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燃料电池用聚芳醚砜阴离子交换膜的制备  
及性能研究

Preparation and Characterization of Anion Exchange  
Membranes based on Poly(arylene ether sulfone) for Fuel  
Cells

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## 摘要

质子交换膜燃料电池(PEMFCs)由于具有高能量密度、高能量转换效率、环境友好和便携等优点,因此被认为是本世纪最具前景的能量转换装置之一。质子交换膜(PEM)作为 PEMFCs 的关键组件,受到众多研究者的关注。然而,PEM 的高燃料渗透性和 PEMFCs 对 Pt 基催化剂的依赖性阻碍了其商业化进程。阴离子交换膜(AEM)与 PEM 相比,传导的离子是氢氧根离子而非质子。因此,AEM 燃料电池是在碱性环境下工作,电极反应活性更高;另外,氢氧根离子和燃料的传递方向相反可以限制电拖曳,降低燃料渗透性。所以,阴离子交换膜燃料电池(AEMFCs)在降低燃料渗透性和催化剂依赖性这两点上具有 PEMFCs 无可比拟的优越性。但是,目前的 AEM 仍存在电导率低和耐碱性差的缺点,因此,制备具有良好电导率和耐碱性的 AEM 就显得十分必要。本文以聚醚砜为主体材料,设计合成了交联型和侧链型 AEM,并进一步探究膜材料的分子结构与膜性能之间的关系。

首先,合成含叔胺的聚芳醚砜(PES-DA)和溴化聚芳醚砜(BPES),然后在 $-40^{\circ}\text{C}$ 下混合均匀后在室温下铸膜,再用浸泡法进行咪唑功能化反应。成膜过程中 BPES 的苜溴基团和 PES-DA 的叔胺基团发生季铵化反应实现交联,避免了小分子交联剂的使用和功能基团的消耗。所制备的膜在  $80^{\circ}\text{C}$  下最高可达  $82.4\text{ mS cm}^{-1}$ ,另外,由于交联网络的形成,该系列膜具有极低的溶胀。氢氧燃料电池测试可得到  $0.82\text{ V}$  的开路电压和  $92.1\text{ mW}\cdot\text{cm}^{-2}$  的最大功率密度。

另外,通过将含溴咪唑离子液体接枝到含羟基的聚醚砜主链上得到侧链型聚醚砜 AEM,柔性长侧链的引入有利于离子簇的聚集从而形成亲疏水微相分离和纳米离子通道,使所制备的侧链型膜具有极高的电导效率。该系列膜的质量 IEC 在  $1.01\text{--}1.90\text{ meq g}^{-1}$  范围内,同时,在  $30^{\circ}\text{C}$  和  $80^{\circ}\text{C}$  下,膜的电导率分别为  $22.13\text{--}59.19\text{ mS cm}^{-1}$  和  $51.66\text{--}108.53\text{ mS cm}^{-1}$ 。该侧链膜也显示出良好的耐碱性和单电池性能。该工作展示了一种温和且具有普适性的 AEM 合成路线。

**关键词:** 燃料电池; 阴离子交换膜; 聚芳醚砜

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## Abstract

Proton exchange membrane fuel cells (PEMFCs) have become one of the most promising energy-conversion devices due to their high power density, high energy conversion efficiency, environmental friendliness and ease of fuel supplement. Proton exchange membranes (PEMs), the key components for PEMFCs, have been extensively studied. However, the widespread commercialization of PEMFCs is impeded by the high fuel permeability of PEM and exclusive dependence on expensive Pt-based catalysts. Anion exchange membranes (AEMs) based fuel cells, in which the charge carriers are hydroxide ions rather than protons, have received a significant interest due to their potential for surpassing those limitations. AEMFCs operate under alkaline conditions, in which the electrode reaction kinetics will be enhanced and the catalysts are not subjected to corrosion. Furthermore, the fuel and water crossover via electro-osmotic drag may also be depressed because the transport of hydroxide ions and fuel are in the opposite directions. But nowadays, AEMs have two major problems: low conductivity and low alkaline stability. Hence, it is essential to fabricate AEMs with high conductivity and good alkaline stability. Here, we designed and synthesized two kinds of AEM (crosslinked-type and side-chain-type), and investigated the structure-property relationship of the membrane.

First of all, a series of anion exchange membranes with high ionic-conductivity and low swelling ratio was prepared from imidazolium-functionalized crosslinked cardo poly(arylene ether sulfone)s for AEMFCs. Two oligomers, tertiary amine-containing poly(arylene ether sulfone) (PES-DA) and bromomethyl-containing poly(arylene ether sulfone) (BPES), are synthesized and then mixed at  $-40\text{ }^{\circ}\text{C}$ . They are spontaneously inter-crosslinked at room temperature to form dense anion exchange membranes (AEMs), in which the quaternary ammonium groups of PES-DA rapidly react with the bromomethyl groups of BPES to form the crosslinked bonds. This avoids the use of crosslinking agents and the expense of functional groups. The resulting membranes show a high hydroxide conductivity up to  $82.4\text{ mS cm}^{-1}$  at  $80\text{ }^{\circ}\text{C}$  and a slight swelling low to traditional AEMs due to its crosslinked network

structure. An open circuit voltage (OCV) of 0.82 V and a maximum power density of 92.1 mW·cm<sup>-2</sup> are achieved in a H<sub>2</sub>/O<sub>2</sub> single cell.

Furthermore, a series of poly(arylene ether sulfone)s containing flexible pendant imidazolium cation was synthesized by grafting bromine-bearing imidazolium-based ionic liquids into hydroxyl-bearing poly(ether sulfone) matrix. The incorporation of the flexible side-chain imidazolium groups is beneficial to the aggregation of the ionic clusters leading to the formation of hydrophilic/hydrophobic phase-separated morphology and nano-channels. As a result, an enhancement in the ion conductivity can be achieved. Therefore, the as-prepared AEMs possess higher ion conductivity than traditional benzyl-type AEMs. The weight-based ionic exchange capacity (IEC<sub>w</sub>) of the membranes was in the range of 1.01–1.90 meq g<sup>-1</sup>. Correspondingly, their ion conductivity was in the range of 22.13–59.19 and 51.66–108.53 mS cm<sup>-1</sup> at 30 and 80 °C, respectively. Moreover, the membranes also exhibit good alkaline stability and an interesting single cell performance. This work presents a facile and universal route for the synthesis of AEMs with superior performance.

**Key words:** Fuel Cells; Anion Exchange Membranes; Poly(arylene ether sulfone).

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