燃料电池用碱性阴离子交换膜链结构调控研究进展

司江菊^{1,2}, 卢善富^{1*}, 相艳^{1*}

1. 北京航空航天大学空间与环境学院, 仿生能源材料与器件北京市重点实验室, 北京 100191;

2. 新乡学院化学化工学院, 新乡 453003

* 联系人, E-mail: lusf@buaa.edu.cn; xiangy@buaa.edu.cn

2018-07-30 收稿, 2018-09-11 修回, 2018-09-30 接受, 2018-11-02 网络版发表

国家自然科学基金(21722601, 21576007)和北京市重点研发计划(Z171100000917011)资助

摘要 碱性阴离子交换膜燃料电池(AAEMFCs)因氧还原动力学快、可使用非Pt催化剂、成本低等优点迅速发展成燃料电池的重点研究领域。作为AAEMFCs的核心组件, 碱性阴离子交换膜(AAEMs)的性能直接影响着燃料电池的输出性能和使用寿命。为保证燃料电池高效、稳定、长时间的运行, AAEMs应具备高的离子电导率、尺寸及化学稳定性。但目前开发的膜尚难同时满足这些要求, 在实际应用中依然面临阴离子传输效率与尺寸稳定性难以兼顾、碱性稳定性较差等问题。本文将结合近年来国内外及本课题组的研究进展, 梳理AAEMs发展中存在的关键问题与解决思路, 展望未来的发展方向。

关键词 燃料电池, 碱性阴离子交换膜, 离子电导率, 碱性稳定性, 微观结构

聚电解质膜燃料电池(PEFCs)因其具有功率密度大、能量转换效率高、结构紧凑、启动快速等优势, 可广泛应用于便携式电源、紧急备用电源、电动汽车等领域, 成为各类燃料电池中发展最快、技术最为成熟的一类燃料电池^[1~4]。目前常用的PEFCs包括基于H⁺传输的质子交换膜燃料电池(PEMFCs)和基于OH⁻传输的碱性阴离子交换膜燃料电池(AAEMFCs)。其中, PEMFCs发展最早, 技术较为成熟, 然而它的高腐蚀性、对贵金属催化剂的依赖性以及高成本等因素限制了其发展。近年来, AAEMFCs因氧还原动力学快、可使用非Pt催化剂、成本低等优点迅速发展成燃料电池领域的一支劲旅^[5~10]。经过10余年的研究AAEMFCs取得了长足的进步, 作为核心组件的碱性阴离子交换膜(AAEMs)离子电导率大幅提升^[11~13], 在80℃达到200 mS cm⁻¹^[14], 已超过Nafion[®]为代表的质子交换膜的电导率; 阴极分别使用Pt/C与Ag/C的AEMFCs最大功率密度在80℃已达到1.9与1.1 W cm⁻²^[15,16]。

但是, AAEMFCs的商业化应用依然面临着严峻的挑战, 尤其是电池的长时间稳定运行仍然是难题^[17~21]。为了保证燃料电池高效、稳定、长时间的运行, 燃料电池中的AAEMs必须具备高的离子电导率, 保持优良的尺寸及化学稳定性, 但目前开发的膜尚难同时满足这些要求。本文将结合近年来国内外及本课题组在碱性阴离子交换膜方面的研究进展, 梳理AAEMs研究的关键问题以及未来发展方向。

1 碱性阴离子交换膜的离子传输及问题分析

在碱性阴离子交换膜中, 阳离子基团在高分子主链的接枝引入OH⁻, 是膜材料导电的根源。然而承担导电功能的OH⁻在25℃稀溶液中的离子淌度为20.64×10⁻⁸ m² s⁻¹ V⁻¹, 仅为同等条件下H⁺的淌度的56.97%^[19,22]。较低的离子淌度、对水的依赖程度高以及聚合物结构中疏水区的阻碍等, 这些因素使得AAEMs中OH⁻传输的效率相对较低。

引用格式: 司江菊, 卢善富, 相艳. 燃料电池用碱性阴离子交换膜链结构调控研究进展. 科学通报, 2019, 64: 153–164

Si J J, Lu S F, Xiang Y. Progress of polymer chain structure regulation of alkaline anion-exchange membranes for fuel cells (in Chinese). Chin Sci Bull, 2019, 64: 153–164, doi: 10.1360/N972018-00767

依据离子独立运动定律, AAEMs中离子传输的电导率可表达为

$$\sigma = F \times \alpha_{\text{OH}^-} \times c_{\text{OH}^-} \times U_{-}, \quad (1)$$

其中, σ 为离子电导率, F 为法拉第常数, α_{OH^-} 为 OH^- 的解离度, c_{OH^-} 为 OH^- 的浓度, U_{-} 为 OH^- 的离子淌度.

如式(1)所示, AAEMs的离子电导率与 OH^- 的浓度、解离度、离子淌度直接相关. 因为季铵碱的强碱性, 在充分水合的情况下 AAEMs 中 OH^- 是完全解离的, α_{OH^-} 可近似为 1^[19]. 为提升 AAEMs 的离子电导率, 通常的方法是通过增大阳离子基团的接枝度 (GD) 来提高 OH^- 的浓度, 但 GD 的过度增大将带来以下三大问题: (1) 膜过度亲水, 在吸入大量的水后膜剧烈溶胀, 尺寸稳定性与机械性能大幅下降; (2) OH^- 浓度的增大, 增强了其对季铵/膦/胍、咪唑鎓等阳离子基团的亲核进攻能力, 加速亲核取代与 β -消去反应的动力学, 从而导致阳离子基团的降解与膜导电性能的下降; (3) 阳离子基团静电场的极化以及主链的亲水性增强使得高分子主链易受到 OH^- 的亲核进攻, 从而导致主链的降解、膜的破坏以及电池短路等.

2 碱性阴离子交换膜链结构调控的研究进展

针对 AAEMs 存在的上述问题, 研究者开展了大量卓有成效的研究工作. 本文将分别就上述 3 个关键问题的解决思路进行阐述.

2.1 AAEMs 电导率与尺寸稳定性的调控

为解决膜离子电导率与尺寸稳定性的问题, 早期通过共混、交联、多孔膜增强与纤维增强等方法引入疏水组分抑制膜材料的过度吸水溶胀^[23]. 近 5 年, 研究者从高分子链结构着手, 通过亲水阳离子基团与疏水链段结构的设计与调控, 获得了一系列高离子电导率与尺寸稳定性的 AAEMs.

2.1.1 侧链阳离子基团的多接枝

侧链阳离子基团的接枝方式可以调控 AAEMs 的电导率与尺寸稳定性. 在前期一个接枝位点引入单个阳离子基团 (简称单一接枝) 的基础上 (图 1), 庄林课题组^[24]和本课题组^[25]的双接枝, 刘庆林课题组^[26]与白如科课题组^[27]的三接枝, 徐铜文课题组^[28]的多接枝, 均在低的 GD 下获得高的离子交换容量 (IEC), 从而在较低的溶胀度下实现膜电导率的大幅提高.

