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碱性阴离子交换膜的碱稳定性

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摘要 碱性阴离子交换膜(AEMs)是碱性阴离子交换膜燃料电池的核心部件之一, 目前已成为制约碱性阴离子交换膜燃料电池发展的关键因素. 离子传导基团在碱性条件下, 容易受到氢氧根离子的攻击发生降解. 本文主要从以下3个方面介绍了近期AEMs在耐碱稳定性方面的研究成果: (1) 开发稳定的离子传导基团, 并通过提高离子传导基团的电子密度和增大缺电子位置的空间位阻提高离子基团的稳定性; (2) 在离子传导基团与聚合物主链之间引入长烷基侧链; (3) 合成不含醚氧键的聚合物主链, 改善AEMs的耐碱稳定性.

关键词 阴离子交换膜, 燃料电池, 碱稳定性, 离子传导基团, 长侧链, 无醚键主链

聚合物电解质膜燃料电池是一种清洁高效的能源技术, 可作为建筑备用电源、发动机动力电源、便携式电源等, 具有广阔的应用前景[1,2]. 聚合物电解质膜燃料电池可分为质子交换膜燃料电池(PEMFCs)和碱性阴离子交换膜燃料电池(AEMFCs). 与PEMFCs相比, AEMFCs的电极反应动力学更快, 可以使用非贵金属催化剂, 避免了Pt贵金属催化剂的使用, 降低了电池成本[3]. 此外, 碱性条件下, 催化剂的稳定性得到了很大的改善[4]. 因此, AEMFCs受到了越来越多的关注.

阴离子交换膜(AEMs)是碱性阴离子交换膜燃料电池的核心部件之一, 很大程度上决定着电池的性能和寿命[5]. AEMs应具备离子传导率高、碱稳定性好等优点, 以满足燃料电池运行的要求. 近年来, 学者通过对膜材料的改进, 显著提高了AEMs的离子传导率, 已基本达到燃料电池的使用要求[6]. 然而, AEMs在电池中的运行寿命和稳定性仍然存在重大挑战. 美国能源部在2018年资助项目公告中提出的AEMFCs发展要求: 在600 mA/cm^{2}的工作电流密度下, 稳定运行2000 h, 电池电压降幅低于10%[7]. 现有商业化AEMs的稳定性仍不能满足要求, 这主要由于氢氧根离子具有强亲核性, 会进攻膜材料的缺电子基团, 从而导致其降解. 目前, 改进AEMs碱稳定性的研究主要集中在3个方面: 开发稳定的离子传导基团; 优化离子传导基团与聚合物主链的连接方式; 设计碱稳定性好的聚合物主链.

1 开发稳定的离子传导基团

从2001年发展至今, 离子传导基团的研究已经由最初的三甲胺发展到很多种类, 主要包括季铵类[8~14]、咪唑类[15~18]、胍[19~21]、季鏻[22]、季锍[23]、金属络合阳离子[24,25]等. 由于离子传导基团带正电, 在碱性条件下容易受到氢氧根离子的亲核攻击, 发生亲核取代、霍夫曼降解, 或形成叶立德中间体, 诱导

