侧链有序交联型咪唑功能化阴离子交换膜

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摘要 利用甲基氢醌和4,4'-二氟二苯基甲酮的缩聚反应, 合成了含苯甲基的聚芳醚酮二元有序结构的聚合物。随后, 利用*N*-溴代琥珀酰亚胺(NBS)溴代, 溴代产物同时接枝1-甲基咪唑和1-乙烯基咪唑制备了一系列侧链有序交联型的阴离子交换膜(Im-PEEK-*x*)。透射电子显微镜图显示Im-PEEK-0.7膜具有较好的微相分离结构。Im-PEEK-0.7膜的离子传导率为 6.68×10^{-2} S/cm, 拉伸强度达到60.03 MPa, 并且在80℃的吸水率、溶胀率分别为16.56%, 18.2%。在耐碱稳定性测试中, Im-PEEK-0.7膜浸泡在80℃, 1 mol/L NaOH 溶液中200 h后, 其IEC值仍为泡碱前的81.5%, 表现出优异的耐碱稳定性。说明侧链有序具有微相分离结构的交联型阴离子交换膜具有优异的离子传导率和稳定性。

关键词 阴离子交换膜, 交联结构, 相分离结构, 1-乙烯基咪唑

碱性燃料电池因其减少了贵金属铂的使用, 可以使用镍和银或者具有简单含氮配体的过渡金属螯合物用以代替传统贵金属催化剂而受到广泛关注^[1,2]。在碱性环境下, 由于碱性燃料电池拥有更快的反应动力学等优点受到广泛关注。另一方面, 碱性燃料电池中氢氧根离子与燃料传递方向相反, 它降低了燃料的渗透性, 降低了成本^[3,4]。因此, 碱性燃料电池的发展前景良好, 而阴离子交换膜(AEMs)作为碱性燃料电池的核心部件存在离子传导率不高、稳定性较差等问题。许多阳离子基团已被广泛研究, 如季铵^[5,6]、咪唑^[7-9]、胍^[10]。季铵基团和咪唑基团是最常用的阳离子基团。严锋课题组^[11,12]证明咪唑型阴离子交换膜优异的耐碱稳定性。这是由于在独特的*N*-杂环结构中存在共轭 π 键, 咪唑功能化后不仅具有高离子电导率, 而且具有优异的化学稳定性和热稳定性。AEMs的离子传导率与离子交换容量(IEC)和氢氧

根离子的迁移率直接相关^[13]。提高离子传导率, 最直接的方法为增加离子交换容量^[14]。但是随着IEC增加会导致溶胀率过高, 尺寸稳定性下降。为解决这个问题, 谢晓峰课题组^[15]合成了一个含有双键的聚合物骨架, 通过双键热交联形成交联结构。网状结构的形成有利于抑制离子交换膜的膨胀, 从而改善膜的尺寸稳定性。另一种方法为制备侧链型微相分离结构, 侧链亲水结构有助于提高离子传导率。刘庆林课题组^[16]通过制备嵌段型共聚物, 形成微相分离结构, 在80℃的离子传导率达到0.1467 S/cm。

本文通过制备二元有序聚合物, 并在聚合物上接枝咪唑功能基团, 从而形成侧链有序具有微相分离结构的阴离子交换膜来提高离子交换膜的离子传导率。引入1-乙烯基咪唑双键交联, 形成的致密网络结构使得膜具有良好的力学性能和尺寸稳定性, 提高了离子交换膜的耐碱稳定性。

