Sulfonated Polyimides for Polymer Electrolyte Membrane Fuel Cell Application

Jianhua Fang*[1], Xiaoxia Guo[1] and Morton Litt[2]

[1]School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, P.R. China.
Fax: 86-21-54741297, e-mail: jhfang@sjtu.edu.cn

[2]Department of Polymer Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, USA

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention in the past decade because they provide cleaning, quiet and portable power for vehicular transportation and for other applications [1, 2]. The key component of a PEMFC is the polymer electrolyte membrane. At present, sulfonated perfluoropolymers such as DuPont's Nafion are typical membranes that are used in practical systems due to their high proton conductivity, good mechanical properties, and high thermal, electrochemical and chemical stability. However, the high cost, low conductivity at low humidity and/or high temperature, and high methanol crossover are the major drawbacks for these perfluoropolymers. The development of low cost and high performance polymers as alternative materials is strongly desired. Recent researches have demonstrated that six-membered ring sulfonated polyimides are promising membrane materials for PEMFC application [3-9]. In particular, highly sulfonated polyimides derived from the diamines with pendent alkoxy-sulfonic acid groups (side chain-type) showed extremely high water stability and high proton conductivity [6, 7]. In this paper, we report on the preparation of wholly aromatic side chain-type sulfonated polyimides as well as their thermal stability, proton conductivities, water stability, and methanol permeability.

EXPERIMENTAL

Sulfonated polyimides were synthesized by one-step polymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), side chain-type sulfonated diamines 3,3'-bis(4-sulfophenoxy)benzidine (BSPOB) and common nonsulfonated diamine monomers in m-cresol in the presence of triethylamine (Et$_3$N) and benzoic acid at 80 °C for 4 h and 180 °C for 16 h. The resulting highly viscous mixtures were diluted with additional m-cresol and precipitated from acetone. The fiber-like precipitate was filtered off, washed with acetone for a few times, and dried in vacuo. Films were prepared by casting the sulfonated polyimide (in triethylammonium salt form) solutions onto glass plates and dried at 80 °C for 10 h. The as-cast films were soaked in methanol at 60 °C for 6 h. Proton exchange was performed by immersing the films into 1.0 N hydrochloric acid at room temperature for two days. The proton exchanged films were washed with deionized water and then dried in vacuo at 100 °C for 20 h.

RESULTS AND DISCUSSION

High molecular weight BSPOB-based polyimides (Scheme 1) were successfully prepared by conventional one-step polymerization method in m-cresol in the presence of triethylamine (Et$_3$N) and benzoic acid. The resulting polyimides showed extremely high inherent viscosity. NTDA-BSPOB/mBAPPS(9/1), for example, had an inherent viscosity of 8.9 dL/g in DMSO at 35 °C (concentration: 0.5 g/dL). TG-MS measurements revealed that for NTDA-BSPOB/mBAPPS(9/1) the decomposition of sulfonic acid groups started from around 270 °C indicateing fairly high thermal stability of this copolyimide.

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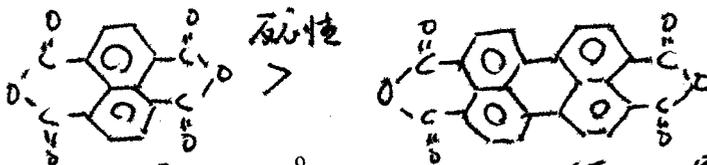
The copolyimide membranes were fabricated by the conventional solution cast method. The as-cast films were in their triethylammonium form and converted to their proton form by soaking the films in 1.0 N hydrochloric acid solution with magnetic stirring for two days. The completion of proton exchange for all the samples was confirmed from their ^{1}HNMR spectra.

Scheme 1
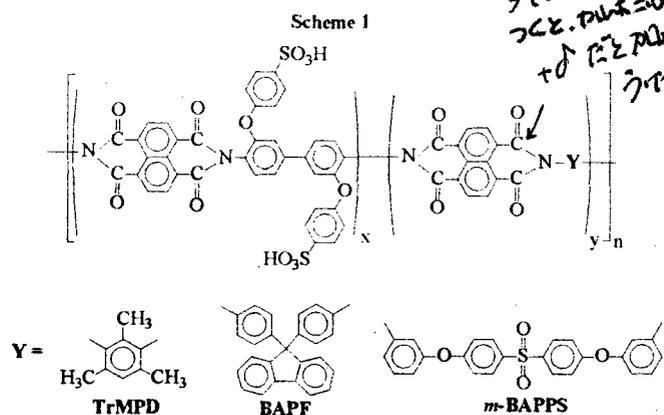
The proton conductivity of BSPOB-based polyimide membranes was investigated. For NTDA-BSPOB/TrMPD(9/1), at high relative humidity (RH > 70%), the membrane showed fairly high conductivities (> 10^{-2} S/cm), whereas at low RH (e.g. 20%), the conductivities are in rather low level (in the order of 10^{-4} S/cm). In the whole humidity range, no significant reduction in proton conductivity decrease as the temperature increased up to 160 °C, which is very favorable for use in medium-temperature (120 – 150 °C) fuel cells. In liquid water, NTDA-BSPOB/mBAPPS(9/1) showed a conductivity of 0.18 S/cm at 25 °C and increased to 0.31 S/cm at 70 °C which is higher than that of Nafion 117.