图 1 (网络版彩色) 阳离子基团在主链上的单接枝(a)、双接枝(b)与三接枝(c)

Figure 1 (Color online) Schematic illustration of single (a), double (b) and triple (c) cations grafted on one site of polymer backbone

该策略是一种简单、有效平衡碱性阴离子交换膜离子电导率与尺寸稳定性的方法.

2.1.2 离子通道的构筑

如前文式(1)所示, 电解质的离子电导率除了与膜中 OH^- 的浓度有关, 还与 OH^- 在膜环境下的离子淌度相关. 在聚电解质膜中, OH^- 的离子淌度由于受到疏水聚合物链的阻碍, 传导路径的曲折系数大, 致使离子在膜中的传导受阻, 表现为较低的电导率^[29]. 因此, 除了提高 OH^- 的浓度外, 还可以通过两亲性聚电解质的微相分离构建离子通道提高 OH^- 的有效离子淌度, 实现膜离子电导率的大幅提升.

与表面活性剂分子类似, 两亲性聚电解质分子在焓或熵的驱动下, 亲水基团与疏水基团自组装形成了局部的亲水和疏水区域, 形成了微观相分离结构, 亲水区域相互连通便构成了水通道, 实现离子的高速传输. 两亲性聚电解质在溶液中的自组装是一个复杂的热力学和动力学过程, 受环境如溶剂、温度以及高分子链结构等因素的影响, 研究聚电解质的自组装行为与机制对于理解离子通道形成的分子机制有着重要意义.

(i) 成膜溶剂的调控. 在大分子自组装的研究中, 溶剂诱导是调控高分子聚集行为的有效方法, 但目前在碱性聚电解质的研究中尚未得到广泛的应用. 庄林课题组^[30]对成膜过程中混合溶剂的种类和比例进行调控, 发现使用二甲基甲酰胺(DMF)、水与异丙醇的混合溶剂制备的膜电导率大幅提升, 因为成膜溶剂的选择显著影响所制备膜的微观结构.

(ii) 两亲性高分子链结构的调控. 商业化质子交换膜中的 Nafion[®] 膜, 独特的两亲高分子链结构以及由其构建的微观相分离结构是膜具有优异离子导电性能和稳定性的根源^[31]. 受 Nafion[®] 膜构效关系的

启发,研究者开始在AAEMs中设计两亲高分子链结构来构建亲/疏水相分离的微观结构,并调节聚合物拓扑结构以及亲疏水基团之间的平衡来调控离子簇的尺寸与形态。Frank课题组^[32]在疏水的聚砜主链上接枝亲水的聚二醇侧链和季铵基团构建了5~10 nm的离子通道;李南文课题组^[33,34]、刘庆林课题组^[35]、Kim课题组^[36]与丁运生课题组^[37]等分别制备了“梳形”的AAEMs,通过调节GD和疏水链段长度实现离子簇尺寸从5到33 nm的增大;庄林课题组^[38]在未接枝季铵基团的位点引入烷基链构建了高速离子传输通道,将AAEMs的离子电导率提高到100 mS cm⁻¹(80℃);除了烷基链的长度和季铵基团的GD, Dang 和 Jannasch^[39]发现烷基链与季铵基团的组合方式影响膜微观结构与性能,通过引入疏水烷基链与阳离子基团多接枝制备的AAEMs其离子电导率在80℃达到221 mS cm⁻¹^[41]; Lee课题组^[40]发现通过端基3个乙炔基的交联可以增大亲水区域的尺寸。本课题组^[41]在聚醚醚酮(PEEK)主链上接枝季铵基团的同时引入十二烷基长链,通过同步增大亲疏水2个组分的浓度,实现了离子簇的尺寸由5~50 nm的增大,发现大尺寸的离子簇相互交叠更容易形成三维连通的离子通道网络;并首次通过二维核奥弗豪泽增强谱(NOESY)谱对合成的长链季铵化聚醚醚酮在溶液中的聚集行为进行初步探索,如图2,发现了疏水烷基链的相互聚集以及季铵基团之间的相互聚集,此外聚电解质分子内/间存在多重氢键以及季铵基团与苯环之间的

cation- π 作用,这些相互作用有助于特定分子构象以及微观结构的形成。

在聚电解质的多种拓扑结构中,两亲性嵌段共聚物比无规聚合物更容易实现有序的周期性离子通道的构建,近年来多种嵌段共聚物被用来构建微相分离的AAEMs^[26,42~53]。刘庆林课题组^[26,54]合成了具有柔性多接枝侧链的三嵌段共聚物,验证了离子簇尺寸的增大更有助于膜电导率的提升以及OH⁻传输活化能的降低;除对离子簇尺寸的调控外,李南文课题组^[47,51]、郑利强课题组^[55]与Coughlin课题组^[56]通过嵌段共聚物中两亲性链段比例的调节,实现离子簇形态从球状、六方柱状,层状以及双连续相之间的转变,相对于球状和六方柱状的结构,层状结构更有利于离子的传输,并且晶界对连续的离子通道的形成有重大影响,在达到一定的湿度和温度时,亲水相膨胀,晶界减小,从而形成了高效的连续离子通道。

以上这些研究均证实亲/疏水相分离的微观结构可以实现膜离子电导率的大幅提升,同时,膜的吸水率和溶胀度也降低,尺寸稳定性得到提升,表明相分离微观结构可以在较低的吸水率下实现离子传输效率的提升。然而,膜的吸水率过低,将导致亲水区域无法充分溶胀,呈现“孤岛”状分布,不能形成长程有序的离子通道,反而不利于OH⁻的传输。因此,如何表征碱性阴离子交换膜中离子通道的连通性就变得尤为重要。本课题组^[41]首次采用TEM与STEM半定量的方法比较了离子簇的尺寸(d_1)和距离(d_2),

图2 (网络版彩色)相分离的季铵化聚醚醚酮的NOESY图谱(a)与聚集结构示意图(b)

Figure 2 (Color online) 2D nuclear overhauser effect spectroscopy (NOESY) for quaternary ammonium Poly (ether ether ketone) (MQ-PEEK) with phase-segregated morphology (a) and schematic of MQ-PEEK aggregation structure (b)

发现大尺寸的离子簇相互交叠更容易构筑三维连通的离子通道网络,并在此基础上,又利用渗流理论评价离子通道的连通性.