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1 实验

(i) 膜的制备. 以甲基氢醌和4,4'-二氟二苯基甲酮为单体, K_2CO_3 作盐剂, *N*-甲基吡咯烷酮(NMP)为溶剂, 混合后加入到100 mL三口烧瓶中. 在氮气氛下将混合物加热至130℃, 除水4 h, 随后升温到170℃, 当溶液黏度显着增加时, 将溶液倒入水中, 随后将聚合物烘干后即得到聚醚醚酮(PEEK). 然后取1 g PEEK和25 mL 1,1,2,2-四氯乙烷于三口烧瓶中机械搅拌. 当聚合物完全溶解后, 加入1.18 g *N*-溴代琥珀酰亚胺(NBS)和0.08 g过氧化二苯甲酰(BPO). 在氮气氛下, 混合物在80℃反应5 h. 溶液冷却至室温后, 将其倒入乙醇中. 得到黄色沉淀物为聚醚醚酮的溴化物(BPEEK), 用乙醇洗涤沉淀4次, 在50℃下干燥24 h. 将BPEEK, 1-甲基咪唑和1-乙烯基咪唑的混合物加入到100 mL三颈烧瓶中并在氮气保护下, 40℃磁力搅拌24 h. 反应完成后, 所得棕色固体用乙醇洗涤4次, 再次用去离子水彻底洗涤并在50℃下干燥24 h. 将一定量的棕色固体溶解在NMP中形成8%的溶液(质量百分比), 并加入适量的BPO. 将混合物溶液浇铸在清洁的平板玻璃板上, 100℃下干燥24 h后取出, 将膜浸入1 mol/L NaOH溶液中24 h, 并用水洗涤几次直至膜表面呈中性, 从而获得一系列阴离子交换膜(Im-PEEK-*x*), *x*代表1-甲基咪唑所占的摩尔比. 图1是Im-PEEK-*x*的合成示意图.

(ii) 结构表征与性能测试. DMSO- d_6 和氯仿- d 作为溶剂, 通过核磁共振氢谱(1H NMR, Bruker Avance III光谱仪)表征聚合物以及膜结构. 透射电子显微镜(TEM, JEM-1011)观察样品的微观结构, 样品通过KI溶液进行染色, 浸泡在KI溶液中24 h后, 用蒸馏水清洗后烘干. 通过红外光谱(FT-IR)测试泡碱前后膜结构的变化. 测试吸水前后的重量及尺寸变化测试Im-PEEK-*x*膜的吸水率和溶胀率. 通过四探针交流(AC)阻抗技术测量离子传导率. 反滴定法测Im-PEEK-*x*膜的离子交换容量(IEC), 其具体过程为: 把Im-PEEK-*x*膜浸没在0.1 mol/L盐酸溶液中24 h, Cl^- 完全交换 OH^- ; 之后, 剩余 H^+ 用0.1 mol/L NaOH溶液滴定. 计算方法如下式. 万能拉伸机(Instron 5965)测量Im-PEEK-*x*膜的机械性能, 拉伸速度1 mm/min, 尺寸30 mm×4 mm, 多次测试取平均值. 通过热重分析(TGA, Perkin Elmer Pyris 1)测试Im-PEEK-*x*膜的热稳定性, 温度范围为40~650℃, 加热速率为10℃/min; 80℃, 膜浸泡1 mol/L NaOH溶液一段时间后, 测试

图1 Im-PEEK-*x*合成过程

Figure 1 Synthesis processes of Im-PEEK-*x*

其离子交换容量(IEC), 通过泡碱前后IEC值的变化测试Im-PEEK-*x*的耐碱稳定性:

$$IEC = \frac{C_{HCl} V_{HCl} - C_{NaOH} V_{NaOH}}{W_d}$$

2 结果与讨论

图2为Im-PEEK-1, PEEK, BPEEK和Im-PEEK-0的 1H NMR谱. 如图2(b)所示, δ 2.3附近的峰为苯甲基的质子, 证实了二元有序共聚物的成功合成. 对于BPEEK(图2(c)), 观察到 δ 4.5出现新峰, 证实了PEEK成功溴化合成BPEEK. BPEEK的溴甲基化程度可由 $-CH_2Br$ 的积分面积与 $-CH_3$ 和 $-CH_2Br$ 的总和之比计算. 将1-乙烯基咪唑接枝到BPEEK上后(图2(d)), δ 4.5附近的峰完全消失, δ 5.4和9.6附近出现新峰分别归属于咪唑上 $-CH_2-$ 和 $=CH-$ 的质子. Im-PEEK-1(图2(a))的核磁图中, δ 3.8左右处为1-甲基咪唑上的甲基的质子.

