



一体式再生燃料电池的研究进展与展望

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摘要 一体式再生燃料电池(unitized regenerative fuel cell, URFC)在同一装置内集成了燃料电池(fuel cell, FC)发电和水电解(water electrolyzer, WE)制氢双功能, 具有高比能量、高能量转换率、清洁高效等优势. 随着氢能的发展, URFC在储供能、长时动力系统、空间电源等领域极具应用价值. 然而, URFC规模化应用存在诸多瓶颈, 如双工作模式往返效率低、催化剂贵金属载量高、性能衰减快和运行不稳定, 主要原因是关于URFC的研究尚在起步阶段, 对于URFC反应机制和水热管理调控仍不明确. 本文从URFC工作原理及分类出发, 重点关注恒定气体构型URFC的部件及材料研究进展, 阐述双功能模式对催化剂、多孔传输层和极板的材料、结构和寿命的影响机制, 分析两种工作模式带来的水气传输规律及模式切换需求, 旨在为提升URFC综合性能提供方法指导. 本文系统地对URFC双功能部件的研究进展进行总结, 并对未来高功率、高效率的URFC发展进行展望.

关键词 一体式再生燃料电池, 发电模式, 电解模式, 双功能, 双极板, 水气传输

我国提出了“碳达峰、碳中和”的发展路线, 发展绿色清洁能源是解决能源危机和环境污染问题的理想方案^[1]. 氢能由于热值高、能量输出稳定、产物零污染等优势, 被认为是21世纪化石燃料的替代能源. 氢能与可再生能源融合, 利用太阳能、风能等进行水电解制氢, 从而实现长时存储和远距离运输^[2]. 一体式再生燃料电池(unitized regenerative fuel cell, URFC)是一种将燃料电池(FC)及电解槽(WE)耦合的电化学装置, 可实现在FC模式放电和WE模式制氢之间自由切换, 具有高比能量、快速启动及高转换率等优势, 在分布式储能、电网调峰、长续航动力系统、航空航天等领域均有应用前景.

根据电解质类型和工作温度, URFC可以分为质子交换膜URFC(PEM-URFC)、碱性URFC(ALK-URFC)和固体氧化物URFC(SO-URFC). 其中PEM-URFC具有

工作温度低、启动快、动态载荷响应快、耐久性好等优势, 且技术更加成熟. 因此, 自21世纪以来, PEM-URFC逐渐受到国内外学者的关注, 本研究也以PEM-URFC综述为主, 其比能量密度有望达到0.4~1.0 kWh/kg(含储氢、储氧装置), 能量转化效率超50%^[3~5]. 日本宇宙航空研究开发机构(JAXA)^[6]设计了100 W级的URFC, 可在40~60°C的温度范围内运行. 俄罗斯Kurchatov研究所^[7]开发了500 W的URFC(有效面积256 cm²), 在WE模式电功率为1.5 kW, 但在电流密度为0.5 A/cm²时往返效率(round-trip efficiency, RTE)仅有30%. 美国劳伦斯伯克利国家实验室^[8,9]开发了多尺度分层结构催化剂, 在1 A/cm²时RTE超过50%. 上海交通大学^[10]研究了双功能水气传输规律, 开发了kW级URFC电堆, FC模式功率6.01 kW, WE模式功率18.16 kW. 2022年, 美国联邦航空局(FAA)^[11]公布了URFC在飞机上应用的实验数

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据. 随着氢能的发展, URFC逐渐由实验室材料级别的研究, 向高功率的实际应用场景如储能、空间能源等拓展(表1).

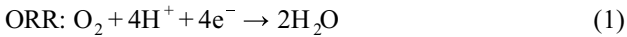
然而, URFC的规模化应用仍面临诸多的挑战, 存在RTE低、材料衰减快、成本高等瓶颈. 一方面, URFC部件难以兼顾FC模式和WE模式的双向反应和水气传输需求, 使得贵金属载量需求大、传质损耗高, FC模式和WE模式的效率无法达到单模式燃料电池和电解槽的现阶段效率^[4]; 另一方面, URFC在长期运行中, 恶劣的工作环境和频繁的循环操作易导致性能衰减加速^[14]. 本文对国内外URFC研究现状进行了总结评述, 并展望了未来URFC研究的重点.

1 一体式再生燃料电池分类及原理

URFC的结构如图1所示, 主要包括双极板(bipolar

plates, BPP)、多孔传输层(porous transport layer, PTL)、催化层(catalyst layer, CL)和质子交换膜(proton exchange membrane, PEM). 根据FC和WE两种模式下的氢氧传输方式, 可将URFC构型分为两种: 恒定气体(constant gas, CG)构型和恒定电极(constant electrode, CE)构型^[8], 两种构型的示意图分别如图1(a), (b)所示.

如图1(a)所示, 在CG构型中, FC模式下通氧产水, 发生氧还原反应(oxygen reduction reaction, ORR)的一侧在WE模式下通水产氧, 发生析氧反应(oxygen evolution reaction, OER), 通常被定义为氧侧^[15,16], 反应方程式分别为



同理, WE模式时通入氢气, 发生氢氧化反应(hy-

表 1 典型URFC技术现状^[12,13]

Table 1 Technology status of different URFCs^[12,13]

类型	工作温度(°C)	往返效率(RTE, %)	特点	优势	瓶颈
PEM-URFC	10~120	40~55	离子聚合物电解质、贵金属催化剂	启动速度快、响应快、技术相对成熟	成本高、双向效率较低、部件耐久性不足
ALK-URFC	20~120	30~40	碱性溶液电解质/阴离子离子聚合物电解质、非贵金属催化剂	结构简单, 无电解质泄漏, 非贵金属催化剂	电解质离子电率低、动态响应差、催化剂耐久性差、往返效率低
SO-URFC	600~1000	60~80	陶瓷电解质、高转化效率、非贵金属催化剂	高往返效率、非贵金属催化剂	启动慢、耐久性低

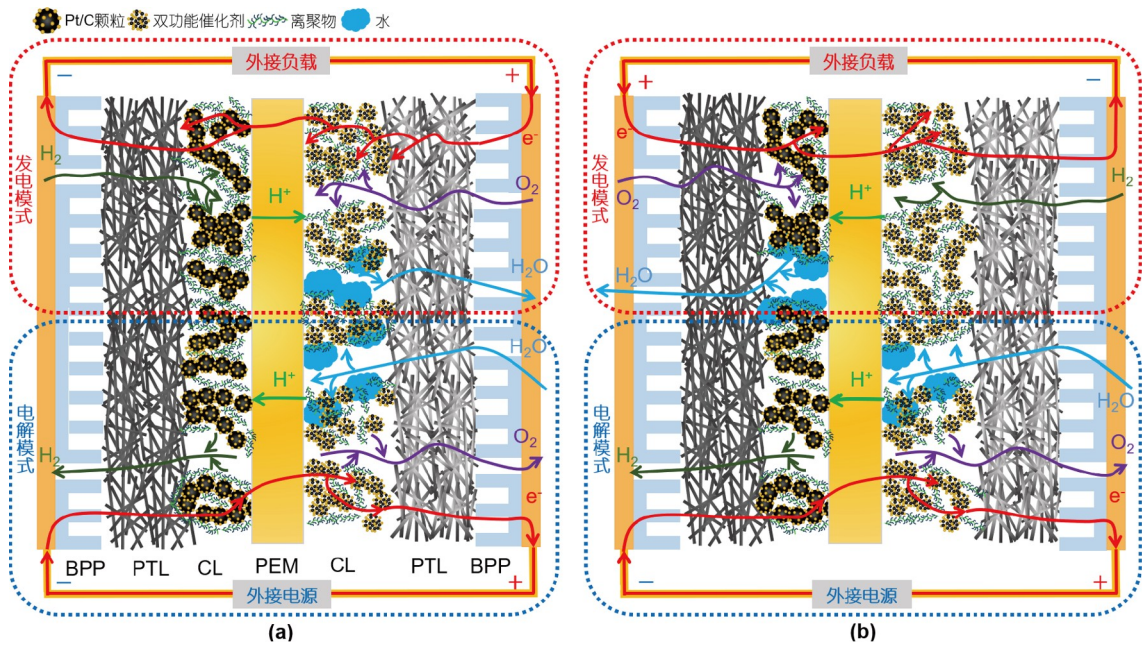


图 1 (网络版彩色)URFC结构及不同构型示意图. (a) 恒定气体(CG)构型; (b) 恒定电极(CE)构型

Figure 1 (Color online) URFC structure and different configurations. (a) Constant gas (CG) configuration; (b) constant electrode (CE) configuration

drogen oxidation reaction, HOR)的一侧在WE模式下产生氢气, 发生氢还原反应(hydrogen evolution reaction, HER), 通常被定义为氢侧, 反应方程式分别为



对于CG构型, 两种模式下氧侧一直处于高电位状态, 氢侧一直处于低电位状态。

对于CE构型, 如图1(b)所示, FC模式下通氧产水, 发生ORR的一侧在WE模式下产生氢气, 发生HER, 两种模式下均为还原反应, 电极从高电位状态转变为低电位状态; FC模式下承担HOR的另一侧, 在WE模式下通水产氧, 发生OER, 两种模式下均为氧化反应, 电极从低电位状态转变为高电位状态。

