基于螺环季铵盐的阴离子交换膜的制备与性能

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摘要 合成了 N,N -二烯丙基吡咯烷溴盐([DAPy][Br]), 采用光引发聚合的方式制备了基于[DAPy][Br]的聚合物膜, 经过离子交换后得到OH⁻型阴离子交换膜. 改变原料配比调控膜的离子交换容量, 发现膜的溶胀度、吸水率、离子交换容量与电导率都随着[DAPy][Br]含量的增加而增大. 该阴离子交换膜具有良好的机械性能和热稳定性, 拉伸强度在室温下为10.6~19.8 MPa. 80℃下最高离子电导率可达 7.29×10^{-2} S/cm. 在成膜过程中[DAPy][Br]发生交联, 形成拥有两个五元环的 N -螺环结构阳离子, 有效提高了膜的耐碱性能, [PSAN]₇₀-[DAPy][OH]₃₀膜浸泡于80℃下1 mol/L KOH溶液中240 h, 电导率仅下降了11%. 上述结果表明, 拥有 N -螺环季铵盐的脂肪主链的阴离子交换膜有望应用于燃料电池.

关键词 N -螺环, 阴离子交换膜, 耐碱性, 燃料电池, 电导率

阴离子交换膜(AEM)是碱性阴离子交换膜燃料电池(AEMFC)的核心部件, 起到分隔燃料和氧化剂、传导离子的双重作用^[1,2]. 典型的AEM的结构是季铵阳离子基团通过共价键的方式连接在聚合物主链上. 通常认为聚合物主链结构决定AEM的力学性能、热稳定性等, 而阳离子基团则影响膜的电导率及耐碱性^[3,4]. 为了满足AEMFC的运行条件, 理想的AEM必须具备较高的OH⁻电导率、良好的热稳定性、优异的机械性能和耐碱性. 然而, OH⁻固有的离子迁移率和季铵基团的解离程度都偏低, 导致AEM电导率低; 并且季铵类AEM在高温强碱条件下存在Hofmann降解和亲核取代降解等反应导致其耐碱性较差^[5-8]. 这两个缺点限制了AEMFC应用和发展.

通过对AEM进行合理的分子结构设计能够有效

提高其电导率和耐碱性^[9]. 近年来, 许多研究团队致力于提高AEMs电导率和耐碱性. 聚苯乙烯、聚砜、聚苯醚、聚丙烯等聚合物已被用于制备AEMs^[10-13]. 但这些AEM大多都是季铵阳离子的聚合物, 制备过程通常需要氯甲基化过程, 对人体和环境都有很大危害. 因此, 开发新的AEM的制备方法势在必行.

近年来, 有别于传统季铵盐类阴离子交换膜的研究取得了较大的研究进展. Marino和Kreuer^[14]合成了26种不同的小分子阳离子, 研究表明哌啶阳离子和 N -螺环阳离子具有优异的耐碱性. 基于他们对这些小分子阳离子耐碱性的研究, 研究人员将 N -螺环阳离子修饰到芳香族聚合物侧链并将其用于制备AEM^[15-17], 这些膜均展现出较好的耐碱性. Nunez和Hickner^[18]的研究表明, AEM的主链结构也会影响其

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耐碱性. 然而, 对于具有脂肪主链结构的基于 N -螺环阳离子的AEM的研究并不多.

本文合成了 N,N -二烯丙基吡咯烷溴化盐[DAPy][Br], 并将其与苯乙烯、丙烯腈混合均匀后, 通过紫外光引发共聚制备出一系列基于脂肪主链结构的含 N -螺环阳离子的AEMs. 研究了[DAPy][Br]含量对AEMs性能的影响, 包括吸水率、溶胀度、热稳定性、机械性能、耐碱性和离子电导率等.

