科学通报 2024 年 第 69 卷 第 25 期: 3705 ~ 3714
能源电催化专题(I) 进 展
《中国科学》杂志社 SCIENCE CHINA PRESS

钌基氧化物酸性析氧电催化剂

万仁典, 黄广幸, 刘庆勋, 赵伯特*

华南理工大学环境与能源学院, 广州 510006

* 联系人, E-mail: botezhao@scut.edu.cn

2024-02-29 收稿, 2024-03-13 修回, 2024-03-21 接受, 2024-03-26 网络版发表
国家自然科学基金(52102248)、广东省基础与应用基础研究基金(2022A1515010231)、广州市基础研究计划(2023A04J1568)、国家重点研发计划(2021YFA1502400)和广东省引进创新创业团队计划(2021ZT09L392)资助

摘要 质子交换膜(proton exchange membrane, PEM)电解水技术是一种很有前景的绿色制氢技术, 但其酸性操作环境对催化剂的性质提出更苛刻的要求. 目前, 可商业化应用于PEM电解水技术酸性析氧反应(oxygen evolution reaction, OER)的催化剂主要为贵金属铱(Ir)基材料. 与Ir基材料相比, 钌(Ru)基氧化物催化剂具有成本相对较低的优势. 然而, Ru基氧化物催化剂在酸性介质中的稳定性较差. 因此, 迫切需要研制出在酸性电解质中高效稳定的Ru基氧化物OER催化剂. 本文综述了Ru基氧化物催化剂的理论稳定性、析氧反应机理和理论活性, 随后探讨了该催化剂在析氧反应过程中的性能衰减机理, 并进一步讨论了提高其反应活性和稳定性的设计策略. 本文最后总结了Ru基氧化物催化剂目前面临的挑战, 并提出了相应的展望.

关键词 电解水, 钌基氧化物, 衰减机理, 催化剂设计策略

电解水制氢技术作为一种绿色的制氢技术, 被认为在克服人类面临的能源和环境问题中将扮演重要的角色[1~5]. 电解水包括两个半反应, 即阳极析氧反应(oxygen evolution reaction, OER)和阴极析氢反应(hydrogen evolution reaction, HER). 通常而言, 多电子转移的OER要比两电子转移的HER动力学缓慢[6]. 因此, 迫切需要开发具有高活性和稳定性的OER催化剂来提升商业电解槽的能效.

目前, 商业低温电解槽主要使用碱性液体电解质或质子交换膜(proton exchange membrane, PEM)电解质. 与使用液体电解质的电解槽相比, PEM电解槽具有更紧凑的设计、更高的气体操作压力、更高的产氢纯度、能实现快速的动态电压响应并达到更高的电流密度[7]. 然而, 在阳极侧OER产生的H^+使得催化剂表面局部环境呈酸性(pH 2~4)[8]. 与碱性条件相比, 酸性条件在热力学上不利于阳极侧的氧电催化, 这对活性材料的选择提出了更高的要求[9]. 因此, PEM电解槽技术的发展及其规模化应用在很大程度上依赖于先进酸性OER催化剂材料的开发和技术突破. 目前, 在商业PEM电解槽中相对成熟的酸性OER催化剂主要来源于全球储量较低的贵金属Ir[7,10,11]. 近五年来, Ir的价格快速增长(从约23000 USD lb^{-1}增长到最高约92000 USD lb^{-1}), 而Ru在价格上有明显的优势, 其最高价格只有约11000 USD lb^{-1}(图1(a)).

据文献[13]报道, RuO_2可以表现出比IrO_2更好的OER活性. 因此, Ru具有替代Ir作为酸性OER催化剂的潜力. 近年来, 研究人员通过各种策略对Ru基氧化物催化剂进行改进, 已经在提高其酸性OER的活性和稳定性方面取得了实质性进展. 然而, 如何合理设计能够在酸性介质中长期稳定使用的Ru基OER催化剂仍然充满

引用格式: 万仁典, 黄广幸, 刘庆勋, 等. 钌基氧化物酸性析氧电催化剂. 科学通报, 2024, 69: 3705–3714
Wan R D, Huang G X, Liu Q X, et al. Ruthenium-based oxides as electrocatalysts for acidic oxygen evolution (in Chinese). Chin Sci Bull, 2024, 69: 3705–3714, doi: 10.1360/TB-2024-0233