CE构型将OER和ORR分离到PEM的两侧, 便于对两侧催化层进行独立优化, 相同贵金属催化剂载量下CE构型的RTE往往比CG构型的RTE更高^[8,17]。因此, CE构型成本相对更低, 在分布式储能、电网调峰等领域具有广阔的应用前景。然而, CE构型进行双向模式切换会使氢氧传输通道发生交换、系统辅件变得更为复杂; 且容易发生氢氧混合, 进而导致催化剂材料降解加速, URFC耐久性降低^[13]。相比而言, CG构型避免了FC-WE模式切换时氢氧的混合^[13], 系统更加简单, 因此在长续航无人机、小型航天飞行器、空间及地外星系储能等方面应用潜力巨大。为此, 研究者进行了广泛而深入的研究, 本文将围绕CG构型的URFC研究展开综述。

2 URFC双功能部件及材料研究

2.1 双功能催化剂的研究进展

双功能催化剂的催化活性、稳定性及利用率是决定URFC效率和成本的关键因素。本节将从双功能催化机理出发, 对催化剂的构效关系进行分析, 介绍其研究现状及发展趋势。目前, 关于双功能催化剂的代表性研究如表S1所示。

2.1.1 双功能氢催化剂

已有文献^[18-22]表明, 双功能氢催化剂WE模式下所承担的HER的催化机制遵循Volmer-Heyrovsky机制或Volmer-Tafel机制, 在FC模式下所承担的HOR的催化机制遵循相应的逆反应, 即Heyrovsky-Volmer机制或Tafel-Volmer机制。Razzaq等人^[18]结合微观动力学建模和数据驱动方法, 发现双功能氢催化剂在两种模式下的

反应机制往往是电化学机制-化学机制相耦合, 而非遵循某个单一机制。长期以来, Pt一直是URFC中最高效、最稳定的双功能氢催化剂材料, 其负载已经降低到0.3 mg/cm²以下^[23,24]。为进一步降低成本, 超低贵金属载量或无贵金属的双功能氢催化剂材料成为趋势。在超低贵金属载量的双功能氢催化剂研究方面, Hunt等人^[25]制备了由掺钛碳化钨纳米颗粒涂有单层贵金属原子(Pt或PtRu)的催化剂, 如图2(a)所示, 其性能与商用的Pt/C(~20 wt%)催化剂相近, 如图2(b)所示, 并在酸性电解质条件下具有更好的耐久性。Liang等人^[26]将超小Ru纳米颗粒负载在泡沫镍上生长的Ni₃N纳米片上, 成功合成了一种用于HOR和HER的Ru/Ni₃N-NF双功能氢催化剂, 如图2(c)所示, HOR活性是商业Pt/C的近2倍, HER过电位低于Pt/C和其他Ru基催化剂。在非贵金属双功能氢催化剂研究方面, Liu等人^[27]在泡沫铜上生长高熵合金(NNM-HEA@CF)作为自支撑催化电极, 该催化剂通过优化活性中心的电子结构, 极大地促进了HER/HOR催化过程, 如图2(d)所示, 成本低于商用Pt/C基电池的1/6。虽然许多金属基(磷化物、碳化物、硫化物、氮化物、硼化物)和无金属(杂原子掺杂碳)催化剂表现出较高的HER活性, 但大多数材料HOR活性较差^[28,29]。总体而言, 非贵金属催化剂在催化活性、稳定性上相较于贵金属催化剂仍有一定差距, 距离商业化应用仍有较大的进步空间。

2.1.2 双功能氧催化剂

已有研究表明, 在较高氧覆盖浓度下, 双功能氧催化剂在FC模式下承担的ORR遵循联合机理^[30,31], 当催化剂对*OOH吸附较强而对*OH吸附较弱时, ORR活性较强^[32]。但迄今为止, 大量的实验表明, 多数材料的 ΔG_{*OOH} 和 ΔG_{*OH} 之间存在一定的正相关关系, 如图3(a)所示, 导致无法在增强*OOH吸附能的同时降低*OH吸附能^[33]。图3(b)为以 ΔG_{*OH} 为描述符的材料ORR活性火山图。从图中可以看出, Pt金属较为接近顶点, 是较理想的ORR催化材料。另一方面, 研究者常用吸附物演化机制(adsorbate evolution mechanism, AEM)来描述WE模式下的反应机理^[34-36], 当催化剂对*O吸附较强而对*OH吸附较弱时, OER活性越强, $\Delta G_{*O} - \Delta G_{*OH}$ 也常被作为OER活性的通用描述符。根据图3(a)可知, ΔG_{*O} 与 ΔG_{*OH} 之间存在正相关关系, 因此得到如图3(c)所示以过电位 η 为纵坐标, 以 $\Delta G_{*O} - \Delta G_{*OH}$ 为横坐标的OER活性火山图^[37]。从图中可以看出, IrO₂和RuO₂接近火山图顶点, 对*O和*OH具有合适的吸附能, 并且二者在酸性

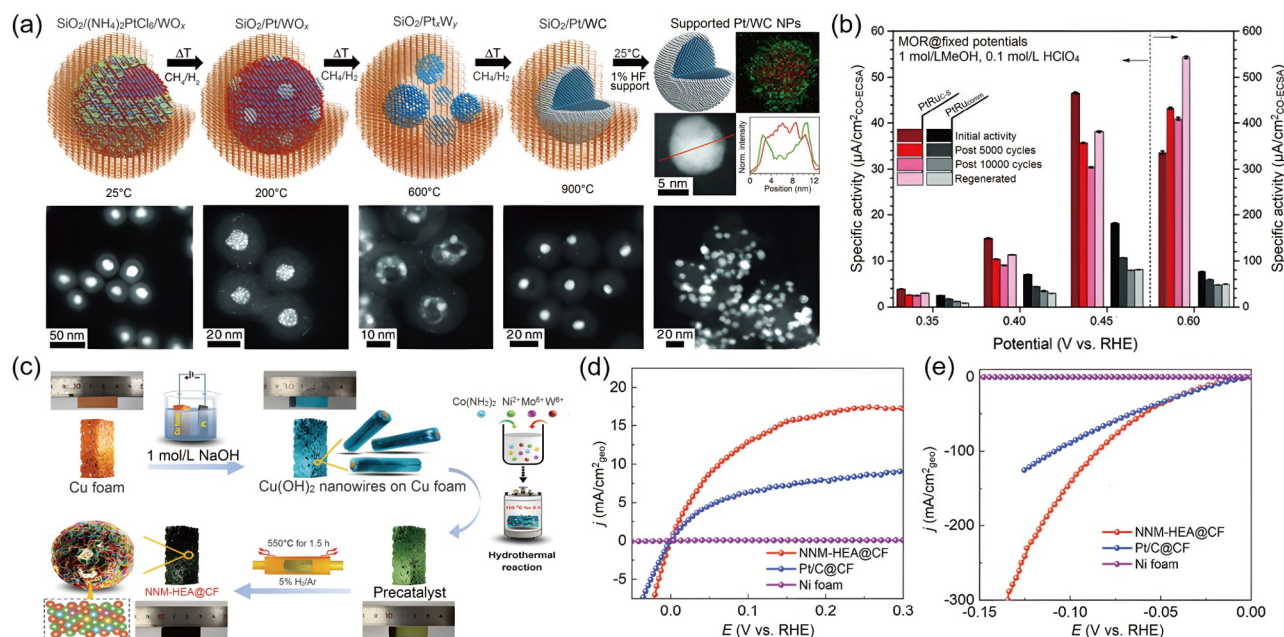


图 2 (网络版彩色)双功能氢催化剂研究进展。(a) 超低贵金属载体Pt/WC催化剂合成与表征及耐久性测试^[25]；(b) HOR/HER活性和耐久性结果^[25]；(c) 高熵合金(NNM-HEA@CF)作为自支撑催化电极合成^[27]，以及该电极、Pt/C电极和泡沫镍电极的HER(d)和HOR(e)线性扫描伏安特性曲线^[27]

Figure 2 (Color online) Research progress of bifunctional hydrogen catalysts. (a) Synthesis and characterization of Pt/WC catalysts with ultra-low noble metal loading^[25]; (b) HOR/HER activity and durability results^[25]; (c) schematic diagram of non-precious metal high entropy alloy (NNM-HEA@CF) as a self-supported catalytic electrode synthesis method^[27], and the linear sweep voltametric curves for the HER (d) and HOR (e) of the self-supported catalytic electrode, Pt/C electrode and nickel foam electrode^[27]

环境下具有较强的稳定性^[38]，如图3(d)所示，因此是较为理想的OER催化剂。

然而，ORR及OER两种反应速度控制步骤并不相同，且不同含氧产物在金属表面的结合能存在一定的正相关关系，导致材料难以兼具最佳ORR活性和最佳OER活性^[39]。为此，通常将Pt和IrO₂两种材料复合制备双功能氧催化剂^[40–46]。Da Silva等人^[46]通过甲酸合成法将Pt沉积在由氨诱导法制备的IrO₂上，ORR活性较商业Pt黑提升近两倍，但OER活性较商业IrO₂有所下降；Lim等人^[42]制备了以Pt为基底的Pt@IrO₂核壳结构催化剂，如图4(a)、(b)所示，贵金属载量为0.8 mg/cm²，实验结果表明在2 V工况下，改进后的核壳结构催化剂的质量活性为44 A/mg_{Ir}，高于普通电沉积IrO₂的21 A/mg_{Ir}，但催化剂的XPS表征中没有Pt出现，如图4(c)所示，表明Pt基本被阻碍，导致ORR性能较低，如图4(d)所示。除了上述方法以外，还可以通过调整含氧中间产物吸附能线性关系提高双功能催化剂活性，Doyle等人^[47]提出通过结合RuO₂(或IrO₂)与沸石，构建一种三维纳米结构来为反应提供一种受限或束缚的环境，以形成的氢键来稳定*OOH，打破*OOH与*OH吸附能的线性关系。另一种