1 实验

(i) [DAPy][Br]的合成. 将溴丙烯在冰水浴下缓慢滴入吡咯烷中(滴加速度0.4 mL/min), 两者摩尔质量比为2:1, 乙酸乙酯作溶剂. 滴加完全后在室温下继续搅拌反应10 h, 生成黄色沉淀. 过滤取滤液, 旋转蒸发除去乙酸乙酯得到淡黄色液体即 N -烯丙基吡咯烷.

将溴丙烯在冰水浴下缓慢滴入生成的 N -烯丙基吡咯烷中(滴加速度0.4 mL/min), 两者摩尔质量比1:1, 乙酸乙酯作溶剂, 滴加完全后在室温下继续搅拌反应12 h, 得到淡黄色沉淀. 将粗产物以乙酸乙酯洗涤3次, 室温下真空干燥, 得到[DAPy][Br].

(ii) AEMs的制备. 将苯乙烯/丙烯腈(SAN, 质量比1:3, 占聚合单体总质量分数70%~90%)、[DAPy][Br] (占聚合单体总质量分数30%~10%)、二乙烯基苯(交联剂, 占聚合单体总质量分数4%)、安息香乙醚(光引发剂, 占聚合单体总质量分数0.5%)混合均匀. 将透明的混合溶液倒入聚合模板中, 将其置于紫外灯下聚合30 min, 得到聚合物膜. 取出聚合物膜将其浸泡于60℃下1 mol/L KOH溶液中24 h进行阴离子交换, 随后将膜浸泡于去离子水去除膜内残留的KOH, 得到碱性AEMs, 具体过程如图1所示. 将制备得到的AEMs命名为[PSAN] $_x$ -[DAPy][OH] $_y$, 其中 x , y 分别表示苯乙烯/丙烯腈与[DAPy][Br]的质量分数.

(iii) 表征. Varian CP-3800红外光谱仪对AEM进行结构表征, 波数范围为4000~400 cm^{-1} ; Varian 400 MHz核磁仪对[DAPy][Br]的化学结构和耐碱性

进行表征; 热稳定性是利用Universal Analysis 2000热重分析仪测试, 测试条件: 氮气氛围, 温度范围为50~650℃, 加热速率为10℃/min; 室温下利用Instron万能试验机对AEMs机械性能进行测试, 拉伸速率为5 mm/min, 测试3次, 取平均值; 利用Agilent原子力显微镜对AEMs微观结构进行表征.

AEMs的溶胀度(SR)测试方法如下: 室温下, 将干燥后的膜样品浸泡于去离子水中24 h保证膜充分吸水, 测量样品膜泡水前后的长度分别记为 L_{dry} , L_{wet} . 计算方法见公式(1):

$$SR = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%. \quad (1)$$

AEMs的吸水率(WU)的计算方法如下: 将干燥后的膜样品浸泡于去离子水中24 h保证膜充分吸水, 称量样品膜在干态和湿态时的质量分别记为 W_{dry} , W_{wet} . 计算方法见公式(2):

$$WU = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%. \quad (2)$$

离子交换容量(IEC)通过反滴定法测试得到, 具体测试方法如下: 将干燥的膜样品室温下浸泡于0.01 mol/L标准HCl溶液中24 h, 用0.01 mol/L标准KOH溶液滴定, 以酚酞试剂为指示剂, 直至混合液变为粉红色. 具体计算方法见公式(3):

$$IEC = \frac{C_{\text{HCl}} \times V_{\text{HCl}} - C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}}, \quad (3)$$

其中, C_{HCl} , V_{HCl} 分别代表标准HCl的浓度与体积, C_{NaOH} , V_{NaOH} 分别代表标准NaOH的浓度与体积.

AEMs的电导率(σ)通过测量交流阻抗计算而得, AEMs的阻抗可利用电化学工作站测得, 测试温度为20~80℃:

$$\sigma = \frac{l}{R \times S}, \quad (4)$$

其中, l 为电极间距离, R 为阻抗, S 为膜样品的截面积.

[PSAN] $_x$ -[DAPy][OH] $_y$ 的耐碱性测试是将膜浸泡于80℃下1 mol/L KOH溶液中, 每隔一定时间测量其在室温下的电导率以及最终离子交换容量的变化.