The water stability test for the sulfonated polyimide membranes was performed by immersing the membranes into deionized water at 80 °C or 100 °C (boiling) and the stability was characterized by the elapsed time when the hydrated membranes lost mechanical properties. Table 1 lists the water uptake, water stability, and dimensional stability of BSPOB-based copolyimide membranes. It can be seen that despite the high ion exchange capacity (IEC: 2.40 meq/g)) NTDA-BSPOB/mBAPPS(9/1) could maintain film form after being soaked in deionized water at 100 °C for more than 3000 h indicating very high water stability. Furthermore, the area change in planar direction of the membrane is less than 7 % at 100 °C which is much smaller than many other sulfonated polymers.

Table 1 Water uptake, water stability, and dimensional changes of sulfonated polyimide membranes at 100 °C.

Polyimide[a]	IEC [meq/g]	Water uptake [g/100g polymer]	Water stability [h]	Dimensional changes [%]		Ref
				ΔL	ΔA	
NTDA-BSPOB/mBAPPS(9/1)	2.40	160	>3000	150	7	e
NTDA-BSPOB/TrMPD(9/1)	2.49	143	600	110	32	e
NTDA-BSPOB/TrMPD(2/1)	2.10	72[b]	>720[b]	22[b]	32[b]	e
NTDA-BAPBDS	2.63	107[b]	1000	16[f]	15[d]	9
NTDA-3,3'-BSPB	2.89	250[c]	700	180[f]	11[d]	6
NTDA-2,2'-BSPB	2.89	222[c]	2500	220[f]	0[d]	6

[a]BAPBDS, 3,3'-BSPB and 2,2'-BSPB refer to 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid, 3,3'-bis(3-sulfopropoxy)benzidine and 2,2'-bis(3-sulfopropoxy)benzidine, respectively.
[b]80 °C;   [c]50 °C;   [d]measured at room temperature.   e: This study.

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燃料电池质子交换膜用磺化聚酰亚胺材料

房建华*[1]，郭晓霞[1]，Morton Litt[2]

[1] 上海交通大学化学化工学院, 上海市, 200240

Fax: 86-21-54741297, e-mail: jhfang@sjtu.edu.cn

[2]Department of Polymer Science and Engineering, Case Western Reserve University, Cleveland, Ohio

44106-7202, USA

引言

聚合物电解质膜燃料电池 (PEMFCs) 由于其能够提供清洁、安静和便携的能源，并在汽车，手机和笔记本电脑等方面有着广泛的应用前景，而在上世纪末开始备受关注[1, 2]。PEMFC 中的关键部件是聚合物电解质膜。目前，磺化全氟聚合物（如：杜邦公司的 Nafion 膜）是典型的可以实际应用的一类膜材料。因为这类膜材料具有较高的质子导电率，优良的机械性能，良好的热、电化学和化学稳定性。然而价格昂贵，在低湿度以及高温下质子导电率急剧下降，很高的甲醇透过率是这类膜材料的致命缺点，也就限制了其应用范围。开发价格低廉综合性能优异的聚合物膜材料来替代现有的磺化全氟聚合物势在必行。近年来，相关研究证明了六元环的磺化聚酰亚胺是很有希望应用于 PEMFC 的一种膜材料[3-9]。尤其是一类由磺酸基接在侧链上的二胺单体（侧链型二胺）制备而得的高磺化度的磺化聚酰亚胺表现了极高的耐水性和质子导电率[6, 7]。本文介绍了一种全芳香类侧链型磺化聚酰亚胺的制备，以及这些磺化聚酰亚胺的热稳定性，质子导电率，耐水性和甲醇透过性能。

实验

磺化聚酰亚胺是由一步法制备而得的, 具体是由 1,4,5,8-萘四酸二酐 (NTDA),侧链型磺化二胺单体 3,3'-双（4-磺酸基苯氧基）联苯二胺（BSPOB）和一些非磺化二胺单体，以间甲酚作溶剂，在三乙胺以及苯甲酸的存在下先在 80 ℃ 反应 4 小时然后在 180 ℃ 反应 16 小时聚合制备而得。聚合所得的高粘度的混合物加入间甲酚稀释后沉析到丙酮中。纤维状聚合物用丙酮反复洗涤后，过滤，然后置于真空烘箱中干燥。用溶液浇注法进行制膜，具体是将磺化聚酰亚胺溶液（三乙胺型）均匀地涂在玻璃板上，在烘箱中 80 ℃ 干燥 10 小时。所得的膜在 60 ℃ 的甲醇中浸泡 6 小时。然后将所得的三乙胺型膜在 1.0 N 的盐酸溶液中浸泡两天进行质子交换。质子型的膜用去离子水洗涤后在真空烘箱中于 100 ℃ 干燥 20 小时。