方法是建立新的反应机制来突破火山图的顶点，Tarascon^[37]设计了La₂LiIrO₆催化剂，发现OER不再遵循AEM机制，如图4(e)所示，而遵循图4(f)所示的晶格氧参与机制(lattice-oxygen-mediated mechanism, LOM)。LOM机制在评价OER活性时无需考虑*OOH与*OH吸附能的线性关系，所设计的催化剂可以具有更高的OER活性，但稳定性降低^[34]。综上所述，将Pt和IrO₂两种材料复合仍是制备双功能氧催化剂最常用的方法之一，但作为支撑的催化剂材料的活性将受到抑制。

高比面积的载体是提高双功能氧催化剂利用率的有效方式，可提升催化活性，阻止贵金属迁移、溶解和团聚带来的性能衰减。然而，FC模式常用的碳载体在电解的高电位下腐蚀严重，并不适用于双功能氧催化剂^[13,48]。为此，高电位环境下耐久性较好的过渡金属氧化物成为载体的研究热点。Park课题组^[49]利用钴前驱体置换法制备了Ti₄O₇载体材料，降低了催化剂的O-O吸附能，提高了ORR催化活性。然而，这种催化剂的OER活性低于商用IrO₂，可能是由于载体导电性不足、Ir利用率不高导致。为了抑制贵金属的溶解，Ko等人^[50]以导电纳米氧化铟锡(ATO)为载体，结合树突状Pt和Ir

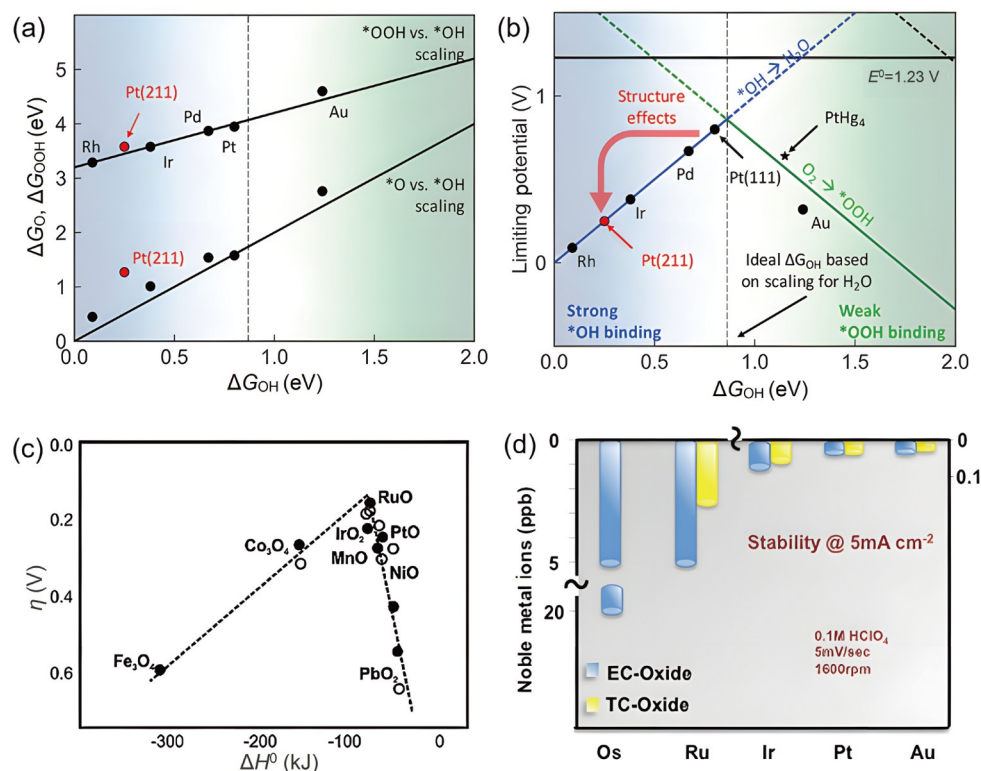


图3 (网络版彩色)双功能氧催化剂理论分析. (a) *OOH 、 *O 、 *OH 三种含氧中间产物之间吸附能关系图^[33]; (b) ORR活性火山图^[33]; (c) OER活性火山图^[37]; (d) 五种材料在酸性环境下的贵金属元素溶解率^[38]

Figure 3 (Color online) Theoretical analysis of bifunctional oxygen catalysts. (a) Adsorption energy relationship between *OOH , *O , *OH three oxygen-containing intermediates^[33]; (b) ORR active volcano map^[33]; (c) OER active volcano map^[37]; (d) solubility of precious metal elements in acidic environment of five materials^[38]

催化剂制备电极,发现与PtIr/C催化剂相比,ATO与催化剂的结合更强,强酸性环境中的溶解速率降低了一个数量级。然而,现有研究的金属氧化物载体比表面积和电导率均低于商用碳载体,且先将Pt和 IrO_2 复合再沉积到载体上,可能会导致Pt和 IrO_2 对彼此活性位造成阻碍,低于单种模式催化剂。

双功能氧催化剂的稳定性是实现URFC规模化应用的必要前提。Da Silva等人^[45]发现在Pt/Ir O_2 催化剂在双向模式中,Pt和Ir元素的溶解对催化剂活性降低产生重要影响,所引发的微粒聚集是造成催化剂分解和性能衰减的主要原因。他们通过研究还发现^[46],随着循环电位从0.6~1.1 V扩大到0.6~1.6 V时,Pt的溶解速率提高了近20倍,Pt衰减的加剧是影响URFC寿命的主要因素之一。然而,URFC双功能氧催化剂衰减的研究仍较少,亟须设计合理的加速衰减实验方案,并借助原位表征技术探究降解机理。

2.2 质子交换膜的研究进展

PEM在URFC中作为固体电解质起到传导质子、

抑制电子传输和隔绝反应物/产物传输的作用,需要具备化学惰性和足够稳定的机械性质。现阶段最常见的PEM是全氟磺酸(perfluorinated sulfonic-acid, PFSA)膜,其结构如图5(a)所示,由电中性的半结晶聚合物主链(聚四氟乙烯(polytetrafluoroethylene, PTFE))和带有悬垂离子基 $-\text{SO}_3^-$ (聚磺酰氟乙烯醚)的无规则侧链组成。PFSA主链为 $-\text{CF}_2-$ 组成的共价键相,化学惰性和机械稳固性较强,导电性差,可以抑制电子和氢氧传输;支链末端为 $-\text{SO}_3^-$ 组成的离子键相,导致相分离,且在引入水或溶剂分子时相分离得到加强。如图5(b)所示,在充分润湿的PFSA膜中,质子首先与 $-\text{SO}_3^-$ 形成配对离子,通过氢键作用在水合域中运输、分离,从而实现质子传导。

对PEM-URFC而言,为了确保WE模式下更低的气体渗透率,往往要求PEM足够厚(>120 μm),但会显著增加欧姆损失;此外,发电和电解两种模式下PEM的水热状态差别较大,导致PEM寿命衰减加快。从表S1可以看到,PEM-URFC所采用的PEM主要为Nafion 212,厚度约为50 μm ,但是其在双向模式的耐久性仍需探究。目

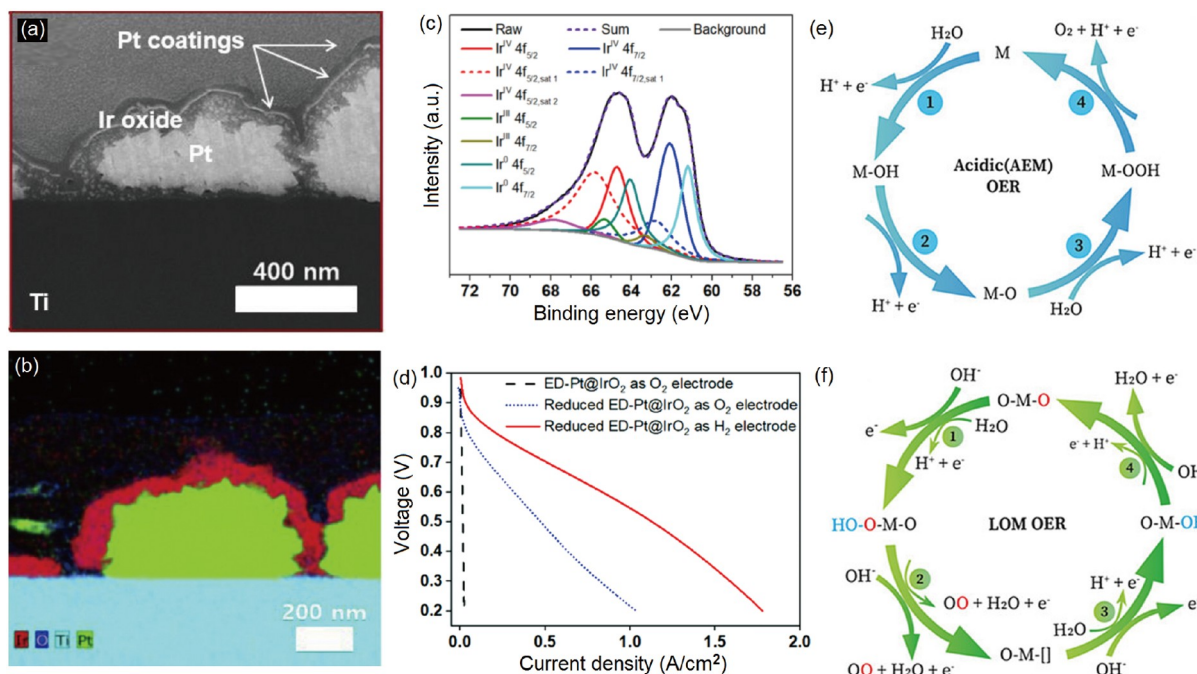


图4 (网络版彩色)Pt@IrO₂核壳结构催化剂。(a) SEM图像^[42];(b) EDS能谱图像^[42];(c) XPS谱图^[42];(d)发电性能曲线^[42];(e) AEM机制^[34,37];(f) LOM机制^[34,37]