图1 [PSAN] $_x$ -[DAPy][OH] $_y$ 的制备流程图

Figure 1 Reaction scheme for the preparation of [PSAN] $_x$ -[DAPy][OH] $_y$

2 结果与讨论

2.1 [DAPy][Br]的核磁表征

N-烯丙基吡咯烷和[DAPy][Br]的核磁氢谱图见图S1. 在 δ 6.0与5.2处的多重峰为烯丙基($\text{CH}_2=\text{CH}$ -)上的H的化学位移; 2.5和1.75处的峰代表吡咯烷环上的H的化学位移. [DAPy][Br]有2个烯丙基, 结构对称, 化学位移略微发生变动. 如图S1所示, 在5.9和5.6处表示烯丙基上 $\text{CH}_2=\text{CH}$ -的化学位移; 3.4和2.0处的化学位移表示吡咯烷环上的H. 核磁表征表明成功制备了*N*-烯丙基吡咯烷和[DAPy][Br].

2.2 红外表征

苯乙烯和丙烯腈共聚物(PSAN)具有良好的成膜性能, 并具有优异的热稳定性和机械性能, 因此本文以PSAN为基体材料制备了AEMs. 图2是PSAN基膜和 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 的红外吸收光谱图, 在 $1450\sim 1600\text{ cm}^{-1}$ 处的峰证明了聚苯乙烯的存在; 在 2235 cm^{-1} 为丙烯腈上的 $\text{C}\equiv\text{N}$ 的伸缩振动峰. 而阴离子交换膜在 1322 cm^{-1} 多出来的峰为 $\text{C}-\text{N}$ 的伸缩振动峰, $3000\sim 3500\text{ cm}^{-1}$ 处出现的宽峰为 $\text{O}-\text{H}$ 的伸缩振动峰. 红外吸收光谱证明成功制备了 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 系列AEMs.

2.3 热稳定性分析

图3是 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 在氮气氛围下的典型的热降解曲线图, 随着温度的升高, 3种膜降解趋

图2 (网络版彩色)PSAN基膜和 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 的红外光谱图
Figure 2 (Color online) FT-IR spectra of PSAN membrane and $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$

图3 (网络版彩色) $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 热重分析曲线
Figure 3 (Color online) TG curves of $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$

势一致: 都有3个热降解平台. 在 100°C 左右的质量下降是由于膜内水分的蒸发造成的, 随着[DAPy][Br]含量的增大, $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 在此处的失重越明显, 这也证明 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 的吸水率随着[DAPy][Br]含量的增大而增加. 在 300°C 左右的质量下降是由于AEMs侧链(苯基、腈基和阳离子等)的降解; 在 400°C 左右膜的质量大幅度下降(约下降了50%)表示膜的主链开始降解. 但该类膜在 200°C 以下是稳定的, 这足以应用于AEMFCs.

2.4 机械性能

应用于燃料电池的阴离子交换膜必须要具有足够的机械强度, 便于通过热压法制备膜电极. $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 的机械性能测试结果如表1所示, 膜的拉伸强度为 $10.6\sim 19.8\text{ MPa}$, 拉伸模量为 $413.2\sim 519.9\text{ MPa}$, 断裂伸长率为 $5.9\%\sim 16.7\%$. [DAPy][Br]为亲水性物质, 随着膜内[DAPy][Br]含量的增多, AEMs内阳离子增多, 膜的拉伸强度与拉伸模量都发生下降, 而断裂伸长率上升. 以上测试结果表明, $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 具有不错的韧性和延展性, 该类膜还可以通过改变[DAPy][Br]的含量来适当调控其机械性能.

