



New application of polymer inclusion membrane based on ionic liquids as proton exchange membrane in microbial fuel cell



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ABSTRACT

In the present work is evaluated for the first time the potential use of polymer inclusion membranes based on ionic liquids as proton exchange membranes in microbial fuel cell. Specifically ionic liquids based on 1-octyl-3-methylimidazolium hexafluorophosphate and methyl trioctyl ammonium chloride were used. It has been demonstrate that polymer inclusion membranes based on ionic liquids could act as proton exchange membrane in microbial fuel cell. In the case of ammonium based supported ionic liquid membrane (70% (w/w) ionic liquid), the power and the chemical oxygen demanded removal reached values of 450 mW/m³ and more than 80% respectively. An increasing of the amount of ionic liquid immobilized in the membrane involved an increasing in the microbial fuel cell power which means that the ionic liquid plays a role as active proton transport through the membrane.

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1. Introduction

In a Microbial Fuel Cell (MFC), microbes oxidize organic matter under anaerobic condition in the anodic compartment and transfer electrons resulting directly to a cathode, where the protons and electrons produce in the anode could be combined with oxygen forming water (see Fig. 1).

Current may be produced from simple substratum (e.g. acetate, lactate or glucose) but what is really innovative was the finding that current can also be generated from complex substrates like domestic and industrial wastewaters. By using organic matter in wastewaters as a fuel, we can simultaneously produce energy and purify wastewater [1]. For that, this biotechnology is presented as a good alternative to face both two major problems in the world: energy crisis and water availability. However, higher power generation and less expensive material are severely required for practical implementation of MFC in wastewater treatment and energy production. In order to improve economic feasibility and current yield, new materials for the electrodes and separator should be explored. MFCs could be configured with separator electrode assembly (SEA) or spaced electrode (SPA) [2]. The use of a separator between the electrodes avoids electrode contact. The electrode contact results in short circuiting as well as increases the oxygen

transfer from the cathode to the anode and the fuel transport from the anode and the cathode and consequently decreases the columbic efficiency. The use of SPA has been found that electrodes have to be separated in order to avoid short circuit. In this sense when SPA is used, placing the electrodes within 2 cm or less can result in a reduction of power [3,4]. On the other hand, for low conductivity solutions, such as domestic wastewater, it is important to use MFC designs with little separation between the electrodes in order to minimize ohmic losses [5]. For that, it is necessary to found an optimal distance. Furthermore, in SPA microbial fuel cell oxygen could pass to the anode compartment where anaerobic conditions are needed.

The proton exchange membrane (PEM) is often used in MFC. Perfluorinatedionomer membranes such as Nafion[®] (Dupont) have been widely used as proton exchange membrane in MFCs, because of their high proton conductivities. However, these membranes are still expensive which makes their use prohibitive in large-scale applications. Furthermore, cation species (e.g. Na⁺, K⁺, NH₄⁺, Ca²⁺, and Mg²⁺) penetrate Nafion at similar efficiencies to that for protons, and concentrations of these cationic species are higher in MFCs than the proton concentration, resulting in the accumulation of these cations in the cathode chamber. This causes an increase in pH value in the cathode chamber and a decrease in MFC performance [6,7]. Different strategies have been proposed to avoid the problem of the opposite pH change in the cell compartments. Thus, the use of pH-static control [6] or of membrane-free configurations

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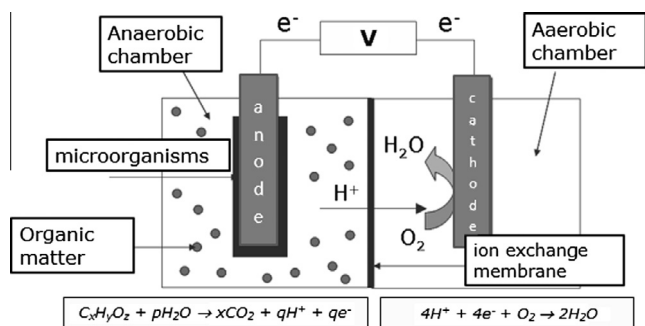


Fig. 1. General outline of the operation of a MFC.

[8,9] has been suggested with the consequently problem of the oxygen crossover. As an alternative strategy, the use of different membrane materials such as cation exchange membranes (CEM), anion exchange membranes (AEM), bipolar membranes (BPM), and ultracentrifugation membranes (UCM) [10–13].