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化学重排. 减少吸电子基团并相应地增加给电子基团, 提高离子传导基团的电子密度, 以及增大缺电子位置的空间位阻, 可降低氢氧根离子的攻击, 从而改善离子传导基团的碱稳定性[16,26,27]. Yan课题组[22]将三(2,4,6-三甲氧基苯基)磷引入聚砜主链, 作为离子传导离团, 制备了季鏻功能化聚砜AEMs. 2,4,6-三甲氧基苯基是强给电子基团, 而且与鏻阳离子共轭, 降低鏻阳离子的正电性; 此外, 2,4,6-三甲氧基苯提供大空间位阻, 降低氢氧根离子对中心磷原子和α-碳原子的进攻, 从而提高了季鏻离子传导离团的碱稳定性. Coates课题组[15]合成了一系列带有不同取代基的咪唑鎓阳离子并测试了其稳定性, 发现咪唑环上的取代基很大程度上改进了咪唑阳离子的稳定性, C2位置的取代可以有效地抑制开环降解, C4, C5位引入甲基或者苯基可进一步提高阳离子的稳定性. Holdcroft课题组[28]研究了在苯并咪唑C2位置接不同取代基对阳离子基团稳定性的影响, 发现C2位置接有间三联苯的苯并咪唑鎓最稳定. 近来, 研究发现环胺作为功能化试剂合成的季铵基团具有更加优异的稳定性. Marino和Kreuer[29]研究了26种含有不同季铵阳离子的模型化合物在强碱性环境(160℃, 6 mol/L NaOH)中的稳定性, 发现环胺构建的季铵基团在所有季铵基团中具有最好的碱稳定性, 半衰期可达到110 h. Jannasch课题组[30]通过戊基侧链将不同环状季铵阳离子连接到聚苯醚主链上, 研究了离子传导基团在AEMs形态下的碱稳定性, 发现哌啶鎓和吡咯烷鎓比较稳定, 在90℃的1 mol/L NaOH中测试16 d不发生降解. 此外他们还发现, 3, 4和5位有取代基对碱稳定性无明显影响, 而2和6位有取代基会降低离子传导基团的碱稳定性. 图1总结了AEMs中常用的阳离子基团的化学结构. 前线轨道理论认为, 最低未占轨道(LUMO)是决定一个体系发生化学反应的关键. AEMs结构中基团的LUMO能量越低, 越容易受到氢氧根离子的攻击而发生降解. 基于密度泛函理论, 计算离子传导基团的LUMO能量, 可辅助选择更稳定的离子传导基团, 从而改善AEMs的碱稳定性. Pan等人[31]在咪唑基团上引入亲水性聚乙二醇低聚物, 提高了离子传导基团的LUMO能量, 改善了以苄基形式连接的咪唑功能化聚砜AEMs的碱稳定性. Yan等人[32]制备了聚醚腈阴离子交换膜, 通过强极性腈基和侧链阳离子基团之间的相互作用, 控制膜的溶胀度, 降低了水合阳离子基团周围的自由体积, 增大了离子基团周围的空间位阻, 从而降低了氢氧根离子对离子基团的攻击, 同时腈基与阳离子基团之间的相互作用也增加了阳离子基团的LUMO能量, 从而显著提高了AEMs的碱稳定性.

2 优化离子传导基团与聚合物主链的连接方式

早期AEMs的研究中, 氢氧根离子传导基团主要是以苄基形式连接到聚合物主链. 在强碱性环境中, 特别是温度在60~80℃时, 苄基不稳定, 容易受到氢氧根离子的亲核攻击, 造成离子交换容量和氢氧根离子传导率的下降. 近年来的研究工作主要是在离子传导基团和聚合物主链之间引入长链, 使离子传导基团远离聚合物主链的苯环. 研究发现: 全烷基、含胺和醚的支链连接结构均具有良好的稳定性, 而含羰基的支链连接结构不稳定. Gao等人[33]通过聚苯醚的酰基化, 再接入1,2-二甲基咪唑离子传导基团, 制备了长烷基链型咪唑鎓化AEMs, 其化学结构如图2(a)所示. 与苄基连接的1,2-二甲基咪唑功能化聚苯醚AEMs相比, 长烷基链连接的AEMs, 其稳定性并没有得到改善, 通过密度泛函理论计算发现: 侧链中所含羰基导致LUMO能量降低, 使其容易受到氢氧根离子的进攻而发生降解. Yan等人[34]通过氯甲基化聚醚醚酮(PEEK)与1-氨基乙基-2,3-二甲基咪唑溴化物的反应, 合成了含有长烷基侧链的咪唑鎓功能化聚醚醚酮((PEEK-AeImBr), 如图2(b)所示. 相比于通过氯甲基化制备的咪唑功能化聚醚醚酮, PEEK-AeImOH膜的碱稳定性得到大幅度提升. Gong等人[35]通过氯甲基化聚砜与合成的含羟基咪唑鎓之间的Williamson醚化反应, 引入了含有醚氧键的柔性烷基侧链, 如图2(c)所示, 烷基侧链的引入改善了AEMs的碱稳定性. Xu课题组[36]采用维蒂希反应在聚苯醚主链上引入了含碳碳双键的柔性长支链, 制备了季铵化聚苯醚AEMs, 如图2(d)所示. 所制备的膜在80℃的6 mol/L NaOH中浸泡240 h, 未发生明显降解. Jannasch课题组[37]通过锂化、接二溴烷基链的方法, 在离子传导基团和主链之间引入烷基支链, 如图2(e)所示, 所制备的含5个碳原子烷基侧链的AEMs在80℃的1 mol/L NaOH溶液中浸泡8 d后未检测到降解. Yan课题组[38]合成咪唑功能化含烷基长侧链的聚芴阴离子交换膜, 如图2(f)所示. 该膜在60℃的1 mol/L