2.5 溶胀度、吸水率和离子交换容量

优异的AEMs能够在保持较低溶胀度时具备较高的电导率. 电导率和膜的吸水率、离子交换容量有关, 通常吸水率和离子交换容量越大, 膜的电导率越高, 但高的吸水率和离子交换容量会导致膜具有较高的溶胀度. 表2列出了 $[\text{PSAN}]_x\text{-}[\text{DAPy}][\text{OH}]_y$ 的溶

表1 [PSAN]_x-[DAPy][OH]_y的拉伸强度、拉伸模量和断裂伸长率Table 1 Tensile strength, tensile modules and elongation at break of [PSAN]_x-[DAPy][OH]_y

样品	拉伸强度(MPa)	拉伸模量(MPa)	断裂伸长率(%)
[PSAN] ₉₀ -[DAPy][OH] ₁₀	19.8±0.2	519.9±50.9	5.9±0.2
[PSAN] ₈₀ -[DAPy][OH] ₂₀	14.1±0.5	451.8±35.3	11.2±0.3
[PSAN] ₇₀ -[DAPy][OH] ₃₀	10.6±1.0	413.2±40.9	16.7±0.1

表2 [PSAN]_x-[DAPy][OH]_y的吸水率、溶胀度与离子交换容量Table 2 Water uptake, swelling ratio and ion exchange capacity of [PSAN]_x-[DAPy][OH]_y

样品	IEC(meq/g)		WU(%)		SR(%)	
	理论值	实验值	20℃	80℃	20℃	80℃
[PSAN] ₉₀ -[DAPy][OH] ₁₀	0.43	0.40±0.02	21.28	58.92	12.42	32.67
[PSAN] ₈₀ -[DAPy][OH] ₂₀	0.86	0.83±0.01	45.41	111.18	30.55	51.17
[PSAN] ₇₀ -[DAPy][OH] ₃₀	1.28	1.26±0.01	65.17	139.26	45.63	80.40

胀度、吸水率与离子交换容量. 由表2可知, [PSAN]_x-[DAPy][OH]_y的溶胀度、吸水率及离子交换容量都随着[DAPy][Br]含量的增大而增加. [PSAN]_x-[DAPy][OH]_y的离子交换容量可以很简单地通过改变聚合单体的配比来调控, 其范围在0.40~1.26 meq/g, 与理论值相近. [PSAN]₉₀-[DAPy][OH]₁₀膜在20℃的吸水率和溶胀度分别为21.28%和12.42%. 同等条件下[PSAN]₇₀-[DAPy][OH]₃₀的吸水率和溶胀度分别升高到65.17%和45.63%. 另外, 随着温度的升高, 膜的吸水率和溶胀度也呈现增大的趋势.

2.6 离子电导率

离子电导率是AEMs的重要性能之一, 其大小直接影响AEMFCs的性能. 由图4可知, 在20~80℃, [PSAN]_x-[DAPy][OH]_y的电导率均超过 1×10^{-2} S/cm. 膜的电导率随温度的升高而上升, 一方面是因为温度越高, 离子运动越快; 另一方面温度上升, 膜的吸水率增大(表2), 导致膜内结构疏松, 有助于离子在膜内的传输. 在相同温度下, 膜的电导率随[DAPy][Br]含量的增多而增大, 如20℃下[PSAN]₉₀-[DAPy][OH]₁₀电导率为 1.44×10^{-2} S/cm, 而[PSAN]₇₀-[DAPy][OH]₃₀的电导率达到 3.01×10^{-2} S/cm.

AEMs的微结构对膜的性能有重要影响, 特别是疏水/亲水微观相分离的形成有助于提高膜的电导率. 图5为[PSAN]₇₀-[DAPy][OH]₃₀的原子力显微镜照片. 相位图反映了阴离子交换膜表面的弹性、黏性等性能的变化, 通过比较两张图可以发现高度图与相位图

图4 (网络版彩色)[PSAN]_x-[DAPy][OH]_y的电导率随温度变化曲线Figure 4 (Color online) The curves of conductivity of [PSAN]_x-[DAPy][OH]_y as a function of temperature

并没有相关性, 可排除膜的表面形貌对相位图的影响, 相位图上可见明显的深色和浅色区域, 深色区域是螺环阳离子形成的亲水相而浅色区域是聚合物主链形成的疏水相^[19], 从相位图上可以看出不同的亲水区域相互贯通, 证明了连续网络离子传输通道的形成. 在成膜过程中, [DAPy][Br]和苯乙烯/丙烯腈混合形成均一相, 这种均匀混合有利于连续亲水相的形成, 亲水的螺环阳离子相互聚集形成亲水相, 从而形成如图5所示的连续的微观相分离结构, 这种结构为离子传输提供了通道, 有利于提高AEMs的电导率.