The use of membranes based on ionic liquids could open up this field of improvement in MFCs. Ionic liquids (ILs) are organic salts remaining as liquids near room temperature. They consist of an organic cation such as imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, and a polyatomic inorganic anion or organic anion such as tetrafluoroborate, hexafluorophosphate, chloride, trifluoromethylsulfonate, bis((trifluoromethyl)sulfonyl)imide) [14]. The structures of common cations and anions of ILs are shown in Fig. 2.

The main advantage of these media are their near-zero vapour pressure and their good chemical and thermal stabilities, having a large temperature range where they are stable with a negligible vapor pressure. Additionally, the properties of ionic liquids (hydrophobicity, viscosity, solubility, etc.) can be varied by altering the substitutive group on the cation or the combined anion [14,15] to make them more widely applicable in many physical and chemical fields making ILs a task-specific material [16]. Indeed, ionic liquids have been used in replacement of volatile organic solvents in a wide variety of chemical processes at laboratory scale, such as separation and purification [17–24], reaction media in biochemical [25–28] and chemical catalysis [29–32]. Other interesting properties of ILs in the context of proton exchange membranes are their

high ion conductivity [33], specifically their proton conductivity [34] and high solvent power [35].

Ionic liquids could be immobilized as membranes [36]. Among membranes based on ionic liquids supported liquid membranes (SILMs), porous supports whose pores are impregnated with a solvent, have been showing tremendous potential in different applications such as separation of organic compounds [37] and metal ions [24]. The use of ILs as liquids phase instead organic solvents in SLM resulted in the stabilization of the liquid membrane [38–41]. However instable supported ionic liquid membranes were found when polar solvent like water were used as contacting phases [41]. In order to obtain membranes stable in a universal and polar solvent, as water, and thereby extend the industrial applications to processes that mainly occurs in aqueous media, casting methods could be used to prepare polymeric inclusion membranes based on ionic liquids (PILIMs). PILIMs are obtaining by mixing the relatively inert polymeric supports with ionic liquids. Recently, it has been demonstrated the higher stability of PILIMs compared with SILMS against high polar medium [42] and PILIMs have been applied to different fields such us separation of organic compounds [43], metal ions [44] and in ions selective electrodes [45].

In this work we evaluate for the first time the potential use of polymer ionic liquids inclusion membranes as proton exchange membranes in a single-chamber MFC with cathodes of platinum sprayed on carbon cloth working with a 1 kΩ external resistor. Polymer inclusion membranes were prepared by casting methods using polyvinyl chloride (PVC) and ionic liquids. Nafion® membrane where used as a reference proton exchange membrane. The effect of the ionic liquid on the power generation and water deperation was analyzed.

2. Experimental

2.1. Fuel and chemicals

Substrate used as an energy source for the experiments was wastewater after the lamellar settler of the local Wastewater Treatment Plant. Water was characterized with a soluble chemical oxygen demand (COD) of 430 mg/L. For each experiment, soluble COD content was adjusted to the desired starting level by mixing

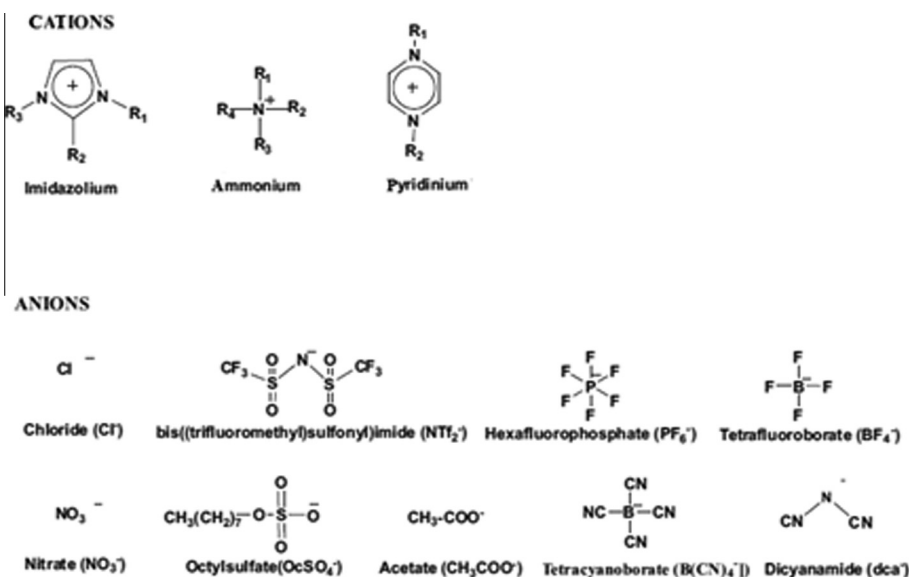


Fig. 2. Examples of ions involve in ionic liquids.

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