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Alternatives toward proton conductive anhydrous membranes for fuel cells: Heterocyclic protogenic solvents comprising polymer electrolytes

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ABSTRACT

Fuel cells are gaining increasing attention as a clean and promising technology for energy conversion. One of the key benefits of fuel cells compared to other methods is the direct energy conversion that enables the achievement of high efficiency. The electrolyte membrane is the most essential parts of a fuel cell unit, and consequently has been the subject of considerable research and development. Among the various types of proton conducting electrolytes examined for fuel cell applications, polymer electrolyte membranes (PEMs) are regarded as viable candidates since they enable operation of the cells at desirably low temperatures. This review describes recent progress in the design and development of high performance proton conducting PEMs, including the analysis of the design requirements and strategies for development of advanced PEMs for operation in anhydrous conditions. Some of the most widely used types of azole heterocycles are introduced and compared, particularly in terms of their performance characteristics in polyacids containing different functional groups. In addition, the latest research studies and progress in the field of azole-containing and azole-functionalized electrolyte systems are discussed and reviewed.

Contents

Abbreviations: PEMFCs, polymer electrolyte membrane fuel cells; PEMs, polymer electrolyte membranes; MEAs, membrane electrode assemblies; RH, relative humidity; PBI, polybenzimidazole; Im, imidazole; MeIm, 1-methylimidazole; BnIm, benzimidazole; Py, pyrazole; Tri, triazole; ATri, 3-amino-1,2,4-triazole; Tet, tetrazole; ATet, 5-aminotetrazole; FTIR, Foruer Transform Infrared Radiation; TGA, Thermogravimetric Analysis; DSC, Differential Scanning Calorimeter; AA, adipic acid; PAA, polyacrylic acid; AL, alginic acid; PVPA, poly(vinyl phosphonic acid); MDP, monododecyl phosphate; PEGMAP, poly(ethyleneglycol methacrylate phosphate); VTF, Vogel–Tamman–Fulcher; WLF, Williams-Landel-Ferry; PSSA, poly(styrene sulfonic acid); sPSU, sulfonatedpolysulfone; PAMPSA, poly(2-acrylamido-2-methyl-1-propane sulfonic acid); P4VI, poly(4-vinylimidazole); PVT, polyvinyltetrazole; PVTri, polyvinyl triazole; TA, trifilic acid; PTSA, p-toluenesulfonic acid; PEGMEA, poly(ethylene glycol)methyl ether acrylate; PEO, poly(ethylene oxide); MeSOH, methane sulfonic acid; TFA, trifluoroacetic acid; AcOH, acetic acid; TEOS, tetraethoxysilane; PGMA, polyglycidyl methacrylate.

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1. Introduction

Fuel cell systems are regarded as key components for exploitation of the energy stored in hydrogen molecules. In principle, fuel cells offer a number of key advantages over conventional energy conversion devices, including: high energy conversion efficiency (due to direct conversion of chemical energy into electricity), low emissions and noise, flexibility in fuel selection, cogeneration capability, economy of scale, and, last but not the least, low maintenance requirements. These attractive features have led to numerous initiatives toward the realization of fuel cell technology for practical applications. Despite the progress and achievements made over the past years, fuel cell technology suffers from critical aspects that have hampered its widespread acceptance. Further research and development is required in order to overcome the obstacles, and enhance the economic viability and operational reliability of fuel cell systems.

Fuel cells come in a number of types and designs; typically characterized by their electrolyte, which can be made from a polymer membrane, alkaline, phosphoric acid, solid oxide, or other materials. The most important design features in a typical fuel cell system are:

- The fuel, which may be an alcohol, hydrocarbon or its derivatives;
- The electrolyte substance, which is tightly related to the fuel type;
- The anode and cathode catalysts, with the former used to obtain electrons and ions from the fuel while the latter is used to convert the ions into waste chemicals like water.

It can be found that the majority of fuel cells operate based on the proton conductivity mechanism, in which H^+ acts as the mobile ion supplied through the oxidation of hydrogen at the anode catalyst.

Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attention, particularly as promising candidates for variety of power generation applications [1]. This is largely attributed to several advantageous features, such as high energy density (especially compared to that of battery systems) and high conversion efficiencies, up to 60%. In addition, PEMFCs are more environmentally friendly than alternatives, operating with hydrogen as a clean fuel, with essentially no discharge of pollutants. These benefits have created many opportunities for further development, aiming to improve the overall efficiency of PEMFCs. PEMs are also attractive for their use in solid state electrochromic devices. In such devices, PEMs are required to be dry, transparent and compatible with the electrodes [1].

The potential use of PEMFCs is often limited by the poisoning effect caused by traces of carbon monoxide in the fuel. It is found that the presence of even minimal levels of carbon monoxide can dramatically affect the performance and longevity of the anode catalyst. Savinell et al. [2] demonstrated that fuel cell operation at elevated temperatures can improve the tolerance of anode catalysts with respect to fuel impurities. Therefore, suitable candidates as high performance PEMs not only require outstanding thermal and mechanical stability, but also require other important characteristics, such as film forming potential, high ionic conductivity and low gas permeability. These factors contribute effectively to the overall costs associated with both capital and operational expenditures of a fuel cell unit. In this respect, various technological developments are in progress to address the immediate challenges, such as:

- The development of high performance membrane materials,
- Selection of more effective electrode materials,
- Improvements in the design characteristics and operational longevity of the membrane electrode assemblies (MEAs), and
- Enhancement of the performance of hydrogen storage materials.

For instance, the conversion efficiency in MEA maybe altered by changing the type and thickness of both membranes and gas diffusion materials, the nature of the binder used in the electrodes and the binder to catalyst ratio. Research on new and improved fuel cell electrodes and