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评 述

燃料电池聚合物电解质膜的研究进展

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摘要 本文根据聚合物电解质膜燃料电池操作温度、使用的电解质和燃料的不同, 将其分为高温质子交换膜燃料电池、低温质子换膜燃料电池、直接甲醇燃料电池和阴离子交换膜燃料电池, 综述了它们所用电解质膜的最新进展. 第一部分简要介绍了这 4 种燃料电池的优点和不足. 第二部分首先介绍了 Nafion 膜的结构模型, 并对平行柱状纳米水通道模型在介观尺度上进行了修正; 接着分别对应用于不同燃料电池的改性膜的改性思路作了分析; 最后讨论了用于不同燃料电池的新型质子交换膜的研究, 同时列举了性能突出的改性膜和新型质子交换膜. 第三部分介绍了阴离子交换膜的研究现状. 第四部分对未来聚合物电解质膜的研究作了展望.

关键词
聚合物电解质膜
燃料电池
研究进展

1 引言

燃料电池是一种不经过燃烧, 直接以电化学反应方式将燃料和氧化剂中的化学能转变为电能的发电装置. 聚合物电解质膜燃料电池是燃料电池的一种, 作为有着广阔应用前景的新能源技术而备受关注. 除了具有其他燃料电池的优点外, 它还具有常温下快速起动、结构简单紧凑、可靠性高等特点.

根据运行温度、使用燃料和聚合物电解质膜的不同, 聚合物电解质膜燃料电池可以分为高温质子交换膜燃料电池(high temperature proton exchange membrane fuel cell, HT-PEMFC)、低温质子换膜燃料电池(low temperature proton exchange membrane fuel cell, LT-PEMFC)、直接甲醇燃料电池(direct methanol fuel cell, DMFC)和阴离子交换膜燃料电池(anion exchange membrane fuel cell, AEMFC). 除了 AEMFC 使用碱性阴离子交换膜(AEM)外, 其余使用的都是酸性质子交换膜(PEM). 这 4 种聚合物电解质膜燃料电池的特性比较见表 1.

2 质子交换膜

质子交换膜是以含酸性基团(如磺酸、磷酸和羧酸基团等, 其中以磺酸基团为主)的高分子为材料的固体电解质膜, 在燃料电池中起到分隔燃料和氧化剂、传导质子和绝缘电子的作用(图 1 和图 2).

理想的 PEM 通常应当满足以下条件: ①良好的质子传导率, 以降低电池内阻并提高电流密度; ②燃料渗透性低, 能有效阻隔燃料和氧化剂, 避免二者在电极表面直接反应, 造成电池局部过热, 影响电池的库仑效率; ③较好的化学和电化学稳定性, 在氧化/还原、酸性和自由基作用下不降解, 以保证电池的工作寿命; ④出色的机械性能和热性能, 可以承受电池加工和运行中机械和热量冲击; ⑤优异的形貌和水稳定性, 有利于 PEM 吸收充足的水分而不过度溶胀, 进而使水和质子在膜内可快速迁移, 避免膜局部缺水或浓度梯度过大; ⑥干-湿转换的可逆性要好, 否则容易引起 PEM 的局部应力增大或变形; ⑦膜的表面适于和催化剂结合制备膜电极(membrane electrode

表 1　四种聚合物电解质膜燃料电池的比较

Parameters	LT-PEMFC	HT-PEMFC	DMFC	AEMFC
Electrolyte	PEM	PEM	PEM	AEM
Operating temperature (°C)	60–80	120–180	60–80	<60
Charge carrier	H^+	H^+	H^+	OH^-
Fuel	H_2	H_2	CH_3OH	H_2
Oxidant	O_2	O_2	O_2	O_2
Relative humidity (%)	100	25–50	100	100
Advantages	high power density; quick start up; low noise; low temperature operation	reduced parasitic loads and system; faster electrode kinetics; improved tolerance to CO impurities; higher efficiency of heat recovery	liquid fuel; compact design; no compressor or humidification	less corrosive alkaline environment; potentially simplified water management; faster kinetics of oxygen reduction reaction; non-precious metal catalysts
Drawbacks	insufficient proton conductivity under low humidity conditions; complex and expensive heat and water management system; expensive pt catalysts and their poor performance; sensitive to CO impurities	low water retention; harsher operating environment	low efficiency and power density; high fuel permeability; catalyst poisoning; slow load response times	inherently high thermodynamic voltage loss; low-performance AEMs; relatively low mobility of OH^-; unaccommodated binder for MEA

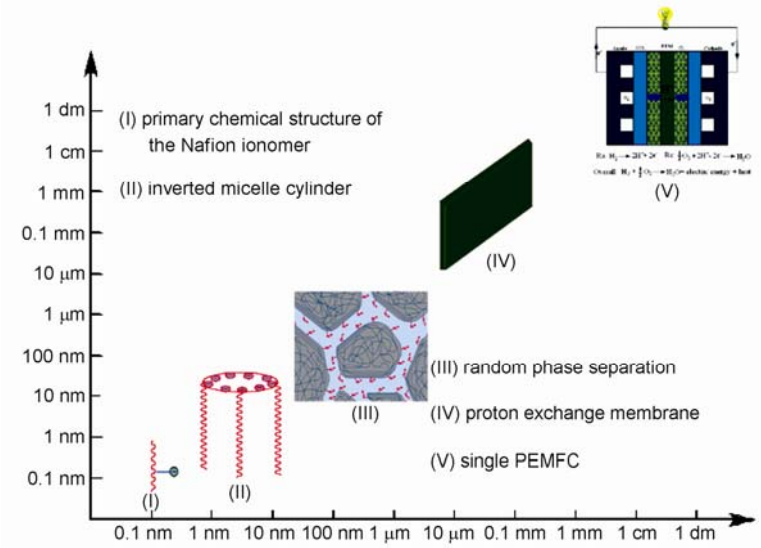

图 1　PEMFC 中尺寸演化示意图

assembly, MEA); ⑧具有竞争力的低价格.

目前广泛使用的质子交换膜是以 Du Pont 公司生产的 Nafion 系列膜(图 3)为代表的全氟磺酸膜(包括 Nafion, Hyflon Ion, Dow, Flemion, Aciplex-S 和 3 M 等). 从分子水平上看, Nafion 膜材料的结构是憎水的聚四氟乙烯(PTFE)骨架上通过醚键连接着末端带亲水磺酸基的全氟支链. Nafion 膜吸水后, 膜内形成亲水/憎水两相, 其中憎水相为其提供强度、稳定性等物理性能, 以保证膜形貌和尺寸的稳定性; 亲水相则为质子迁移提供连续的传输通道. 这种独特的纳米相分离结构赋予了 Nafion 膜出色的机械性能、优异的电化学稳定性、适宜温度下充分润湿时的高质子传导率、良好的热稳定性和化学稳定性[1].

2.1　Nafion 的结构模型

恰当的结构模型有利于深入理解材料形貌结构

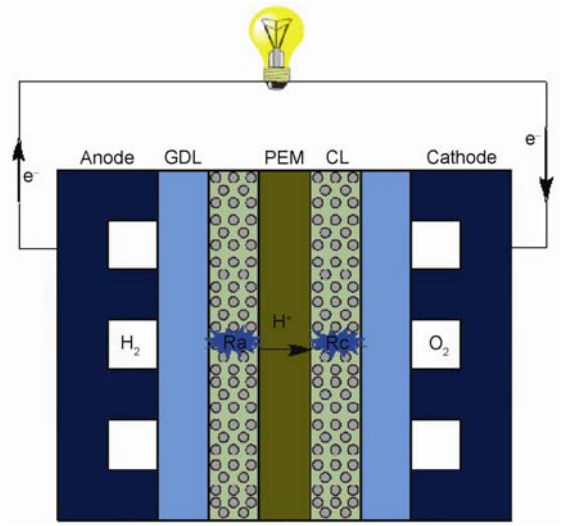

图 2 PEMFC 结构及原理示意图

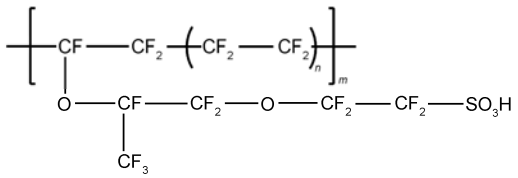

图 3 Nafion 的化学结构式

与性能间的复杂关系, 将分子结构和宏观性能有机联系起来. 研究人员基于小角和广角 X-射线散射、中子散射、红外和拉曼光谱、时变傅立叶变换红外光谱、核磁共振谱、电子显微镜、正电子湮没谱、扫描探针显微镜和扫描电化学显微镜等实验所获得的信息, 提出了各种各样的 Nafion 膜结构模型, 如簇-网络模型[2]、局部有序模型[3]、壳-核模型[4]、层状模型[5]、狭长聚合物束模型[6,7]、三明治结构模型[8]和三相区模型[9]. 这些结构模型大多是在簇-网络模型(图 4)的基础上发展而来, 该模型认为反胶束结构的球状离子簇(直径 3~5 nm) 通过狭窄水通道(直径 1 nm)相互连接, 并被包埋于半晶、憎水的氟碳链中. 不过簇-网络模型存在着很大的局限, 首先, 模型中反胶束结构的球状离子簇可被实验证实, 而狭窄水通道并没有直接的实验证据支持; 其次, 1 nm 宽的水通道过于狭窄, 其间的水分子与通道内表面磺酸基的作用将使得质子传导率很难达到本体水的水平, 这显然与实验现象不符[10, 11]; 最后, 也是最重要的一点, 包括簇-网络模型在内的上面各模型的 SAXS 模拟曲线与 Nafion 膜的 SAXS 实验数据并不能很好地吻合[12].