通过TEM图像观察所制备的阴离子交换膜的微观形貌. 如图3所示, 暗区代表亲水区域的咪唑离子簇, 而明亮区域为疏水骨架. 显然, 膜具有良好的相

图2 (网络版彩色) ^1H NMR谱. (a) Im-PEEK-1; (b) PEEK; (c) BPEEK; (d) Im-PEEK-0

Figure 2 (Color online) ^1H NMR spectra of Im-PEEK-1 (a), PEEK (b), BPEEK (c) and Im-PEEK-0 (d)

分离结构,在水合状态下,咪唑基团与水分子形成离子簇,并与疏水主链形成微相分离,从而为水合氢氧根离子在其中传导提供了传输通道,传输通道的形成成为传导率的提高创造了条件,因此提高了传导率.

离子传导率的大小是评估阴离子交换膜性能的

图3 Im-PEEK-0.7(a)和Im-PEEK-1(b)的TEM图

Figure 3 TEM images of Im-PEEK-0.7 (a) and Im-PEEK-1 (b)

重要依据之一, Im-PEEK- x 的传导率如图4(a)所示. 随着温度的升高,离子传导率增加,这主要由于升温促进阴离子在膜内的运动和水的扩散. 从TEM图中可以看出, Im-PEEK-0.7膜具有明显的微相分离结构, 交联结构有利于形成更大的离子簇. Im-PEEK-1的离子传导率最高($7.12 \times 10^{-2} \text{ S/cm}$, 80°C), 随着1-乙基咪唑含量增加, Im-PEEK-0.7在 80°C 的离子传导为 $6.68 \times 10^{-2} \text{ S/cm}$. 离子传导率有所下降但仍具有较高离子传导率. 这主要由于随着1-乙基咪唑含量增加,膜内自由体积减少,形成了更为致密的交联结构,抑制了水的吸收,因此离子传导率下降. OH^- 传输路径如图4(b)所示, 氢氧根离子通过亲水咪唑基团和 H_2O 进行传输,具体的传输过程为氢氧根离子与 H_2O 结合成 H_3O_2^- ,随后 H_3O_2^- 可以分解为 H_2O 和 OH^- ,从而进一步的传递氢氧根离子.

Im-PEEK- x 的离子交换容量(IEC)如图5(a)所示, IEC值越大,吸水率越大,离子传导率越高. 高吸水率有利于提高膜的离子电导率^[17], 增加膜中的水含

图4 (网络版彩色)Im-PEEK- x 的离子传导率(a)和 OH^- 的传输路径图(b)

Figure 4 (Color online) Hydroxide conductivity of Im-PEEK- x (a) and the OH^- transportation paths (b)

图5 (网络版彩色)Im-PEEK-*x*的IEC值(a), 吸水率(b)和溶胀率测试(c)
Figure 5 (Color online) IEC values (a), water uptake (b) and swelling ratio (c) of Im-PEEK-*x*

量有助于提高水的局部流动性和渗透亲水相域以提高有效的离子传导^[5,18]。然而, 过量的水吸收会引起溶胀, 从而降低膜的尺寸稳定性。膜材料的尺寸稳定性不仅对膜的力学性能有很大的影响, 而且对膜的使用寿命和电池效率也有至关重要的影响。Im-PEEK-1未交联膜具有较高的吸水率(17.19%, 80 °C)和溶胀率(36.29%, 80 °C)。随着1-乙烯基咪唑含量增加, Im-PEEK-0.3的吸水率(12.57%, 80 °C)及溶胀率(8.52%, 80 °C)均有下降(图5)。这主要是由于形成致密网络交联结构抑制了水的吸收与膜的溶胀, 同时交联限制了膜中分子链的热运动。