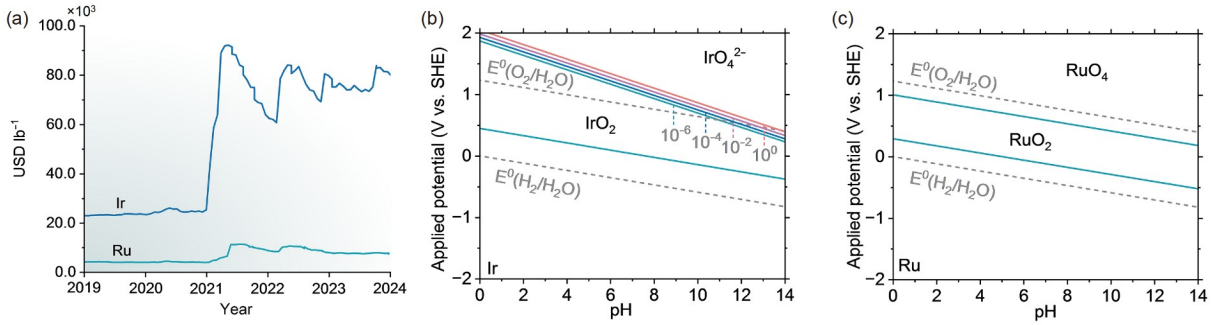

图 1 (网络版彩色)Ru和Ir价格及Pourbaix图. (a) Ru和Ir近5年的价格趋势图. 这些数据来自于Umicore Precious Metals Management (https://pmm.umicore.com/en/). Ir(b)和Ru(c)在25°C水溶液中的Pourbaix图. 离子浓度从10^{-6}到10^{0} mol L^{-1}变化. 数据来自Materials Project (https://next-gen.materialsproject.org/)[12]

Figure 1 (Color online) The price and Pourbaix diagrams of Ru and Ir. (a) The price of metallic Ru and Ir within a 5-year range. These data were derived from Umicore Precious Metals Management (https://pmm.umicore.com/en/). Pourbaix diagrams for Ir (b) and Ru (c) in aqueous solution at 25°C. The ion concentration is varied from 10^{-6} to 10^{0} mol L^{-1}. The data were generated from the Materials Project (https://next-gen.materialsproject.org/)[12]

挑战.

本文从Ru基氧化物催化剂的理论研究出发, 重点讨论了其理论稳定性、酸性OER反应机理和理论活性. 然后, 总结了其在酸性环境下的主要衰减机理, 提出了解决这些与稳定性相关问题的催化剂设计策略, 并通过对近期报道的高性能Ru基催化剂的性能进行汇总来简要讨论提高催化剂活性的策略. 最后, 我们提出了新一代Ru基氧化物催化剂设计面临的挑战和未来展望.

1 Ru基氧化物催化剂的理论研究

1.1 理论稳定性

Pourbaix图是通过理论计算算得一定条件下(即pH、外加电位和离子浓度)催化剂的水溶性物质状态和固体物质状态的形成能来构建而成的[12,14,15]. Pourbaix图可以评估材料结构在特定条件下的热力学稳定性[16]. 图1(b), (c)是通过Materials Project (https://next-gen.materialsproject.org/)[12]获得的Ru和Ir的Pourbaix图. 如图1(b)所示, 随着离子浓度的增加, 固态IrO_2的稳定区域更大, 表明Ir的相关离子浓度可以影响固体物质中阳离子的溶解平衡. 在一定的电压范围内, 固态IrO_2可以在酸性OER条件下保持稳定, 这也是其作为酸性条件下的基准催化剂的原因之一. 而在较高电压下, 催化剂会溶解形成IrO_4^{2-}离子. 不同于Ir的情况, Ru在给定的pH和电压范围内不会随着离子浓度(10^{0}~10^{-6} mol L^{-1})的变化而发生变化(图1(c)). 在OER条件下, Ru主要以RuO_4的形式存在, 而RuO_4被认为是不稳定的化合物(详情见2.1节)[17,18], 这可能是导致Ru基氧化物催化剂不稳定的因素之一.