平行柱状纳米水通道模型(图 5)[12]则很好地解决了这些问题, 在这一模型中, 水通道由 Nafion 的侧链包围、聚四氟乙烯分子支撑, 形成了长柱状的反胶束, 这些反胶束柱在微观尺度上相互平行, 互不相连. 含水量为 20 vol%的 Nafion 膜中, 反胶束柱的直径为 1.8~3.5 nm, 平均直径为 2.4 nm, 为质子迁移提供通道. 此外, 模型中还考虑到了 Nafion 微晶, 这些平均截面为 5 nm^2 的狭长微晶平行于反胶束柱, 总量约为 10 vol%, 嵌在膜内形成物理交联, 为 Nafion 膜提供良好的机械性能. 平行柱状纳米水通道模型不仅 SAXS 模拟曲线与 SAXS 的实验数据十分吻合, 还能有效地解释 Nafion 膜的快速水扩散和质子迁移等现象.

美中不足的是这一模型对介观尺度(>20 nm)上的结构没有给予足够的考虑, 因为在介观和宏观尺度上反胶束柱肯定会出现分岔或合并, 此时需要对

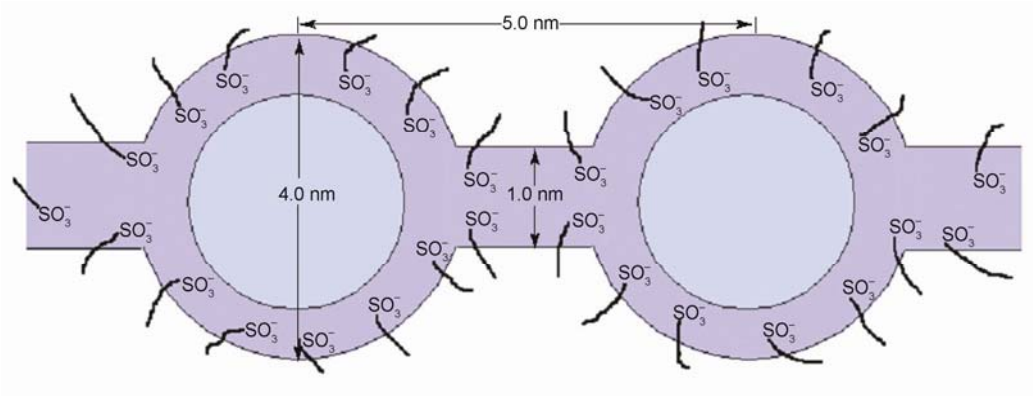

图 4 Nafion 膜的簇-网络模型[2]

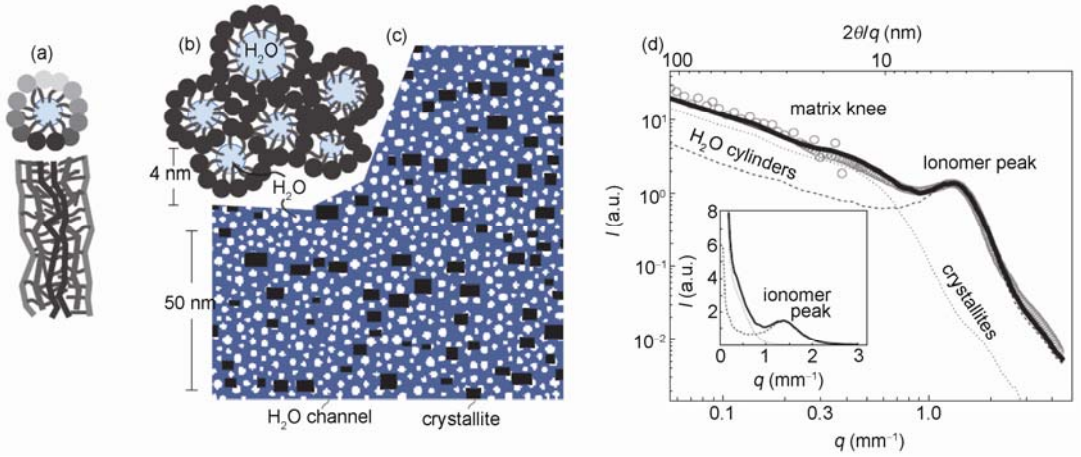

图 5　Nafion 膜的平行柱状纳米水通道模型[12]. (a) 反胶束柱的断面和侧面透视; (b) 反胶束柱的的团聚; (c) 该模型的断面, 水通道(白色), Nafion 微晶(黑色)和无定形 Nafion(蓝色); (d) 平行柱状纳米水通道模型的 SAXS 模拟曲线与小角 X-射线散射的实验数据的对照

该模型进行必要的修正.

在介观和宏观尺度上, 反胶束柱团聚体中每个反胶束柱都可能会发生弯曲或分岔(每个反胶束柱发生弯曲或分岔的位置未必相同), 然后分别与另外的反胶束柱团聚体中的反胶束柱合并或组成新的平行反胶束柱团聚. 图 6 是介观尺度上 Nafion 膜的平行柱状纳米水通道模型, 其中为了表示方便, 反胶束柱团聚体在图中被简化为单一的反胶束柱, 青色代表反胶束柱中吸收的水分, 灰色代表憎水相, 与水通道平行的链代表 Nafion 微晶.

根据 Nafion 膜的平行柱状纳米水通道模型, Nafion 膜从干态到完全溶胀过程中介观结构和微观结构的变化分别如图 7 和图 8 所示. 水在 Nafion 膜中起着至关重要的作用, 不仅决定着膜内可以获得的质子载体数; 还参与膜形貌的形成, 决定着膜内迁移通道的连通性. 它在膜内有 3 种存在状态: 强键合水、弱键合水和自由水, 据此可以将饱和吸水的 Nafion 膜亲水区分为强键合水区、弱键合水区和自由水区, 其中弱键合水区质子传导以结构扩散机理(structural diffusion or Grotthus mechanism)为主, 而自由水区质子传导则以运输扩散机理(vehicle diffusion mechanism)为主, 甲醇主要也是通过此区渗透.

2.1.1　介观尺度(图 7)

当 Nafion 膜为干态时, 膜内仍然存在柱状纳米通道, 只是直径较完全溶胀时有所减小, 此时膜不传导质子; 当有少量吸水时, 水分子分散地吸附在 Nafion 膜中柱状纳米通道的内表面, 彼此间距离较大, 不能形成有效的质子通道; 随着吸水量的增加, 当达到逾渗阈时, 水分子在柱状纳米通道内表面上形成了部分的质子通道, Nafion 膜开始传导质子; 继续增加吸水, 当柱状纳米通道全部被水充满, 不能再容纳更多的水时, 宏观上 Nafion 膜开始发生明显的溶胀, 膜内则发生结构重组, 开始建立连续的质子传输网络, 膜的质子传导率显著增加; 当 Nafion 膜达到完全溶胀时, 膜内形成了完善的质子传输网络, 质子传导能力进一步得到增强.

2.1.2　微观尺度(图 8)

在 Nafion 膜未吸水时, 磺酸根存在于柱状纳米通道内, 没有质子传导能力; 当有少量吸水时, 水分子主要以强键合水存在于磺酸根周围, 且相互间处于分离状态, 仍不能传导质子; 随着吸水量达到逾渗阈, 少量的质子通道被建立, Nafion 膜开始传导质子, 不过质子传导率相当低, 因为大部分的水分子仍都存在于磺酸根的第一水合壳层内, 其中的每个水分子都受到多个磺酸根形成的离子笼的约束, 少量的自由水与质子结合成水合质子通过运输扩散机理从一个磺酸根迁移到邻近的磺酸根[13~15]; 当 Nafion 膜内发生重组以后, 弱键合水的增加使得建立 $H_9O_4^+$-$H_5O_2^+$-$H_9O_4^+$传导链以结构扩散机理传输质子成为可能[16], 不过此时仍以运输扩散机理为主; 在 Nafion 膜达到完全溶胀的过程中, 随着 Nafion 膜的不断溶