在渗流理论中,网络具有临界概率(pc),当不超过 pc 时,网络由孤立的节点集群组成,但是当超过 pc 时,巨大节点集群将扩展到整个网络. Hsu等人^[57]用此理论验证了Nafion®膜的三维连通性,白色的空网格指Nafion®膜由碳氟链构成的疏水相,黑色已填充网格代表亲水的离子簇相,如图3所示. 在低浓度时,离子簇相被分隔成“孤岛”状(图3(a)),这时离子从网格的一端传输到另一端难度较大. 当浓度增大(图3(b)),这些“孤岛”逐渐增大,但是,如图中标记为L的关键节点还是缺失的,尚未形成长距离连通的离子通道. 当浓度进一步提高达到阈值,关键节点连通形成了真正三维连通的通道网络,实现了离子的畅通传输. 此外,在阈值时,电导率 σ 与亲水相的体积分数 c 满足以下指数关系:

$$\sigma = \frac{(c - c_0)^n}{\sigma_0}, \quad (2)$$

其中, c_0 是指亲水相体积分数的阈值, n 是关键指数因子, n 在1.3~1.7之间的体系是三维连通的体系.

渗流理论揭示了膜中亲水相体积分数-离子通道连通程度-离子电导率三者之间的关系,当膜中的含水量达到亲水相体积分数的阈值时,离子通道呈现三维连通状态,膜的离子电导率随亲水相体积分数呈指数增长.

2.2 侧链阳离子基团稳定性的研究进展

针对侧链季铵/膦/胍、咪唑鎓等阳离子基团碱性稳定性较差的问题,研究者主要从2个方向着手:(1)

理解这些阳离子基团碱性降解的分子机制,通过分子结构的设计提高它们的碱性稳定性;(2)寻找新型的高稳定阳离子基团.

为了提高季铵/膦/胍、咪唑鎓等阳离子基团的碱性稳定性,严锋课题组^[58-62]、Marino课题组^[63]与Bae课题组^[64]系统研究了这些阳离子基团的碱性降解机制,发现降解的路径主要包括亲核取代反应与 β -消去反应,这两类反应受 OH^- 的水合数、 β -H的数量、取代基的场效应、空间位阻效应与几何构象等因素的综合影响^[19,65]. 以降解机制为指导,研究者们开始通过分子结构的设计如引入供电子基团^[63]、增大空间位阻^[66,67]、减少 β -H的数量^[68,69]以及促进 OH^- 的充分水合^[70,71]等方法降低亲核取代反应与 β -消去反应的动力学,提高阳离子基团的碱性稳定性. 常见的阳离子基团的碱性稳定性总结见表S1.

近期发现,环状季铵碱中环的张力也将影响季铵碱的稳定性,其中无张力的六元单/螺环的哌啶季铵碱虽含有多个 β -H,并容易形成反叠构象,但它们均具有非常优异的碱性稳定性,用6 mol L⁻¹的NaOH水溶液在160℃下处理时半衰期分别可达到87.3与110 h, β -消去反应仅在160℃以上发生^[63]. 在此基础上,朱红课题组^[72]与Jannasch课题组^[14,44,73,74]制备了一系列基于单环与螺环哌啶季铵碱的AAEMs,发现它们在80℃均具有较好的碱性稳定性. 高稳定哌啶季铵碱的出现为AAEMs的进一步发展带来新的希望,基于哌啶季铵碱的AAEMs是下一阶段高稳定AAEMs的设计方向.

2.3 高分子主链化学稳定性的调控思路

除侧链阳离子基团的降解外,AAEMs高分子主

图3 渗流理论示意图. 黑色网格是已经被填充的网格,交叉的网格是即将被填充的网格,标记L的网格是指达到渗流阈值必须被填充的网格,从(a)~(d),网格的填充率分别是18%,31%,45%与53%^[57]

Figure 3 A two-dimensional illustration for percolation theory. The shaded and crossed areas correspond respectively to sites that were previously occupied and sites that have just been occupied whereas those marked L in (b) are some empty sites that must be occupied before the onset of ion transport. The percentages of occupancy of the grid for cases (a) to (d) are 18%, 31%, 45%, and 53%, respectively^[57]

链的降解也逐渐引起关注,它对于电池的长期稳定运行起着至关重要的作用,主链的降解不仅造成膜结构的破坏,导致电导率的下降,还可能引起电池短路,从而带来系列安全问题。

AAEMs主链的主要降解路径为阳离子两侧的醚键与季碳的水解断裂^[75,76],周围吸电子基团(如砷基、羰基)的存在加速了主链的降解^[77-79]。阳离子静电场的极化以及吸电子基团的诱导效应是AAEMs主链降解的关键因素,目前的解决思路是通过高分子链结构设计降低甚至避免吸电子基团与阳离子对主链的负面影响,主要包括以下3方面:(1)针对醚键易水解的问题,研发基于无醚键主链的AAEMs是提高其稳定性的一个方向,国内外的科研工作者研究制备了一系列刚性的聚芳香、柔性的聚烷烃、半导体聚(3,4'-二烷基噻吩)等作为主链的AAEMs^[66,67,73,74,80-91],这些膜都展现了良好的碱性稳定性,如表S2所示;(2)为避免羰基等吸电子基团对主链醚键和季碳的诱导效应,贺高红课题组^[78]与刘庆林课题组^[26]将羰基还原为亚甲基从而提高了膜的稳定性;(3)为降低阳离子基团对主链的影响,Bae课题组^[92]、Jannasch课题组^[39]、张所波课题组^[48]、贺高红课题组^[78]、刘庆林课题组^[42,93]通过烷基长链将季铵基团远离主链接枝,增大季铵基团与主链的空间距离,提高了主链的稳定性。

通过以上对侧链阳离子基团与高分子主链的设计与调控,获得了系列高稳定性的AAEMs。但是有个问题被忽略了,高分子链结构的调控势必影响到AAEMs的微观结构,膜的微观结构也将影响其稳定性,相关的研究目前还尚未系统性的开展。在小分子季铵碱化学稳定性的研究中,Marino和Kreuer^[63]发现当烷基链的长度大于6个碳时,季铵基团的碱性稳定性反而大幅降低,认为可能的原因在于较长的烷基链有助于相分离微观结构的形成,这种微观结构中类似胶束的聚集体不仅影响到OH⁻的亲核进攻速率,也将影响到离去基团的离去速率。此外,Bae课题组^[77]发现相同组成的聚合物,以膜形态存在时碱性稳定性提高,表明成膜过程中形成的微观结构也将影响膜材料的化学稳定性。这些结果表明AAEMs的化学稳定性不仅受高分子链化学组成的影响,也取决于高分子链在微观尺度上的聚集状态即膜材料的微观结构。但是,离子簇的尺寸、形态等对侧链阳离子基团、主链稳定性的影响规律是什么?作用机制是什么?这