Figure 4 (Color online) Pt@IrO₂ core-shell structure catalyst. (a) SEM image^[42], (b) EDS spectral images^[42], (c) XPS spectra^[42], (d) performance curve for FC mode^[42]; (e) AEM mechanism^[34,37]; (f) LOM mechanism^[34,37]

前,相关学者对PEM在URFC中的气体渗透率、耐久性开展了深入的研究。

2.2.1 质子交换膜气体渗透研究

在URFC中,理想的PEM应该具有更薄的厚度,以减少欧姆损失,但厚度的减薄造成更大的气体渗透率,尤其导致氧侧的氢渗透变得更加严重。为了减轻这种影响,Klose等人^[52]将Pt载量为0.02 mg/cm²的复合中间层喷涂在两层Nafion膜中间,如图5(c)所示,使得渗透进膜内的氢和氧在复合中间层催化剂的作用下形成水,具有复合中间层的MEA在1 A/cm²工况下运行245 h后氧中氢含量仅为140×10⁻⁶ vol%/h,显著低于不含复合中间层MEA的1250×10⁻⁶ vol%/h,如图5(d)所示。Briguglio等人^[53]在阳极催化剂层中加入PtCo合金颗粒作为重组催化剂,消除了氧气中99.5%的氢含量,使得电池(WE模式)在电流密度低至0.15 A/cm²,压力差为20 bar (1 bar=10⁵ Pa)的工况下,90 μm厚的Nafion膜依然可以支撑MEA正常工作,并大幅降低氢渗透量。除了Nafion之外,学者考虑开发离子交换容量更高的膜材料,在降低气体渗透率的同时提高膜的电导率^[54]。例如,Daryaei等人^[55]合成了二磺化聚芳醚砜无规共聚物作为高温水电解槽的PEM,发现其质子导通率显著提高,且氢气渗

透性在30~100℃的宽温度范围内都得到了很好的控制。

2.2.2 质子交换膜稳定性研究

影响PEM稳定性的主要因素可以分为化学降解和机械降解^[51,56]。化学降解主要是由于气体渗透形成的羟基自由基等攻击主链和侧链引起的主链压缩、侧链氟化等,而机械降解主要是由于温湿溶胀、气体压差等引起的PEM材料疲劳、蠕变,以及表面裂纹、孔洞、剥离等。机械衰减和化学衰减往往互相关联,因为发生化学降解的地方更易发生厚度减薄和应力集中,使该区域更易发生机械降解;同理,发生机械降解的区域更容易发生气体渗透,产生更多的过氧化氢,加剧化学降解。研究人员对PFSA膜湿热老化进行了深入研究,认为湿热老化过程中可能引起了功能物质(如酸酐)的形成,这些功能物质在污染物的催化下在离子基团之间形成交联,影响了PFSA膜的相分离形态,抑制了PFSA膜的质子传导能力、透水能力等,导致耐久性降低^[57]。Shi等人^[58]通过傅里叶变换红外光谱仪研究PFSA膜湿热老化后在1440 cm⁻¹处的峰值变化(研究人员认为该峰代表由于-SO₃⁻基团缩合导致的S-O-S交联),发现相对湿度越高,膜的老化越明显。对PEM-URFC来说,从WE模式切换到FC模式前必须先将氧侧

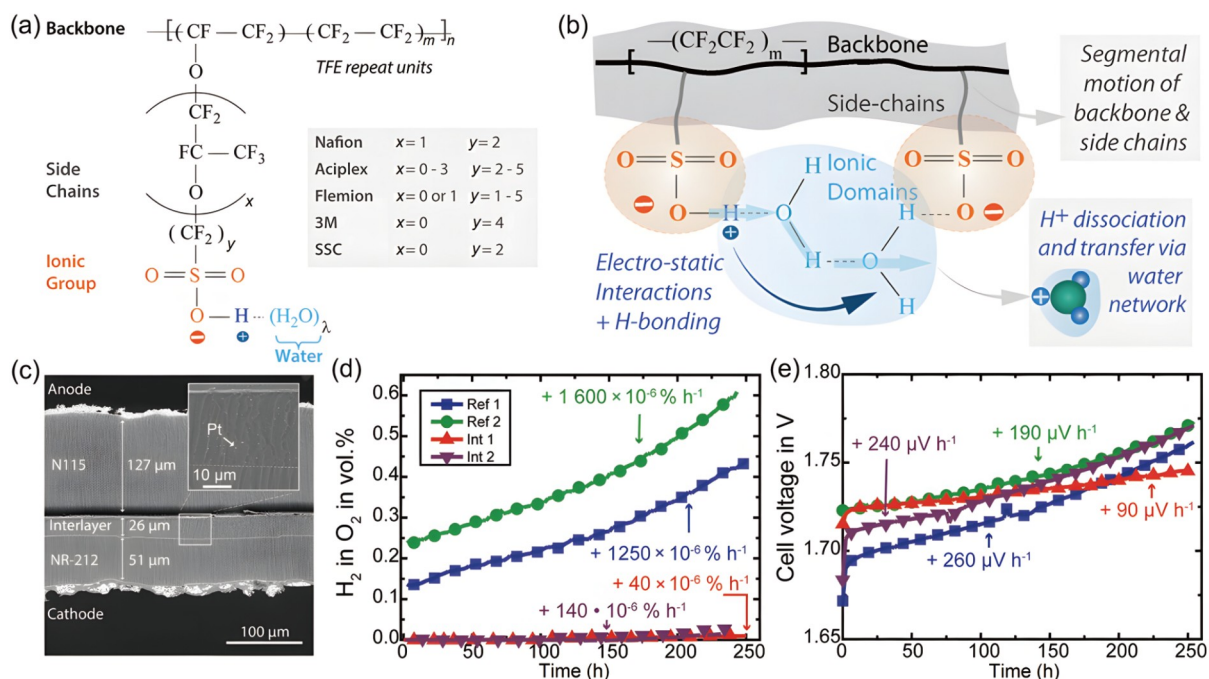


图5 (网络版彩色)PFSA膜的功能及气体渗透改善研究. (a) PFSA架构示意图及不同产品(如Nafion, 短侧链(SSC)等)对应的侧链参数^[51]; (b) 质子在充分润湿的PFSA膜中传输过程示意图^[51]; (c) 在两层Nafion中间喷涂Pt载量为0.02 mg/cm²的复合中间层^[52]; (d) 具有复合中间层的MEA与常规MEA在1 A/cm²工况下运行过程中的氧中氢含量^[52]; (e) 在工况为1 A/cm²情况下保持10 d, 不同PFSA膜对应MEA的电压变化曲线^[52]

Figure 5 (Color online) Research on function and gas permeability reduction for PFSA membranes. (a) Schematic diagram of PFSA architecture and side chain parameters corresponding to different products (such as Nafion and short side chain (SSC))^[51]; (b) schematic diagram of proton transport in a sufficiently wetted PFSA membrane^[51]; (c) spraying a composite intermediate layer with Pt load of 0.02 mg/cm² in the middle of two Nafion layers^[52]; (d) hydrogen content in oxygen during the operation of MEA with composite intermediate layer and conventional MEA at 1 A/cm²^[52]; (e) voltage curves of MEA corresponding to different PFSA membranes at 1 A/cm² for ten days^[52]

的水排除, PEM温湿度变化更为剧烈, 导致机械及化学降解、湿热老化加剧, 因此需要从结构及材料上提升PFSA膜的耐久性, 提高其使用寿命. 例如, Liu等人^[59]通过采用溶液浇铸法在PFSA膜中引入了双层e-PTFE刚性增强层, 与未增强的原始PFSA膜和具有单层增强层的PFSA膜相比, 具有双层增强层的PFSA膜的抗塑性变形能力得到提高, 干湿交替3000次后, 膜的力学耐久性显著增强. 然而, 目前的研究主要集中在FC或WE单个模式的PEM设计上, 关于PEM-URFC双模式条件下PEM的衰减机理及应对策略的研究仍较少.