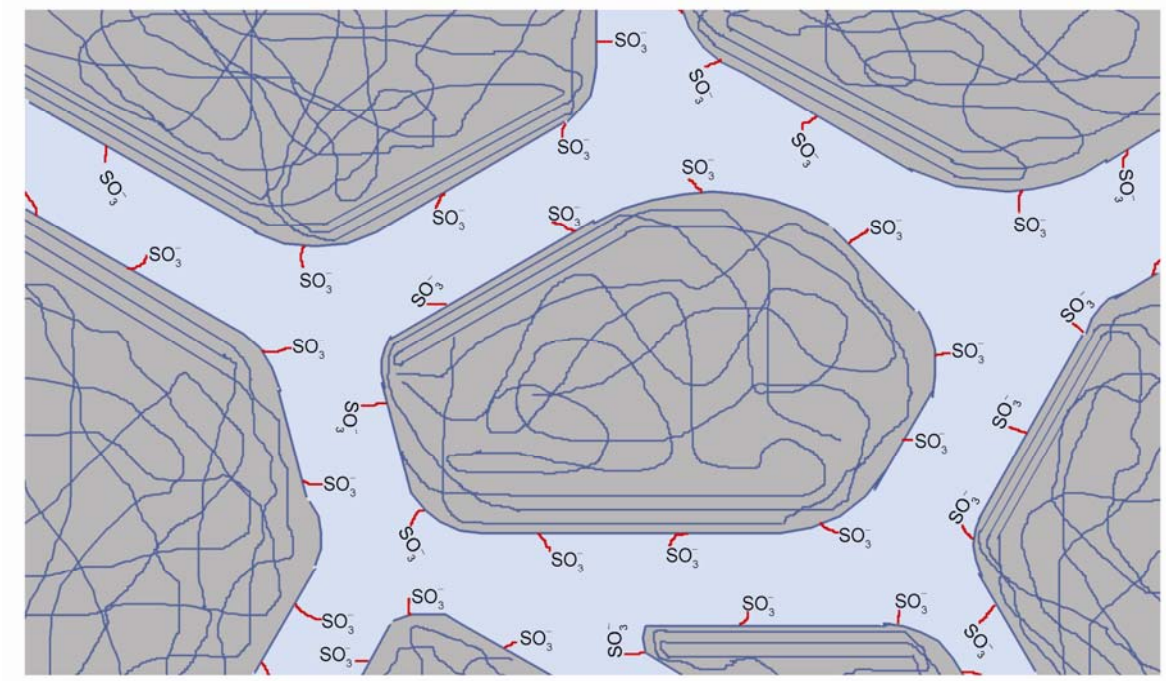

图 6 介观尺度上 Nafion 膜的平行柱状纳米水通道模型

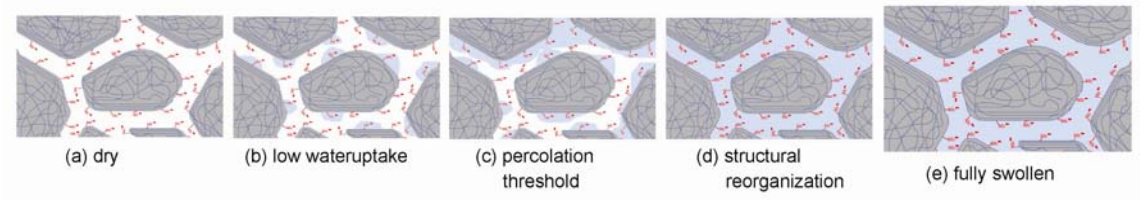

图 7 介观尺度上 Nafion 膜结构随水含量的变化

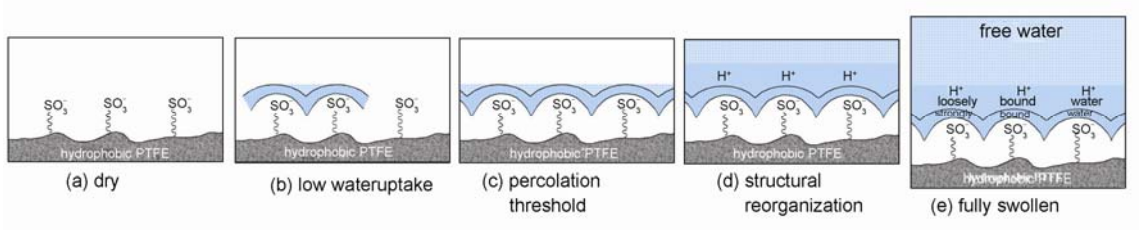

图 8 分子水平上 Nafion 膜从干态到完全溶胀状态结构的变化

胀, 膜内柱状纳米通道的直径逐渐增加, 结构扩散机理也逐步地取得了主导地位, 最终以运输扩散机理迁移的质子在质子传导中只占到 1/5 左右[13].

2.2 改性 PEM

Solvay 公司生产的 Hyflon Ion 膜分子结构与 Nafion 膜相似, 只是 Hyflon Ion 膜分子链中支链较短, 故也被称为短支链全氟磺酸膜. 与分子量相近的 Nafion 膜相比, Hyflon Ion 膜有更高的磺酸基含量, 即它的离子交换容量(IEC)更高, 从而使其质子传导率要高于 Nafion 膜; Hyflon Ion 膜的结晶度也因为分子链排列更规整而增加, 结晶度的增加进一步导致了 Hyflon Ion 膜更高的机械强度和玻璃化转变温度(~160 ℃), 使得它有可能用于 HT-PEMFC[17, 18]. 不

过文献中使用短支链全氟磺酸膜的报道非常少见, 仍都是以 Nafion 膜为主. 但是 Nafion 系列膜存在着诸如价格高、甲醇渗透严重和耐温性能差(玻璃化转变温度低)等不足, 这限制了其在 PEMFC 和 DMFC 中的应用, 也在一定程度上阻碍了 PEMFC 的大规模商品化. 为了解决这些问题, 两种方案被广为采用, 一是对现有的 PEM 材料进行改性, 增加耐温性能或阻甲醇性能; 另一个是开发新型 PEM 材料.

改性 PEM 材料主要包括 Nafion 膜或树脂和商品非氟聚合物(如聚醚醚酮(PEEK)[19~42]、二氮杂萘酮结构的聚芳醚[43]和聚醚砜(PES)[44~46]等)的磺化产物以及少量新合成的磺化非氟聚合物[47~56].

2.2.1 用于 HT-PEMFC 的改性膜

HT-PEMFC 的运行温度还可分为 100~120 ℃和 160~180 ℃. 其中 100~120 ℃运行的 HT-PEMFC 的潜在应用对象是电动汽车, 表 2 列出了美国能源部(U.S. DOE)对这类 PEM 的技术要求.

用于 HT-PEMFC 的改性膜的改性思路比较简单, 就是通过掺杂亲水的或(和)导质子的无机粒子制备复合膜, 增强其在高温条件下的保水性或(和)降低质子传导对水含量的依赖. 复合膜制备方法主要包括模板法和溶胶-凝胶法, 前者不改变 PEM 的原有结构, 后者无机粒子则参与复合膜结构的形成, 需要改善无机粒子和聚合物分子链间的相容性, 避免相界面间孔腔的生成.

通常使用的亲水的无机粒子包括纳米氧化铪(HfO_2)和氧化钽[58~60]、纳米二氧化硅(SiO_2)和介孔 SiO_2[61~65]、纳米二氧化钛(TiO_2) [66]、介孔 TiO_2 和 TiO_2 纳米管[67~71]、氧化锆[72]、水合氧化锌[73]、沸石[74]、和粘土[75, 76]等. 小于 5 nm 的固体粒子可以在分子水平上改变膜的结构; 而 10 nm 左右的固体粒子则可以起到填充自由体积和稳定有机基体的作用[40]. 固体粒子的形貌对复合膜的性能也有重要影响, 具有规则结构和孔通道的固体粒子比无规的固体粒子更有效地促进复合膜的水吸收, 改善复合膜的保水能力[51]. 对于固体粒子均匀分散的复合膜, 这些粒子在复合膜亲水通道内起到保水或提供额外质子迁移通道的作用, 使得复合膜质子传导率仅略有减小或增强.

HfO_2 含量为 5 wt%的 Nafion 复合膜在 125 ℃和 100%相对湿度(RH)下, 质子传导率仍可达 3.2×10^{-2} S cm^{-1} [60]; 通过 Nafion 和 SiO_2 纳米粒子自组装技术制备的 Nafion 复合膜在 100 ℃运行的 PEMFC 中的测试显示, 电池性能和寿命都有了明显提高, 电压衰减速率为 0.12 mV min^{-1}, 几乎比同等条件下的 Nafion112 膜低 20 倍[62]; 含 3 wt%介孔 TiO_2 的 Nafion 复合膜用于氢氧 PEMFC, 在 120 ℃和 50% RH 条件下运行, 0.4 V 时的功率密度是 669 mW cm^{-2}, 此值为 Nafion 重铸膜的 5.7 倍高[67]. 这些都表明在改性膜中添加亲水的无机粒子有助于复合膜在高温下保持较高质子传导率, 进而改善 PEMFC 的性能.

表 2 美国能源部关于高温低湿操作的 PEM 的技术标准[57]

Characteristic	Units	2015 Target
Operating temperature	℃	⩽120
Inlet water vapor partial pressure	kPa	⩽1.5
Membrane conductivity at inlet water vapor partial pressure		
Operating temperature	S cm^{-1}	0.10
Room temperature	S cm^{-1}	0.07
−20 ℃	S cm^{-1}	0.01
Oxygen crossover[a)]	mA cm^{-2}	2
Hydrogen crossover [a)]	mA cm^{-2}	2
Area specific resistance	Ωcm^2	0.02
Cost [b)]	\$$cm^{-2}$	20
Durability with cycling		
At operating temperature ⩽80 ℃	h	5000 [c)]
At operating temperature >80 ℃	h	5000 [c)]
Unassisted start from	℃	−40
Thermal cyclability in presence of condensed water		Yes

a) 标称电堆工作温度下, 在 1 atm 的 O_2 或 H_2 的 MEA 中测试; b) 基于 2002 年的美元购买力的大批量生产测算的价格(每年 500000 个电堆); c) 基于适当的测试方法(待开发)

亲水无机粒子被酸性基团修饰后兼具亲水和传导质子的特性, 应用于改性膜后常常带来更佳的效果. 例如, 含磺酸基团的介孔 SiO_2 与 Nafion 制备的复合膜 95 ℃和 90% RH 时的质子传导率比 Nafion112 膜的高 5 倍以上[77]. Okamoto 等合成了一种侧链型磺化聚酰亚胺(SPI), 然后与 IEC 为 2.3 meq g^{-1} 的介孔 SiO_2 (Si-MCM-41)一起制得 SPI 复合膜, 因为磺酸功能化的 Si-MCM-41 具有良好的保水能力, 其含量为 20 wt%的 SPI 复合膜在高温低湿条件仍具有优异的性能. 相应的 PEMFC 在 110 ℃和 33% RH 条件下最大功率密度为 640 mW cm^{-2}, 比 Nafion 膜高 110 mW cm^{-2} [78].