一系列问题都有待进一步深入研究。

3 AAEMs的发展新动向

近年来,随着AEMs及相关领域的不断发展,研究者开始采用新的结构设计理念,利用新材料来制备综合性能较好的AAEMs。

3.1 基于多孔结构材料的碱性阴离子交换膜

新型多孔材料如金属-有机框架(MOF)、托格乐碱(Tröger's Base)以及大环冠醚化合物等因其自身的三维孔结构,可以为离子传输提供有序的离子通道,从而逐渐被用作AAEMs的功能组分。那辉课题组^[94,95]通过离子热法分别制备了IL@ZIF-8/IL/PVA和PVA-ZIF8i复合阴离子交换膜,将含季铵基团的胆碱分子固定在MOF ZIF-8的有序孔道中,实现了OH⁻的有序传输。除MOF外,V型Tröger's Base自身的多孔结构有助于离子的高效传输,徐铜文课题组^[13]制备了含Tröger's Base的AAEMs,IEC仅为0.82 mmol g⁻¹的膜离子电导率就可以达到164.4 mS cm⁻¹。此外,徐铜文课题组^[12]设计了基于主-客体的聚轮烷超分子结构,含双仲胺与季铵的阳离子侧链客体分子可以在主链的冠醚孔道中穿梭,从而加速了OH⁻在膜中的传输,使得IEC仅为0.68 mmol g⁻¹的膜在90℃的离子电导率高达180 mS cm⁻¹。这些有序离子通道的构筑实现了OH⁻的高效传输,这些新材料的出现也为高性能AAEMs的设计开拓了新的视野。

3.2 基于金属阳离子的碱性阴离子交换膜

因为季铵/膦/胍、咪唑鎓等阳离子较差的碱性稳定性,研究者开始开发新型的高稳定阳离子基团,基于金属络合物的阳离子就是其中的一种。Hickner课题组^[96]制备了基于双(三联吡啶)Ru(II)络合物的AAEMs; Tang课题组^[97]制备了基于二茂钴的AAEMs,此膜在获得较高离子电导率(90 mS cm⁻¹, 90℃)的同时具有优异的化学稳定性,在80℃ 1 mol L⁻¹ NaOH溶液中浸泡1个月后,其IEC的保有率为95%。Yan课题组^[98]将稳定的全甲基二茂钴鎓阳离子通过桥联的二胺共价接枝到聚砒的主链上,将制备的AEM在80℃的1 mol L⁻¹ KOH中进行稳定性测试,1000 h后,其IEC损失率为18%,聚砒主链发生断裂,但阳离子基团的结构没有发生变化,研究结果验证了全甲基二茂钴鎓阳离子的优异稳定性。徐铜文课题组^[99]将离子溅射得到

的阳离子MOFs通过共价结合到多孔的溴甲基化聚(2,6-二甲基-1,4-苯醚)膜中,这种基于MOF的新型三明治结构AAEM在80℃时电导率达到145 mS cm⁻¹,在60℃ 1 mol L⁻¹ NaOH溶液中浸泡100 h后,其电导率没有衰减,化学结构并未发生明显的降解.这些基于高稳定金属络合物阳离子的设计为新型高稳定性AAEMs以及高使用寿命AAEMFCs的发展开辟了新的方向.

4 碱性阴离子交换膜在电池器件中的稳定性

在过去10余年中,AAEMFCs的性能在不断提高,AAEMFC的最大功率密度在70℃已达到1.9 W cm⁻²[41],但是电池的长时间稳定运行依然是AAEMFCs商业化亟待解决的难题.文献[21]报道的大多数AAEMFCs在运行100~200 h后性能出现大幅度的衰减,衰减的速率比相似环境条件下PEMFCs高2个数量级,除了催化剂的因素外,AAEMFCs性能衰减的主要原因是膜的化学降解.

近年来,随着高稳定性AAEMs的出现,AAEMFCs的操作温度提高到80℃,稳定性也大幅提高,下一阶段的目标是实现1000 h的使用寿命.庄林课题组[100]用基于哌啶季铵碱AAEMs(QAPPT)组装的AEMFCs可以在80℃ 0.2 A cm⁻²的条件下稳定放电125 h不衰减(图4(a)). Lee课题组[40]发现高分子链间的交联可以提高AAEMs的稳定性,从而提高AAEMFCs的耐受性,如图4(b)在80℃ 0.2 A cm⁻²的条件下放电,未交联的E-Imds膜组装的电池放电电压下降速度较快,导致电池的使用寿命仅为300 h,然而同样接枝度的交联膜XE-Imds组装的电池稳定性明显提高,在运行800 h后电压由0.6 V下降到0.4 V,验证了AAEMs的稳定性与AAEMFCs耐久性之间的正向关联.但是,李南文课题组[101]得到了相反的结论,在0.1 A cm⁻²的电流密度下,具有优良碱性稳定性的侧链型LSCQA-30膜组装的电池仅有3.3 h的寿命,在电池运行过程中,膜发生了降解,降解的主要路径是季铵基团的亲核取代与β-消去反应.相反,在碱溶液中不稳定的BTMA-30膜在8.3 h的电池运行中未发生明显的降解.

与在碱溶液中的固-液界面行为相比,AAEMs在电池中的气-固-液环境要更为复杂,低的含水量使得OH⁻不能充分水合,催化层中局部OH⁻的浓度远大于

图4 (网络版彩色)基于哌啶季铵碱QAPPT膜(a)[100]与交联前后的E-Imds与XE-Imds膜(b)[40]组装的AAEMFCs稳定性测试. 测试条件: 0.2 A cm⁻²恒流放电, 80℃

Figure 4 (Color online) Durability of AAEMFCs using QAPPT[100] (a), pristine E-Imds and cross-linked XE-Imds (b) membranes under a constant current density of 0.2 A cm⁻² at 80℃[40]

膜体相浓度等,这对膜的碱性稳定性提出了更高的要求.此外,电池运行中产生大量自由基,强氧化性的环境可能进一步降低膜的稳定性,但是,目前对实际运行中AAEMs氧化稳定性的研究尚未展开,影响因素与机制有待深入系统研究,这对于高稳定的AAEMs以及AAEMFCs的发展具有重要的意义.

5 结论和展望

AAEMFCs因阴极氧还原动力学快、可使用非Pt催化剂等优点迅速成为燃料电池的重要发展方向之一.满足燃料电池应用要求的AAEMs的研发是AAEMFCs商业化应用必须解决的首要问题.目前AAEMs面临的主要问题包括电导率与尺寸稳定性难以协同兼备及化学稳定性较低的问题.针对这些问题,寻找新型高稳定性的阳离子基团,通过高分子链

源头设计开发新材料的同时, 对其进行必要的微观结构调控, 从而获得离子电导率、尺寸与化学稳定性兼备的碱性阴离子交换膜, 实现AAEMFCs下一个阶段1000 h使用寿命的目标. 此外, 阴离子在膜中的深

层传输机制、聚电解质在溶液以及成膜过程中的分子相互作用及其自组装机理、微观结构对膜化学稳定性的影响机制、影响AAEMFCs长时间稳定性的因素与机制等这些科学问题是未来研究的着力点.