2.3 双功能多孔传输层的研究进展

PTL是由纤维交联缠绕或粉末烧结而成的多孔材料, 常见的有碳纸、碳布、泡沫钛板、钛毡等, 如图6所示. PTL置于催化层与流道之间, 承担水气传输通道及导电作用. 此外, URFC耦合了FC和WE双模式, 使得PTL对于水气传输的适应性更为复杂, 诸多学者对PTL材料和结构进行了深入研究, 如表S2所示.

2.3.1 氢气侧多孔传输层

URFC氢侧PTL的主要作用为引导氢气的分配, 并将少量来自氧侧的液态水排出. 同时, 双模式氢侧电极为标准氢电极, 对材料的电化学腐蚀影响较低. 但是, 由于氢侧氢气浓度较高, 高压下容易造成金属材料的氢脆^[60], 引起电堆服役寿命衰减. 目前, 氢侧PTL主流的材料为碳纸、碳毡或者碳布. 其中碳纸和碳毡具有良好的机械强度、导电性和导热性^[61], 可与电极表面充分接触, 是URFC氢侧PTL的优选.

2.3.2 氧气侧多孔传输层

URFC氧侧PTL需要能承受WE模式下的高电位(>1.8 V)^[62], 避免过快发生电化学腐蚀. 目前, 防止氧侧PTL快速腐蚀的方法主要分为两类: 一类为传统碳基材料表面做防腐涂层^[63], 另一类为采用化学稳定性更强的钛材料, 如钛毡、泡沫钛、烧结钛网等.

碳基材料是燃料电池中常用的水气传输部件, 然而其在高电位下腐蚀严重($\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$, $E^0 = 0.207 \text{ V vs. RHE}$)^[64], 难以满足URFC氧侧稳定性要

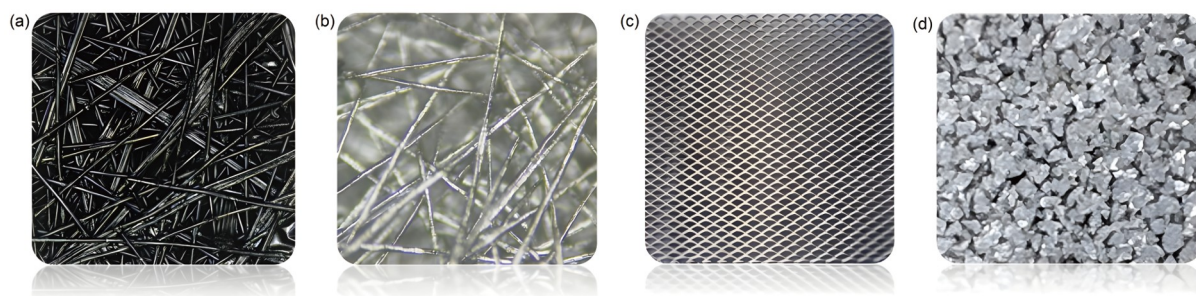


图6 (网络版彩色)不同类型的多孔传输层材料。(a) 碳纸; (b) 钛毡; (c) 钛网; (d) 泡沫钛

Figure 6 (Color online) Different types of porous transport layers. (a) Carbon paper; (b) titanium felt; (c) titanium mesh; (d) sintered titanium

求。Li等人^[14]采用碳纸作为URFC的氧侧PTL,通过双模式下循环伏安法做耐久性测试(132 h@1 A/cm²),发现碳基微孔层(micro porous layer, MPL)发生剥落,造成URFC性能衰减。为此, Song等人^[65]将IrO₂粉末沉积在碳纸表面,形成厚度10 μm的MPL,经过20次模式切换(每个模式运行1 h@0.3 A/cm²), URFC性能从0.730 V下降到0.705 V,而未经处理的碳纸难以支撑5次循环。Chen等人^[66]利用TiC、IrTiO_x粉末在碳纸表面制备了MPL,在双模式循环切换下稳定运行超过60 h(每个模式持续运行2 h@0.2 A/cm²),而未经处理的碳纸快速衰减。可见,在碳基PTL表面制备金属粉末MPL有利于抑制其腐蚀,一方面部分金属粉末具有OER活性,使大量从催化剂涂覆膜(catalyst coated membrane, CCM)中流出的羟基和氧基结合^[67],以抑制其对碳基底的腐蚀;二是金属粉末具有更高耐蚀性,增加了MPL腐蚀壁垒以降低腐蚀速率^[68]。

钛基材料由于优异的耐腐蚀性,已经被广泛用于电解槽,并逐渐在URFC的PTL中获得应用^[69,70]。Lickert等人^[71]对比了钛毡、泡沫钛、钛网作为氧侧PTL的电解槽性能,发现钛毡由于较好的水气传输能力,性能比泡沫钛优越(>10 mV, 3.0 A/cm²)。Panchwnko等人^[72]利用中子成像对比了电解槽中钛毡和泡沫钛的水气传输规律,相同工况下,钛毡和泡沫钛内气体分数分别为13%和20%。这是因为相同孔隙率下,钛毡比泡沫钛拥有更大的孔隙,排气能力更好。Stiber等人^[73]集合泡沫钛和钛网成一个组件,取代电解槽的流场,在150 N/cm²夹紧力下的接触电阻相比钛网下降约43%。可见,泡沫钛缺乏良好的传质特性及钛网的高接触电阻,钛毡成为URFC氧侧PTL的优选。

然而,钛毡作为氧侧PTL的URFC双向性能普遍低于碳纸PTL,这主要是因为钛毡内部孔隙过大,同时缺

乏MPL,致使PTL与催化层的界面接触不足,使得高频阻抗(high frequency resistance, HFR)增加,且影响物质传输及催化剂反应位点^[74-76]。Lopata等人^[77]制备了三种不同粗糙度的泡沫钛,实验表明在低催化剂载量下,PTL与CCM接触界面对性能影响明显,低粗糙度有利于降低界面气体覆盖率,如图7(b)所示,减小塔菲尔斜率。Schuler等人^[78]在泡沫钛上制备超薄MPL(钛粉,厚度<20 μm),采用X射线对接触表面进行表征,发现带有MPL的PTL使得催化剂的利用率提升了2.2~2.8倍,2 A/cm²时极化过电位下降60 mV。随后, Schuler等人^[79]继续在钛毡上制备了两种MPL,如图7(a)所示,相比纯钛毡基底,电解槽电压降低约100 mV@7 A/cm²,如图7(c)所示。可见,在钛毡表面制备MPL可有效提升电解槽性能,提升催化活性。虽然带有MPL钛毡的URFC发电性能测试结果尚不充足,但是考虑到MPL已经在燃料电池中广泛用来提升发电性能,带有微纳孔隙MPL的钛毡可能会成为URFC氧侧PTL的优选。

2.4 双功能极板的研究进展

双极板作为URFC的骨架,负责反应物质的分配(FC模式下通气排水, WE模式下通水排气)及电流的传输。因此,双极板需具备良好的导电性以减少电流传输损失、优秀的流场设计以适应气液分布、良好的耐腐蚀性以应对腐蚀环境,相关研究如表S3所示。

2.4.1 双极板材料

URFC在WE模式下富氧且工作电位高,在1.5~2.0 V范围内,传统的石墨双极板会受到严重腐蚀^[80]。因此,双极板材料的研究重点是如何提高耐腐蚀及导电性能。燃料电池双极板常用石墨、不锈钢、铝合金等材料,并采用涂层方法提高耐腐蚀性能,但这类极板无法适应WE模式高电压带来的强腐蚀环境。重量

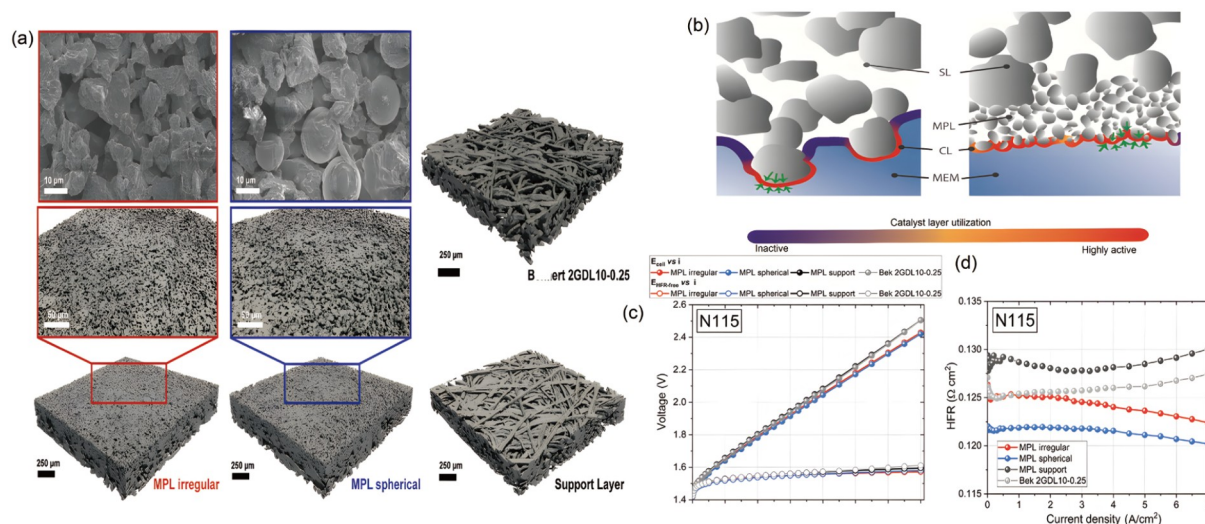


图7 (网络版彩色) PTL表面MPL对电解槽性能影响研究^[78,79]。(a) 不同PTL(带非规则颗粒MPL、带规则颗粒MPL、Bekaert商用碳毡、纯碳毡层)的3D结构图; (b) MPL对PTL-CL界面接触影响(左图无MPL, 右图有MPL); (c) 不同PTL对电解槽性能的影响(极化曲线和IR-free曲线); (d) 不同PTL对电解槽高频阻抗的影响