无机质子导体则是以磷酸氢锆(ZrP)为主[79~83], ZrP 含量为 20 wt.%的 Nafion 复合膜质子传导率在 100 ℃和 30%~90% RH 的范围内一直低于 Nafion 膜, 不过复合膜稳定传导质子的温度范围却比 Nafion 膜高 20 ℃[81], 因为 ZrP 的存在提高了复合膜的耐温性能, 避免其发生高温变形. 若 ZrP 中部分的磷酸基被磺化苯膦酸基取代后再与 Nafion 掺杂, 则复合膜的质子传导率可达到 Nafion 膜的水平, 同时其稳定传导质子的温度范围仍与 Nafion/ZrP 相当[84].

虽然杂多酸也是很好的无机质子导体, 但由于杂多酸在复合膜内存在随 PEMFC 生成水流失的问题, 因而很少在改性膜中直接使用. 一般先用铯离子部分取代杂多酸中的质子形成不溶于水的杂多酸盐(如 $Cs_{2.5}H_{0.5}PWO_{40}$), 然后再用于掺杂[85, 86].

此外还有掺杂磷酸、离子液体、咪唑和三唑等的报道[87~97], 但这几种非水的导质子介质易于随反应生成的水流失的问题仍有待解决.

160~180 ℃运行的 HT-PEMFC 是燃料电池的未来发展方向之一, 此温度范围内使用的 PEM 仍然以聚苯并咪唑(PBI)膜掺杂磷酸体系为主[98~103], 因为它们的 HT-PEMFC 可以产生更高的功率密度, 如 Kongstein 使用改进的电极和 PBI/H_3PO_4 膜, 常压供气的 H_2/O_2(干态)PEMFC 在 175 ℃和 0.4 V 条件下最大功率密度达到 830 mW cm^{-2} [103], PBI/H_3PO_4 体系的研究现状已经被详细地综述[104, 105]. 研究人员在膜材料和掺杂介质等方面也做了新的探索[106~109]. Li 等在 PBI 中掺杂少量杂多酸盐($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$)后再吸收 H_3PO_4, 其质子传导率在 160 ℃和 8.4% RH 下为 0.15 S cm^{-1}; 常压干态 H_2/O_2 供气的 PEMFC 最大功率密度 150 ℃为 700 mW cm^{-2}, 比未掺杂 $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ 的 PBI/H_3PO_4 膜提高近 300 mW cm^{-2} [106]. Kallitsis 合成了含吡啶基的聚芳醚, 掺杂 H_3PO_4 后可以获得较好质子传导率; 用于干态 H_2/空气 PEMFC 中, 在 180 ℃的性能与 PBI/H_3PO_4 膜相当, 并且至少可稳定运行 2000 h, 电压衰减速率为 4 μV h^{-1} [107]. Lin 等制备了含质子型离子液体的杂化膜, 160 ℃无水质子传导率为 1×10^{-2} S cm^{-1}, 不过经水洗后, 仅能保留约 20 wt.%的离子液体, 160 ℃无水质子传导率下降为 10^{-4} S cm^{-1} [108]. 由于这些新体系的性能都要比 PBI/H_3PO_4 体系的差[108, 109], H_3PO_4 依旧是用于 160~180 ℃的 PEM 必不可少的导质子介质, 故而 H_3PO_4 随生成水流失的风险依然存在, 仍是亟待解决的一个问题.

2.2.2 用于 LT-PEMFC 和 DMFC 的改性膜

LT-PEMFC 和 DMFC 的结构基本相似, 除了在使用的燃料上有所不同外, 对改性膜的要求也各有侧重. 前者强调降低膜对水的依赖, 进而简化水管理; 后者则强调阻甲醇渗透能力的改善, 从而提高燃料利用率和 DMFC 的性能. 不过这两种用途的改性膜之间的分界并不严格, 用于 LT-PEMFC 的改性膜中的无机粒子同样可以起到阻甲醇渗透的作用, 而用于 DMFC 的改性膜中的亲水粒子不仅可以减弱膜对外部润湿的依赖, 还可以对气体渗透起到抑制作用.

用于 LT-PEMFC 的改性膜主要改性思路是赋予其自润湿特性, 以减少气体增湿装置. 具体地就是通过添加亲水的粒子, 如 SiO_2 粒子[110]、SiO_2 粒子支撑的硫酸化二氧化锆(SiO_2-SZ) [111]、载有铂(Pt)纳米颗粒的沸石[112]、酸功能化的多壁碳纳米管[113~115]、蒙脱土[116]和磺化碳球[117]等, 使 Nafion 复合膜在干态进气条件仍能保持足够的润湿, 从而保证 LT-PEMFC 的性能. Bi 等制备的 Naifon/SiO_2-SZ 复合膜用于干态 H_2 和 O_2 进气的 LT-PEMFC, 60 ℃时的最高功率密度达 980 mW cm^{-2}, 比 Nafion 重铸膜的 640 mW cm^{-2} 增加 50%以上[111]. Zhao 等先制得磺酸修饰 SiO_2 粒子与二氧化锰(MnO_2) 催化剂粒子的多功能纳米混合物, 再与 Nafion 一起制备复合膜. 由于 MnO_2 作为变价金属氧化物易于在三价锰和四价锰间进行可逆氧化还原反应, 这使得通过分解 H_2O_2 来淬灭自由基在热力学成为可能. 原位氟排放速率测试表明, 这种 Nafion 复合膜的氟放出速率约为 Nafion 膜的 1/10, 有效地延长了 Nafion 改性膜的寿命; 而由于磺酸修饰 SiO_2 粒子的存在, 复合膜的 LT-PEMFC 性能

仅略低于未改性 Nafion 膜[118].

用于 DMFC 的改性膜的改性思路则较多, 包括:

①在 PEM 表面形成异质的阻甲醇层, 这些阻甲醇层可以是通过 PEM 在庚烷气氛中用氩等离子体处理形成的氟碳层[119~121]和溅射形成钯或其合金纳米层[122], 也可以是 PEM 表面磺酸基通过化学方法转化后形成的羧酸基层[123]和单体聚合形成的纳米层[124~126], 还可以是层层自组装(LBL)形成的自组装层等[127~130]. 其中钯或其合金纳米层因为与 PEM 膜间溶胀的差异, 导致阻甲醇层出现很多裂隙, 减弱了其阻甲醇效果; 氟碳层和羧酸基层在减少了甲醇透过的同时伴随着质子传导率的明显下降; 聚合纳米层和自组装层在有效降低甲醇渗透的同时, 对质子传导率影响较小, 如 Zhao 等用 LBL 法在含羧基侧链的磺化聚芳醚酮(SPAEK-COOH)膜表面沉积了最大厚度为 2 μm 的壳聚糖/磷钨酸阻甲醇层, 80 ℃的溶胀从 60%以上降至不足 20%, 改善了其尺寸稳定性; β 值更是有了极大增长, 比 Nafion117 膜高两个数量级[131].

Li 等用高 IEC 的含悬垂磺酸的聚芳醚酮(SPAEK)和低 IEC 的磺化聚芳醚砜(SPAES)制备了 SPAEK/SPAES/SPAEK 三明治结构的阻甲醇膜, 该膜总的厚度为 60 μm, 其中 SPAES 层厚 15 μm[132]. 它的 DMFC (1 M CH_3OH/O_2) 功率密度在 80 ℃时达到 140 mW cm^{-2}, 比 Nafion 115 膜提高 58 mW cm^{-2}.

②在改性膜的亲水通道中引用有机[133~135]、无机或金属粒子[136~144], 通过增加通道曲折度和缩小通道尺寸, 达到降低甲醇渗透的目的. 有机粒子如聚乙烯基咪唑(PVI)[133]、聚对苯乙炔(PPV)[134]和聚酰胺树脂[135]的引入主要是通过原位聚合完成, 这些有机粒子对 DMFC 性能的改善有限. 在所使用的无机粒子中, 如 SiO_2 粒子[137]、沸石粒子[138]、氢氧化锶[139]、蒙脱土[140, 141] $Cs_{2.5}H_{0.5}PWO_{40}$ 粒子[142]、富勒烯[143]和 ZrP 粒子[144]等, 高长宽比的鳞片状 ZrP 对 DMFC 性能的改进最为显著, 这种 Nafion/ZrP 复合膜的选择性 β 达到 Nafion 膜的 7 倍左右[144].

Lin 等将 3-缩水甘油丙基三甲氧基硅烷(KH-560)接枝到 SPAEK-COOH 并成膜, 然后通过水解-缩聚制得含 Si–O–Si 交联结构的有机-无机复合膜[52]. 这种复合膜展示了增强的机械性能和抗自由基氧化稳定性, 可在 3%的 H_2O_2 溶液中 60 ℃保持 168 h 而不破裂. 80 ℃和 100% RH 下的最高质子传导率达 0.155 S cm^{-1}, 常温甲醇透过率仅为 Nafion 的 1/10, β 值是 Nafion 的 5 倍以上. Lee 等将 SPAES 与 SiO_2 粒子混合成膜后, 又经过了 30 min 的表面氟化处理将表面 20%左右的 C-H 键转化为了 C–F 键, 获得了高尺寸稳定性和低甲醇透过的复合膜. 其 DMFC 运行 1400 h 的电势损失比未氟化的复合膜明显减少; 90 ℃时 DMFC(1 M CH_3OH/O_2)功率密度峰值为 190 mW cm^{-2}, 为 Nafion 117 膜的 3 倍多[56].

③通过交联, 抑制改性膜的溶胀, 降低自由水含量, 缩小自由水通道尺寸, 从而减少甲醇渗透. 交联的改性膜内有多种相互作用(图 9)[145], 但最受关注的则是离子交联(静电作用)和共价交联(化学键作用). 离子交联可以在分别带有酸性和碱性基团的两种聚合物的混合膜内形成[146~152], 也可以在同时带有酸性和碱性基团的酸-碱聚合物膜内形成[153~161]. 不过这种离子交联容易受温度影响, 在 70~90 ℃以上常会遭到破坏, 导致膜过度吸水和溶胀. 共价交联则稳定得多, 不易受到温度影响.