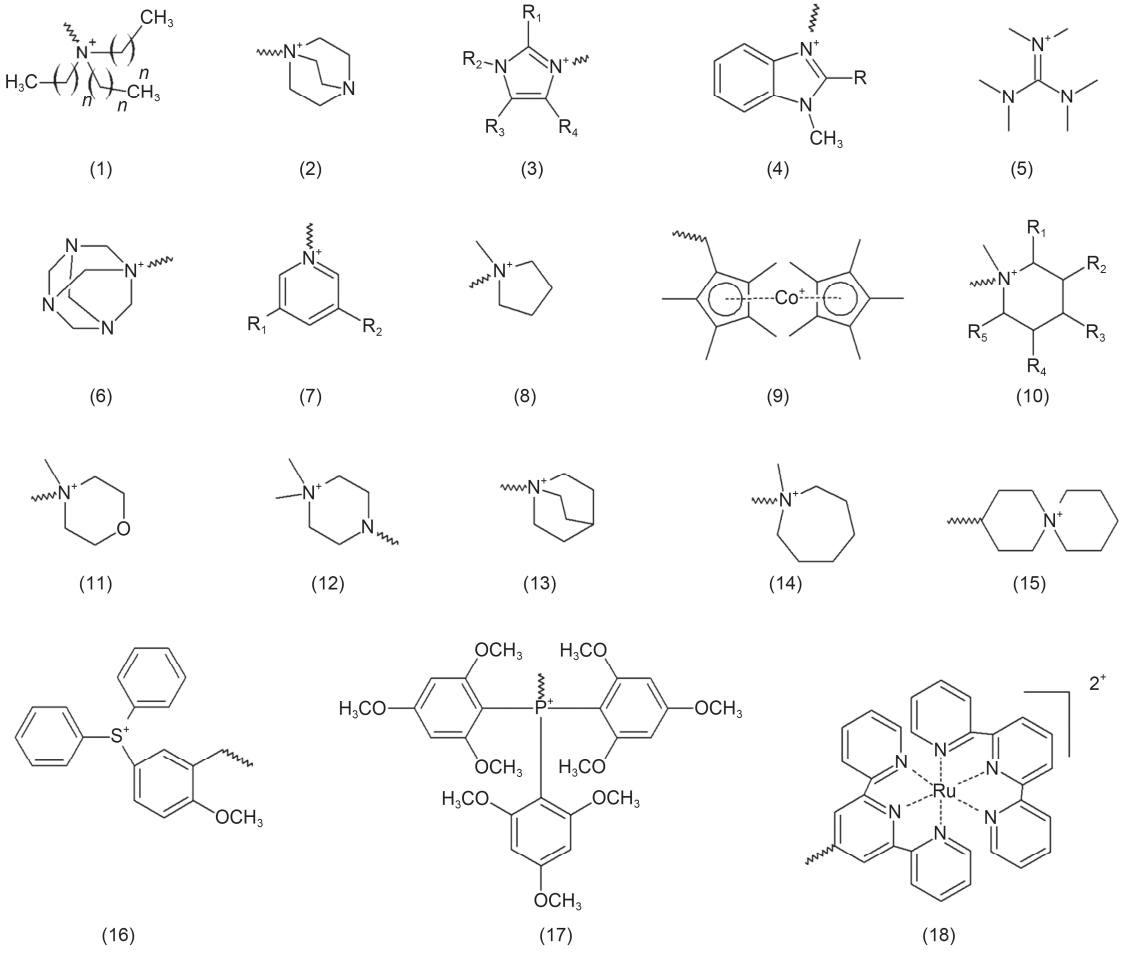


图 1 AEMs的离子传导基团. (1) 三烷基季铵; (2) 1,4-二氮杂双环[2.2.2]辛烷; (3) 咪唑; (4) 苯并咪唑; (5) 胍; (6) 乌洛托品; (7) 吡啶; (8) 吡咯烷; (9) 钴阳离子; (10) 哌啶; (11) 吗啉; (12) 哌嗪; (13) 奎宁; (14) 高哌啶; (15) 螺环季铵; (16) 季锍; (17) 季鏻; (18) 钌阳离子

Figure 1 Functional groups for anion exchange membranes. (1) Quaternary ammonium; (2) DABCO based ammonium; (3) imidazolium; (4) benzimidazolium; (5) guanidium; (6) hexamethylenetetrammonium; (7) pyridinium; (8) pyrrolidinium; (9) permethyl cobaltocenium; (10) piperidinium; (11) morpholinium; (12) piperazinium; (13) quinuclidium; (14) azepanium; (15) 6-azonia-spiro[5.5]undecane based ammonium; (16) methoxy-substituted triarylsulfonium; (17) tris(2,4,6-trimethoxyphenyl) phosphonium; (18) bis(terpyridine)ruthenium(II)