1.2 反应机理

目前被研究者广泛接受的OER反应机制如图2(a)~(c)所示, 主要包括吸附演化机制(adsorbates evolution mechanism, AEM)、晶格氧介导机制(lattice oxygen-mediated mechanism, LOM)和氧化路径机制(oxide path mechanism, OPM)[19,22]. 在AEM路径中, 催化剂表面金属活性中心与吸附物种作用[9]. 如图2(a)所示, AEM路径从吸附的水分子中裂解形成HO*表面中间体开始, 接着去质子化生成O*物种, 然后H_2O分子与*O中间体反应形成HOO*中间体, 脱质子后进一步释放O_2分子. 有学者提出了HO*和HOO*结合能呈线性相关, 并遵循一般固有关系, 即$\Delta G_{HOO*}-\Delta G_{HO*}=3.2\pm0.2$ eV[20,23]. 基于AEM机理和以上线性固有关系计算出的OER理论极限过电位约为370 mV[21]. 如图2(b)所示, 在LOM路径中, 开始的HO*中间体的吸附和脱质子过程与AEM类似, 其区别在于催化剂中的晶格氧会参与反应, 与表面O*中间体结合形成O–O键并释放O_2分子[9]. 然后, HO*会重新填充晶格氧释放后留下的空位. LOM路径中没有HOO*中间体的参与, 不受传统AEM中固有关系的限制, 因此可以实现更低的理论OER过电位. 然而, LOM路径下的OER催化剂可能会产生金属离子快速溶解等稳定性问题. 除了AEM和LOM机理外, 研究者还提出一些其他机理, 比较代表性的是OPM, 此机理可用于解释催化剂高活性和高稳定性的情况[19]. 在OPM路径

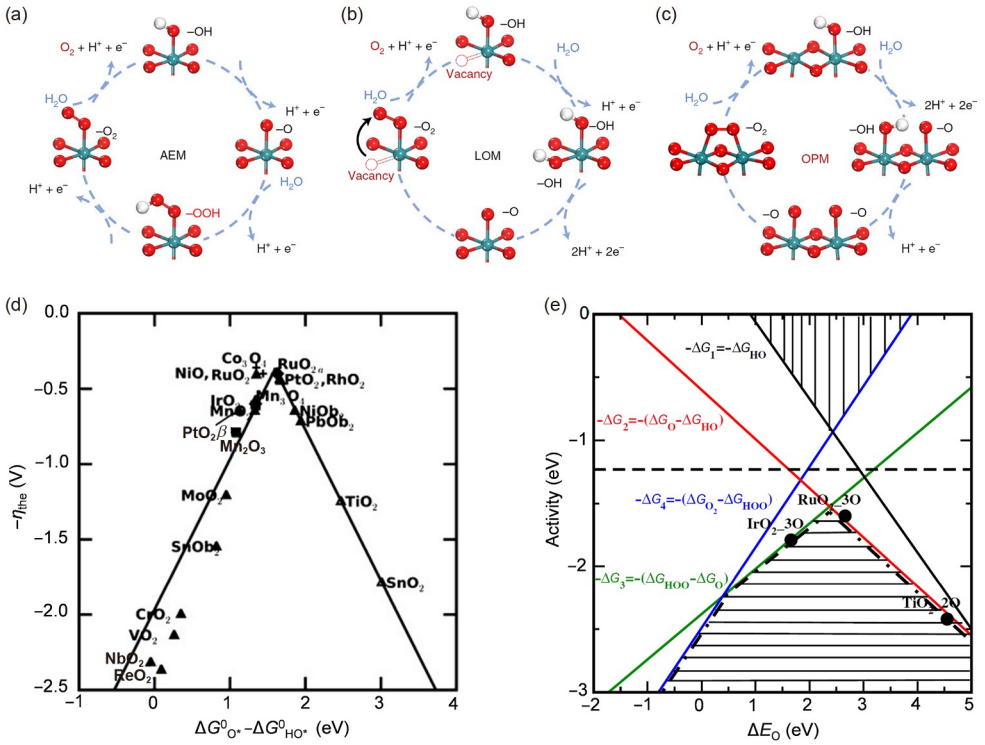

图 2 (网络版彩色)OER机理和理论活性. OER机理示意图[19]: (a) AEM; (b) LOM; (c) OPM. Copyright © 2021, Springer Nature. (d) 理论过电位(负值)与$\Delta G_{O^*}-\Delta G_{HO^*}$标准自由能的关系[20]. Copyright © 2011, Wiley-VCH. (e) 负的吉布斯自由能变化值($-\Delta G$)与氧结合能的函数[21]. Copyright © 2007, Elsevier

Figure 2 (Color online) OER mechanisms and theoretical activity. Schematic illustration of OER mechanisms including (a) AEM, (b) LOM and (c) OPM[19]. Copyright © 2021, Springer Nature. (d) Theoretical overpotential (negative value) as a function of the standard free energy of $\Delta G_{O^*}-\Delta G_{HO^*}$[20]. Copyright © 2011, Wiley-VCH. (e) The negative change of the free energy ($-\Delta G$) as a function of the oxygen binding energy[21]. Copyright © 2007, Elsevier

中, 与AEM和LOM的区别在于两个金属活性中心的O*可以直接耦合形成O_2分子[19]. 该机制下的OER催化剂没有HOO*中间体和氧空位产生, 因此理论上可以在不牺牲稳定性的情况下突破AEM理论活性的极限.

