

Short communication

## Conductivity in zeolite–polymer composite membranes for PEMFCs<sup>☆</sup>

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### Abstract

Structured materials, such as zeolites can be candidates to be used as electrolytes in proton exchange membrane fuel cells (PEMFC) to substitute polymeric membranes, taking advantage of their higher chemical and thermal stability and their specific adsorption properties. The possibility to work at temperatures of nearly 150 °C would make easy the selection of the fuel, decreasing the influence of CO in the catalyst poisoning, and it would also improve the kinetics of the electrochemical reactions involved. In this work, four zeolites and related materials have been studied: mordenite, NaA zeolite, umbite and ETS-10. In special, the influence of relative humidity and temperature have been carefully explored. A conductivity cell was designed and built to measure in cross direction, by using the electrochemical impedance spectroscopy. The experimental system was validated using Nafion<sup>®</sup> as a reference material by comparing the results with bibliography data. Samples were prepared by pressing the zeolite powders, with size of 1 μm on average, using polymer PVDF (10 wt.%) as a binder. The results here obtained, in spite of not reaching the absolute values of the Nafion<sup>®</sup> ones, show a lower effect of the dehydration phenomenon on the conduction performance in the temperature range studied (from room temperature to 150 °C). This increase of the operation temperature range would give important advantages to the PEMFC. ETS-10 sample shows the best behaviour with respect to conductivity exhibiting an activation energy value comparable with reported for Nafion<sup>®</sup> membrane.

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### 1. Introduction

The proton exchange membranes (PEM) more widely used are those based on polymer of the perfluorosulphonic acid (PFSA) [1]. This kind of polymer requires hydration to exhibit proton conductivity and, for that reason, the maximum conductivity values take place at 100% relative humidity for every temperature [2]. Transport of protons and associated water molecules within PEMs is strongly dependent on the membrane's microstructure: Eisenberg [3] postulated the existence of ion clusters in Nafion<sup>®</sup> membranes in 1970. A "cluster-network" model for Nafion<sup>®</sup> was proposed by Gierke et al. [4], in which the solvent and ion-exchange sites separate from the perfluorinated polymer backbone forming inverted micelles (~5 nm in diameter) which are connected via short, narrow channels

(~1 nm in diameter). When Nafion<sup>®</sup> membranes dehydrate, the size of the water clusters within the polymer microstructure decreases, leading to a narrowing of the interconnecting channels. The mobility of the proton through the membrane becomes restricted and consequently conductivity falls [5]. Therefore, the operation temperature to use the PFSA polymer as electrolyte for proton exchange membrane fuel cells (PEMFCs) is limited to the water boiling point. Although operating at high pressures can overcome this drawback, the mechanical resistance of the polymer prevents an essential improvement in performance.

The possibility of operating at higher temperature than PFSA (range 120–200 °C) would allow several advantages. One of them is that hydrogen obtained from reforming gas could be used as a fuel due to the poisoning effect of CO traces in Pt electrocatalyst reduces noticeably with temperature. It has been proved that CO poisoning takes place from 10 ppm at room temperature, but at 150 °C the CO tolerance reaches values around 1% [6]. So, power densities similar to pure hydrogen (more expensive and difficult to produce) could be obtained operating

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