2.7 耐碱性

AEMs的耐碱性影响到AEMFCs的性能和寿命,

图5 (网络版彩色)[PSAN]₇₀-[DAPy][OH]₃₀ 原子力显微镜图。(a) 高度图; (b) 相位图

Figure 5 (Color online) AFM height image (a) and phase image (b) of [PSAN]₇₀-[DAPy][OH]₃₀

是AEMs最重要的性能之一。[PSAN]_x-[DAPy][OH]_y的耐碱性是通过测试其在80℃下1 mol/L KOH溶液中浸泡不同时间后的电导率和IEC值的变化来评估。图6(a)显示了在1 mol/L KOH溶液中浸泡不同时间后, [PSAN]_x-[DAPy][OH]_y在室温下的电导率变化, 耐碱性测试发现[PSAN]_x-[DAPy][OH]_y的电导率没有明显下降, 即使在泡碱240 h后, 所有样品的电导率下降不超过11%。[PSAN]_x-[DAPy][OH]_y的耐碱性要优于季铵盐修饰的聚苯醚型AEMs^[17](浸泡于1 mol/L NaOH中240 h后电导率下降约14%)和咪唑盐接枝的聚醚砜型AEMs(浸泡于2 mol/L KOH中240 h后电导

率降低超过50%), 这表明[PSAN]_x-[DAPy][OH]_y具有良好的碱性稳定性。

本文还测试了IEC值的变化进一步研究[PSAN]_x-[DAPy][OH]_y的耐碱性, 测试结果见图6(b)。[PSAN]₇₀-[DAPy][OH]₃₀的IEC在1 mol/L KOH溶液中浸泡240 h后从1.26降低到1.21 meq/g, IEC值测试泡碱后变化与电导率的变化趋势一致, 进一步表明[PSAN]_x-[DAPy][OH]_y具有良好的耐碱性。这是由于成膜过程中[DAPy][Br]发生闭环交联, 形成拥有2个五元环的螺环结构, 提高了阳离子的耐碱性^[14]。

3 总结

本文成功合成了*N,N*-二烯丙基吡咯烷溴盐, 并通过简单的光引发聚合方法成功制备了一系列基于脂肪主链结构、IEC可控的AEMs, IEC的范围为0.40~1.26 meq/g。AEMs的吸水率、溶胀度和离子交换容量都随着膜内[DAPy][Br]含量的提高而增大。该系列AEMs同时还具有较高的电导率、良好的热稳定性、机械性能及优异的耐碱性。80℃时[PSAN]₇₀-[DAPy][OH]₃₀最高电导率可达 7.29×10^{-2} S/cm, 在80℃ 1 mol/L KOH溶液中浸泡240 h, 膜的电导率与离子交换容量都没有明显下降, 说明该系列AEMs有望应用于碱性燃料电池。

图6 (网络版彩色)[PSAN]_x-[DAPy][OH]_y电导率随泡碱时间变化曲线(a)与[PSAN]_x-[DAPy][OH]_y IEC泡碱(240 h)前后变化(b)

Figure 6 (Color online) The curves of conductivity (a) and change of IEC of [PSAN]_x-[DAPy][OH]_y after treatment of 1 mol/L KOH at 80℃ (b)

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补充材料

图 S1 *N*-烯丙基吡咯烷与[DAPy][Br]的核磁谱图

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Summary for “基于螺环季铵盐的阴离子交换膜的制备与性能”