参考文献

- 1 Lu S F, Peng S K, Xiang Y. Perspectives on the research progress of bipolar interfacial polyelectrolyte membrane fuel cell (in Chinese). *Acta Phys Chim Sin*, 2016, 32: 1859–1865 [卢善富, 彭思侃, 相艳. 双极界面聚合物膜燃料电池研究进展. *物理化学学报*, 2016, 32: 1859–1865]
- 2 Peng S K, Xu X, Zhang J, et al. Bipolar interfacial polyelectrolyte membrane fuel cell I: Structure of membrane electrode assembly (in Chinese). *Acta Chim Sin*, 2015, 73: 137–142 [彭思侃, 徐鑫, 张劲, 等. 双极界面聚合物膜燃料电池 I: 膜电极构型. *化学学报*, 2015, 73: 137–142]
- 3 Xu X, Peng S K, Zhang J, et al. Bipolar interfacial polyelectrolyte membrane fuel cell II: Optimization of cathode catalyst layer (in Chinese). *Acta Chim Sin*, 2016, 74: 271–276 [徐鑫, 彭思侃, 张劲, 等. 双极界面聚合物膜燃料电池 II: 阴极催化层结构优化. *化学学报*, 2016, 74: 271–276]
- 4 Lu S F, Xu X, Zhang J, et al. Progress of phosphoric acid doped high temperature proton exchange membrane for fuel cells (in Chinese). *Sci Sin Chim*, 2017, 47: 565–572 [卢善富, 徐鑫, 张劲, 等. 燃料电池用磷酸掺杂高温质子交换膜研究进展. *中国科学: 化学*, 2017, 47: 565–572]
- 5 Lu S, Pan J, Huang A, et al. Alkaline polymer electrolyte fuel cells completely free from noble metal catalysts. *Proc Natl Acad Sci USA*, 2008, 105: 20611–20614
- 6 Wang Y, Li L, Hu L, et al. A feasibility analysis for alkaline membrane direct methanol fuel cell: Thermodynamic disadvantages versus kinetic advantages. *Electrochem Commun*, 2003, 5: 662–666
- 7 Varcoe J R, Slade R C T. Prospects for alkaline anion-exchange membranes in low temperature fuel cells. *Fuel Cells*, 2005, 5: 187–200
- 8 He G, Li Z, Zhao J, et al. Nanostructured ion-exchange membranes for fuel cells: Recent advances and perspectives. *Adv Mater*, 2015, 27: 5280–5295
- 9 Wang Y, Wang G, Li G, et al. Pt-Ru catalyzed hydrogen oxidation in alkaline media: Oxophilic effect or electronic effect? *Energy Environ Sci*, 2015, 8: 177–181
- 10 Yuan Y, Shen C H, Chen J Q, et al. Research progress of alkaline anion exchange membranes (in Chinese). *Chem Ind Eng Prog*, 2017, 36: 3336–3342 [袁园, 沈春晖, 陈继钦, 等. 用于燃料电池的碱性阴离子交换膜研究进展. *化工进展*, 2017, 36: 3336–3342]
- 11 Pan J, Chen C, Zhuang L, et al. Designing advanced alkaline polymer electrolytes for fuel cell applications. *Acc Chem Res*, 2011, 45: 473–481
- 12 Ge X, He Y, Guiver M D, et al. Alkaline anion-exchange membranes containing mobile ion shuttles. *Adv Mater*, 2016, 28: 3467–3472
- 13 Yang Z, Guo R, Malpass-Evans R, et al. Highly conductive anion-exchange membranes from microporous tröger's base polymers. *Angew Chem Int Ed*, 2016, 55: 11499–11502
- 14 Dang H S, Jannasch P. High-performing hydroxide exchange membranes with flexible tetra-piperidinium side chains linked by alkyl spacers. *ACS Appl Energy Mater*, 2018, 1: 2222–2231
- 15 Wang L, Brink J J, Liu Y, et al. Non-fluorinated pre-irradiation-grafted (peroxidated) LDPE-based anion-exchange membranes with high performance and stability. *Energy Environ Sci*, 2017, 10: 2154–2167
- 16 Wang L, Brink J J, Varcoe J R. The first anion-exchange membrane fuel cell to exceed 1 W cm^{-2} at 70°C with a non-Pt-group (O_2) cathode. *Chem Commun*, 2017, 53: 11771–11773
- 17 Yang Z, Ran J, Wu B, et al. Stability challenge in anion exchange membrane for fuel cells. *Curr Opin Chem Eng*, 2016, 12: 22–30
- 18 Cheng J, He G, Zhang F. A mini-review on anion exchange membranes for fuel cell applications: Stability issue and addressing strategies. *Int J Hydrog Energy*, 2015, 40: 7348–7360
- 19 Varcoe J R, Atanassov P, Dekel D R, et al. Anion-exchange membranes in electrochemical energy systems. *Energy Environ Sci*, 2014, 7: 3135–3191
- 20 Gottesfeld S, Dekel D R, Page M, et al. Anion exchange membrane fuel cells: Current status and remaining challenges. *J Power Sources*, 2018, 375: 170–184
- 21 Dekel D R. Review of cell performance in anion exchange membrane fuel cells. *J Power Sources*, 2018, 375: 158–169