KOH溶液中测试400 h, 其IEC从0.98~0.92 mequiv/g, 显示出优异的化学稳定性. Coates课题组[39]合成咪唑鎓稠合的环辛烯单体并使其开环易位聚合, 获得大环低聚物, 通过交联大环化合物制备了高性能AEMs, 如图2(g)所示. 与以往的咪唑阳离子与主链的连接方式不同, 咪唑基团是通过C4和C5位连接到聚合物主链, 所制备的AEMs在80℃的1 mol/L KOH中测试, 30 d后检测到微小的离子传导率下降(<3 mS/cm). Liu课题组[40]通过将溴代烷基咪唑鎓离子液体接枝到带有酚羟基的聚醚砜主链中, 合成了一系列含有柔性侧链的咪唑鎓阳离子的聚芳醚砜阴离子交换膜, 如图2(h)所示, 在60℃的2 mol/L KOH浸泡504 h, 仍保留了约80%的咪唑鎓基团.

3 设计碱稳定性好的聚合物主链

聚芳醚类具有热稳定性好、机械强度高、易改性等优点, 在AEMs中得到了广泛的研究. 但是随着研究的深入, 学者发现离子传导基团的引入会导致此类主链的稳定性降低, 使其容易受到氢氧根离子的攻击而断链. Kim课题组[41]通过研究苄基三甲基铵(BTMA)功能化的聚芳醚(PAE)和聚苯(PP)的主链稳定性, 发现在强碱性环境中, PAE主链的芳基醚键出现降解, PP主链未降解. PAE主链降解显着降低了膜的机械性能. Ramani课题组[42]研究了碱性环境中, 季铵功能化聚砜AEMs主链的稳定性. 研究发现, 聚砜和氯甲基化聚砜在碱性条件下是稳定的, 但是功能

