main conduction mechanisms: vehicle -type mechanism (with H2O as proton carrier) and hopping- type mechanism (through -SO3H terminal groups + H2O molecules).

Similarly, the presence of Im008b in the NaY framework structure also enhances the membrane conduction properties due to the hydrophilicity of NaY crystals and the new conduction pathways provided by proton donor-acceptor sites encapsulated within its framework. A parametric study on the inorganic loading effect onto conduction performance of dense membranes has been carried out to identify an optimum value around 3% wt. referred to the polymer in the studied range (1-20% wt.). In a subsequent step, with the aim to further promote the conductivity of hybrid membranes, porous based PBI membranes with porosity values ranging from 30% to 75% have also been prepared by leaching out a porogen (DBP or TPP). Higher proton conductor uptakes values do not necessary involve higher conductivity. This fact is related to the phosphoric acid leakage during handling and the limited number of percolating pathways. It is important to remark that 3% of inorganic loading was identified as the optimum value for the 30% porous data set19; and it seems likely that higher porosity values would demand a higher amount of filler to ensure the beneficial effects.

The analyses of intrinsic proton conductivity values (expressed per phosphoric acid doping %wt.) versus porosity values for the two porogen molecules (i.e. pore connectivity degree) has allowed to quantify the 'porous structure' effect for a given inorganic filler. In particular, a most effective acid doping is shown by porous membranes prepared from TPP porogen.

Different porous membranes have been assembled on Freudenberg Carbon Paper recommended for High temperature H2 PEMFCs and DMFCs. Among the tested, the most outstanding H2 PEMFC performance is exhibited by MEAs prepared for porous PBI membranes, 60% DBP content (0.5 V/ 0.704 A/cm2 vs. 0.5 V/ 0.47 A/cm2 at 160ºC and non humidified conditions). This result is in accordance with the reported values for commercial and state of the art HT H2-PEMFCs. Eventually, further improvements are expected in the short-term by means of electrode and MEA assembly optimization.

A similar work-programme has been followed for high temperature DMFCs. In this case the electrolyte membrane porosity seems to have an adverse effect over DMFC performance and time on stream behaviour (cracks formation). Among the samples tested, the best high temperature DMFC performance was exhibited by MEAs prepared for dense PBI membranes (0.3 V/ 0.170 A/cm2 at 150ºC), which can be considered as an outstanding result.

6) Electrolyte Membranes from three main components: Protic Ionic Liquids embedded in Hybrid Porous PBI Membranes

Hybrid membranes based on PBI and microporous materials impregnated with protic ionic liquid have been also tested. This membrane system could be considered as a supported liquid membrane, where the porous hybrid PBI is the inert container and the protic ionic liquid is the selective carrier from proton transport. Therefore, the pore connectivity of the PBI framework has to ensure a continuous conduction pathway through the protic ionic liquid network. Unfortunately, the exhibited conduction performance is far below the ZEOCELL requirements, whatever the porosity and porogen used in spite of the reported Im008b uptake values.

7) Electrolyte Membranes from four main components: Protic Ionic Liquids embedded in Phosphoric Acid Doped Porous PBI Membranes with Zeolite Coatings

The ZEOCELL project puts forward an innovative electrolyte membrane concept based on the synergic combination of porous PBI supports containing protic ionic liquids as intrinsic conductors and zeolite coatings ETS-10 as diffusional barriers over PBI top surfaces to prevent the conductor leakage/dragging with time on stream. Due to the technical difficulties to fabricate ordered porous PBI supports, all the experimentation on this topic has been carried out with randomly porous PBI prepared either by leaching out DBP or TPP porogen molecules (CIDETEC route) or by phase separation process (UTWENTE route).

From the preliminary results, it appears that membrane porosity values higher than 60% provide the best conduction performances. TPP porogen renders sponge-like pores more adequate for ionic liquid filling but also more prone to leakage. On these samples, a trade-off between durability and conductivity should be considered. Thus, the most interconnected porosity attained on TPP samples, the higher embedding and proton transport properties, at the expense of a higher leakage risk during operation. Moreover, electrolyte membranes based on porous PBI 80% prepared by delayed de-mixing outperform CIDETEC membranes.

In addition, two different coatings have been deployed over the polymer surface. The FORTH procedures involve the infiltration of colloidal NaY seeds, whereas, ETS10 coatings by covalent-linkage over acid doped PBI polymer were prepared by INA. In the former case, conductivity values up to 10 mS/cm have been reported. On the other hand, up to 100 mS/cm and 60 mS/cm at 150ºC for in plane and through plane conductivities respectively have been attained by following optimized INA procedures over porous PBI 80% prepared by delayed de-mixing. The optimized preparation method comprises four main steps:
- Phosphoric Acid Doping of porous PBI membranes with 11M solution for 24 h at room temperature followed by drying at 120ºC under vacuum for 12 hours.
- Immobilization of ionic liquid by assisted vacuum filtration at 170ºC onto doped PBI membranes previously evacuated. The filtration procedure is carried out during 8 h at the fixed temperature. Finally, the system is evacuated at 0.5 mbar until most of the ionic liquid pass through the membrane ensuring that the pores are filled with it. The resulted composite membrane is dried at room temperature for 3 hours. Sweeping the excess of ionic liquid of the PBI surface was then performed using sorbent paper soaked in dry acetone.
- Two steps of covalent linkage of functionalized epoxy-ETS10 crystals over the PBI surface.
- Phosphoric acid doping of composite IL-ETS10-PBI membranes with 11M solution for 15 minutes at room temperature followed by drying at 120ºC under vacuum for 3 hours.