1.3 理论活性

催化反应往往涉及多个反应中间体, 活性中心与中间体的结合能遵循Sabatier原理, 即结合能既不能太强也不能太弱[20]. 因此理想的催化剂应该拥有最合适的中间体吸附能[20]. OER的理论活性可以由理论过电位来反映, 其中理论过电位可以通过DFT计算OER多步反应中所需自由能能量最大的步骤(即电位决定步骤(potential-determining step))得到[20]. OER理论活性与特定中间体结合能的函数图显示出火山形状(图2(d), (e))[20,21]. 如图2(d)所示, RuO_2的位置接近火山图顶点, 表明具有优异的理论OER活性. 图2(e)中以金红石氧化物中最稳定的(110)晶面为模型, RuO_2接近火山图(虚线围绕的阴影区域)顶点[21]. 与RuO_2相比, IrO_2的位置落在火山图顶点的左侧位置, 因此IrO_2与O*中间体的过强吸附(结合能为1.66 eV)导致了其相对较低的理论活性(图2(e))[21].

2 Ru基氧化物催化剂的衰减机理

对于钌基催化剂而言, 其表观OER活性的衰减可以认为由两部分组成. 一部分来自催化剂本身活性的衰减, 主要原因为催化剂的溶解造成的活性位点减少[24]. Ru的过氧化[25,26]、瞬时溶解[18]或晶格氧缺陷[27,28]等都会导致Ru的溶解. 另一部分则是电接触不良造成的衰减, 主要原因为基底的钝化和催化剂层的机械损伤[29,30].

2.1 热力学驱动溶解

在较高的氧化电位下, 催化剂中的Ru在热力学驱动下被氧化为高价态(>Ⅳ)的不稳定物种(图3(a)). 因为

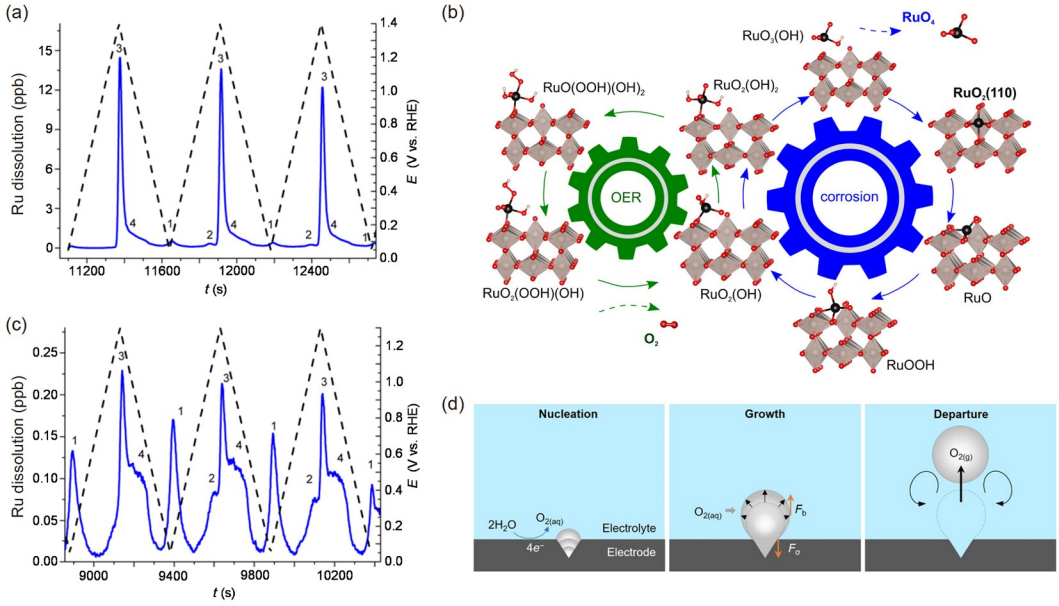

图 3 (网络版彩色)Ru基氧化物催化剂的溶解行为和催化层机械损伤. (a), (c) RuO_2在0.1 mol L^{-1} $HClO_4$, 5 mV s^{-1}下的电压-溶解关系图[18]. (a)和(c)的扫描电压区间分别为0.05~1.4 V vs. RHE和0.05~1.3 V vs. RHE. 蓝色实线对应于Ru溶解的浓度(左坐标轴), 黑色虚线是相应的电压(右坐标轴). 峰3表示热力学驱动溶解, 峰1、2和4表示瞬时溶解. (b) Ru腐蚀过程与OER催化过程之间耦合机制的图示[31]. RuO_2(110)上的中间体由从头算分子动力学模拟得到. (d) O_2气泡生成的不同阶段示意图[25]