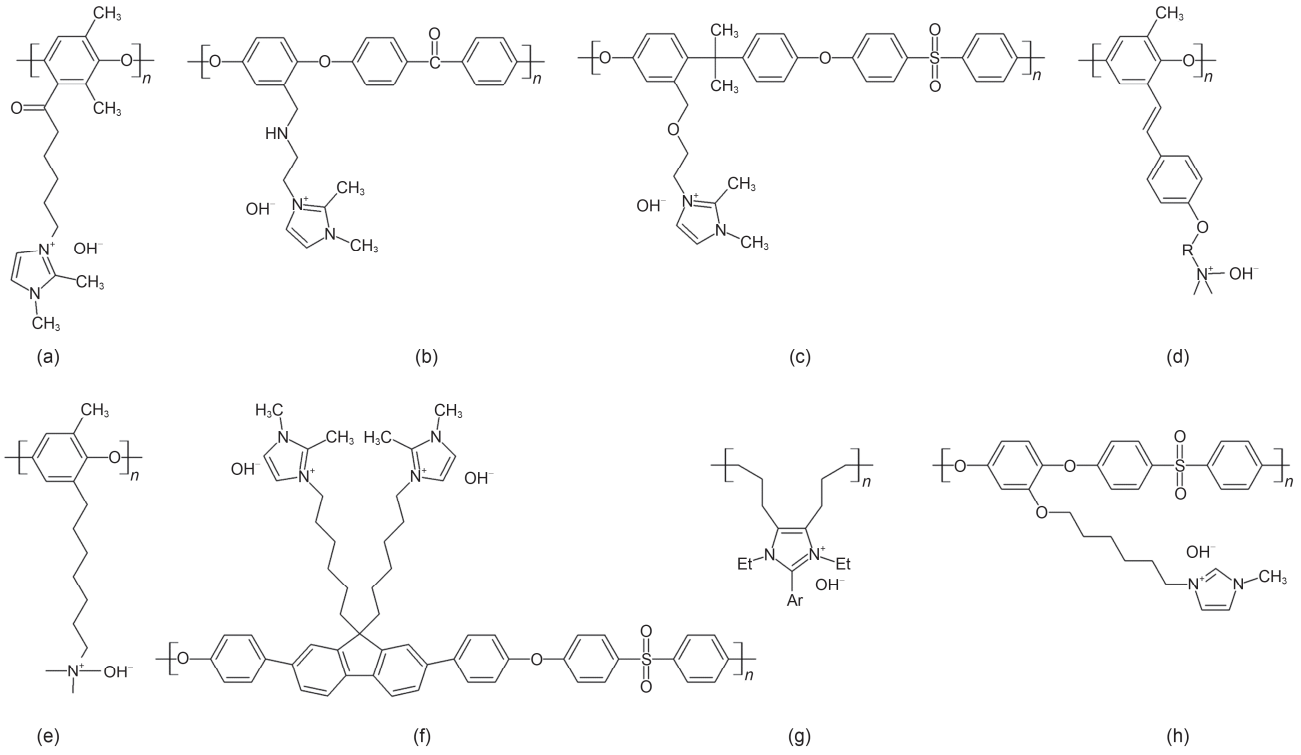


图 2 支链型AEMs的化学结构

Figure 2 Chemical structures of branched AEMs

化以后, 聚砜主链中的烷基碳和醚氧键发生了降解. 这颠覆了离子传导基团的稳定性决定AEMs稳定性的观念, 将主链稳定的重要性带入人们的视野. 典型的AEMs主链(聚芳醚砜)是通过芳香族二卤化物和二羟基单体之间的缩聚反应制备的, 其主链均含有醚氧键. 研究表明醚氧键在强碱性条件下不稳定[42~44], 导致聚合物主链降解, 从而使AEMs的机械性能降低, 严重影响了AEMs的使用. 因此, 选择合适的聚合物主链对碱性阴离子交换膜的耐碱稳定性起至关重要的作用.