Im-PEEK-1的最大应力及断裂伸长率分别为58.9 MPa, 13.69%; Im-PEEK-0.3的最大应力和断裂伸长率分别为66.57 MPa, 7.86%(表1)。随着交联结构进一步增加, 膜的杨氏模量和拉伸强度增加, Im-PEEK-*x*表现出优异的机械性能。

膜的热性能决定了阴离子膜使用的温度范围。图6为Im-PEEK-*x*膜的TGA曲线, 从曲线中可以明显的看到其具有3个失重平台。在200 °C之前的第1次轻微的重量损失是由于膜中残留水分、溶剂和BPO的损失; 第2个失重平台为200~350 °C, 主要是由于侧链咪唑阳离子基团的降解造成的^[19,20]; 第3个失重平台在400 °C左右, 可能是由于聚醚醚酮主链的分解。因此, 膜的热稳定性远高于碱性燃料电池的操作温度(~80 °C)^[21]。综上所述, TGA测试表明Im-PEEK-*x*具有良好的热稳定性。

膜的耐碱稳定性是膜实际应用中的重要因素之一。咪唑鎓阳离子容易受到强亲核OH⁻的攻击, 导致咪唑阳离子开环反应, 从而降低了膜的离子电导率^[22,23]。膜中1-乙烯基咪唑含量越高, 膜的耐碱稳定

表1 Im-PEEK-*x*的机械性能^{a)}

Table 1 Mechanical properties of the Im-PEEK-*x*

样品	杨氏模量(GPa)	最大压力(MPa)	断裂伸长率(%)
Im-PEEK-1	1.678±0.05	58.90±1.87	13.69±0.46
Im-PEEK-0.7	1.725±0.04	60.03±2.39	12.59±1.08
Im-PEEK-0.5	1.797±0.03	64.12±2.13	10.76±0.35
Im-PEEK-0.3	1.939±0.06	66.57±2.57	7.86±0.93

a) 干膜室温下测得

图6 (网络版彩色)Im-PEEK-*x*的TGA曲线
Figure 6 (Color online) TGA curves of the Im-PEEK-*x*

性越好(图7(a))。在80 °C泡碱200 h后, Im-PEEK-1的IEC值为泡碱前IEC值的76.8%, 而Im-PEEK-0.7的IEC值为泡碱前的81.5%。泡碱200 h后的Im-PEEK-0.7的红外光谱图(b2曲线)与泡碱前(b1曲线)相比, 并无明显变化(图7(b))。这主要是由于交联后形成致密的网状结构, 该致密的结构提高了阴离子交换膜的内部稳定性, 有利于防御OH⁻的攻击^[24]。说明交联结

图7 Im-PEEK-x的耐碱稳定性测试. (a) IEC值; (b) Im-PEEK-0.7的泡碱前(b1)和泡碱后(b2)的红外光谱

Figure 7 Alkaline stability test of Im-PEEK-x. (a) IEC values; (b) FT-IR spectra of Im-PEEK-0.7 (b1) before immersed in NaOH and (b2) after immersed in NaOH solutions

构有利于提高阴离子交换膜的化学稳定性.

3 结论

本制备了一系列交联咪唑功能化阴离子交换膜, 其侧链微相分离结构提高了阴离子交换膜的离子传

导率. 当膜被浸泡在80℃, 1mol/L NaOH溶液中200 h后, Im-PEEK-0.7的IEC值仍为泡碱前的81.5%. 说明交联结构改善了膜的尺寸稳定性, 提高了膜的耐碱稳定性. 基于聚芳醚酮制备的侧链有序交联型咪唑功能化的阴离子交换膜有望应用于碱性燃料电池.