- 22 Fu X C, Shen W X, Yao T Y, et al. Physical Chemistry. 5th Ed, Volume II. (in Chinese). Beijing: Higher Education Press, 2006 [傅献彩, 沈文霞, 姚天扬, 等. 物理化学(第五版)下册. 北京: 高等教育出版社, 2006]
- 23 Xiang Y, Si J J. Strategies for reconciling tradeoff between conductivity and swelling in alkaline polymer electrolytes membrane (in Chinese). J Beijing Univ Aeron Astron, 2015, 41: 961–968 [相艳, 司江菊. 高电导率、低溶胀的碱性聚电解质膜的实现策略. 北京航空航天大学学报, 2015, 41: 961–968]
- 24 Pan J, Li Y, Han J, et al. A strategy for disentangling the conductivity-stability dilemma in alkaline polymer electrolytes. Energy Environ Sci, 2013, 6: 2912–2915
- 25 Si J, Lu S, Xu X, et al. A gemini quaternary ammonium poly (ether ether ketone) anion-exchange membrane for alkaline fuel cell: Design, synthesis, and properties. ChemSusChem, 2014, 7: 3389–3395
- 26 Lin C X, Wu H Y, Li L, et al. Anion conductive triblock copolymer membranes with flexible multication side chain. ACS Appl Mater Interfaces, 2018, 10: 18327–18337
- 27 Li Q, Liu L, Miao Q, et al. A novel poly(2,6-dimethyl-1,4-phenylene oxide) with trifunctional ammonium moieties for alkaline anion exchange membranes. Chem Commun, 2014, 50: 2791–2793
- 28 Ran J, Wu L, Wei B, et al. Simultaneous enhancements of conductivity and stability for anion exchange membranes (AEMs) through precise structure design. Sci Rep, 2014, 4: 6486
- 29 Pan J. A study of alkaline polymer electrolytes for fuel cell application (in Chinese). Doctor Dissertation. Wuhan: Wuhan University, 2012 [潘靖. 燃料电池用碱性聚合物电解质研究. 博士学位论文. 武汉: 武汉大学, 2012]
- 30 Peng Y, Lyu K, Wang Y, et al. Effect of H₂O on the phase separation of PEEK. Wuhan: Beijing Forum 2016 on Electrochemical Frontier, 2016. 6–9
- 31 Mauritz K A, Moore R B. State of understanding of Nafion. Chem Rev, 2004, 104: 4535–4586
- 32 He S S, Frank C W. Facilitating hydroxide transport in anion exchange membranes via hydrophilic grafts. J Mater Chem A, 2014, 2: 16489–16497
- 33 Li N, Yan T, Li Z, et al. Comb-shaped polymers to enhance hydroxide transport in anion exchange membranes. Energy Environ Sci, 2012, 5: 7888–7892
- 34 Li N, Leng Y, Hickner M A, et al. Highly stable, anion conductive, comb-shaped copolymers for alkaline fuel cells. J Am Chem Soc, 2013, 135: 10124–10133
- 35 Lin C X, Zhuo Y Z, Lai A N, et al. Comb-shaped phenolphthalein-based poly(ether sulfone)s as anion exchange membranes for alkaline fuel cells. RSC Adv, 2016, 6: 17269–17279
- 36 Rao A H N, Nam S, Kim T H. Comb-shaped alkyl imidazolium-functionalized poly(arylene ether sulfone)s as high performance anion-exchange membranes. J Mater Chem A, 2015, 3: 8571–8580
- 37 Chen Y, Tao Y, Wang J, et al. Comb-shaped guanidinium functionalized poly(ether sulfone)s for anion exchange membranes: Effects of the spacer types and lengths. J Polym Sci Polym Chem, 2017, 55: 1313–1321
- 38 Pan J, Chen C, Li Y, et al. Constructing ionic highway in alkaline polymer electrolytes. Energy Environ Sci, 2014, 7: 354–360
- 39 Dang H S, Jannasch P. Exploring different cationic alkyl side chain designs for enhanced alkaline stability and hydroxide ion conductivity of anion-exchange membranes. Macromolecules, 2015, 48: 5742–5751
- 40 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
- 41 Si J, Wang H, Lu S, et al. *In situ* construction of interconnected ion transfer channels in anion-exchange membranes for fuel cell application. J Mater Chem A, 2017, 5: 4003–4010
- 42 Lin C X, Wang X Q, Li L, et al. Triblock copolymer anion exchange membranes bearing alkyl-tethered cycloaliphatic quaternary ammonium-head-groups for fuel cells. J Power Sources, 2017, 365: 282–292
- 43 Zhang X, Li S, Chen P, et al. Imidazolium functionalized block copolymer anion exchange membrane with enhanced hydroxide conductivity and alkaline stability via tailoring side chains. Int J Hydrogen Energy, 2018, 43: 3716–3730
- 44 Strasser D J, Graziano B J, Knauss D M. Base stable poly(diallylpiperidinium hydroxide) multiblock copolymers for anion exchange membranes. J Mater Chem A, 2017, 5: 9627–9640
- 45 Cha M S, Lee J Y, Kim T H, et al. Preparation and characterization of crosslinked anion exchange membrane (AEM) materials with poly(phenylene ether)-based short hydrophilic block for use in electrochemical applications. J Membr Sci, 2017, 530: 73–83
- 46 Xue B, Dong X, Li Y, et al. Synthesis of novel guanidinium-based anion-exchange membranes with controlled microblock structures. J Membr Sci, 2017, 537: 151–159
- 47 Zhu M, Zhang X, Wang Y, et al. Novel anion exchange membranes based on quaternized diblock copolystyrene containing a fluorinated hydrophobic block. J Membr Sci, 2018, 554: 264–273