Figure 3 (Color online) Dissolution behaviors of Ru-based oxide catalysts and mechanical damage of catalyst layer. (a), (c) The diagram of relationship between voltage and Ru dissolution for RuO_2 at 0.1 mol L^{-1} $HClO_4$ and a scanning rate of 5 mV s^{-1}[18]. The voltage ranges in (a) and (c) are 0.05–1.4 V vs. RHE and 0.05–1.3 V vs. RHE, respectively. The solid line corresponds to the concentration of Ru dissolution (left *y*-axis), and the dashed line represents the corresponding voltage (right *y*-axis). Peak 3 represents thermodynamic dissolution, while peaks 1, 2, and 4 represent transient dissolution. (b) Diagram of the coupling mechanism between Ru corrosion and OER[31]. The intermediates on RuO_2(110) were obtained from *ab initio* molecular dynamics simulations. (d) The different stages of O_2 bubble generation[25]

高价钌物种可以溶于电解液, 使催化剂失活, 所以高价钌(>Ⅳ)的生成是一种过度氧化或过氧化(over-oxidation)[25,26]. 通过在线质谱(online mass spectrum)和原位差分反射光谱(*in-situ* differential reflectance spectrum)的相关研究证明了在电解液中存在性能衰减后的产物RuO_4[32]. RuO_4是一种不稳定的化合物, 可溶于水, 甚至被认为是OER过程中的中间体(因其可分解为O_2和RuO_2)[18].

Ru(Ⅵ)中间体$RuO_2(OH)_2$的相对稳定性在早期研究中就被认为是影响腐蚀过程的重要因素[32]. 此后, 结合分子动力学方法与热力学方法, 发现在原子尺度上Ru的腐蚀与其位点上的OER催化过程之间存在明显的耦合机制(图3(b)), 即两种过程共享反应中间体($RuO_2(OH)_2$和$RuO_2(OH)$)[31]. 在腐蚀过程中, 水的亲核攻击和化学键的断裂会导致表面Ru原子的价态升高并形成中间体, 其中$RuO_2(OH)_2$会转变成$RuO_3(OH)$并最终形成RuO_4而导致溶解问题[31]. 因此, 我们可以调控可溶性的高价Ru中间物种的相对稳定性来抑制腐蚀过程[31]. 同时, $RuO_2(OH)_2$在OER循环中发挥重要作用, 计算模拟表明可溶性的高价Ru反应中间体能与晶格氧相互作用而稳定在催化剂表面并贡献OER活性, 这与实验中观察到的表面形成非晶化层提升活性的结果相符合[31].

2.2 瞬时溶解(transient dissolution)

除了在确定电位下发生的传统热力学驱动的溶解之外, 性能衰减现象也与Ru位点氧化态变化所伴随的晶体结构扰动有关. 例如, 当氧在氧化/还原反应中插入或脱离结构时, Ru可能会溶解[18]. 配位程度较低与亚稳态转变的物种更可能溶解并脱离结构[18,24]. 图3(a)中峰3的强度明显高于其他峰, 表明高电压(1.4 V vs. RHE)下RuO_2的溶解以热力学驱动为主, 而在较低的电压区间(<1.3 V vs. RHE)峰3相对减弱后能观察到瞬时溶解(对应峰1, 2和4)的发生(图3(c)). 值得一提的是, 瞬时溶解行为在重复的循环伏安测试间存在差异[33]. 因而, 瞬时溶解还受电极历史状态所影响.

2.3 LOM促进溶解

基于LOM路径的OER催化剂的晶格氧参与反应，同时伴随着氧空位的生成[9,34]. 虽然氧空位可以被OH^-填充并实现动态平衡，但是氧空位填充的速度通常慢于LOM路径中氧空位的产生速度，因此相邻的金属离子会从催化剂表面浸出到电解液中以补偿电荷平衡[25,34]. 例如, 有晶格氧参与OER的RuO_x催化剂表现出较差的稳定性，即在1.7 V vs. RHE电压下稳定性测试5 h就失活了约81.2%[27].

2.4 电接触不良

OER催化剂通常会通过沉积、旋涂、滴涂等方式与基底形成良好的电接触. 除了催化剂本身之外, OER表观活性的衰减也可能来自于OER条件下造成的不良的电接触. 例如, 在2.2 V vs. RHE电位下, 玻碳电极在0.1 mol/L H_2SO_4中极化2 min, 就会形成钝化层, 从而造成电接触问题[35]. 此外, OER产生的气泡可能会因体积膨胀而加剧催化剂层的机械损伤(图3(d))[24,25]. 在大电流操作条件(1000 mA cm^{-2})下, 催化剂的剥离相比于催化剂的溶解对OER表观活性衰减的影响更甚[36].