参考文献

- McLean G F, Niet T, Prince-Richard S, et al. An assessment of alkaline fuel cell technology. *Int J Hydrog Energy*, 2002, 27: 507–526
- Varcoe J R, Slade R C, Wright G L, et al. Steady-state dc and impedance investigations of H₂/O₂ alkaline membrane fuel cells with commercial Pt/C, Ag/C, and Au/C cathodes. *J Phys Chem B*, 2006, 110: 21041–21049
- Tang D, Pan J, Lu S, et al. Alkaline polymer electrolyte fuel cells: Principle, challenges, and recent progress. *Sci China Chem*, 2010, 53: 357–364
- Spendlow J S, Goodpaster J D, Kenis P J, et al. Mechanism of CO Oxidation on Pt(111) in alkaline media. *J Phys Chem B*, 2006, 110: 9545–9555
- Dang H S, Jannasch P. Anion-exchange membranes with polycationic alkyl side chains attached via spacer units. *J Mater Chem A*, 2016, 4: 17138–17153
- He S Q, Liu L, Wang X C, et al. Azide-assisted self-crosslinking of highly ion conductive anion exchange membranes. *J Membr Sci*, 2016, 509: 48–56
- Gong X, Yan X M, Li T T, et al. Design of pendent imidazolium side chain with flexible ether-containing spacer for alkaline anion exchange membrane. *J Membr Sci*, 2017, 523: 216–224
- Zhuo Y Z, Lai A L, Zhang Q G, et al. Enhancement of hydroxide conductivity by grafting flexible pendant imidazolium groups into poly(arylene ether sulfone) as anion exchange membranes. *J Mater Chem A*, 2015, 3: 18105–18114
- Lee K H, Cho D H, Kim Y M, et al. Highly conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross-linking. *Energy Environ Sci*, 2017, 10: 275–285
- Sajjad S D, Liu D, Wei Z, et al. Guanidinium based blend anion exchange membranes for direct methanol alkaline fuel cells (DMAFCs). *J Power Sources*, 2015, 300: 95–103
- Lin B, Qiu L, Qiu B, et al. Correction to a soluble and conductive polyfluorene ionomer with pendant imidazolium groups for alkaline fuel cell applications. *Macromolecules*, 2011, 44: 9642–9649
- Zhao J, Feng Y, Chen Z, et al. Microemulsion polymerization of cationic pyrroles bearing an imidazolium-ionic liquid moiety. *J Polym Sci Part A Polym Chem*, 2010, 47: 746–753

- 13 Liu L S, Ahlfield J, Tricker A, et al. Anion conducting multiblock copolymer membranes with partial fluorination and long head-group tethers. *J Mater Chem A*, 2016, 4: 16233–16244
- 14 Agel E, Bouet J, Fauvarque J F. Characterization and use of anionic membranes for alkaline fuel cells. *J Power Sources*, 2001, 101: 267–274.
- 15 Li C P, Wang S B, Wang W P, et al. A cross-linked fluorinated poly(aryl ether oxadiazole)s using a thermal cross-linking for anion exchange membranes. *Int J Hydrog Energy*, 2013, 38: 11038–11044
- 16 Lai A N, Wang L S, Lin C X, et al. Phenolphthalein-based poly(arylene ether sulfone nitrile)s multiblock copolymers as anion exchange membranes for alkaline fuel cells. *ACS Appl Mater Interfaces*, 2015, 7: 8284
- 17 Han K W, Ko K H, Abu-Hakme K, et al. Molecular dynamics simulation study of a polysulfone-based anion exchange membrane in comparison with the proton exchange membrane. *J Phys Chem C*, 2014, 118: 12577–12587
- 18 Zhu L, Pan J, Wang Y, et al. Multication side chain anion exchange membranes. *Macromolecules*, 2016, 49: 815–824
- 19 Fang J, Lyu M, Wang X, et al. Synthesis and performance of novel anion exchange membranes based on imidazolium ionic liquids for alkaline fuel cell applications. *J Power Sources*, 2015, 284: 517–523
- 20 Ngo H L, LeCompte K, Hargens L, et al. Thermal properties of imidazolium ionic liquids. *Thermochim Acta*, 2000, 357: 97–102
- 21 Merle G, Wessling M, Nijmeijer K. Anion exchange membranes for alkaline fuel cells: A review. *J Membr Sci*, 2011, 377: 1–35
- 22 Meek K M, Elabd Y A. Alkaline chemical stability of polymerized ionic liquids with various cations. *Macromolecules*, 2015, 48: 7071–7084
- 23 Meek K M, Nykaza J R, Elabd Y A. Alkaline chemical stability and ion transport in polymerized ionic liquids with various backbones and cations. *Macromolecules*, 2016, 49: 3382–3394
- 24 Guo D, Zhuo Y Z, Lai A N, et al. Interpenetrating anion exchange membranes using poly(1-vinylimidazole) as bifunctional crosslinker for fuel cells. *J Membr Sci*, 2016, 518: 295–304

