Advances in Hydrogen Energy Technologies: Key to Sustainable Energy Markets

5th International Seminar
November 29-30, 2012, Taguspark - Portugal

Synthesis and Characterization of New Azaheterocyclic Aromatic Phosphonates for Hybrid Materials for Fuel Cell Applications

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Abstract

This work reports the synthesis and characterization of new azaheterocyclic aromatic phosphonates derivated from benzimidazole and benzotriazole by nickel-catalyzed Arbuzov reaction of 4,7-dibromo-2,1,3-benzothiadiazole with triethyl phosphite, followed by reductive sulfur extrusion reaction and cyclization. The compounds were characterized by NMR and mass spectrometry (low and high resolution). These azoles will be incorporated into proton conductive inorganic-organic hybrid membranes of mesoporous silica to produce novel membranes materials with high proton conductivity for intermediate temperature PEMFCs.

Keywords: *PEMFC, PEM, benzimidazole, benzotriazole, phosphonylation*

1 Introduction

The development of cleaner and sustainable sources of energy is one of the major challenges of the 21st century. Alternative energy systems are crucial in order to deal with environmental threat of global warming and the declining reserves of fossil. Fuel cells are electrochemical devices that convert the chemical energy stored in a fuel directly into electrical energy. Fuel cells can provide electrical energy with high efficiency and low environmental impact. Their performance depends crucially on the properties of component materials [1-6].

Among the various kinds of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) are considered promising power sources, due to their high power density and high power-to-weight ratio. A key material for the operation of PEMFC is the proton-exchange membrane (PEM). Usually, these 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 90ºC. These limitations have fostered the interest in research and development of new alternative membranes for the operation of fuel cells at temperature above 100ºC which increases its performance due to faster electrode reaction without CO poisoning of the Pt electro-catalyst, easier heating, water management and high energy efficiency [1-6].

New alternative membranes include polybenzimidazole (PBI)-doped, composites of Nafion and metal oxides, sulfonated polymers based on aromatic hydrocarbons, and organosiloxane-based on inorganic-organic hybrids with various acidic species [1-6].

Recently we have reported the synthesis of several new precursors 4,7-dibromobenzoazoles substituted at N-1 or N-2 position with phosphonate-, hydroxybisphosphonate- and aminobisphosphonate to be precursors of mesoporous silica host to produce novel membranes materials with high proton conductivity for intermediate temperature PEMFCs [7]. Phosphonic acids are considered to be promising proton carriers because of their good proton donating and accepting properties. In addition to their high proton conductivities, phosphonic acids have better thermal stabilities than sulfonic acids [8]. To modify the properties of the hybrid membranes, herein we report the preparation of new azaheterocyclic aromatic phosphonates of the general formula $(EtO)_2(O)P\text{-}R\text{-}P(O)(OEt)_2$, where R is a benzimidazole or benzotriazole.