3 提升活性和稳定性的策略

3.1 活性

在酸性体系中，催化剂的OER活性可以通过掺杂/取代、相结构设计、异质结构工程、电化学锂化、形貌控制、载体设计和缺陷工程等策略得到显著提高(图4(a)). 其中一些策略可以调控Ru的局部结构和电子结构, 从而优化中间物种的吸附能[37~41].

如图4(a)所示, 大部分策略都可以使催化剂达到高活性, 最终使得过电位≤200 mV. 而在更高活性区域(比如过电位≤180 mV, Tafel斜率≤50 mV dec^{-1})，我们可以看到掺杂/取代、相结构设计、缺陷工程等策略设计改性的催化剂，说明了这些策略在提升催化剂活性方面具有显著优势. 值得一提的是, 催化剂的载量也是影响活性的重要因素，比如过电位≤180 mV的催化剂载量均≥0.25 mg cm^{-2}_{geo}. 对比调控前后的催化剂活性，我们可以发现个别初始活性相对较差的催化剂在经过掺杂/取代策略改性后, 性能得到大幅提升, 比如使用掺杂/取代策略的Sr–Ru–Ir–O的过电位相比于初始的RuO_2降低了205 mV[52](图4(a)). 图4(b)中列举了使用最广泛的掺杂/取代策略改性的催化剂性能，使用该策略的催化剂相比于其他策略而言可以达到更高的活性，其中过电位最低的Si和W共掺杂的Ru基氧化物催化剂表现出最低的过电位(142 mV). 因此，掺杂/取代策略是提升Ru基氧化物催化剂酸性OER活性的较优选择. 除此之外, 针对同一催化剂的多策略合用可能可实现更高的催化活性(图4(a)); 例如, 同时使用表面包覆、缺陷工程和载体设计三种策略的碳包覆RuO_{2-x}@CNT催化剂在10 mA cm^{-2}_{geo}电流密度下的过电位只有170 mV[59].

3.2 稳定性

3.2.1 抑制过氧化

针对Ru基催化剂在热力学驱动的过氧化导致的溶解问题, 我们需要设计策略来抑制过氧化. 已报道的策略有掺杂/取代、电化学锂化、缺陷工程(如氧空位)和表面包覆等, 其中应用最广泛是掺杂/取代. 通过引入杂原子到RuO_2的晶格中可以降低Ru的价态[37]或实现杂原子在高电流密度下向Ru原子进行电子转移[38,45]. 例如，RuO_2中引入Zn和氧空位可以优化Ru的电子结构, 降低Ru的价态，形成的稳定Zn–O–Ru局域结构能增强催化剂稳定性[37]. 除此之外，有研究发现在RuO_2中掺杂Re[45]或Nb[38]能在OER条件下作为电子供体向Ru转移电子从而稳定Ru的价态，使催化剂稳定性得到显著提高.

3.2.2 稳定晶格氧或抑制晶格氧参与OER

针对Ru基氧化物LOM机理中晶格氧参与反应导致的稳定性问题，稳定晶格氧或抑制晶格氧参与OER可以显著增加其稳定性. 与抑制过氧化相似，掺杂/取代是目前应用最广泛的策略. 杂原子可以提高Ru基氧化物中Ru–O键的稳定性[41,43]或者调节Ru的电荷平衡[27]. 例如, 用不同电负性的金属离子掺杂到RuO_2中可以调节OER的反应机制，其中Sn掺杂可以抑制RuO_x催化剂LOM路径，使其主要按照AEM路径进行，从而提升了稳定性；掺杂后的催化剂在100 mA cm^{-2}电流密度下稳定性测试时间可以达到250 h[27]. 除此之外，Ni的掺杂可以稳定RuO_2晶格, 使其OER路径完全遵循AEM; 与未掺杂的RuO_2相比，Ni–RuO_2的稳定性得到显著提升[43].

3.2.3 不同策略催化剂的稳定性比较

图4(c)为不同策略Ru基氧化物催化剂的稳定性. 从图中可知，大多数Ru基氧化物催化剂是在10 mA cm^{-2}电流密度下进行稳定性测试，且接近一半的催化剂的