The H2-FC performance (with 2.5cm*2.5cm of electroactive area) has been evaluated at temperatures up to 180ºC. By comparison with pure PBI MEAs and commercial MEAs from Advent, the 'proof of concept' could be considered as demonstrated. However, better results are expected following electrode-electrolyte interphase optimization due to the nanostructured membrane roughness.

A preparation procedure for 3-layer integrated MEA by CCM (Catalyst Coated Membrane) relying on the catalytic properties of zeolite coatings has been established. The nanostructured electrolyte membrane preparation procedure already described has been slightly modified for catalytic activation purposes. In particular, the second covalent linkage step has been carried out with Vulcan/amine/Pt/amine/ETS-10 instead of amine/ETS-10 crystals to incorporate the Pt and also de Vulcan required for electron transport at the three boundary layer. In this scenario, the zeolitic layers play the two following roles:
i. Catalyst support due to the well-known properties of zeolites as platinum support to provide with higher metal dispersion; and
ii. Microporous barrier to diminish fuel crossover and proton conductor leakage during operation.

The preparation method developed here, involves Vulcan-Pt-zeolite electrocatalysts. Accounting from the gained knowledge, the catalysts here prepared are also amenable to deploy in other catalytic chemical reactions.

Potential Impact:

Potential impact of S&T results and exploration

The main ST outcome from ZEOCELL is the development of three novel electrolyte membranes fulfilling all the ST requirements originally claimed for high temperature PEM fuel cells in stationary applications with the exception of durability issues which are briefly described below:
1) Hybrid randomly porous PBI membranes doped with phosphoric acid (PCT/EP2010/064857; priority date 05/10/2010). The endurance properties of this family are under investigation.
2) Nanostructured Electrolyte Membranes based on randomly porous acid doped PBI membranes with tortuous pores filled up with protic ionic liquid and two microporous ETS10 coatings on top surfaces. The endurance properties a 150º and 200ºC reveals severe performance decay after 150 h operation in presence of 5% H2O
3) Reinforced Polymeric Ionic Liquid Membranes on Porous PBI supports (also being considered for intellectual protection). A continuous stepwise loss in performance is observed during the first 500 h at 200ºC, but thereafter conductivity values remain constant at around 275 mS/cm.

The manufacture requirements have been present throughout the project as a criterion to guide the research and development to obtain a PEM able to be mass manufactured in market competitive conditions. The preliminary industrial evaluation of the basic materials proposed in the project (i.e. PBI, protic ionic liquids and zeolites/zeotypes) reveals that neither raw material and energy costs, not chemicals availability are limiting factors for the commercialization of membranes significantly cheaper than the commercially available membranes for HT applications. Furthermore, the principles of Green Chemistry have been followed to synthesize selected ionic liquids in good agreement with the requirements for a safe and efficient large scale production. Finally, our assessment of intellectual property on the basic materials used indicates that they shouldn't be an obstacle for a potential implementation at industrial level.

CEGASA INTERNACIONAL, leader of work-packages related to industrial manufacturing and exploitation issues, has contributed with knowledge and experience in the field of manufacturing electrodes for PEM fuel cells and lithium ion batteries to establish how the manufacturing process of the new membranes could be performed in a pilot line. Before the coating unit, a mixing unit is required for the preparation of a homogeneous casting solution. The main issue in this process is the reproducibility of the rheological characteristics of the solution in each batch of mixing. At the end of the mixing process, a homogeneous membrane solution will be available. Once the mixing is done, the membrane solution goes to an intermediate vessel from where it will be pumped to the slot die. The second step is the casting of membranes onto an inert material (i.e. Teflon substrate). Once the membrane solution is cast onto the substrate, a conditioning procedure must be applied. A thermal cycle in the oven (I) will be used to eliminate the solvent. The next step is porogen leaching from the casted membrane by Immersion Bath (I) + Oven (II). The membrane manufacturing method also includes coating an electrolyte in the carrier film by Immersion Bath II (Phosphoric acid solution) and final Oven (III) (Evaporation of free water). The last step in the membrane manufacturing consists on the membrane lamination by winding device.