制备无醚氧键的聚合物主链是提高主链稳定性的方法之一. Hibbs课题组[45]通过Diels-Alder反应制备了通过六碳烷基侧链连接的季铵功能化聚苯(TMAC6PP)碱性阴离子交换膜, 如图3(a)所示. 该AEMs在90℃的4 mol/L KOH 溶液中浸泡14 d, 氢氧根离子传导率只降低了5%, 离子交换容量几乎没有发生变化, 显示出很好的碱稳定性. Holdcroft课题组[46]制备了聚芳基咪唑鎓聚合物, 其结构如图3(b). 该阳离子聚电解质在C2位位置形成空间保护, 在100℃的10 mol/L KOH溶液中稳定($t_{1/2}$>5000 h). Bae课题组[47]通过酸催化的缩聚反应制备了无芳基醚氧键的季铵化聚联苯亚烷(PBPA), 如图3(c)所示. 该膜氢氧根离子传导率高达120 mS/cm, 在80℃的1 mol/L NaOH 溶液中浸泡30 d未发生降解. 偶联反应是合成无氧主链的有效方法. Bae课题组[48]合成并表征了具有烷基侧链的季铵功能化的含芴基的聚合物, 如图3(d)所示. 该膜80℃离子传导率高于100 mS/cm, 在 80℃下, 1 mol/L NaOH溶液中测试30 d未发生降解. Jannasch课题组[49]通过成环缩合反应, 合成了含有由中心氮阳离子稠合的N-螺环季铵聚合物膜, 如图3(e)所示. 该膜在80℃的1 mol/L KOD溶液中测试超过1800 h未发生降解. Olsson等人[50]还通过Friedel-Craft反应制备的聚三联苯基二甲基哌啶鎓聚合物膜, 如图3(f)所示. 在60℃下, 2 mol/L NaOH溶液中浸泡15 d, 检测不到结构降解. 在90℃下仅有5%降解.

脂肪族主链在碱性环境中的稳定性较好, 因此, 对其进行改性用于制备AEMs, 也成为一个重要的研究方向. Ponce-González等人[51]采用辐射接枝的方法在乙烯-四氟乙烯共聚物(ETFE)上引入功能支链, 制备了具有不同离子传导基团的AEMs, 在80℃的