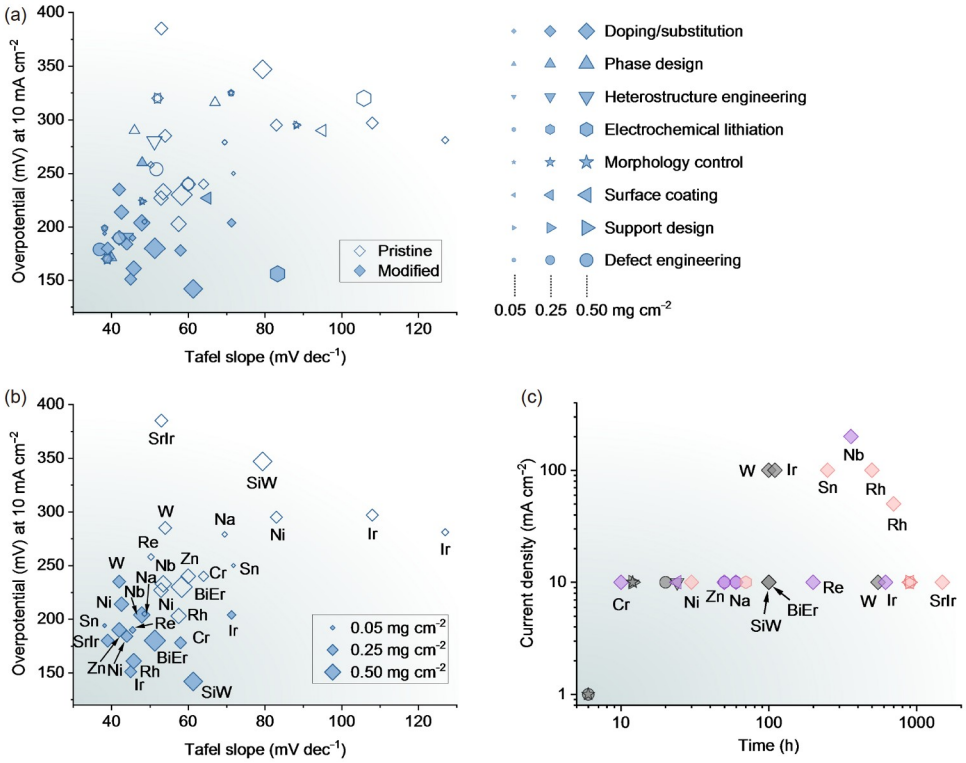

图 4 (网络版彩色)不同策略下Ru基氧化物催化剂的活性和稳定性比较. (a) 不同策略改性的Ru基氧化物催化剂活性前后对比图. (b) 使用掺杂/取代策略的Ru基氧化物催化剂活性对比图. (a)和(b)中形状大小表示催化剂载量, 未填充的符号表示初始催化剂, 对应填充的符号表示使用策略改性后的催化剂. (c) 不同策略的Ru基氧化物催化剂稳定性对比图. 符号的形状代表不同策略, 如(a)中所注释. 符号的颜色代表了不同稳定化思路, 浅紫色符号表示抑制过氧化, 浅红色代表稳定晶格氧或抑制晶格氧参与OER, 浅灰色代表其他或未说明情况. 本图涉及的策略包括掺杂/取代[27,37,38,42~54]、相结构设计[40,55]、异质结构工程[39]、电化学锂化[41]、形貌控制[56,57]、表面包覆[58,59]、载体设计[56,59]和缺陷工程[37,53,57,59,60]. 详见表S1

Figure 4 (Color online) Comparison of activity and stability of Ru-based oxide catalysts with different strategies. (a) Activity comparison of Ru-based oxide catalysts using different strategies. (b) Activity comparison of Ru-based oxide catalysts with the strategy of doping/substitution. The area of symbols in (a) and (b) represents the catalyst mass loading. Unfilled symbols and filled symbols in (a) and (b) represent pristine catalysts and catalysts modified by different strategy. (c) Stability comparison of Ru-based oxide catalysts using different strategies. The shape of symbols represents different strategies as shown in (a). The color of the symbols represents different stabilization ways: Light purple symbols represent inhibiting over-oxidation; light red symbols represent stabilizing lattice oxygen or inhibiting lattice oxygen participation in OER; light grey symbols represent other cases or unclear cases. These strategies include doping/substitution[27,37,38,42–54], phase design[40,55], heterostructure engineering[39], electrochemical lithiation[41], morphology control[56,57], surface coating[58,59], support design[56,59], and defect engineering[37,53,57,59,60]. See details in Table S1