共价交联可以仅通过适当后处理实现(图 10a 和(b)[162~165], 也可以通过在成膜时添加交联剂来实现(图 10(c)和(d))[166~179], 还可以在合成时引入可交联基团如乙烯基、乙炔基和烯丙基等, 成膜后再引发交联来实现(图 10(e))[180~189]. 共价交联可从两方面对交联膜的使用寿命带来改善, 一方面交联膜的结构更加致密, 减少了吸水和溶胀, 限制了自由基在膜内的渗透和扩散; 另一方面共价交联增加了分子链间的纠缠, 减缓了被攻击的分子链从膜内脱落的速度, 从而起到了延长使用寿命的作用.

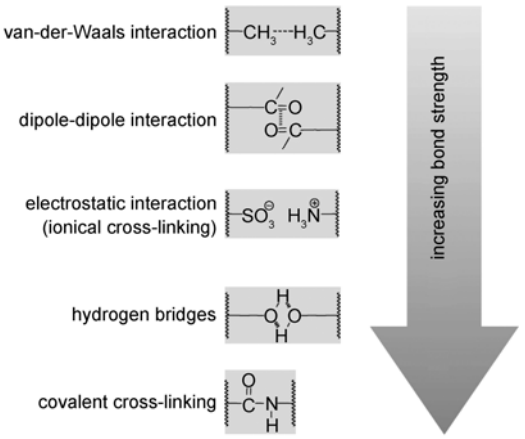

图 9　高分子间的相互作用[145]

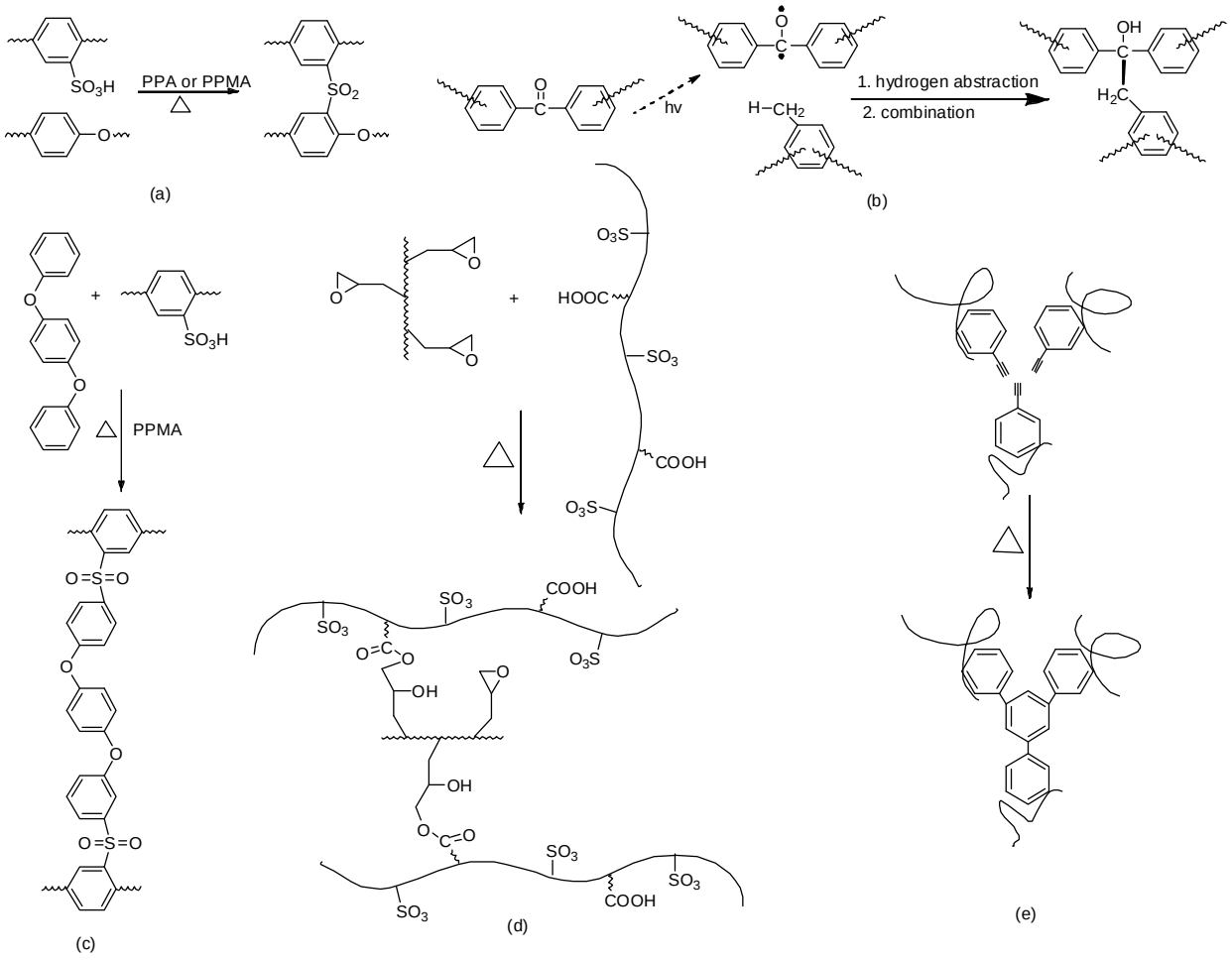

图 10 共价键交联

Yu 等将双酚 A 型磺化聚砜膜(SPSF)在甲基磺酸/五氧化二磷的混合液(PPMA)中浸泡引发交联形成稳定的磺酰基, IEC 为 2.10 meq g^{-1} 的 SPSF 膜交联后, 在 50 ℃水中的溶胀从 80%下降到 10%, 其在 25 ℃和 100% RH 质子传导率仍可达 8.4×10^{-2} S cm^{-1} [164]. Nakabayashi 等将高 IEC 的多嵌段磺化聚醚砜膜(SPES)浸入 PPMA 和 1,4-二苯氧基苯混合物制备交联 SPES 膜, IEC 为 3.40 meq g^{-1} 的膜交联后在 80 ℃和 95% RH 的条件下吸水量为 80.0%, 80 ℃的 Fenton 试剂中保持 6 h 不破裂; 在 80 ℃和 30% RH 的条件下质子传导率仍达 1.0×10^{-2} S cm^{-1}, 且在 30%~95%的 RH 范围内其质子传导率都高于 Nafion 117 膜[170]. Lee 等制备了乙炔基封端的含氟磺化聚芳醚(SPAE-6F)膜, 经热处理后形成苯环交联, IEC 为 1.79 meq g^{-1} 的交联 SPAE-6F 膜的亲水通道具有良好的连通性, 亲水通道尺寸为 5~18 nm, 质子传导率为 0.111 S cm^{-1}, 其 β 值为 Nafion 膜的 4.6 倍左右[187].

但是共价交联限制了分子链的运动, 使交联膜在干态时变得很脆, 容易破碎. 共价-离子交联兼具离子交联和共价交联的优点, 通过调节两种交联在膜内所占比例, 有可能改善和解决这一问题[190~192]. Wang 等分别合成了 SPAEK-COOH 和含胺基的聚芳醚酮(PAEK-Am), 混合成膜后引发羧基和胺基间的反应, 形成了共价交联, 而磺酸基与胺基间则形成了离子交联, 这种共价-离子交联膜展示了很低的水溶胀和甲醇渗透, 同时还极大增强了其抗自由基氧化性能[192]. 其中含 PAEK-Am 为 20 wt%的共价-离子交联膜在 80 ℃的 Fenton 试剂中保持完整的时间从 SPAEK-COOH 膜的 15 min 延长至 152 min, β 值则达到 SPAEK-COOH 膜的 6 倍以上.

④使用增强材料, 如多孔超高分子量聚乙烯(PE)[193]、多孔聚酰亚胺(PI) [194]、聚偏氟乙烯(PVDF)[195]和聚乙烯醇(PVA)静电纺纳米纤维束[196]等, 充填入 PEM 材料的溶液后制备增强膜. 由于高强度支撑材料对导质子材料的约束, 增强膜的吸水和溶胀被有效地减小, 甲醇渗透因此显著地被抑制, 抗自由基氧化性得到了增强[197~201]. Gore 公司在这方面做了大量的工作, 早在 1994 年就开始用全氟磺酸树脂溶液充填多孔交联 PTFE 制备增强膜的研究, 其后 Gore 公司开发了商品名为 Gore-Select 系列增强复合膜[202]. 这些增强膜厚度很小(5~25 μm), 其面内尺寸改变受吸水的影响较小, 使用 25 μm 厚的 Gore-Select 增强膜的 PEMFC 功率密度和寿命都优于商品的 Naion 1035 膜[203, 204].

Nguyen 等制备的 Nafion/PI 增强膜在 80 ℃和 100% RH 下质子传导率为 7.7×10^{-2} S cm^{-1}, 与 Nafion 膜相当(7.9×10^{-2} S cm^{-1}); 而其甲醇渗透系数仅为 3.36×10^{-8} cm^2 s^{-1}, 远低于 Nafion 膜的 2.76×10^{-6} cm^2 s^{-1} [194]. Molla 等制备的 Nafion/PVA 增强膜虽然厚度减小至 19 μm, 70 ℃的甲醇渗透系数仍比 Nafion 膜低一个数量级[196]. 这表明当使用 Nafion 树脂作充填材料时, 不仅可以减少 Nafion 树脂的使用, 降低 PEM 的成本; 还可以减小膜的厚度, 增强 DMFC 的性能. Mittelsteadt 等使用高磺化的全氟磺酸聚合物充填聚砜或聚酰亚胺的三维多孔材料, 这种复合膜显示出很高的质子传导率, 在全 RH 范围内差不多是 Nafion 膜的 5 倍[205]. 遗憾的是这种高磺化的全氟磺酸聚合物是溶于水的, 使得其最终会从多孔材料中流失.