Summary for “侧链有序交联型咪唑功能化阴离子交换膜”

The ordered side chain imidazole functionalized cross-linked anion exchange membrane

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In recent years, the development of alkaline anion exchange membrane fuel cells (AEMFCs) has received widespread attention. On the one hand, non-noble metals can be used as catalysts in alkaline anion exchange membrane fuel cells (AEMFCs), such as silver and nickel which reduced the cost of fuel cell devices. On the other hand, the hydroxide ions move in the opposite direction with the fuel, which reduce fuel permeability and the cost on other aspects. Therefore, the development prospect of alkaline fuel cells is good, while anion exchange membrane, as the core component of alkaline fuel cells, has problems such as the insufficient ion conductivity and alkaline stability, which hinder the successful realization of AEMFCs technology. Until now, many cationic groups have been widely investigated, such as quaternary ammonium, imidazolium, guanidinium and phosphonium. Quaternary ammonium group and imidazolium group are the most commonly used cationic group. The experimental results suggest that imidazole-type anion exchange membrane have better performance. Due to the existence of the conjugated π bond in the unique *N*-heterocyclic structure, imidazolium grafted membranes exhibit not only high ionic conductivity, but also excellent chemical and thermal stability. The formation of cross-linked network structure is advantageous in suppressing the swelling of the membrane, thereby improving the dimensional stability of the membrane. Meantime, we introduce 1-vinylimidazole to improve the performance of the 1-methylimidazole grafted membrane. This monomer contains not only imidazolium cation groups, but also double bonds can be cross-linked. The imidazole group can transfer OH^- ions. The dense network structure formed by double bonds cross-linking makes membranes have good mechanical properties and dimensional stability, and conducive to defense strong nucleophile OH^- attack.

First, a benzylmethyl-containing poly ether (ether ether ketone) (PEEK) copolymer was synthesized through condensation polymerization of 4,4'-difluorobenzopheno and methylhydroquinone. Then, dissolved the PEEK by 1,1,2,2-tetrachloroethane, the yellow precipitate bromination of polyether ether ketone (BPEEK) was synthesized by adding NBS and BPO into the solution and reacted at 80°C for 5 h under the nitrogen atmosphere. The BPEEK was chosen to react directly with the functional reagent, 1-methyl imidazole and 1-vinylimidazole and obtained poly (ether ether ketone) cross-linked anion exchange membranes. The structure was characterized by ^1H NMR spectroscopy. The morphology and microstructure of the resulting samples were characterized using transmission electron microscopy (TEM). The ion conductivity of the Im-PEEK-*x* membrane was measured by four-probe alternating current (AC) impedance technique. The thermal stability was tested by thermogravimetric analysis (TGA). The alkaline solution stability of the Im-PEEK-*x* membrane was evaluated by measuring the changes in IEC values after immersed in 1 mol/L NaOH for a certain time. Water uptake, swelling ratio and mechanical properties of the membranes were also measured.

The results indicated that the Im-PEEK-*x* membrane had been synthesized. After grafting of 1-vinylimidazole, for the membrane of Im-PEEK-0.7, the maximum stress is 60.03 MPa, and the swelling rate is 18.2% at 80°C. After soaking in 1 mol L⁻¹ NaOH solution for 200 h at 80°C, the IEC value was about 81.5% of the initial, which exhibited excellent alkaline stability.

anionic exchange membrane, crosslinking structure, phase separation structure, 1-vinyl imidazole

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