Preparation and properties of anion exchange membranes based on spirocyclic quaternary ammonium salts

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Among various types of fuel cells, alkaline anion exchange membrane fuel cells (AEMFCs) have attracted enormous attention as clean and highly efficient energy conversion devices for vehicles and portable electronic applications. As the key component of AEMFCs, anion exchange membranes (AEMs) act both as a barrier to separate the fuel and an electrolyte to transport hydroxide anion. To fulfill the application of AEMFCs, an AEM should possess good thermal stability, good mechanical properties, high conductivity and excellent alkaline stability. The lack of commercially available AEMs with excellent alkaline stability is limited the application of AEMs in the AEMFCs.

In the recent years, a variety of AEMs based on poly(sulfone)s, poly(styrene)s, polypropylene, poly(arylene ether)s, poly(phenylene)s, poly(phenylene oxide)s and poly(olefin)s, have been synthesized for the application of AEMs. Most of these AEMs showed a similar chemical structure that a polymer backbone with with pendent quaternary ammonium cations. However, quaternary ammonium cations are unstable in alkaline environment due to the Hofmann degradation, the nucleophilic substitution and the ylide reaction, even in high temperature. Therefore, various types of AEMs based on some potential alternative cations, including imidazolium, guanidinium, phosphonium, metal-cation, pyridinium, tertiary sulfonium, and pyrrolidinium cations have been prepared and investigated in the last few years. Recently, different quaternary ammonium small molecules were synthesized and their alkaline stability was thoroughly investigated by Marino and Kreuer. Their study showed that spirocyclic quaternary ammonium have good stability in alkaline condition. To date, there is few work on spirocyclic quaternary ammonium-based AEMs, and to understand the properties of this type of AEMs, a systematic study is needed.

In the present work, *N,N*-diallylpyrrolidinium bromide [DAPy][Br] was synthesized and used as hydrophilic phase in the polymeric membranes. The purity and chemical structure of [DAPy][Br] were confirmed by ¹H NMR measurements. However, poly(*N,N*-diallylpyrrolidinium bromide), the homopolymer of [DAPy][Br], shows poor film forming properties, and it is very soluble in water. Therefore, styrene and acrylonitrile were chose to synthesize the copolymers with [DAPy][Br] due to the ease of processing, good mechanical properties and chemical resistance. A mixture of styrene/acrylonitrile, [DAPy][Br], divinylbenzene and benzoin ethyl ether was stirred to obtain a homogeneous solution. Then, the mixture was casted onto a glass mold irradiation with UV light. The prepared spirocyclic quaternary ammonium-based membranes were immersed in 1 mol/L KOH solution at 60°C for 24 h to convert the anion of membrane from Br⁻ to OH⁻. Then the membranes was immersed in de-ionized water and washed with deionized water until the pH of residual water was neutral.

In summary, a series of spirocyclic quaternary ammonium-based AEMs were successfully designed and prepared via a simple synthetic strategy. The resultant AEMs demonstrated great potential for alkaline anion exchange membrane fuel cell applications based on its good thermal stability, sufficient mechanical properties and high conductivity. The ion exchange capacity can be controlled by change the mixture ratio, and the swelling ratio, water uptake and ion exchange capacity of the spirocyclic quaternary ammonium-based membranes increase with the increasement of the content of [DAPy][Br] in the membranes.

The transparent and mechanically robust spirocyclic quaternary ammonium-based AEMs show high conductivity up to 7.29×10⁻² S/cm at 80°C, and all the membranes showed conductivity up to 1×10⁻² S/cm at room temperature. In addition, all the AEMs synthesize in this work showed excellent long-term alkaline stability at elevated temperature. The spirocyclic quaternary ammonium-based AEMs with an aliphatic backbone exhibit high alkaline stability, which will open up new prospects for the preparation of AEMs with excellent alkaline stability and high conductivity.

***N*-spirocyclic, anion exchange membrane, alkaline stability, fuel cell, Conductivity**

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