Furthermore, the cost analyses of the aforementioned membranes have been carried out considering two main aspects: materials cost and manufacturing cost. It is estimated that the materials cost, especially the PBI ionomer cost would drop by roughly 90% when production scales up from laboratory to industrial production. This estimation is applied in the calculation of both membranes cost from 1 m2 of membrane surface to 2.000.000 m2. Moreover, price evaluation for ionic liquids has been reconsidered using continuous process as a function of annual production rate. On the other hand, there is a reduction in losses associated with the manufacturing process which directly affect the membrane material cost.

The results of the cost assessment clearly indicate that the membranes developed in the ZEOCELL project would be competitive in the high temperature PEMFC stationary applications market. Due to the favourable cost evaluation, the analysis for a 2 kW PEMFC stack manufacturing based on MEAs prepared by CCS method from hybrid porous PBI membranes doped with phosphoric acid has been carried out and compared with state of the art PBI membranes and DOE-EU targets from 1000 to 500000 stack units/year. A power of 2 kW for the stack has been considered as particularly attractive for micro-scale residential applications, such as 'single-family' households, for which the average net electric power requirement is, generally well below 5kW.

In general, the manufacturing process of fuel cell components is still in the development stage and fits into the category of low volumes of high quality production with high production costs. For this, there are several approaches to manufacturing processes, depending on the solutions adopted by each manufacturer, without a generally applicable standardized process. The mass manufacturing scale associated to an automated process reduces the price of 1kW stack (manually assembled) by 95% approximately. In particular, a cost reduction of 4.1 to 1 with manufacturing rates (i.e. from 1000 to 500.000 units) has been estimated. Considering the automated versus manual processing, the manufacturing time is reduced by approximately a 60%. According to our estimations based on the components cost and the automated manufacturing process on 500.0000 units/year basis; the high temperature stack cost (214 EUR/kW) based on ZEOCELL Hybrid Porous PBI membranes would fulfil the European and USA targets, provided that the durability requirements (which are still under investigation) can be met.

The project exploitation plan has provided business analysis of those stacks in the two following markets:
i. Micro-Combined Heat and Power Systems and
ii. Backup/supplemental power for Telecom Applications.

The analysis is based on HT PEMFCs penetration in the market of 10% for micro-CHP and 20% in the case of backups. For a hypothetical scenario in which ZEOCELL membranes would achieve a 20% and 30% share of the market for CHP's units and back-up systems respectively, the surface requirements and the foreseen benefits are quite encouraging. Annual benefits from EUR 9 M to EUR 64 M for 2015 and 2025 have been estimated.

Other exploitable results

Apart from the power generation sector, exploitable foregrounds and potential new applications in different fields for the individual and composite materials and membranes studied in the project have been also identified. Thus, from the properties found for ZEOCELL materials, the potential markets and new research lines not directly related to FC technologies are the following:
- Applications of porous and Dense PBI membranes in the field of gas separations at high temperature and pressure conditions (H2 Separation/ CO2 Precombustion Capture; Natural gas sweetening)

- Porous PBI membranes for Liquid Phase Separations (Solvent stable nanofiltration)
- Straight Porous PBI Membranes prepared by Ion-Track Technology as Separators for Lithium Ion Batteries & Inert Containers for Proton Conductors
- Micropatterned PBI films by Microtransfer Moulding Techniques for micro Fuel Cells and Smart Microsystems (reaction, separation and detection purposes)
- Ionic Liquids as Ion Conductors for PEMFC and Energy Storage Applications
- Ionic Liquids as Solvents/Carriers in Supported Liquid Membranes for Gas and Liquid Separations
- Monomeric and Polymeric Ionic Liquids: Development of Polymer Ionic Liquid Based Membranes for Fuel Cells and Energy Storage
- Polymer Ionic Liquid Based Membranes for Gas Separation Applications
- Functionalized Microporous Materials for Adsorption and Catalytic Applications
- Development of Flexible SU8 and PBI microstructures with advanced functionalities for micro Fuel Cells and Lab on Chip Applications

Diffusion of project results, dissemination and impact (societal, socio-economic, etc.)

The diffusion of project results started with ZEOCELL web site (http://ina.unizar.es/ZEOCELL/) which has been continuously updated with relevant information related to any action of dissemination carried out by any of the partners: attendance to conferences, participation in exhibition fairs, presentations made in some of these events, internal events where ZEOCELL have been presented, meeting communications (abstracts, proceedings, papers). Moreover, some publications directly related to the work within ZEOCELL have been / are being obtained and have been / are being published the main scientific journals of the field. Additional dissemination of the consortium activities is granted due to the fact that some of partners are members of important networks in the field of fuel cells and hydrogen.

All Partners have contributed, along the project, to maximising the potential impact of the knowledge both in terms of the dissemination of results of academic interest to scientific community (nanomaterials, polymer membranes, ionic liquids, microporous materials, and PEMFCs) and of exploitable to potential end-users (materials provider and PEMFC manufacturers).

Project website:
http://ina.unizar.es/zeocell/

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