吡啶接枝的磺化聚芳醚酮砜质子交换膜的制备与性能研究

Preparation and Properties of Pyridine-grafted Sulfonated Poly(aryl ether ketone) Proton Exchange Membranes

摘　要

质子交换膜作为质子交换膜燃料电池的核心部件，兼备传递质子与阻隔燃料和氧化剂的作用，其性能的好坏直接影响着质子交换膜燃料电池的使用情况。目前，使用最普遍的质子交换膜是已经商业化的杜邦公司生产的 Nafion 全氟磺酸膜，该膜本身具有优秀的正电子传导率、化学稳定性以及机械功能，从而备受青睐。但是昂贵的成本，较高是的甲醇渗透性阻碍了 Nafion 膜的进一步发展应用，故而人们把寻找能够替代 Nafion 膜的聚合物材料作为主要研究方向。

磺化聚芳醚酮砜是一种性能优异的工程材料，其出色的耐热性、耐腐蚀性和低廉的价格，使其被认为是 Nafion 最有潜力的替代品。然而传统的质子交换膜当温度高于 80℃时，体系内水份快速流失，质子载体的减少直接影响膜的质子传导率。并且质子的传递与甲醇的渗透途径相同，所以质子传导率较高时常伴随着甲醇渗透系数过高的问题。研究者们想要建立一条不依靠水的质子传输通道，希望通过这种手段打破质子传导率和甲醇渗透率之间的限制，并且摆脱质子传递对水的依赖。

本文首先制备出了含有羧基基团的磺化聚芳醚酮砜聚合物，然后通过接枝的手段将 4-氨基吡啶固定到聚合物链上，希望接枝后的紧密结构能够有效地降低甲醇的渗透，同时利用氮杂环兼备的质子导体与受体的特性，构建一条只能传递质子的新的质子传输途径。通过测试发现随着吡啶接枝量的增加，25℃时膜的甲醇渗透系数由 8.17×10-7cm^2s^{-1} 显著降低到 8.92×$10^{-8}cm^2s^{-1}$。膜的质子传导率和相对选择性与接枝吡啶含量呈正相关。其中，SPP-4 膜在 100℃时质子电导率最高。

关键词：质子交换膜　磺化聚芳醚酮砜　接枝　4-氨基吡啶

Abstract

Proton exchange membrane is the core component of proton exchange membrane fuel cell. It has the function of transmitting protons and blocking fuel and oxidant. Its performance directly affects the application of proton exchange membrane fuel cells. At present, the most widely used proton exchange membrane is the commercial Nafion perfluorosulfonic acid membrane produced by DuPont, which is highly favored for its excellent proton conductivity, chemical stability and mechanical properties. However, the high cost and high methanol permeability hinder the further development and application of the Nafion membrane. Therefore, the search for a polymer material capable of replacing the Nafion membrane has been the main research direction.

Sulfonated poly(arylene ether ketone sulfone)s is an excellent engineering material with excellent thermal stability, chemical stability and low price, making it the most potential alternative to Nafion. However, when the temperature of the proton exchange membrane is higher than 80℃ the water in the system is quickly lost, and the decrease of the proton carrier directly affects the proton conductivity of the membrane. And the proton transfer is the same as the methanol permeation route, so the high proton conductivity is often accompanied by the problem of high methanol permeability coefficient. Researchers want to create a proton transport channel that does not rely on water, hoping to break the limits between proton conductivity and methanol permeability and get rid of the dependence of protons on water.

Firstly, a sulfonated polyarylether ketone sulfone polymer containing a carboxyl group was prepared, and then 4-aminopyridine was immobilized on the polymer chain by grafting. It is hoped that the dense structure after grafting can effectively reduce methanol. The infiltration, while utilizing the properties of proton conductors and acceptors with nitrogen heterocycles, constructs a new proton transport pathway that only transmits protons. It was found by experiments that the methanol permeability coefficient of the membrane decreased significantly from $8.17\times10^{-7}cm^2s^{-1}$ to $8.92\times10^{-8}cm^2s^{-1}$ at 25 ℃ as the amount of pyridine grafting increased. The proton conductivity and relative selectivity of the membrane were positively correlated with the grafted pyridine content. Among them, the SPP-4 membrane had the highest proton conductivity at 100℃,which was 0.088 Scm^{-1}.

Key words: proton exchange membrane sulfonated poly(arylene ether ketone sulfone)s grafted 4-aminopyridine