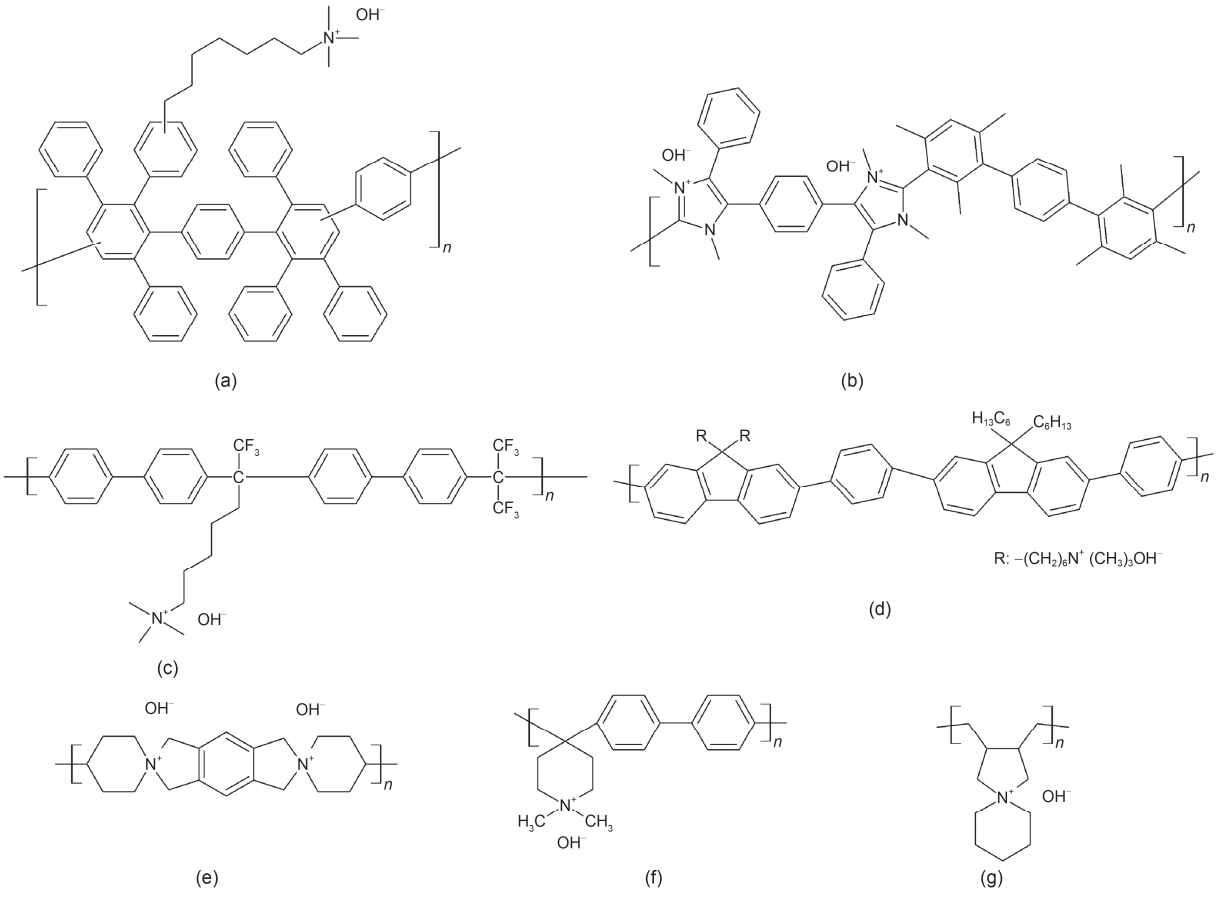


图 3 无氧主链AEMs的化学结构式

Figure 3 Chemical structures of aryl ether-free polymer based AEMs

1 mol/L KOH溶液中测试 28 d, AEMs的IEC有所下降, 但是其ETFE主链却保持了稳定. 聚乙烯主链因其优异的碱稳定性和机械性能, 被认为是理想的AEMs主链[52,53]. Liu等人[54]以全氟磺酸为基材, 引入吗啉作为离子传导基团制备了碱稳定性好的AEMs. 该膜在60℃下的8 mol/L KOH溶液中测试30 d, 仍保有80.1%的离子传导率和85.6%的离子交换容量. Jannasch课题组[55]采用聚烯烃主链制备了聚*N*,*N*-二烯丙基哌啶鎓阴离子交换膜, 如图3(g)所示. 该膜具有很好的碱稳定性, 在120℃的2 mol/L KOD溶液中测试14 d后, 仅有轻微的降解迹象.

4 结论及展望

AEMs在碱性环境中的耐碱稳定性是制约AEMs性能的关键. 研究工作者经过不断积累改进, 对离子传导基团、聚合物主链以及二者连接方式展开了广泛的研究. 目前, AEMs的碱稳定性已取得了令人欣喜的进展. 筛选出三甲胺、五或六元环状胺、取代的咪唑、季鏻等稳定的离子传导基团; 研究出稳定的离子传导基团与聚合物主链的连接方式; 设计出无醚键的芳香族主链以及改性的脂肪族主链. 目前, 所制备的AEMs在强碱性溶液中能够保持数百小时而不发生降解, 这是AEMs在碱稳定性方面的重大突破. 想要制备出如同质子交换膜(Nafion)一样具有代表性的碱性阴离子膜, 仍需要优化膜材料, 使其同时具有高离子传导率和碱稳定性. 在此基础上, 找到简单可控的合成路线, 批量化制备膜材料, 实现工业化. 现有研究中, AEMs的碱稳定性测试方法采用1~10 mol/L的NaOH或KOH溶液, 测试温度和时间也不统一, 因此还需建立标准的膜材料碱稳定性测定方法. 另外, AEMs在燃料电池中实际运行稳定性目前研究较少, 今后的研究中需要重点突破.

