




新型燃料电池用质子交换膜的 合成和性能研究



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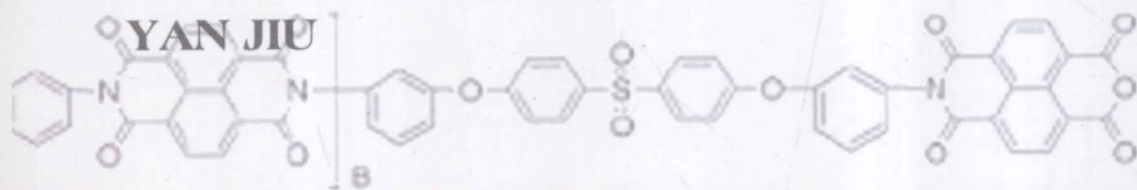
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中文摘要

聚合物电解质膜燃料电池 (PEMFC) 是正在迅猛发展的工作温度最低、比能最高、启动最快、寿命最长和应用范围最广的第五代燃料电池, 在海、陆、空各领域均具有极其重要和广泛的应用前景。质子交换膜是聚合物电解质膜燃料电池 (PEMFC) 的“心脏”。它不同于一般化学电源中的隔膜, 因为它不但起着隔离燃料和氧化剂, 防止它们直接发生反应的作用, 更起着电解质的作用。大多数质子交换膜是由高分子母体和离子交换基团构成, 目前的商售产品还只有 Nafion 系列全氟磺酸膜, 但其价格奇高, 在高温条件下质子传导率低, 阻醇性能差导致电池效率降低。鉴于此, 寻找能够替代 Nafion 等全氟磺酸膜的替代材料成为近年来质子交换膜研究的热点。磺化聚酰亚胺具有极高的耐热性, 高机械强度及模量, 优异的电性能、化学稳定性及很好的成膜性, 是有希望替代 Nafion 等全氟磺酸膜作为质子交换膜的材料之一。另外, 无机-有机复合质子交换膜由于兼具有机膜和无机膜的优点, 已经成为质子交换膜研究的新方向。无机粒子具有很好的亲水性, 它们可以增加聚合物膜对水分子的约束力, 增强水合作用, 确保在高温条件下质子交换膜内仍保持一定的湿度, 从而达到在高温时提高质子传导速率的目的。本书在第二、三、四章利用分子设计制备通过亲核取代路线合成不同磺化度的含醚酮结构的磺化萘型聚酰亚胺, 并制备了 SPEEK/纳米二氧化钛新型有机无机复合质子交换膜材料, 考察了两个系列质子交换膜的性能。

首先, 以发烟硫酸作为磺化试剂, 通过亲电取代反应在二氟二

苯酮引入磺酸钠基团，成功合成磺化二氟二苯酮单体。从萘-1-4-5-8-二酐 (NTDA) 和对氨基苯酚出发，合成了含有酰亚胺环的双酚单体。利用典型的亲核取代缩聚反应，合成了不同磺化度的含有醚酮结构的磺化聚酰亚胺。对聚合物的结构进行表征证实利用亲核取代反应制备磺化聚酰亚胺是切实可行的。

聚合物具有良好的成膜性，说明得到了较高分子量的磺化聚酰亚胺。所得聚合物具有较高的热分解温度 ($T_{10\%} > 400^\circ\text{C}$) 和玻璃化转变温度 ($T_g > 200^\circ\text{C}$)，完全能满足质子交换膜的热稳定性要求；所得聚合物可溶于 m-cresol, NMP 溶剂中，保证了聚合物成膜；SPEK-PI 系列聚合物的拉伸强度、拉伸膜量等力学性能数据说明了所合成的聚合物膜能够达到质子交换膜燃料电池的使用要求；聚合物膜具有良好的质子传导性能，磺化度为 1.0 的 SPEK-PI 膜的质子传导率与 Nafion 膜的质子传导率相差不大；所合成的聚合物膜的阻醇性能优于 Nafion 膜。以上性能测试的结果表明我们制备的聚合物膜将会具有很好的应用前景。

无机-有机复合质子交换膜由于兼具有机膜和无机膜的优点，成为质子交换膜研究的新方向。无机粒子具有很好的亲水性，它们可以增加聚合物膜对水分子的约束力，增强水合作用，确保在高温条件下质子交换膜内仍保持一定的湿度，从而达到在高温时提高质子传导速率的目的。

