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Hybrid membranes of sulfonated poly ether ether ketone, ionic liquid and organically modified montmorillonite for Proton Exchange Membranes with enhanced ionic conductivity and ionic liquid lixiviation protection

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ABSTRACT
Through the fabrication of hybrid membranes, composed by the protic ionic liquid diethylmethylammonium trifluomethane sulfonate (demaTfO), sulfonated poly (ether ether kethone) with degree of sulfonation 73 % (sPEEK73) and montmorillonite modified with $dema^+$ cation (Mmtdema), this work evaluates the effect exerted by the compatibilization between clay and ionic liquid on the morphology and performance of membranes, as a function of Mmtdema proportion. This system of membranes showed high conductivity (78 mS/cm at 70 ºC) with some issues, due to the plasticization effect caused by montmorillonite and ionic liquid; these effects were confirmed through electrochemical impedance spectrometry (EIS), dynamic mechanical analysis (DMA) and proton relaxometry. The membranes showed resistance to ionic liquid lixiviation, which was confirmed through static water immersion and this effect was attributed to the protection effect that interlamellar spaces can provide to the ionic liquid, as it was visualized through TEM and XRD. The conjugation of results from several different techniques as SAXS, EIS, NMR, TEM and XRD permitted to obtain evidences for a proposed descriptive model of proton transporting process, which turns out to be a synergy between Grotthuss mechanism and vehicular mechanism, favored by the structure of Mmtdema and the preparation method, leading thus to high conductivity membranes with lixiviation protection for application as proton exchange membranes.

Keywords
Ionic liquid lixiviation; fuel cell; vehicular mechanism; Grotthuss mechanism; SAXS;

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are being extensively studied nowadays for purposes of alternative energy generation [1]. Fuel cells are electrochemical systems that allow generating electrical energy from a chemical reaction, with a constant supply of a certain fuel [2]. Several types of fuel cells can be made in order to generate electrical energy from a chemical reaction; between those, there is a particular one called PEMFC, which is based on the phenomena of ionic diffusion through a semi-permeable membrane known as proton exchange membrane (PEM) [3]. A PEM is a polymeric membrane and it selectively allows the pass of protons through its structure, isolating anodic and cathodic compartments of the fuel cell. Nowadays nafion polymer membranes are the most widely used Proton Exchange Membranes (PEMs) – which are the core of the PEMFC – due to its high mechanic properties and good ionic conductivity [4].

In order to produce a well performed PEM there are two characteristics of membrane polymer structure that are required: A rigid polymer backbone and ionic species attached to it [4]; in terms of mobility, the membrane structure must have a rigid and a mobile part. The rigid part is represented by the polymer backbone; which gives to the membrane its capacity to maintain its form. The mobile part is also called as Ionic Transporting Agent (ITA), and as its name indicates, it is the substance in charge of transporting protons from anode to cathode through two possible mechanisms of ionic transport [3]. The first one is known as Grotthuss Mechanism and consists on electronic jumps (for which it is necessary that the agent of transport is capable of forming hydrogen bonds). These jumps allow the proton generated at one side of the cell, to be transported to the other side without diffusion of molecules into the membrane structure [5]. The other possible mechanism is called vehicular mechanism [31], and it implies the diffusion of ITA through the membrane structure [6, 7].

For economy purposes it is important to substitute nafion by less expensive polymers which could make more accessible the price of fuel cells [8]. Pristine sulfonated poly ether ether ketone (sPEEK) has been demonstrated to be a less efficient polymer than pristine nafion in terms of ionic conductivity, presenting conductivities of 0,12 and 0,26 mS/cm at 60 and 80 ºC, in contrast with nafion which presents conductivies of 1,3 and 2 mS/cm [9]; in terms of mechanical resistance, nafion presents also significant vantages over sPEEK [12,52-53]. In spite of vantages that nafion membranes have in comparison with sPEEK, its price has made the researchers to look for a different alternative [54]; Ghasemi and co-workers have compared nafion and sPEEK performances, finding that despite power production of 77,3 mW/m^2 for pristine sPEEK is only 77,2% of pristine nafion, the former is at least two times more cost effective [55].

Along years of investigation it has been observed that the higher the degree of sulfonation of the polymer, the higher its ionic conductivity [10]; that behavior is due to the bigger number of ionic species attached to the polymer chains, ionic species that are capable of supporting an ITA (water or ionic liquid) [7]. The problem that has been observed throughout several researches, is that high sulfonation degree (which implies a high amount of ionic species attached to polymer backbone), makes the sPEEK highly hydrophilic, causing big swelling, and consequently poor mechanical properties that make the polymer unsuitable for fuel cell purposes [10]. In order to improve this issue, modified montmorillonite incorporated as reinforcement has proven to be a reliable