Yildirim 等在多孔 PE 膜中充填磺化二氮杂萘酮结构的聚醚酮(SPPEK)制备了 SPPEK/PE 增强膜(~20 μm), 表现出良好的阻甲醇渗透的能力; 尽管质子传导率因不导质子的 PE 存在而大幅下降, 其高浓度甲醇给料的 DMFC(6 M CH_3OH/ O_2, 0.2 MPa, 无润湿)在 80 ℃仍可获得 200 mW cm^{-2} 以上的功率密度[199]. Dai 等制备了厚度为 26 μm 的磺化聚亚苯基砜/多孔 PTFE 增强膜, 研究表明其具有出色的热稳定性和尺寸稳定性; 用于 H_2/O_2 (0.2 MPa, 100% RH)供气的 PEMFC 在 80 ℃的最大功率密度为 1.34 W cm^{-2} [201].

Zhang 等更是将用于 DMFC 的改性膜改性思路与用于 LT-PEMFC 的改性膜的改性思路相结合, 制备出用于 LT-PEMFC 的自润湿膜(图 11) [206]. 组装成 LT-PEMFC, 0.2 Mpa 的 H_2 和 O_2 干态进气条件下, 开路电压为 0.98 V, 60 ℃时的最高功率密度达 800 mW cm^{-2}. 尽管这种膜的长期寿命仍需进一步研究, 但这种膜以 SPEEK 为主体材料, 极大地减少了 Nafion 材料的使用, 从而可大幅降低膜的成本.

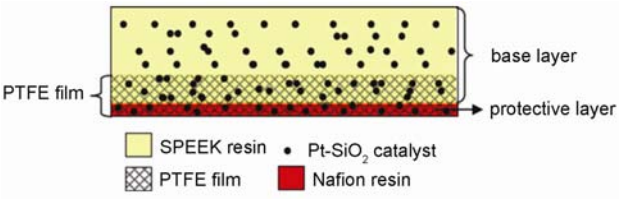

图 11　Pt-SiO_2/SPEEK/PTFE/Nafion/Pt-SiO_2 自润湿膜示意图[206]

⑤形成半互穿网络(SIPN). SIPN 有两种制备方法, 一个是将 PEM 膜在第二组分前体中溶胀, 然后再引发聚合形成网络[207~213]; 另一个是将磺化聚合物与第二组分混合成膜后, 再引发第二组分的聚合或交联[214~217]. 改性膜因为受到 SIPN 网络的约束, 溶胀和吸水减少, 水和质子迁移通道变窄, 从而有效地抑制了甲醇渗透.

Lin 等使用 SPAEK-COOH 与 Nafiion 混合成膜, 然后 160 ℃处理引发 Friedel-Craft 反应在 SPAEK-C 间形成交联制得 SIPN, 其 β 值达到 Nafion 膜 4 倍[210]. Fu 等用磺化四甲基聚醚醚酮(STMPEEK)、环氧乙烷和磺化酚醛一起制备成膜, 经退火后制得 SIPN[217]. 该 SIPN 的 β 值是 STMPEEK 膜的两倍, 在 80 ℃的 Fenton 试剂中保持完整不被破坏的时间增加 67%.

⑥静电纺丝制备制得纳米纤维, 再与同质聚合物复合制备增强膜. Kawakami 等先通过静电纺丝制得一种 SPI 纳米纤维, 然后与这种 SPI 溶液一起制备了 SPI 增强膜[218, 219]. 这种增强膜的自由基稳定性和水解稳定性随着 SPI 纳米纤维的增加而有明显改善; 同时由于 SPI 纳米纤维的轴向取向, SPI 增强膜展现了高质子传导率和低气体透过的特点. 这有可能为解决 PEM 质子传导率与稳定性之间的矛盾指明了一个方向. Dong 等制备的直径为 400 nm 的高纯度 Nafion 纳米纤维在 30 ℃和 90% RH 下, 质子传导率达 1.5 S cm^{-1}, 比商品 Nafion 膜高 10 多倍[220]. 若能以 Nafion 纳米纤维束为骨架, 填充惰性高分子聚合物制备 Nafion 纳米纤维复合膜, 超低的甲醇渗透是可以预见的. 不过由于 Nafion 纳米纤维的质子质子导率随直径增加而迅速下降, 5 μm 的 Nafion 纳米纤维的质子传导率仅与商品 Nafion 膜相当, 如何保持

Nafion 纳米纤维复合膜的高质子传导率仍需要进一步研究.

⑦仅使用物理方法处理, 通过改变膜的形貌(如结晶性、亲水通道尺寸和曲折度等)来实现甲醇渗透的减小. 这些物理方法包括轴向拉伸[221]、热退火处理[222]和超临界二氧化碳处理[223]等, 但对膜性能的改进不及前几种思路.

此外, 还有一类基于脂肪族碳氢主链 PEM 的改性膜, 它们主要用于操作温度不高于 60 ℃的 DMFC. 虽然通过交联、形成 SIPN 和有机/无机杂化等方法[224~231]可以将这类膜的β值最高增加到 Nafion 膜的 8 倍[230], 但因为它们脆弱的脂肪族碳氢主链自由基氧化稳定性, 仍只能作为上述各种 PEM 的不太重要的补充.

2.3 新型 PEM 材料

2.3.1 用于 HT-PEMFC 的新型 PEM

用于 HT-PEMFC 的新型 PEM 的研究思路主要包括以下几点(图 12):

①合成新型含长亲水和憎水链段的多嵌段共聚物(图 12c)[232~238]. PEM 的质子传导率除了依赖于其 IEC, 也即磺化度外, 还依赖于其形貌(图 13)[239, 240]. 通常无规共聚物膜在形貌调节上缺乏有效手段, 仅能通过提高 IEC 来提高质子传导率, 但过高的 IEC 会导致 PEM 过度溶胀, 丧失机械强度和完整性. 而含长亲水和憎水链段的多嵌段共聚物则可以在保持 IEC 不变的前提下通过调节亲水或憎水链的长度来改变 PEM 的形貌, 从而达到调节 PEM 的质子传导率目的[232]. 随着亲水链段长度的增加, 这种多嵌段共聚物膜的相分离就愈明显, 亲水通道也逐渐变宽并且具有更长程的连通性, 最终可以具有与 Nafion 膜相似的形貌结构[233~235]. 良好的相分离形貌赋予了 PEM 在高温低湿条件下优异的质子传导能力, 但如果亲水的链段过长 (如 15 kg mol^{-1}), 形成了分层相结构的膜形貌, 这不仅会导致 PEM 质子传导率明显的各向异性, 使 PEM 面内的质子传导率可以几倍于垂直于表面方向上的质子传导率[236]; 还会导致 PEM 表面可传导质子的区域减小, 从而影响与电极催化剂的接触, 最终损害 PEMFC 的性能[237]. 从现有的文献看, 合适的链段长度应在 7 kg mol^{-1} 左右[238].

②含局部高磺酸浓度的亲水链段和长憎水链段的多嵌段共聚物(图 12(d))[241~247]. 因为亲水链段和憎水链段间极性的巨大反差[241], 含局部高磺酸浓度的亲水链段和长憎水链段的多嵌段共聚物同样可以形