首先在目前众多的成膜材料中，以成膜性好、吸水率高、具有较好的导质子能力为目标筛选出合适的聚合物材料作为成膜基质。由于四甲基型磺化聚醚醚酮 (SPEEK) 膜是众多磺化聚醚醚酮中综合性能较为优异的一类聚合物，具有高热氧化稳定性和良好的机械性，同时具有较高的质子传导率，SPEEK 膜的阻醇性能要优越于 Nafion 膜，所以本文选取了成本较低的本课题组合成的四甲基型磺化聚醚醚酮 (SPEEK) 作为聚合物基质，无机纳米粒子本文也选择了合成工艺已经很成熟的纳米二氧化钛。

通过对不同磺化度、不同无机含量的磺化聚醚醚酮 (SPEEK) / 纳米二氧化钛 (TiO_2) 复合膜的红外表征、扫描电镜测试、透射电镜测试, 说明得到了粒径为几十纳米分散均匀的 SPEEK/ TiO_2 复合膜。复合膜具有良好的热性能、机械性能, 可以满足质子交换膜的使用要求。由于纳米二氧化钛具有大的比表面积、高的表面能, 使得在相同磺化度条件下复合膜的吸水率随膜中无机粒子含量的增加而升高。通过对膜的水扩散系数的考察, 发现 SPEEK/ TiO_2 复合膜的保水能力要明显优于纯的磺化聚醚醚酮膜。这是由于复合膜内含有大量氢键抑制了水的运动, 从而降低其扩散速度; 也可以解释为: 粒径较小的纳米粒子填充到质子交换膜的微观孔洞中, 减小了水扩散界面的曲率半径, 导致饱和蒸汽压升高, 限制了水的蒸发。

对复合膜的甲醇渗透性能进行了研究, 发现由于纳米粒子填充到复合膜的微观孔道, 使膜结构更加致密, 从而阻碍了甲醇分子自由运动, 导致复合膜的甲醇渗透率明显降低。相同磺化度的复合膜, 在相同温度下, 随着纳米二氧化钛含量的增加, 膜的质子传导率呈现了先上升后下降的趋势, 这是由于纳米粒子的加入一方面提高了膜的吸水率和保水能力, 另一方面堵塞了水合质子自由传输的孔道, 当前者占优势时则表现为质子传导率的升高, 而当后者的影响占优势时, 则导致质子传导率的降低。

采用直接缩聚的方法可以合成不同结构和磺化度的新型系列磺化聚芳醚酮和磺化聚芳醚砜等质子交换膜材料, 研究表明它们在 PEMFC, 不过这类材料仍存在着以下缺点: ①对于低磺化度的磺化聚芳醚酮, 虽然其表现出良好的机械性能和阻醇性能, 但其质子传导率太低, 影响了其应用; ②高磺化度的磺化聚芳醚酮质子传导率较高, 但由于吸水率很高, 导致膜的机械性能不好, 阻醇性差等缺点。针对以上问题提出了解决方法: 从序列结构和微观形态入手, 合成嵌段型磺化聚芳醚酮。

在本书的第五章，采用“一锅两步法”，以不同嵌段长度的氟封端的聚芳醚酮齐聚物与生成亲水嵌段的磺化二氟二苯酮和四甲基联苯二酚共聚，合成了不同磺化度和不同嵌段长度的嵌段 SPAEK 共聚物。通过红外和核磁共振谱证实我们所得聚合物的结构。反应得到的嵌段 SPAEK 共聚物都具有良好的溶解性和热稳定性，都能够以溶液铺膜的方式形成韧性比较好的透明膜。

在本书的第六章，利用 TEM 和 SAXS 对磺化聚芳醚酮嵌段共聚物的微观形态进行了研究。TEM 测试可以观察到无规磺化聚芳醚酮聚合物他们能够形成具有相对统一尺寸的球状的离子簇，尺寸一般在 5~15nm 之间，并且随着磺化度的增大而增大。而嵌段聚合物与无规聚合物完全不同。既有一定数量的尺寸比较大的离子簇 (>15nm) 存在，又有大量的尺寸在 5nm 以下的离子簇存在，并且存在着一些颜色较深的类似云带一样的尺寸很宽的离子区域。这一点在其 SAXS 的研究中也能得到证实，即由足够多的尺寸小的离子簇构成了较宽的离子区域。嵌段共聚物在 SAXS 曲线中出现了明显的规则的散射峰，这是由明显的相分离引起的。我们接着对嵌段 SPAEK 膜的性能进行了研究。相同 IEC 下，嵌段共聚物膜的质子传导率高于无规聚合物。另一方面，嵌段 SPAEK 膜的质子传导率随着离子含量和嵌段长度的增加而增大。从而建立起了嵌段 SPAEK 膜的形貌、结构和性能之间的关系。