- 48 Dong X, Xue B, Qian H, et al. Novel quaternary ammonium microblock poly(*p*-phenylene-*co*-aryl ether ketone)s as anion exchange membranes for alkaline fuel cells. *J Power Sources*, 2017, 342: 605–615
- 49 Kim E, Lee S, Woo S, et al. Synthesis and characterization of anion exchange multi-block copolymer membranes with a fluorine moiety as alkaline membrane fuel cells. *J Power Sources*, 2017, 359: 568–576
- 50 Mohanty A D, Ryu C Y, Kim Y S, et al. Stable elastomeric anion exchange membranes based on quaternary ammonium-tethered polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene triblock copolymers. *Macromolecules*, 2015, 48: 7085–7095
- 51 Zhu M, Zhang M, Chen Q, et al. Synthesis of midblock-quaternized triblock copolystyrenes as highly conductive and alkaline-stable anion-exchange membranes. *Polym Chem*, 2017, 8: 2074–2086
- 52 Meek K M, Sun R, Willis C, et al. Hydroxide conducting polymerized ionic liquid pentablock terpolymer anion exchange membranes with methylpyrrolidinium cations. *Polymer*, 2018, 134: 221–226
- 53 Zhang X, Shi Q, Chen P, et al. Block poly(arylene ether sulfone) copolymers tethering aromatic side-chain quaternary ammonium as anion exchange membranes. *Polym Chem*, 2018, 9: 699–711
- 54 Lin C X, Wang X Q, Hu E N, et al. Quaternized triblock polymer anion exchange membranes with enhanced alkaline stability. *J Membrane Sci*, 2017, 541: 358–366
- 55 Gao X, Lu F, Liu Y, et al. The facile construction of an anion exchange membrane with 3D interconnected ionic nano-channels. *Chem Commun*, 2017, 53: 767–770
- 56 Tsai T H, Maes A M, Vandiver M A, et al. Synthesis and structure-conductivity relationship of polystyrene-block-poly(vinyl benzyl trimethylammonium) for alkaline anion exchange membrane fuel cells. *J Polym Sci Polym Phys*, 2013, 51: 1751–1760
- 57 Hsu W Y, Barkley J R, Meakin P. Ion percolation and insulator-to-conductor transition in nafion perfluorosulfonic acid membranes. *Macromolecules*, 1980, 13: 198–200
- 58 Sun Z, Lin B, Yan F. Anion-exchange membranes for alkaline fuel-cell applications: The effects of cations. *ChemSusChem*, 2018, 11: 58–70
- 59 Gu L, Sun Z, Xu D, et al. Progress of alkaline anion exchange membranes (in Chinese). *J Funct Polym*, 2016, 29: 153–162 [顾梁, 孙哲, 徐丹, 等. 碱性阴离子交换聚合物膜研究进展. *功能高分子学报*, 2016, 29: 153–162]
- 60 Si Z, Qiu L, Dong H, et al. Effects of substituents and substitution positions on alkaline stability of imidazolium cations and their corresponding anion-exchange membranes. *ACS Appl Mater Interfaces*, 2014, 6: 4346–4355
- 61 Gu F, Dong H, Li Y, et al. Highly stable N3-substituted imidazolium-based alkaline anion exchange membranes: Experimental studies and theoretical calculations. *Macromolecules*, 2013, 47: 208–216
- 62 Lin B, Dong H, Li Y, et al. Alkaline stable C2-substituted imidazolium-based anion-exchange membranes. *Chem Mater*, 2013, 25: 1858–1867
- 63 Marino M G, Kreuer K D. Alkaline stability of quaternary ammonium cations for alkaline fuel cell membranes and ionic liquids. *ChemSusChem*, 2015, 8: 513–523
- 64 Mohanty A D, Bae C. Mechanistic analysis of ammonium cation stability for alkaline exchange membrane fuel cells. *J Mater Chem A*, 2014, 2: 17314–17320
- 65 Price S C, Williams K S, Beyer F L. Relationships between structure and alkaline stability of imidazolium cations for fuel cell membrane applications. *ACS Macro Lett*, 2014, 3: 160–165
- 66 Wright A G, Holdcroft S. Hydroxide-stable ionenes. *ACS Macro Lett*, 2014, 3: 444–447
- 67 Fan J, Wright A G, Britton B, et al. Cationic polyelectrolytes, stable in 10 mol L⁻¹ KOH_{aq} at 100°C. *ACS Macro Lett*, 2017, 6: 1089–1093
- 68 Long H, Kim K, Pivovar B S. Hydroxide degradation pathways for substituted trimethylammonium cations: A DFT study. *J Phys Chem C*, 2012, 116: 9419–9426
- 69 Chempath S, Einsla B R, Pratt L R, et al. Mechanism of tetraalkylammonium headgroup degradation in alkaline fuel cell membranes. *J Phys Chem C*, 2008, 112: 3179–3182
- 70 Dekel D R, Amar M, Willdorf S, et al. Effect of water on the stability of quaternary ammonium groups for anion exchange membrane fuel cell applications. *Chem Mater*, 2017, 29: 4425–4431
- 71 Liu X, Chen X, Pei S, et al. Evaluation of water in perfluorinated anion exchange membranes with different iec values. *J Phys Chem C*, 2017, 121: 17546–17551
- 72 Chen N, Long C, Li Y, et al. Ultrastable and high ion-conducting polyelectrolyte based on six-membered *n*-spirocyclic ammonium for hydroxide exchange membrane fuel cell applications. *ACS Appl Mater Interfaces*, 2018, 10: 15720–15732
- 73 Olsson J S, Pham T H, Jannasch P. Poly(arylene piperidinium) hydroxide ion exchange membranes: Synthesis, alkaline stability, and conductivity. *Adv Funct Mater*, 2018, 28: 1702758
- 74 Pham T H, Olsson J S, Jannasch P. *N*-spirocyclic quaternary ammonium ionenes for anion-exchange membranes. *J Am Chem Soc*, 2017, 139: 2888–2891

- 75 Arges C G, Ramani V. Two-dimensional nmr spectroscopy reveals cation-triggered backbone degradation in polysulfone-based anion exchange membranes. *Proc Natl Acad Sci USA*, 2013, 110: 2490–2495
- 76 Fujimoto C, Kim D S, Hibbs M, et al. Backbone stability of quaternized polyaromatics for alkaline membrane fuel cells. *J Membrane Sci*, 2012, 423–424: 438–449
- 77 Mohanty A D, Tignor S E, Krause J A, et al. Systematic alkaline stability study of polymer backbones for anion exchange membrane applications. *Macromolecules*, 2016, 49: 3366–3372
- 78 Gao L, He G, Pan Y, et al. Poly(2,6-dimethyl-1,4-phenylene oxide) containing imidazolium-terminated long side chains as hydroxide exchange membranes with improved conductivity. *J Membrane Sci*, 2016, 518: 159–167
- 79 Nuñez S A, Hickner M A. Quantitative ^1H NMR analysis of chemical stabilities in anion-exchange membranes. *ACS Macro Lett*, 2013, 2: 49–52
- 80 Miyanishi S, Fukushima T, Yamaguchi T. Synthesis and property of semicrystalline anion exchange membrane with well-defined ion channel structure. *Macromolecules*, 2015, 48: 2576–2584
- 81 Lee W-H, Park E J, Han J, et al. Poly(terphenylene) anion exchange membranes: The effect of backbone structure on morphology and membrane property. *ACS Macro Lett*, 2017, 6: 566–570
- 82 Olsson J S, Pham T H, Jannasch P. Poly(*N,N*-diallylazacycloalkane)s for anion-exchange membranes functionalized with *n*-spirocyclic quaternary ammonium cations. *Macromolecules*, 2017, 50: 2784–2793
- 83 Park E J, Kim Y S. Quaternized aryl ether-free polyaromatics for alkaline membrane fuel cells: Synthesis, properties, and performance-a topical review. *J Mater Chem A*, 2018, 6: 15456–15477
- 84 Lee W H, Kim Y S, Bae C. Robust hydroxide ion conducting poly(biphenyl alkylene)s for alkaline fuel cell membranes. *ACS Macro Lett*, 2015, 4: 814–818
- 85 Lee W H, Mohanty A D, Bae C. Fluorene-based hydroxide ion conducting polymers for chemically stable anion exchange membrane fuel cells. *ACS Macro Lett*, 2015, 4: 453–457
- 86 Nawn G, Vezzù K, Cavinato G, et al. Opening doors to future electrochemical energy devices: The anion-conducting polyketone poly-electrolytes. *Adv Funct Mater*, 2018, 28: 1706522
- 87 Zhang M, Liu J, Wang Y, et al. Highly stable anion exchange membranes based on quaternized polypropylene. *J Mater Chem A*, 2015, 3: 12284–12296
- 88 Zhang M, Shan C, Liu L, et al. Facilitating anion transport in polyolefin-based anion exchange membranes via bulky side chains. *ACS Appl Mater Interfaces*, 2016, 8: 23321–23330
- 89 You W, Hugar K M, Coates G W. Synthesis of alkaline anion exchange membranes with chemically stable imidazolium cations: Unexpected cross-linked macrocycles from ring-fused romp monomers. *Macromolecules*, 2018, 51: 3212–3218
- 90 Graha H P R, Ando S, Miyanishi S, et al. Development of a novel durable aromatic anion exchange membrane using a thermally convertible precursor. *Chem Commun*, 2018, 54: 10820–10823
- 91 Xu F, Yuan W S, Zhu Y Y, et al. Preparation and properties of anion exchange membranes based on spirocyclic quaternary ammonium salts (in Chinese). *Chin Sci Bull*, 2018, 64: 165–171 [徐斐, 袁文森, 朱媛媛, 等. 基于螺环季铵盐的阴离子交换膜的制备与性能. *科学通报*, 2018, 64: 165–171]
- 92 Dang H S, Jannasch P. A comparative study of anion-exchange membranes tethered with different hetero-cycloaliphatic quaternary ammonium hydroxides. *J Mater Chem A*, 2017, 5: 21965–21978
- 93 Hu E N, Lin C X, Liu F H, et al. Poly(arylene ether nitrile) anion exchange membranes with dense flexible ionic side chain for fuel cells. *J Membrane Sci*, 2018, 550: 254–265
- 94 Liu C, Feng S, Zhuang Z, et al. Towards basic ionic liquid-based hybrid membranes as hydroxide-conducting electrolytes under low humidity conditions. *Chem Commun*, 2015, 51: 12629–12632
- 95 Liu C, Zhang G, Zhao C, et al. MOFs synthesized by the ionothermal method addressing the leaching problem of IL-polymer composite membranes. *Chem Commun*, 2014, 50: 14121–14124
- 96 Zha Y, Disabb-Miller M L, Johnson Z D, et al. Metal-cation-based anion exchange membranes. *J Am Chem Soc*, 2012, 134: 4493–4496
- 97 Zhu T, Xu S, Rahman A, et al. Cationic metallo-polyelectrolytes for robust alkaline anion-exchange membranes. *Angew Chem Int Ed*, 2018, 57: 2388–2392
- 98 Gu S, Wang J, Kaspar R B, et al. Permethyl cobaltocenium (Cp^*_2Co^+) as an ultra-stable cation for polymer hydroxide-exchange membranes. *Sci Rep*, 2015, 5: 11668
- 99 Wu B, Ge L, Yu D, et al. Cationic metal-organic framework porous membranes with high hydroxide conductivity and alkaline resistance for fuel cells. *J Mater Chem A*, 2016, 4: 14545–14549
- 100 Peng H, Li Q, Hu M, et al. Alkaline polymer electrolyte fuel cells stably working at 80°C. *J Power Sources*, 2018, 390: 165–167