Figure 7 (Color online) Effects of MPL on the WE performance^[78,79]. (a) 3D surface rendering based on X-ray tomographic microscopy (XTM) acquired data of the relevant samples (two MPLs (irregular and spherical) as well as of the single-layer support material and a commercial reference from Bekaert (2GDL10N-0.25)); (b) visualization of the MPL effect showing the interfacial cross sections of mechanical deformation of CCM for (left) the coarse PTL and (right) a multilayer PTL with MPL; (c) polarization curves (cell voltage and HFR free cell voltage versus current density); (d) high-frequency resistance measurements

轻、机械性能高、耐腐蚀性更好的金属钛成为URFC极板的理想材料^[81]。然而, 钛基材料在酸性环境表面易产生惰性氧化层, 导电性变差降低双向性能^[70]。为此, 相关学者通过在表面涂覆涂层解决导电性降低的问题。Jung等人^[82]开发了镀金的钛基双极板, 该极板表现出较强的稳定性, 欧姆电阻从纯钛极板电池的 $0.08 \Omega \text{ cm}^2$ 降低到 $0.036 \Omega \text{ cm}^2$ 。通过电化学沉积形成铂、氧化铱、银等材料涂层及钛表面氮化改性的方法也已被证明能够提高极板耐腐蚀性和导电性能^[83~86]。近年来, 金属、金属氮化物、有机物等材料组成的复合涂层成为钛极板表面改性的新方向。Liu等人^[87]利用电泳沉积的方法制备一种纳米尺寸TiN-C涂层, 该涂层显著降低接触电阻, 在 400°C 下将腐蚀电流从裸钛的 $36.02 \mu\text{A}/\text{cm}^2$ 降低到 $1.41 \mu\text{A}/\text{cm}^2$ 。Zhang等人^[88]采用脉冲偏置电弧离子镀膜法制备蜂窝状纳米复合Ti-Ag-N薄膜作为钛表面涂层, 该涂层具有高导电性Ag纳米颗粒、纳米复合微观结构和蜂窝状粗糙表面, 表现出高耐腐蚀性及高导电性。

2.4.2 双极板流场

与传统的燃料电池不同, URFC需要综合FC模式排水和WE模式供水的需求。图8展示了燃料电池中常用的一些传统流场模式。Hwang等人^[89]讨论了单蛇形、

双蛇形、平行流场对URFC性能的影响。结果表明, 在FC模式下, 单蛇形流场能够提供高速度和高压降, 有效地排除产生的水, 而平行通道和双蛇形通道在低电流密度下出现了液态水积聚问题, 导致电池性能下降。但在WE模式下, 平行通道供水性能较佳, 而单蛇形流场在较高电流密度下局部供水不足。Zhang等人^[90]研究了圆形、矩形流场中气液流动, 通过流道形状、挡板等参数优化提升了URFC传质能力, 使得电池极化性能增强。Song等人^[91]研究了五种氧侧流道分布在FC和WE模式下的物质分布、电流密度和功率变化, 结果表明流线型流道和浅深度流道在FC模式下可有效降低浓差极化, 在WE模式下可提高总功率。此外, 许多学者对仿生流场、复合流场等复杂流场在燃料电池的应用进行了分析^[92~94], 但目前针对URFC流场的研究主要集中在流道横截面的设计, 如流道设置挡板、波浪流道、梯度流道设计、亲水性调控等^[95]。近年来, 相关学者提出采用多孔金属泡沫替代传统流道^[96]。Afshari等人^[97]发现多孔流场的高孔隙率能增强对流, 提高阴极催化剂表面的电流密度, 并且几乎不影响温度分布。Fly等人^[98]通过高速相机观测了金属泡沫的疏水性、泡沫孔径和空气流速对液态水的流动影响, 结果表明疏水性和孔径是影响多孔流场内的水分布的主要因素。

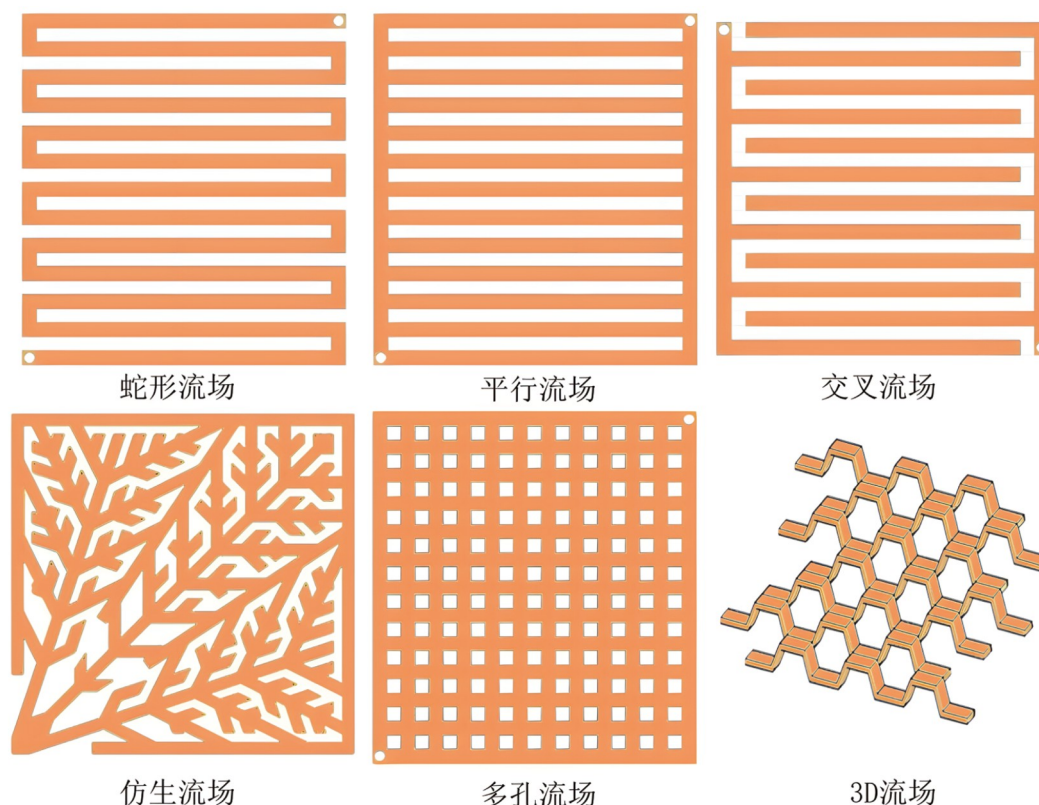


图8 (网络版彩色)常见流场模式示意图^[99]

Figure 8 (Color online) Common flow field patterns^[99]

双极板流场直接影响FC模式下的排水性能和WE模式下的供水情况。当前研究主要围绕单一模式下气液两相传输情况,综合考虑两种模式的研究尚不充分。因此,URFC流场设计需进一步考虑两种工作模式下的综合特征,以实现更高的能量转化效率和系统稳定性。

3 URFC水热管理的研究

3.1 双向模式的水气传输

如何协调双向模式的水气传输直接影响URFC往返反应效率,是其性能提升的关键。在FC模式,发生ORR与HOR反应,氢侧及氧侧需要气体供给,同时及时排水;在WE模式,发生OER及HER反应,氢侧生成氢气排出,而氧侧需要液态水流入和氧气排出。

在FC模式中,水气两相流在质子交换膜、催化层、PTL和极板流通,传输机制复杂。质子交换膜水传输的机制包括热拖拽、电渗迁移、液压渗透及扩散^[51,100-102]。催化层由纳米催化剂及离聚物组成,水气传输机制与质子交换膜相似。燃料电池的水淹主要发

生在PTL及其与CCM界面^[103],这里将重点陈述PTL对水气管理的影响。孔径及孔隙率是PTL的重要参数,高孔隙率(>70%)有利于提升排水速率,降低PTL内部的液态水饱和度^[104],但是同时会降低机械强度和导电性^[105]。渗透率是评价PTL水气传输性能的重要指标,高渗透率将有利于避免水淹^[106-108]。Holzer等人^[108]通过X射线计算机断层成像(X-ray computed tomography, XCT)定量描述了碳纸参数与平面、厚度方向上渗透率之间的关系,发现厚度方向的渗透率大于平面方向,主要是由于孔隙造成的水力半径差异。Koresawa和Utaka^[109]通过X射线探究了不同PTFE含量对碳纸中氧气扩散率及水分布的影响,结果表明10 wt%~20 wt%的PTFE使得碳纸的有效氧扩散率提升3倍,PTFE过多将造成碳纸孔隙堵塞从而阻碍氧传输。为满足高效率排水,防止水淹,在PTL表面制作疏水MPL是一种常用方法。MPL内部的微纳孔隙通过毛细作用加速水的排出,降低界面液态水饱和度,提高了氧气输出效率^[110]。Nanadeganni等人^[111]认为MPL厚度越薄,孔隙率越高,发电性能越好。

在WE模式中, PTL是影响水气传输性能的重要部件. Lee等人^[112]采用孔隙网络方法建立梯度孔隙率PTL电解槽水气传输模型, 发现在CCM与PTL之间的大孔被氧气填满, 从而造成液态水渗透降低, 因此建议在PTL表面制作MPL以避免气泡堵塞. Ito等人^[113]测试了氧侧采用不同孔隙率和孔径钛毡的电解槽性能, 结果表明当PTL孔径大于10 μm 时, 电解性能随着孔径的减小而提高, 但是当孔隙率超过50%时, 孔隙率的变化对性能影响不明显. Lee等人^[114]采用等离子喷涂技术制作了梯度孔隙率PTL, 结果表明梯度孔隙率将氧气饱和度降低50%, 在4.5 A/cm²的过电位降低29%. Zhao等人^[115]制作了超亲水的PTL(接触角<45°), 使得电解槽的效率提升超过11%.