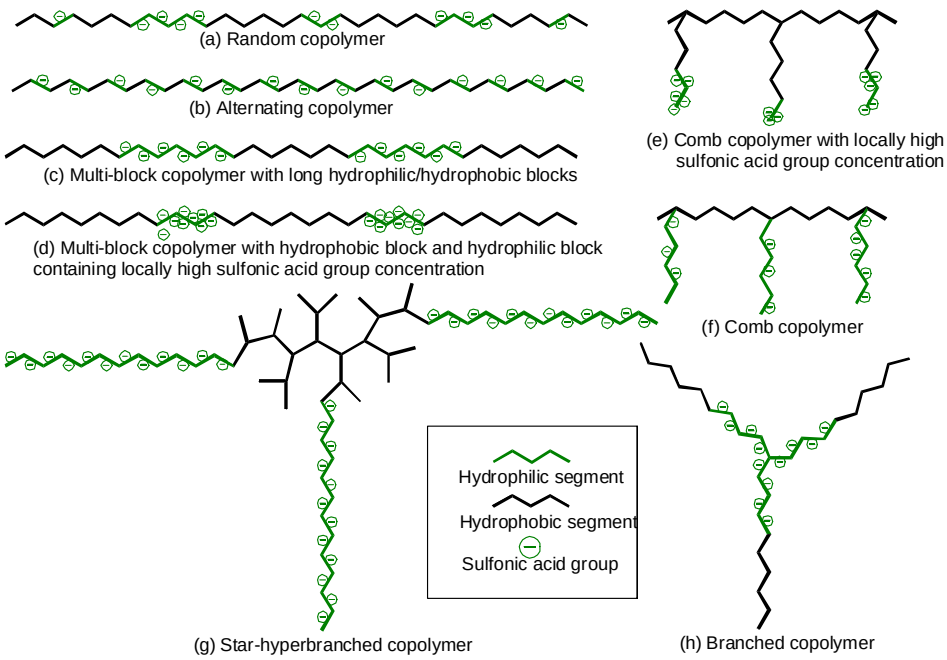

图 12 用于 PEMs 的共聚物构造示意图

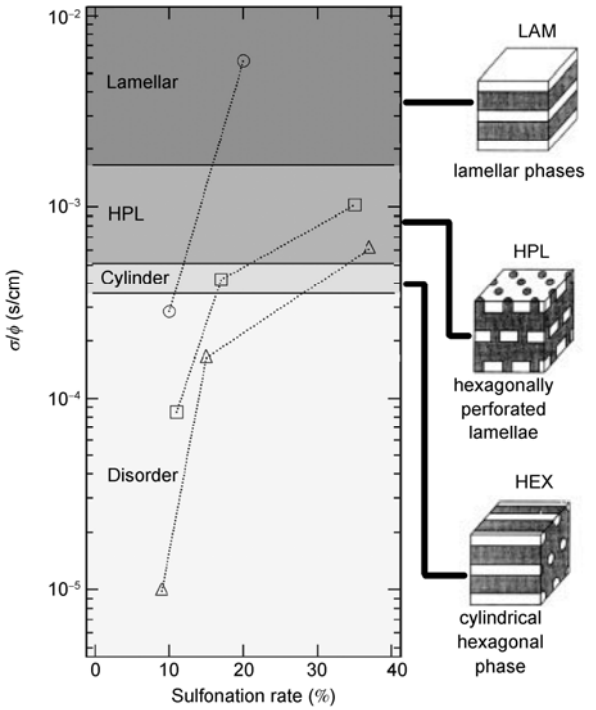

图 13　三个系列的 sPS-PMMA 双嵌段共聚物膜归一化的质子传导率与磺化度间的关系[239]

成与 Nafion 膜相似的形貌结构. 与图 12(c)结构的多嵌段共聚物不同的是, 图 12(d)结构的共聚物亲水链段长度较短, 但其上所含磺酸数目却很多, 因而体积很大, 单一的亲水链段就能形成尺寸为数个纳米的簇[242]. 而且图 12(d)结构的多嵌段共聚物膜的形貌很少出现分层相结构[244~246], 因而质子传导率的各向差异不大, 有利于 PEMFC 性能的提高. Bae 等合成了图 12d 结构的多嵌段磺化聚芳醚砜酮(SPESK), IEC 为 1.62 meq g^{-1} 的 SPESK 膜, 在 110 ℃时仍具有与 Nafion 膜相当(<40% RH)或略高(>40% RH)的质子传导率[246]. Zhang 等合成的图 12(d)结构的多嵌段磺化聚酰亚胺(SPI)由于在酰亚胺环上引入了四个供电子的苯氧基, 显著增强了这类 SPI 膜的水解稳定性, 在 140 ℃的水蒸汽中处理 100 h 仍可基本保持其机械性能; IEC 为 2.22 meq g^{-1} 的这种 SPI 膜 100 ℃的质子传导率略高于 Nafion 膜, 其常温下的 β 值为 Nafion 膜的 20 倍以上[247].

③梳状聚合物(图 12(e)和(f))[248~252]. 与磺酸基位于聚合物主链的 PEM(主链型)相比, 磺酸基位于聚合物侧链的 PEM(侧链型)由于侧链具有更高的运动自由度, 可以形成比主链型 PEM 更明显的相分离, 因而也具有更高的质子传导率. 若结合侧链型聚合物与局部高磺酸浓度思路(图 12(e)), 则可以进一步增强 PEM 的相分离. 在 IEC 相近的图 12(e)结构的 PEM 中, 随着侧链长度和局部磺酸浓度的增加, 亲水相尺寸逐渐增大, 相间距也逐渐增大, 但亲水相数量减小[249]. Lafitte 等合成了图 12(e)结构的系列磺化聚醚砜(SPAES)膜, IEC 为 1.45 meq g^{-1} 的 SPAES 膜在 20~120 ℃的范围内仅略低于 Nafion 膜, 而 IEC 高于 1.70 meq g^{-1} 的 SPAES 膜质子传导率在整个温度区间内都高于 Nafion 膜[250]. 图 12(f)结构的 PEM 质子传导率更为突出, Yamazaki 等制备的 IEC 为 2.41 meq g^{-1} 的梳状型 SPI 膜在 90 ℃和 98% RH 条件下质子传导率为 Nafion 膜的 5 倍以上, 达到 0.69 S cm^{-1}, 并且具有中等的抗自由基氧化性和在 80℃水中 1300 h 才完全溶解的耐水解性能[252].

④超支化聚合物(图 12(g))[253~256]. 树枝状和超支化聚合物因为分子量不高的原因很少单独用作 PEM 材料. Suda 等采用以憎水的超支化结构为核, 以亲水的线性链作为壳制备了具有壳-核结构(图 12(g))的 PEM 膜, 这种膜的质子传导率取决于亲水线性链的分子量, 且随之缓慢增加, 可惜该系列膜抗自由基氧化的稳定很差, 在 25 ℃的 Fenton 试剂中 1 h 就会破裂[255]. 而 Matsumoto 等合成的星形磺化嵌段聚醚酮(SPES)膜(图 12(h)), 其亲水链被憎水链包围, 有高吸水和高键合水的特点, 保水性能也较好, 在 50%~95% RH 范围内质子传导率与 Nafion 膜相当[256].

需要指出的是, 上述各类具有良好相分离结构的 PEM 在较高温度(>100 ℃)的水中常会发生过度溶胀, 同时良好的相分离结构也有利于甲醇和自由基在膜内的渗透和扩散, 给 PEM 的长期稳定性带来不利影响, 因而在未来的研究中有必要采取交联或增大分子量等手段来解决或减轻这些问题.

2.3.2　用于 LT-PEMFC 和 DMFC 的新型 PEM

因为 LT-PEMFC 和 DMFC 的运行环境比 HT-PEMFC 要温和, 所以用于 LT-PEMFC 和 DMFC 的新型 PEM 合成思路还包括了辐射接枝共聚和原子转移自由基共聚(ATRP). 具体如下:

①成新型非氟磺酸聚合物. 出于降低 PEM 对润湿依赖的目的, 用于 LT-PEMFC 的新型非氟磺酸聚合物相当一部分也具有图 12(c)或图 12(d)的结构[257~271]; 其余的无规共聚物和侧链共聚物也各具特

点[272~278]. 与 IEC 相近的无规共聚物膜相比, 长链多嵌段共聚物膜链段长度越长, 达到近似的质子传导率所需的水含量就越少, 因为随着链段长度的增加, 膜内相分离发育就越完善, 也越有利于自由水的形成[266]. Li 等合成了一种图 12(c)结构的 SPI, IEC 为 2.69 meq g^{-1} 的这种 SPI 膜在 70 ℃和 50% RH 的条件下质子传导率仍可达到 3.22×10^{-2} S cm^{-1}, 而相同 IEC 的无规 SPI 共聚物膜在相同条件下仅为 1.10×10^{-3} S cm^{-1} [268]. Bae 等制备了图 12d 结构的磺化聚芳醚砜膜(IEC 为 2.20 meq g^{-1})在 80% RH 和 40% RH 的条件下, 80 ℃的质子传导率分为 0.14 和 0.02 S cm^{-1} [271].

Tan 等合成了含六氟异叉丙基的磺化聚苯并噻唑(SPBT), 相应的 SPBT 膜具有良好的相分离形貌且亲水通道的尺寸有随磺化度增加而减小的趋势, 狭窄的亲水通道意味着较低的溶胀和良好的尺寸稳定性, SPBT 膜同时还具有出色的抗自由基氧化和水解稳定性. 其中磺化度为 65%的 SPBT 膜在 80 ℃的条件下质子传导率为 0.11 S cm^{-1}, 而其溶胀仅为 15.5%[274]. 含三苯基氧膦结构的磺化聚芳醚(SPOPAE)膜因为三苯基氧膦结构的钝化用及其与在磺酸基团间氢键的共同作用, 同样具有良好的抗自由基氧化的能力[275]. SPOPAE 膜具有纳米相分离形貌, 亲水相间的连通性随磺化度增加而增强, 但亲水通道尺寸并没有随磺化度而明显增加[276], IEC 为 1.44 meq g^{-1} 的膜 80 ℃吸水率为 30.8 wt%, 溶胀仅为 15.8%, 质子传导率则为 8.7×10^{-2} S cm^{-1} [277]. 不过 SPOPAE 膜的质子传导对 RH 依赖严重, 仅在 80% RH 以上时才能有与 Nafion 膜相当的质子传导率[278].

此外两种具有全芳香主链、以全氟烷基磺酸为侧链的膜(PES-PSA[279]和 PAEK-PSA[280])也值得关注, IEC 为 1.34 meq g^{-1} 的 PES-PSA 膜在 80 ℃和 90% RH 的条件下质子传导率为 7.7×10^{-2} S cm^{-1}, 它的 PEMFC(润湿的氢气和空气)功率密度达到 805 mW cm^{-2}, 与 Nafion 212 膜相当; 而 IEC 为 1.29 meq g^{-1} 的 PAEK-PSA 膜同样条件下质子传导率则可达 0.13 S cm^{-1}, 因为其膜内存在更明显的相分离结构, 亲水通道尺寸约为 10 nm, 有利于水和质子的迁移.

用于 DMFC 的新型非氟磺酸聚合物则以无规共聚物和侧链型共聚物为主[281~292]. Zhang 等合成了一系列非对称全芳香磺化聚酰亚胺(SPPI), 相应的 SPPI 膜具有溶胀低、耐水解和自由基氧化的特点. IEC 为 1.89 meq g^{-1} 的膜 100 ℃吸水率仅为 48 wt%, 在 30 ℃的 Fenton 试剂中可保持 51h 不破碎, 并且其 β 值为 Nafion117 膜的 17 倍以上[291]. Yoon 等制备了含全氟己基链节的聚芳醚砜膜, 有效地减小了甲醇渗透和吸水, 用于 DMFC (2 M CH_3OH/O_2, 无润湿)在 80 ℃可获得 250 mW cm^{-2} 以上的功率密度[292].