-
- 101 Liu L, Chu X, Liao J, et al. Tuning the properties of poly(2,6-dimethyl-1,4-phenylene oxide) anion exchange membranes and their performance in H_2/O_2 fuel cells. *Energy Environ Sci*, 2018, 11: 435–446
-

补充材料

表 S1 常见阳离子基团的碱性稳定性

表 S2 主链不含醚键的阴离子交换膜及其碱性稳定性

本文以上补充材料见网络版 csb.scichina.com. 补充材料为作者提供的原始数据, 作者对其学术质量和内容负责.

Summary for “燃料电池用碱性阴离子交换膜链结构调控研究进展”

Progress of polymer chain structure regulation of alkaline anion-exchange membranes for fuel cells

Jiangju Si^{1,2}, Shanfu Lu^{1*} & Yan Xiang^{1*}¹ Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Space and Environment, Beihang University, Beijing 100191, China;² School of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453003, China

* Corresponding authors, E-mail: lusf@buaa.edu.cn; xiangy@buaa.edu.cn

Alkaline anion-exchange membrane fuel cells (AAEMFCs) have attracted worldwide interest due to their advantages including fast oxygen reduction kinetics, high compatibility with non-precious-metal catalyst and low cost. As one of the key components in AAEMFCs, the performance of alkaline anion exchange membranes (AAEMs) directly affects the power output and durability of the fuel cells. During fuel cell operating, AAEMs require high ionic conductivity, excellent dimensional and chemical stability to ensure high efficiency and outstanding durability. However, it is still difficult for any type of the AAEMs to meet all these requirements. This monograph summarizes recent development around the world for AAEMs, especially for the trade-off effect between ionic conductivity and stability of AAEMs as well as the proposed strategies for this issue. The charge carrier in AAEMs is OH^- , and it has a lower transporting efficiency owing to its lower mobility, higher dependence on water molecular and the blocking of many hydrophobic domains in AAEMs. The improvement of ion-exchange capacity (IEC) by increasing the grafting degree (GD) of cationic functional groups can, to some extent, solve this issue. However, a high GD always brings the following negative issues: (1) Excessive swelling of AAEMs and significant reducing in the dimensional stability of membranes; (2) the increase of OH^- concentration accelerates the kinetics of nucleophilic substitution and Hofmann elimination, leading to the degradation of cationic groups; (3) the enhanced polarization of the cationic groups and the hydrophilicity of the main chain enable the polymer backbone susceptible to nucleophilic attack by OH^- , resulting in the degradation of the membrane, and even short-circuit of the fuel cells.

In order to solve these issues, various of polymer chain architectures have been designed and regulated. To balance the ionic conductivity and the dimensional stability in AAEMs, double, triple and multi-cations are grafted on one site of polymer backbone to achieve a sufficiently high IEC at relatively low GD. Another realistic strategy is constructing 3D anion channels by the segregated hydrophilic/hydrophobic phase. The alkali stability of the cationic groups is affected by many factors including field effects, steric effects and conformation of substituent groups, and so on. The improvement of chemical stability of AAEMs has been another formidable scientific challenge. Researchers reduce the kinetics of the nucleophilic substitution and elimination reactions, and improve the basic stability of the cationic groups by modulating the structure of substituent groups such as the introduction of electron-donating groups, increased steric hindrance, and adequate hydration of OH^- . Among various cationic groups, the piperidinium-based cations show high resistance against both nucleophilic substitution and elimination in alkaline conditions and at elevated temperature. Furthermore, the polymer backbones without ether band and electron-withdrawing groups have been synthesized and exhibit highly resistant to alkali hydrolysis. Recently, new strategy for constructing ordered ion channels in AAEMs by novel porous materials such as metal-organic frameworks (MOF), Tröger's base, and macrocyclic crown ether compounds, provide for efficient ionic transport. Additionally, highly stable metal complexes have been used as cationic group in AAEMs. These new trends will open up an exciting opportunity to design high-performance AAEMs.

The appearance of highly stable AAEMs enables the AAEMFCs to be operated at 80°C , and the cell works stably in a period of study over 100 h. Although this progress is encouraging, there still remains work for improving the cell performance and stability. A 1000 h of stable operation at elevated temperatures will be the next mission for AAEMFCs. In addition, there are some fundamental issues necessary to explore, such as the transport mechanism of OH^- in the membrane, the molecular interaction of polyelectrolytes and their self-assembly mechanism in solution and film formation, the mechanism of the influence of morphology on the chemical stability of AAEMs, and the factors affecting the long-term stability of AAEMFCs. These scientific issues will be the focus of future research.

The development of AAEMFCs is on its way, and it calls for more efforts in fundamental study, polymer chain architectures and morphology designing, and fuel cell engineering to make it viable.

fuel cells, alkaline anion-exchange membrane, ionic conductivity, alkaline stability, microstructure

doi: 10.1360/N972018-00767