SYNTHESIS AND STUDY OF PROPERTIES OF NOVEL PROTON EXCHANGE MEMBRANE FOR FUEL CELLE

ABSTRACT

The polymer electrolyte membrane fuel cell (PEMFC) is the rapidly developing fifth-generation fuel cell. With the lowest working temperature, the highest specific energy, the fastest startup, the longest service life, and the widest applications, PEMFC has very important applications and good prospects in the fields of the sea, the land and the air. The proton-exchange membrane is the core component of PEMFC. It differs from the membranes used in chemical cells in that it not only acts as an insulator between the fuel and the oxidant, but also works as an electrolyte. Most proton-exchange membranes consist of a polymer matrix and ion-exchange groups. At present, the only available commercial products of proton-exchange membrane are the Nafion series of perfluorosulfonic acid membranes from Dupont. Although Nafion has good chemical and physical properties for use in fuel cell fields. It has three major

draw backs, including low conductivity at low humidity or high temperature, as well as high methanol permeability. Unreacted methanol at the anode can diffuse through the membrane and react at the cathode, lowering the voltage efficiency of the cell and reducing the system's fuel efficiency. The drawbacks limited application in the direct methanol polymer Electrolyte membrane fuel cells. Besides, the perfluorinated membranes are very expensive, which is also regarded as a limiting factor. Thus new polymer electrolyte membranes for fuel cell are being explored. Synthesis and study of properties of novel proton exchange membrane for fuel cells.

Sulfonated polyimide is a promising candidate of Nafion for proton-exchange membranes due to its outstanding thermal and chemical stability, high mechanical and electrical property as well as good film-forming capability. Additionally, the organic-inorganic composite proton exchange membranes have received a great deal of attention because they possess the excellence of organic and inorganic membranes. The incorporation of inorganic components in polymer electrolyte materials improves the water uptake and water retention, which caused the high proton conductivity of membranes at high temperature. Meanwhile, the introduction of inorganic particles also reduces the methanol permeability.

In this thesis, a series of sulfonated polyimides were synthesized by condensation of bis (p-hydroxyphenyl) -1,4,5,8-

naphthalenetetracarboxylic di-imide with various ratios of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone to 4,4'-dichlorodiphenyl-sulfone and were prepared for proton exchange membranes. At the same time, the SPEEK/TiO₂ hybrid membranes with various contents of TiO₂ were prepared through sol-gel reactions. Both of them were evaluated for proton exchange membrane fuel cell application. The sodium 5,5-carboxylbis (2-fluorobenzene-sulfonate) was synthesized by dissolving 4,4-difluorobenzophenone in 30% fuming sulfuric acid through electron-withdrawing substitute reaction. The bisphenol monomer containing the imide ring was synthesized by NTDA and p-aminophenol. In addition, a series of sulfonated polyimides containing ether ketone structure were synthesized successfully by typical nucleophilic substitution reactions. The results of characters proved that sulfonated polyimides can be synthesized by nucleophilic substitution reactions.

The resulting polymers showed good film-forming capability, which indicated high molecular weight of sulfonated polyimides. Besides, the polymers possessed high thermal decomposition temperature ($T_{10\%} > 400^{\circ}\text{C}$) and T_g ($T_g > 200^{\circ}\text{C}$). The polymers had good solubility and easily dissolved in m-cresol and NMP. The data of tensile modulus and tensile strength of SPEK-PI membranes indicated that they were suitable as membrane materials for proton exchange membranes. SPEEK-PI membranes showed favorable proton conductivity and the proton

conductivity of membrane with $DS = 1$ was close to that of Nafion. All the membranes showed lower methanol permeabilities compared with Nafion117. Consequently, the proton exchange membranes were promising for PEMFC applications.

In this thesis, the SPEEKs containing tetramethyl were selected as matrix owing to their good mechanical properties, low methanol permeability, high thermo-oxidative stability and proton conductivity. At the same time, nanosized TiO_2 was selected as additive due to its classical procedure of synthesise.

A series of SPEEK/ TiO_2 composite membranes with various DS and contents of TiO_2 were prepared and characterized by FTIR, SEM and TEM. It could be conclude that TiO_2 particles were homogeneously distributed in the membrane. and the diameters of TiO_2 particles were below 100 nm. The composite membranes displayed excellent thermal stability and mechanical properties, which could suit the use of proton exchange membrane.

The water uptake of composite membranes improved with increasing TiO_2 at the same DS owing to large specific surface area and high surface energy. We noticed that SPEEK/ TiO_2 composite membranes showed better water retention than SPEEK membranes. It could be explained that abounding O—H restrained the movement of water in composite membranes, and further reduced water diffusion speed. It was also because that the introducing of nanosized TiO_2 to proton exchange mem-

branes can decrease radius of curvature of water diffuse interphase, further resulted in the enhancement of saturated vapor tension, which restricted the evaporation of water.