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Summary for “碱性阴离子交换膜的碱稳定性”

Alkali stability of anion exchange membrane

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Anion exchange membrane fuel cells (AEMFCs) are attractive alternatives to proton exchange membrane fuel cells due to using non-noble metal catalysts and faster cathode reaction kinetics. Anion exchange membranes (AEMs) are one of the key materials composed of AEMFCs. The hydroxide conductivity of AEMs has been able to meet operating requirements of fuel cells. Although the hydroxide conductivity is no longer a problem, the stability of AEMs is still a notable challenge. This work mainly introduces the development of alkaline stability of AEMs.

AEMs mainly consist of functional groups, side chains and polymer backbones. The degradation of functional groups causes by attacking of hydroxide ion through Hofmann elimination, nucleophilic substitution and ylide-intermediate degradation pathways. Numerous functional groups have been developed in order to improve the alkaline stability of AEMs. The introductions of appropriate electron donors and steric shielding are effective ways to weaken the attack of hydroxide ion. Developing new functional groups is a very important way. In addition, the development of novel stable groups is an important way for long-lived AEMs. For example, hetero-cycloaliphatic quaternary ammonium cations (QAs) are proved to be especially stable in both model compound studies and even AEM studies.

The most commonly studied AEMs were synthesized by chloromethylation/bromination of the aromatic backbones, followed by a Menshutkin reaction to introduce QAs. Benzylic groups, electron-withdrawing groups, are prone to degrade by nucleophilic substitution on the benzylic carbon/α-carbon, Hofmann elimination and N-ylide intermediate formation in the presence of hydroxide ion. Therefore, the tethering linkage between the polymer backbone and functional groups is quite important. Recent studies have mainly introduced long side chains between functional groups and polymer backbones, leaving functional groups away from the benzene ring of the polymer backbone. The all-alkyl, amine- and ether-containing branched-chain structures are proved to be stable.

Poly(arylene ether)s have been extensively studied in AEMs due to the advantages of good thermal stability, high mechanical property and easy modification. Frequently employed polyaromatic electrolytes are quaternized poly(aryl ether sulfone)s, which are prepared via the nucleophilic polycondensation reaction. The introduction of functional groups leads to degrade of these main chains containing aryl ether bonds, which are unable to avoid in the polycondensation reaction. It is necessary that main chains are devoid of aryl ether bonds so as to develop AEMs with excellent alkaline stability. Diels-Alder reaction, coupling reaction and acid-catalyzed Friedel-Craft polycondensation are effective methods for synthesizing aromatic backbones devoid of aryl ether bonds. In addition, aliphatic backbones, such as poly(ethylene-co-tetrafluoroethylene), are proved to have good stability in alkaline conditions, so its modification for AEMs has also become an important research direction.

At present, the alkaline stability of AEMs has made great progress. Three major aspects have been studied in an effort to develop stable AEMs: (1) screening stable functional groups such as five- or six-membered cyclic amines, substituted imidazoles; (2) developing effective linkages between functional groups and polymer backbones; (3) designing aryl ether-free aromatic backbones and stable aliphatic backbones. The designed AEMs can remain for hundreds of hours without degradation in alkaline solution, which is a significant advancement in increasing alkaline stability of AEMs.

anion exchange membrane, fuel cell, alkaline stability, functional group, long side chain, backbone without ether bond

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