结果与讨论

高分子量的含 BSPOB 的磺化聚酰亚胺 (Scheme 1) 由一步法在间甲酚溶剂中，在三乙胺以及苯甲酸的存在下制备得到。所得到的聚酰亚胺具有很高的特性粘度，例如：NTDA-BSPOB/mBAPPS(9/1) 的二甲基亚砜溶液（0.5 g/dL）在 35 ℃ 时的特性粘度为 8.9 dL/g 。TG-MS 测试得到的 NTDA-BSPOB/mBAPPS(9/1)中磺酸基的分解温度高于 270 ℃ ，这就表明了该类磺酸聚酰亚胺具有较好的热稳定性。

本文所研究的这些基于 BAPPSDS 的磺化聚酰亚胺膜的质子导电率（σ）对于相对湿度（RH）有很强的依赖关系。在低相对湿度条件下，这些聚酰亚胺的质子导电率比较低。但在较高的相对湿度条件下（RH>70%）或在水中，这些磺化聚酰亚胺膜表现出较高的质子导电率。表 1 列出了一系列磺化聚酰亚胺和 Nafion 117 的质子导电率和甲醇透过率（P_M）以及这两者的比值 ϕ（$=\sigma/P_M$）。在 30 °C 和 50 °C 时，NTDA-BAPPSDS/mBAPPS(2/1)的 P_M 值要远小于其它的磺化聚酰亚胺以及
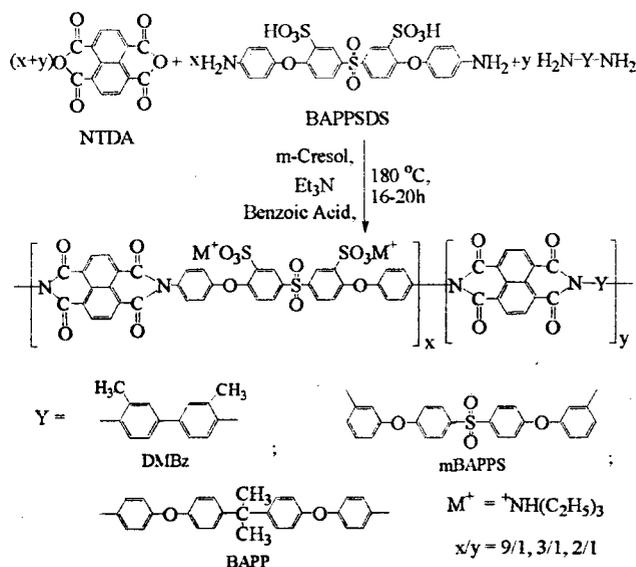
Nafion 117 。因此可以看到 NTDA-BAPPSDS/mBAPPS(2/1)的 ϕ 值大于 Nafion 117。但由于 NTDA-BAPPSDS/mBAPPS(2/1)的质子导电率相对较低，其 ϕ 值要小于其它类型的磺化聚酰亚胺。

耐水性的测试是将磺化聚酰亚胺膜浸入去离子水中，分别在不同温度下（80 °C 或 100 °C）进行测量，将膜在热水中开始变脆的时间作为衡量膜的耐水性的依据。实验表明，耐水性具有温度依赖性，比如：BAPPSDS/mBAPPS(3/1)在 80 °C 的去离子水中能保持 600 小时不变脆，体现了良好的耐水性，然而同一种膜在 100 °C 的去离子水中 5 小时后就开始溶解了。材料的耐水性可以通过降低聚合物的离子交换容量（IEC）值得到改善。例如：NTDA-BAPPSDS/mBAPPS(2/1)能在 100 °C 的去离子水中保持 200 多小时不变脆，这一结果大大优于 BAPPSDS/mBAPPS(3/1)。

表 1 磺化聚合物膜的离子交换容量，质子导电率，甲醇透过系数和两者的比值。

Membranes	IEC [meq g^{-1}]	σ (S/cm)[a]		P_M(10^{-6}cm^2/s)[b]		$\phi = \sigma/P_M$(10^4 S.cm^{-3} s) (30°C)	Ref.
		90%RH	In water	30°C	50°C		
NTDA-BAPPSDS/mBAPPS(2/1)	1.73	0.071	0.07	0.84[b]	1.64[b]	8.3	c
NTDA-BAPBDS	2.63	0.031	0.19	1.14	-	18	4, 5
NTDA-2,2'-BSPB	2.89	0.11	0.18	1.05	2.06	13	5, 7
Nafion 117	0.91	0.085	0.12	2.21	3.32	4.8	5

[a] Measured at 50 °C; [b] Methanol concentration in feed: 8.6wt%, [bl] 10wt%; [c]This study.

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