We can see that the introduction of nanosized TiO_2 increased the density of membrane and impeded the moving of methanol, which resulted in obvious decrease of methanol permeability. First the proton conductivity of composite membranes increased with enhance content of nanosized TiO_2 , and then they decreased depending on same DS and temperature. It was because that the proton conductivity was influenced by nanosized TiO_2 in two aspects: one is to improve water uptake and water retain; another is to block the channels of protons. The proton conductivity enhanced when the former play a dominant role, whereas, the proton conductivity decreased.

Recently our groups have explored several sulfonated poly (aryl ether)s (SPAEs) for proton exchange membranes usages. Although they show very good potential usages in PEM, there still have several drawbacks to solve. (1) SPAEs with low IEC exhibited good mechanical strength and methanol resistance. However, their low proton conductivity restricts the performance in fuel cell. (2) SPAEs with high IEC exhibited superior proton conductivity. However, the brittleness of the membranes at evaluated temperatures, excessively swelling properties and the relatively high methanol crossover in membranes has limited their usages.

In order to solve these problems and improve selected PEM properties, two methods were proposed in this dissertation: (1) block copolymers; (2) acid-base blend membranes.

In chapter 5, block SPAEK copolymer ionomers were successfully synthesized by a two-stage process. First, the hydrophobic block with controlled length on average was prepared. And then, the monomers with desired stoichiometry were added in order to prepare and control the length of the hydrophilic block. Each block copolymer was then composed of an alternating sequence of several hydrophilic and hydrophobic blocks. Further we have characterized the structures in detail.

In chapter 6, the morphology of block SPAEK membranes was detailed investigated by various measurements, including small angle X-ray scattering (SAXS) and transmission electron microscope (TEM). As observed by TEM, spherical ionic clusters uniformly dispersed through the random SPAEK polymer backbone matrix. The ionic cluster size was in the range of 5 ~ 15nm, which is dependent of the degree of sulfonation. On the other hand, a large number of smaller ionic clusters (< 5nm) and a certain amount of bigger ionic clusters (20 ~ 35nm) appeared for block SPAEK membranes. However, the amount of these silver clusters was less than that of random membranes. Instead, the dark colored ionic domains spreading as a cloud-like belt were also observed. These wide ionic domains were well-connected each other by a mass of bigger and

smaller ionic clusters together with medium size clusters. This observation was also confirmed by the SAXS analysis. The ionomer peaks in SAXS profiles indicated the presence of large ionic domains for most of polymers. The results showed that the block copolymers exhibited larger size of ionic domains or more clearly phase-separated microstructures with the increase of ionic content and hydrophobic sequence length. Further, we have studied the properties of the resulted block SPAEK membranes in detail. Then, the relationship between morphology and proton conductivity of block SPAEK membranes was then established according to experimental data.

目 录

第一章 绪论	1
引言	1
第一节 燃料电池介绍	2
一、简介	2
二、燃料电池发展历程	2
三、燃料电池分类、特点	3
四、燃料电池发展趋势	4
第二节 质子交换膜燃料电池介绍	5
一、质子交换膜燃料电池工作原理	5
二、质子交换膜燃料电池的优缺点	6
三、质子交换膜燃料电池的发展	7
四、质子交换膜燃料电池的应用实例	8
第三节 质子交换膜介绍	11
一、质子交换膜概述	11
二、PEMFC 电池对质子交换膜的技术要求	11
三、全氟磺酸膜	12
四、改进的全氟磺酸型膜	15
五、非全氟化质子交换膜	21

六、非氟质子交换膜	21
七、嵌段聚合物在质子交换膜中的应用	32
八、PEMFC 质子传导机理	48
第四节 研究内容	51
一、含有醚酮结构的磺化聚酰亚胺	51
二、纳米二氧化钛/SPEEK 复合膜	52
三、嵌段型磺化聚芳醚类质子交换膜	52
参考文献	54
第二章 以亲核反应路线制备磺化聚酰亚胺	60
引言	60
第一节 含有醚酮结构的磺化聚酰亚胺的合成及表征	61
一、单体的合成	61
二、含有醚酮结构的磺化聚酰亚胺(SPEK-PI)的合成	66
参考文献	74
第三章 磺化聚酰亚胺质子交换膜性能研究	75
引言	75
第一节 表征技术与试验方法	76
一、力学性能	76
二、离子交换容量	76
三、吸水率	77
四、甲醇渗透性	77
五、膜的电性能测试	78