可见, URFC双模式水气传输的方向不同, 对部件的结构参数及表面特性需求也不同. 如何使PTL同时满足双向模式下的水气传输需求, 成为URFC性能提升的挑战. Lim等人^[116]提出利用超薄聚二甲基硅氧烷(PDMS)作为疏水剂, 通过掩膜形成亲疏水交替的两亲性PTL, 如图9所示. 两亲性的PTL为水气分别提供传输通道, 满足WE和FC模式的不同需求, 与未经处理的钛毡相比发电性能提升4.3倍(0.6 V), 电解性能提升1.9倍(1.8 V). Zhang等人^[117]用掩膜夹紧未经PTFE处理的碳纸两侧, 反复浸渍PTFE同时经过高温处理后, 形成包含不同接触角的交替图案(亲水区76°, 疏水区125°), 发电性能提高了11.5%(0.65 V), 电解性能提高了4.8%(1.65 V). 可见, 两亲性的PTL有利于解决双向模式的水气传输矛盾.

3.2 双向模式的热管理

温度是电化学反应的重要参数, 直接影响URFC的反应效率. URFC是多材料、多界面、多物质的耦合体, 不合理的热管理包括导热效率低、温度分布差、局部温度过高等, 这将导致电堆性能急剧下降, 甚至出现CCM损伤、电堆烧坏等灾难性后果. URFC反应包括可逆热、不可逆热, 其中可逆热来自FC及WE模式的焓变, FC是放热反应, WE是吸热反应. 不可逆热是由欧姆阻抗及活化阻抗等所致. Xiao等人^[118]建立了瞬态URFC传热模型, 发现双模式下氢侧温度均低于氧侧温度. 其中FC模式下, 温度最高点在催化层; WE模式下, 最高温度首先出现在催化层, 随后转移到质子交换膜. 虽然电解的可逆反应是吸热反应, 但是欧姆阻抗等产生的焦耳热超过可逆反应热, 使得双模式下URFC均是

放热过程.

探究URFC温度分布是提升热管理的重要基础. 针对FC模式, Zhou等人^[119]通过印刷电路板(printed circuit board, PCB)原位观测技术探究了大面积燃料电池内部温湿度分布, 实验结果表明: 燃料电池内部温度与冷却液流向相关, 冷却液末端的温度较高, 温度极差超过8°C@1.8 A/cm². 针对WE模式, Möckl等人^[120]通过建立一维传热模型, 揭示了从MEA到流场通道的热传输行为, 温差达到9.9 K, 产热量为7.8 W/cm². Li等人^[121]通过对7节69 cm²的电解槽进行敏感性实验测试, 发现温度从60°C提升到80°C, 电解槽性能明显提升, 这是因为高温提升了反应动力. 综上, 温度对URFC性能具有显著影响, 但仍存在大面积下温度分布不均的问题造成局部性能差异, 如何提升热管理将是URFC研究的重要方向之一.

3.3 双向模式切换

与单模式的燃料电池或电解槽不同, URFC需要在FC模式与WE模式互相切换. 如何加快切换速度, 提升切换的安全性和稳定性是影响URFC往返效率和寿命是研究的关注点.

目前, FC模式切换为WE模式的研究较少. 电解启动过程中, 气体的排出是较为容易的, FC模式下残留的液态水可用于WE模式. Yuan等人^[122]使用透明电池, 对比了在反应气切断和电解水通入过程中切换负载时的URFC电压动态响应; 提出发电结束, 要在电解水通入前切断负载, 电解启动, 要在电解水充分流入后切换电路, 避免局部反应物欠缺而损伤电池. 李辉艳等人^[123]提出供水流量增大有利于提升模式切换的稳定性.

WE模式切换为FC模式的研究较多. WE模式结束, 残留的电解水使电池处于水淹状态, 反应气体流通受到阻碍, 易导致FC模式启动失败^[5]. 目前通常采用反应气体或惰性气体吹扫的方法将残余的电解水排出电池, 同时使膜电极处于湿润状态, 以利于FC模式的高效启动. 吹扫气体流速过大, 可能会导致膜电极过干, 造成气体浪费; 气体流速过小, 则会增加模式切换时间. 吹扫策略的设计包括吹扫终止状态的界定和吹扫过程参数的优化两个方面. 现有研究主要通过间接测量方法表征电解水排出和膜电极润湿状态, 从而分辨电堆是否可以转为FC模式. Tajiri等人^[124,125]、Sinha等人^[126,127]提出使用高频阻抗表征电池中残余水量和质子交换膜内的水含量. Ito等人^[128]建立吹扫过程中URFC膜电极干湿状态变化的数值模型, 以高频阻抗值

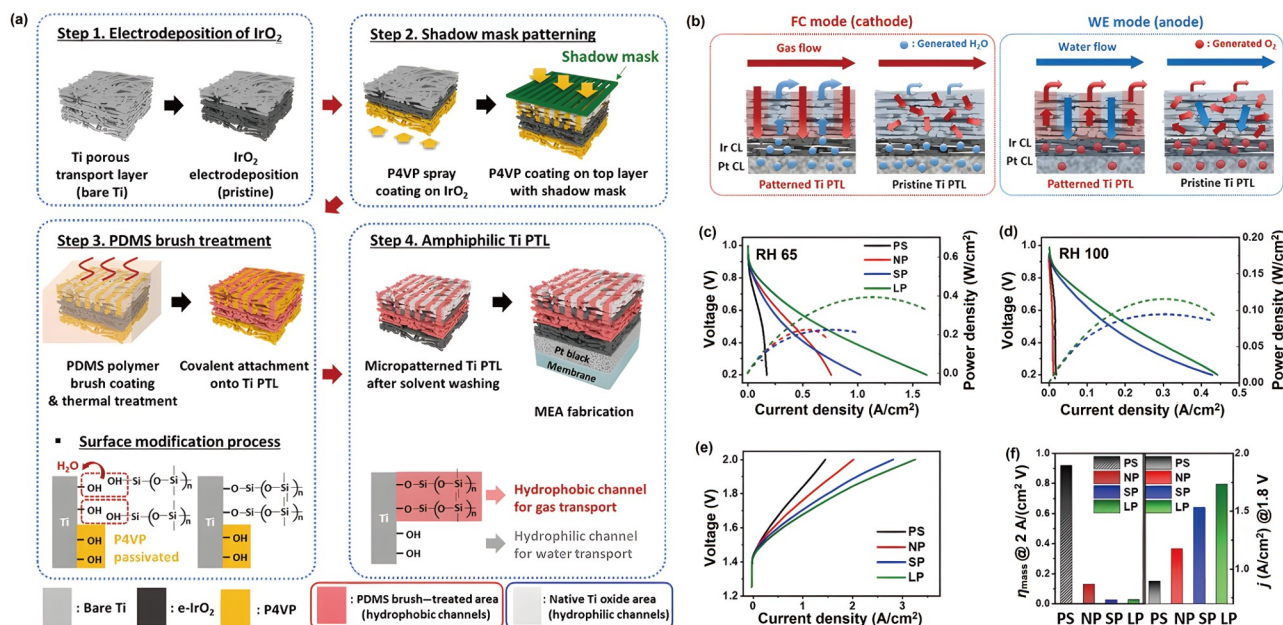


图9 (网络版彩色)两亲性的钛基PTL性能分析^[116]。(a) 两亲性PTL制备工艺; (b) 两亲性PTL与亲水PTL(0°)水气传输机制对比; 四种PTL在65%湿度(c)和100%湿度(d)下的发电 I - V 曲线和功率密度对比; 四种PTL电解 I - V 曲线(e)及2 A/cm²的传质损失和1.8 V的电流密度(f)。PS: 原始亲水PTL, NP: 145°疏水PTL, SP: 小间隔两亲性PTL, LP: 大间隔两亲性PTL

Figure 9 (Color online) Effect of the amphiphilic Ti PTLs on URFC performance^[116]. (a) Fabrication procedure of amphiphilic PTL; (b) mass transfer pathways in the patterned and hydrophilic Ti PTL under FC and EC modes; comparison of I - V performance and power density for four PTLs in the FC mode at RH 65 (c) and RH 100 (d); (e) comparison of I - V performances of four PTLs in the EC mode; (f) comparison of overvoltage from mass transport resistance at 2 A cm⁻² and current density at 1.8 V for PS, NP, SP, and LP. PS: Pristine hydrophilic PTL, NP: Hydrophobic PTL with 145°, SP: Amphiphilic PTL with small pattern; LP: Amphiphilic PTL with large pattern