②辐射接枝共聚通常要经过初始材料辐射预处理(如电子束和 γ 射线照射)形成活性点、在活性点引发苯乙烯单体或其衍生物的聚合和磺化等步骤, 最后得到 PEM. 其中的初始材料主要是商品的含氟聚合物膜[293~308], 如 PVDF、PTFE 和乙烯-四氟乙烯共聚物(ETFE)膜等, 因为它们比碳氢聚合物膜具有更好化学和热稳定性, 并且易于产生稳定的自由基. 由于聚苯乙烯接枝链对自由基攻击敏感, 易于降解, 因而交联[297]、使用更稳定的单体共聚(如 α-甲基苯乙烯和甲基丙烯腈等)[306]和离子潜痕技术[308]被单独或联合使用来延长辐射接枝共聚 PEM 的寿命, 但目前仍鲜有令人满意的报道.

③ATRP 是一种有效的活性/可控聚合方法[309], 在含氯或溴基团的聚合物膜表面或溶液中引发单体的 ATRP 反应都可以将导质子基团引入起始材料, 并最终获得 PEM[310~315]. 对偏氟乙烯和三氟氯乙烯共聚物(P(VDF-co-CTFE))膜 ATRP 接枝聚苯乙烯磺酸的研究表明, 接枝聚苯乙烯链长较短的 PEM, 增加 IEC 会导致亲水簇尺寸增加, 离子簇密度保持不变; 而接枝聚苯乙烯链长较长的 PEM 则相反, 簇尺寸基本不变, 簇密度增加. 另外, 高分子量起始膜材料、低接枝密度和长聚苯乙烯链有利 PEM 获得较窄的亲水通道, 低吸水的特性, 从而使其在高 IEC(>2.5 meq g^{-1})时抗溶胀性能较好[312, 313]. 不过 ATRP 反应制备的 PEM 和辐射接枝共聚制备的 PEM 一样存在接枝的脂肪链不耐自由基攻击的弱点, 同样面临着增加 PEM 寿命的问题.

3 阴离子交换膜

与 PEMFC 相比, AEMFC 的发展仍处在起始阶段, 所面临的问题主要包括: 以季铵基作 OH^- 离子交换基团的 AEM 不稳定, 易于发生 Hofmann 脱除和 S_N2 取代反应; 缺少如 PEMFC 的 MEA 制备中 Nafion 树脂那样的通用粘合剂用于制备 AEMFC 的 MEA; 需要开发与 AEMFC 相匹配的催化剂体系. 因为高性能 AEM 的可以为后两种问题的研究提供更好的研究平

台, 因此 AEMFC 的研究焦点集中在了新型 AEM 的开发上[316~334], 其中以异于传统季铵基的 AEM(图 14)最为引人注目.

Pan 等将氯甲基化的 PES 部分地进行叔胺化处理, 制备了季铵化/叔胺化的 PES(图 14(b)), 最终形成了自交联的 AEM. 含叔胺 50%的 AEM 在 80~90 ℃水中溶胀很小, 且 500 h 后 OH^-传导率未见明显降低, 其 OH^-传导率 20℃为 1.5×10^{-2} S cm^{-1}, 90 ℃则增加到 4.3×10^{-2} S cm^{-1} [329]. Lin 等制备了含咪唑环的 AEM(图 14(c)), 60 ℃下在 1 M 的 KOH 溶液中浸泡 400 h 仍能保持其性能, 室温下的 OH^-传导率在 10^{-2} S cm^{-1}以上[332]. Gu 等合成的以三(2,4,6-三甲氧基苯基)季鏻盐为 OH^-离子交换基团的 PES(TPQPOH)(图 14(e))不仅可以制备高性能的 AEM, 还可以作为出色的粘合剂用于 MEA 的制备[334, 335]. TPQPOH 膜 60 ℃下在 2 M 的 KOH 溶液中可保持 48 h 不破坏, 20 ℃时的 OH^-传导率高达 4.5×10^{-2} S cm^{-1}; 同时使用 TPQPOH 作为 MEA 粘合剂和 AEM 材料的 AEMFC(H_2/O_2) 70 ℃的最高功率密度为 258 mW cm^{-2}.

此外, PEM 和 AEM 联用的杂化燃料电池也值得关注(图 15)[336], 这种结构的燃料电池不仅具有自润湿特性, 还因为 H^+和 OH^-仅需要迁移膜厚的一半就可完成反应, 而燃料和氧化剂要完成渗透则需要通过整个膜的厚度, 因而具有更好的阻隔燃料渗透的性能, 这在使用甲醇作燃料时尤其有利. 同时 AEM

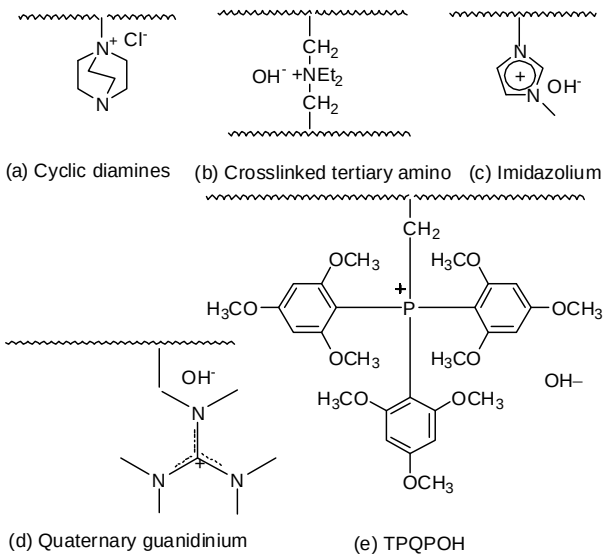

图 14　AEM 中新型的 OH^-离子交换基团

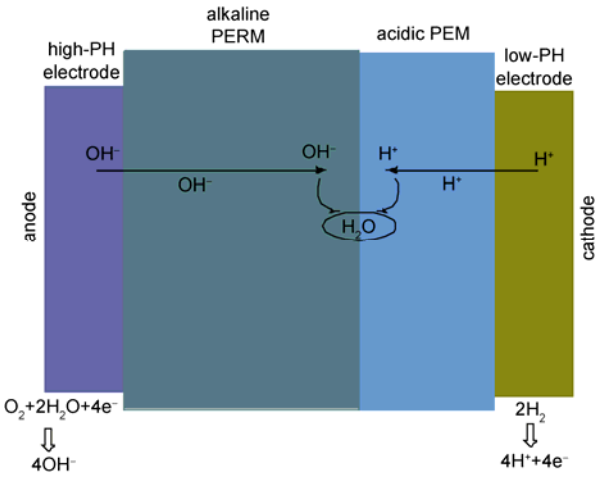

图 15　PEM 和 AEM 联用的杂化燃料电池

侧的电极可以使用非铂催化剂, 有望进一步降低 MEA 组件的成本. 不过由于受 AEM 的影响, 这种燃料电池性能还无法与 PEMFC 相比, 相信随着 AEM 的进步, 其性能会逐步得到提高, 优势也将会更明显地表现出来.

4　结论

尽管聚合物电解质膜的研究取得了长足的进展, 但与聚合物电解质膜燃料电池大规模应用两个主要障碍(价格和寿命)的解决仍有距离. 根据不同的应用要求, 未来聚合物电解质膜研究的侧重点应有所不同. 对于用于 HT-PEMFC 的 PEM 而言, Nafion 膜的价格和性能并无明显优势, 因而应侧重于新型 PEM, 如, 含局部高磺酸浓度的亲水链段和长憎水链段的多嵌段全芳香共聚物的研究. 不过由于非氟膜的碳氢键强比碳氟键弱, 易被自由基破坏, 其使用寿命仍有待进一步增强. 通过高分子结构设计, 利用空间效应, 保护非氟聚合物碳碳主链不被自由基氧化; 利用杂原子提高聚合物的稳定性; 通过交联限制自由基在非氟膜内的扩散等都是提高非氟膜耐久性的可行方法. 而对于用于 LT-PEMFC 和 DMFC 的 PEM 而言, 由于 Nafion 膜性能上的优势, Nafion 多孔材料增强膜将是一种高性价比的选择; 辐射接枝共聚膜若能解决自由基氧化稳定性的问题, 也将是一个不错的选择. 至于用于 AEMFC 的 AEM, 相关的研究还处于起步阶段, 最好能借鉴 PEM 研究中成熟的经验和技术, 如长链段多嵌段共聚物的合成等, 来制备高性能的 AEM.

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Progress of polymer electrolyte membranes for fuel cells

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Abstract: According to their operation temperature, polymer electrolyte membrane and fuel, the polymer electrolyte membrane fuel cells (PEMFCs) are sorted as high temperature proton exchange membrane fuel cell, low temperature proton exchange membrane fuel cell, direct methanol fuel cell and anion exchange membrane fuel cell. In this review. the advances of the polymer electrolyte membranes for these fuel cells are presented. In the first section, the four types of fuel cells are introduced briefly. In the second section, the model of Nafion membrane is discussed and a revised model based on parallel water-channel (inverted-micelle cylinder) model at mesoscopic scale is proposed. Then the modified strategies of Nafion for proton exchange membrane fuel cells and DMFCs are described. Lastly, the strategies of preparing proton exchange membranes alternatives to Nafion are presented. Furthermore, the highlights of them are also listed. In the third section, the development of anion exchange membranes is given. In the last section, the research trends of this field in the future are predicted.

Keywords: polymer electrolyte membrane, fuel cell, advancement