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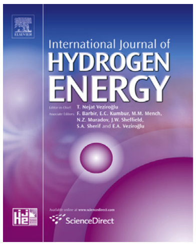

LoLiPEM: Long life proton exchange membrane fuel cells

G. Barbieri [a,*], A. Brunetti [a], M.L. Di Vona [b], E. Sgreccia [b], P. Knauth [c], H.Y. Hou [c], R. Hempelmann [d], F. Arena [d,1], L.D. Beretta [e], B. Bauer [f], M. Schuster [f], J.O. Ossó [g,2], L.F. Vega [g,h,3]

[a] National Research Council — Institute on Membrane Technology (ITM—CNR), Via Pietro BUCCI, c/o The University of Calabria, cubo 17C, 87036 Rende CS, Italy
[b] Università Roma “Tor Vergata”, Dip. Scienze e Tecnologie Chimiche, 00133 Roma, Italy
[c] Aix Marseille Université, CNRS, Madirel (UMR 7246), Campus St Jérôme, 13397 Marseille, France
[d] Saarland University, Physical Chemistry, D-66123 Saarbrücken, Germany
[e] EDISON — Centro Ricerca e Sviluppo di Trofarello, via G. LA PIRA 2, 10028 Trofarello TO, Italy
[f] FuMA-Tech GmbH, Am Grubenstollen 11, 66386 St. Ingbert, Germany
[g] MATGAS Research Center, Campus UAB, 08193 Bellaterra, Barcelona, Spain
[h] Carburos Metálicos, Air Products Group, C/ Aragón 300, 08009 Barcelona, Spain

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ABSTRACT

This paper presents the main results obtained during the European project (FCH-JU) “LoLiPEM — Long-life PEM-FCH & CHP systems”. The paper describes significant improvements in the polymer electrolyte by tailored heat treatments for cross-linking of Sulfonated Poly(ether ether ketone) (SPEEK), obtained without any addition of cross-linker species. The reported properties of the ionomers include mechanical properties, gas permeability and ionic conductivity.

Innovative gas-diffusion electrodes are fabricated by the electrochemical deposition of Pt catalyst; the fuel cell current—voltage characteristics are reported with Nafion and SPEEK-based binder.

The fuel cell performances at 80 °C of membrane-electrode-assemblies containing a SPEEK membrane with a cross-linking degree of 32% are among the best in the literature compared with the PEMFC using membrane alternative than Nafion.

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[*] *Corresponding author*. Tel.: +39 0984 492029; fax: +39 0984 402103.
E-mail addresses: g.barbieri@itm.cnr.it, giuseppe.barbieri@cnr.it (G. Barbieri).

[1] Current address: MECADI GmbH, Industriegebiet in der Kolling, In der Kolling 9, 66450 Bexbach, Germany.

[2] Current address: BASF New Business GmbH, BNB — Lu-Benckiserplatz BE 1, 67059 Ludwigshafen, Germany.

[3] Current address: Alya Technology & Innovation, Centre de Promoció Empresarial, C/Tres Creus, 236, 08203 Sabadell, Barcelona, Spain.

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Introduction

Stationary power generation and combined heat and power systems (SPG&CHP) based on fuel cells (FC) can help to reduce petrol dependence and CO_2 emissions in the atmosphere. They can also be useful to decrease pollution, especially in large towns, and in the case of electrical black-out. These co-generation systems can use very thin and flexible ionomer membranes, which exhibit high proton conductivity at relatively low temperature without any addition of mineral acids. The specific characteristics of the ionomer membranes facilitate the development of small co-generation systems, very suitable for small buildings.

Although the potential of fuel cells is well established, the enthusiasm for this technology has decreased in recent years for various reasons, including its limited durability and the too high total price [1–6]. Research to further accelerate their deployment on the market should be focused on these two issues: increasing the durability and reducing the cost of the current systems [7,8]. It is therefore important to develop membranes with high durability and low price as well as new catalytic electrodes that are more stable at the operating temperature of the fuel cells.

The proton exchange membrane (PEM) is typically phase-separated into a percolating network of hydrophilic nano-pores embedded in a hydrophobic polymer-rich phase domain [9–13]. The hydrophilic nano-pores contain acidic moieties, which ensure the proton conductivity. The hydrophobic phase domain provides mechanical strength to the membrane. Nowadays extensive research is devoted to finding ionomer membranes with high durability and low cost that can work at a higher temperature [14–17].

