Synthesis and characterization of new benzimidazole phosphonates for hybrid materials for fuel cell application

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Abstract
Fuel cells are electrochemical devices that convert the chemical energy stored in a fuel, directly and efficiently into electrical energy and are a promising and clean alternative to traditional energy fuels [1]. The proton-exchange membrane fuel cells (PEMFCs) are considered a promising type of electrochemical device for power generation. The proton exchange membrane (PEM) is a key part for the operation of PEMFC. Usually, the proton exchange membranes are made of organic polymers containing acidic functionalities (ex. Nafion®), but the proton transport properties of these membranes strongly depend on their water content and, consequently, limit their operation temperatures up to 90°C. These limitations have fostered the interest in research and development of new alternative membranes [1].

Phosphonic acids are considered to be promising proton carriers due to their good proton donating and accepting properties, furthermore they present better thermal stabilities than sulfonic acids [2]. This work reports on the synthesis and characterization of a series of mono-, bis- and trisbenzimidazole phosphonates derivatives, prepared from the new diaminebenzene diphasphonate, by cyclization with differents reagents. These benzimidazole phosphonates derivatives were prepared by a new strategy which involves nickel-catalyzed Arbuzov reaction of 4,7-dibromo-2,1,3-benzothiadiazole with triethyl phosphite, followed by reductive sulfur extrusion to afford the new diaminebenzene diphasphonate [3], followed by cyclization with different reagents, such as acyl chlorides or orthoformate derivatives. The synthesized compounds have different spacers with different lengths between benzimidazole rings (Fig. 1). All compounds have been fully characterized by \(^1\)H, \(^{31}\)P and \(^{13}\)C NMR, IR spectroscopy and mass spectrometry (low and high resolution).

![Chemical structure of bisbenzimidazole derivatives.](image)

The influence of different spacers with different length in the properties of benzimidazole rings with phosphonate groups is discussed. Evaluation of their molecular packing structures and effective proton transfer is also sought.

Keywords: PEMFC, proton exchange membrane, benzimidazole, phosphonate, spacer

Acknowledgements
To FCT and FEDER (QREN-COMPETE) for provision of funding (PTDC/CTM-CER/109843/2009).

References