作为参考,可以计算不同气体流速下吹扫所需的时间。Chen等人^[129]以吹扫时间和启动电压下冲值作为评价依据,对比了不同吹扫气体湿度的影响,指出吹扫气体湿度在52%~83%之间可以缩短吹扫时间并减小电压下冲值,使模式切换更快更稳定。Guo等人^[130]通过实验测量了不同吹扫流量下URFC高频阻抗的变化规律,综合吹扫时间、耗气量和安全性三个评估指标,提出了分段式动态吹扫策略。

也有学者通过优化电池结构、系统运行策略等提高吹扫效果。Guo等人^[95]对比了不同流道结构对水气传输的影响,发现优化的T型流道相比矩形流道,FC模式启动时不易出现性能急剧下降,增强了模式切换的稳定性。Qiao等人^[131]设计了阶梯状流道,可以通过流道宽度的缩小加快出口流速,增强排水效果,加快FC模式的启动速度。Liu等人^[132]提出在吹扫前期可以继续维持电解状态,通过电解消耗掉部分残留水,从而加快模式切换。综上,以高频阻抗为监测电URFC水含量的指标,优化吹扫策略中气体流量、湿度等参数,辅以流道构型的优化和系统运行策略的优化,可以有效提升

切换效率。

4 总结与展望

URFC具有高比能量、高能量利用率及快速启动等优势,在储能转换方面具有巨大的应用潜力。目前,URFC研究仍在初步阶段,存在贵金属载量高、FC/WE模式兼容性差、性能衰减快等瓶颈,研究者通过实验和仿真等手段对双功能部件及水气传输进行了深入研究,取得了卓有成效的成果。

(1) 在双功能氢催化剂材料方面,开发高活性非贵金属催化剂是未来研究方向,目前在催化活性、稳定性上相较于贵金属催化剂仍有差距;双功能氧催化剂需兼顾ORR和OER,将Pt和IrO₂两种活性较高的材料复合仍是最常用的方法,但催化活性受到抑制。在载体材料方面,金属氧化物可能是理想的双功能氧催化剂载体材料,但现有研究的载体比表面积和电导率均低于商用碳载体,催化剂利用率、稳定性仍有待提高;在催化剂衰减方面,双向模式下Pt溶解速率提高是加剧URFC衰减的重要因素之一,但其降解机制尚不清楚。

探究双向模式下的催化剂衰减机制,设计高比表面积、高导电性、强耐久性介孔金属氧化物载体,并基于金属氧化物-催化剂强相互作用或结构有序化载体对催化剂的限域效应开发高活性、高利用率、长寿命超低载量贵金属催化剂,是提升PEM-URFC双向性能和耐久性的重要研究方向。此外,对于双功能氧催化层,如何设计分离式的ORR和OER催化剂,充分发挥双向催化活性和减小衰减速率,也是有效的途径。

(2) PEM-URFC的双向运行模式给PEM提出了更高的要求:一方面,PEM应该足够薄,以降低双向模式运行过程中的欧姆损失,但这可能会加剧氢渗透,使得氧中氢含量升高,造成安全隐患和PEM退化;另一方面,电解-发电切换给PEM带来了较为剧烈的温湿度变化,湿热老化加速,但鲜有关于PEM-URFC干湿变换条件下PEM的衰减机理及应对策略的研究。未来应结合PEM-URFC的运行特点,一方面通过元素掺杂、聚合物共混等方式开发离子交换容量更高的PFSA膜材料,另一方面引入强度更高、韧性更强的支撑层,设计厚度薄、具有增强层结构且能够满足抗气体渗透需求的PEM,兼顾双向性能和耐久性。

(3) 在氢侧PTL方面,为了避免发生氢脆,同时保证优良的机械性和导电性,碳纸具有较高的认可度。在氧侧PTL方面,考虑到高电位、酸性等腐蚀环境及高气压

工作要求,钛基材料仍是较为理想的材料,带有微纳孔隙金属MPL的钛基PTL在提升极化性能及抵抗衰减方面已经得到验证,但距离长时间稳定服役的目标仍存在较大差距,针对MPL材料及制备工艺的研究仍较少。PTL及MPL的厚度、孔隙结构、导电性及机械强度等兼顾FC和WE双向水气传输及电化学反应要求,材料达到耐蚀性要求,是URFC的主要研究方向之一。

(4) 在URFC水气管理方面,如何调控双模式的水气传输是URFC设计的关键问题,也是目前URFC研究发展的瓶颈。面对双模式截然相反的水气传输需求,现有部件从材料特性、结构参数方面难以同时满足。两亲性PTL为WE模式和FC模式分别提供水气传输通道,为解决URFC水气管理提供了借鉴。然而这方面的研究仍较少,适应两种模式的高效水热管理通道设计仍有待确定。针对两种模式的差异,例如电子导向、温度差异变化等,寻找可随此发生亲疏水敏感性的材料或将是未来解决URFC水气管理问题的路线之一。

(5) URFC模式切换不合理,将导致催化剂性能衰减、气体利用率降低等问题。WE模式向FC模式切换,是URFC模式切换的关键。目前,模式切换的评估方法较为单一,大多仅注重切换速度和启动电压的响应情况,还需要综合考虑耗气量、安全性等多方面需求,对切换策略进行智能化动态调节。

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补充材料

表S1 现有双功能催化剂及质子交换膜研究现状

表S2 现有双功能多孔传输层研究对比

表S3 现有双功能双极板研究对比

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Summary for “一体式再生燃料电池的研究进展与展望”

Research progress and prospects of unitized regenerative fuel cells

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With its high calorific value, stable energy output, and zero-emission byproducts, hydrogen energy is seen as a leading alternative to fossil fuels in the 21st century. By combining hydrogen energy with renewable sources such as solar and wind power, hydrogen can be produced through water electrolysis, allowing for long-term storage and long-distance transportation. Unitized Regenerative Fuel Cells (URFCs) combine the functionalities of both fuel cells (FC) for power generation and water electrolyzers (WE) for hydrogen production in a single device, providing benefits such as high specific energy, high conversion efficiency, and zero emissions. With advancements in hydrogen technology, URFCs are poised to play a crucial role in energy storage and supply, long-duration power systems, and space applications. Despite these advantages, several challenges hinder their large-scale implementation. One major obstacle is the difficulty URFC components face in simultaneously handling the bidirectional reaction and gas-water transport required in both FC and WE operations. The high usage of costly metals and the relative inefficiencies of the bifunctional modes, compared to dedicated fuel cells and electrolyzers, present significant barriers. Additionally, the severe operational conditions and frequent cycling can lead to accelerated degradation, affecting long-term performance.

This paper summarizes the current state of research on URFCs both domestically and internationally, and offers insights into future research directions. It begins by discussing the working principles and classifications of URFCs, then delves into the advancements in component and material research for URFCs with a constant gas configuration. The study details how bifunctional modes influence the materials, structure, and lifespan of CLs, PTLs, and BPPs. For bifunctional oxygen catalysts to efficiently support both ORR and OER, the use of Pt and IrO is common, though this combination tends to reduce the activity of the supporting material. Metal oxides are preferred as they provide better support than commercial carbon supports, despite having lower specific surface areas and conductivity. The increased dissolution rate of Pt in a bidirectional mode significantly contributes to URFC degradation, although the specific mechanisms of degradation are not fully understood. An important research focus for improving the bidirectional performance and durability of PEM-URFCs is the development of ultra-low loading noble metal mixed catalysts on metal supports or the creation of separate OER and ORR catalysts. For the PEM, existing membrane materials have difficulty simultaneously achieving high proton conductivity, low gas permeability, and strong mechanical strength for FC and WE modes. There remains a need for better membrane materials and reinforced structural designs. For the PTL at oxygen side, typical materials include carbon-based substances with anti-corrosion coatings and chemically stable titanium-based materials. Titanium felt with an MPL is favored for the oxygen side in URFCs, but its porosity, wettability, and conductivity require further optimization. For the BPPs, surface treatments such as coating with gold, silver, or platinum, and nitridation are common methods to improve durability of BPPs.

Analyzing the water-gas transmission requirements and the mode-switching demands of dual working modes is essential for enhancing overall performance. Water-gas transmission behavior under dual-mode operation necessitates coordinated regulation of materials and structures for membrane, CLs, PTLs, and BPPs to satisfy the requirements of both operational modes. Amphiphilic PTLs facilitate water-gas transmission for both WE and FC modes, providing solutions for URFC water-gas management. In addition, a promising approach is to explore materials that can dynamically adjust their hydrophilic and hydrophobic properties in response to differences between the two modes, such as changes in electron flow and temperature. Transitioning from WE mode to FC mode is critical for URFCs, requiring comprehensive consideration of gas consumption, safety, and additional factors.

This paper systematically reviews the research advancements in bifunctional components of URFCs and delineates future research directions. These insights are crucial for guiding the enhancement of URFC performance.

unitized regenerative fuel cells, fuel cell mode, electrolyzer mode, bifunctional catalyst, bipolar plates, water and gas transport

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