Sulfonated Aromatic Polymers (SAPs [11,18,19]) can be valid materials for this purpose, provided the degradation problems that affect this class of polymers are solved. The main distinctive feature of SAPs is the fact that the water filled channels are narrow and tortuous with a small separation between hydrophilic and hydrophobic domains. One positive effect is the permeability reduction for reactants, such as methanol or hydrogen. Conversely, the distance between adjacent sulfonic groups is large and, for this reason, SAPs need a higher ion exchange capacity (IEC) compared with perfluorinated ionomers to achieve the required conductivity [13,20]. However, the high IEC leads to morphological instability and large swelling at high humidity. Water uptake increases with the degree of sulfonation (number of SO_3H groups per repeat unit) thereby improving the conductivity of the hydrated membrane, but highly polar water molecules act also as a plasticizer, undermining the electrostatic interactions between SAP macromolecular chains and favoring membrane swelling. Highly sulfonated aromatic polymers swell rather strongly in water and become even soluble if the sulfonation degree is high enough [21,22]; this has made the long-term stability of highly sulfonated membranes questionable until now.

Cross-linking reactions are one of the most powerful ways to control and improve the properties of polymeric materials [23–27], such as swelling and mechanical behavior [28–30]. However, reticulation often relies on the presence of cross-linker species and special procedures, such as grafting by irradiation [23,31–35]. Furthermore, some cross-linker species might be attacked under the harsh conditions of an operating fuel cell [16]. The possibility of achieving reticulation between chains via sulfone bridges, directly by thermal treatment of cast membranes using sulfonic acid groups already present in SAP, is an appealing way to obtain stable ionomeric membranes [36,37]. This method also allows overcoming problems associated with the insolubility of cross-linked polymers in common solvents that make the casting procedure difficult. Furthermore, cross-linking by thermal treatment without any addition of cross-linker molecules can be performed in a cost-effective mode from an industrial point of view.

Another objective is the development of more efficient noble metal electrocatalysts, reducing the platinum loading of the electrodes significantly [38,39] and, in this way, the overall cost of the fuel cell. The common preparation technique for catalyst layers in fuel cell electrodes starts from carbon black covered with platinum (pre-catalysation) [38–46]. Thus only low catalyst utilization can be obtained, because a considerable fraction of the catalyst material is not in direct contact with the three-phase boundary. The objective of our work is to increase the catalyst utilization by localizing the catalysts particles exclusively in the three-phase boundary. This is only possible a posteriori: a platinum precursor salt is brought into the microlayer during the layer preparation and platinum is site-selectively electrochemically deposited *in situ* on the carbon surface, without expensive outer plating baths. With improvements in the deposition route described in the following sections, non-aggregated platinum nanoparticles with diameters down to 2 nm can be prepared directly in the microporous layer (MPL) of Gas Diffusion Layers (GDLs), thus transforming GDLs into Gas Diffusion Electrodes (GDEs) [50]. In this way, both noble metal costs and processing costs can be saved, because the electrochemical route to GDEs exhibits fewer processing steps than the conventional route. A further advantage is that in the same way platinum alloy catalysts can easily be prepared, even in medium-throughput.

This paper presents examples of membrane improvement by thermal cross-linking of Sulfonated Poly(ether ether ketone) (SPEEK), including mechanical, hydrolytic, electrical and mass transport properties, the innovative preparation of GDEs by electrodeposition of platinum catalyst as well as characteristics of the assembled fuel cells.

Experimental

Membrane preparation

Sulfonated Poly(ether ether ketone) (SPEEK) was prepared by reaction of PEEK (Victrex 450P, MW = 38,300 g/mol) with concentrated sulfuric acid (96%) in ratio 1:35 ($g\ mL^{-1}$) under N_2 at 50 °C for 2–4 days in order to obtain a large degree of sulfonation. After this time, the solution was poured, under continuous stirring, into an excess of ice-cold water thereby obtaining a white precipitate [47]. After resting overnight, the precipitate was filtered and washed in a dialysis membrane (Sigma-Aldrich D9402) until neutral pH in order to eliminate the residual sulfuric acid completely. The sulfonated polymer