稳定性测试时间小于100 h, 表明Ru基氧化物催化剂的稳定性问题依然充满挑战. 研究者通过抑制过氧化和稳定晶格氧或抑制晶格氧参与OER等来提升催化剂稳定性, 使得稳定性测试时间大于200 h. 掺杂/取代策略能达到这一目的, 如在Ru氧化物中掺杂Re[45]、Nb[38]和Ir[46]等原子可以抑制Ru的过氧化; 掺杂Sn[27]、Rh[47]和SrIr[52]等原子可以稳定晶格氧或抑制晶格氧参与OER. 稳定晶格氧或抑制晶格氧参与OER的催化剂表现出更好的稳定性, 尤其是SrIr掺杂的Ru氧化物, 其局部结构Ru–O–Ir具有较强的相互作用能抑制OER过程中的LOM路径, 从而使稳定性测试时间达到1500 h[52]. 然而, 使用缺陷工程和形貌控制策略调控的催化剂RuO_2纳米片表现出较差的稳定性, 其在1 mA cm^{-2}电流密度下的稳定性测试时间只有6 h, 表明此RuO_2催化剂并未因为这两种策略的使用而达到特别理想的稳定性[57]. 其中缘由可以归结于: (1) 缺陷导致的潜在结构不稳定而加速催化剂溶解[28]; (2) 形貌控制增加了催化剂的比表面积, 使其暴露更多的位点在电解质中, 这可能会促进催化剂在酸性条件下的溶解.

4 挑战与展望

本文首先综述了Ru基氧化物催化剂在酸性介质中

的理论稳定性、反应机理和理论活性. 同时讨论了其衰减机理以及提升稳定性和活性的策略. 虽然目前文献中已经报道了一些高活性和稳定性的Ru基氧化物催化剂, 但如何合理设计其组分以及打破活性和稳定性之间的权衡关系仍存在关键挑战.

(1) 如何找到合适的指导原则来合理设计Ru基氧化物催化剂组分仍具挑战. 目前已有许多元素被报道用于Ru基氧化物催化剂的掺杂/取代, 且可显著提升催化剂性能(图4(b), (c)). 然而, 如何选择合适的掺杂原子目前并没有可靠的参考准则, 更多的是通过试错实验得到优化的掺杂组分, 这种开发方式往往非常耗时. 掺杂原子的常见基本性质(比如价态和离子半径等)会如何影响Ru基催化剂性能与机理并不清楚, 这为催化剂的理性设计带来了困难. 例如, 一价的Na^{+}[53]与五价的Nb^{5+}[38]掺杂到RuO_2中都可以显著提升活性和稳定性(图4). 除此之外, 研究非贵金属掺杂Ru基氧化物催化剂是降低贵金属使用量的有效策略, 然而目前性能表现更好的掺杂剂依然是贵金属(如Ir和Rh) (图4). DFT计算和Pourbaix图可以预测催化剂的活性和稳定性. 但是催化剂的结构在反应过程中可能会发生动态变化(如阳离子价态、结晶度、缺陷), 因此对初始催化剂的稳定性的理论预测并不完全可行. 需要通过先进的表征技术对动态变化后或者反应过程中的Ru基氧化物催化剂结构进行表征, 来解读控制和影响催化反应的主导因素, 再将相关结论与理论计算相结合来对组分的设计进行指导. 此外, 机器学习作为有一种有前景的工具, 可以实现催化剂的高通量筛选. 例如, 可以通过机器学习技术从众多离子掺杂的RuO_2中筛选出具有最高OER性能的Ru基氧化物催化剂.

(2) 如何打破Ru基氧化物活性和稳定性之间的权衡关系也充满挑战. 从催化剂本征性质出发, 理论计算和实验均证明OER过程中晶格氧的参与能显著提升活性, 但是同时不可避免地造成了Ru的溶解, 因而晶格氧参与反应被认为是Ru稳定性差的原因之一[61]. 金属离子的溶出也可增加活性位点的暴露量, 从而利于催化活性, 但是带来稳定性问题. 从催化剂表观而言, 纳米化是提升催化活性的有效途径, 但同时带来了稳定性降低的问题. 基于此, 我们需要深入了解Ru基氧化物催化活性和稳定性之间的关系. 虽然已经报道了一些单一策略可以提升Ru基氧化物催化剂的活性和稳定性, 但依旧不足以满足商业化长期使用的需求. 针对同一催化体系的多种策略合用可以实现相对更好的活性和稳定性, 将组分合理设计与其他多种策略相结合可能是设计下一代Ru基氧化物酸性OER催化剂的有效思路.

用Ru基氧化物催化剂替代Ir基催化剂能降低PEM电解槽的成本, 从而更有利于其商业化应用. 但Ru基氧化物催化剂在稳定性方面依然存在较大的挑战, 解决这些挑战还需要研究者付出更多努力. 我们相信, 在逐步解决以上两大挑战的基础上, 研究者可以开发出高活性和稳定性的Ru基氧化物催化剂, 从而促进PEM电解水制绿氢的大规模应用.

参考文献

1 Turner J A. Sustainable hydrogen production. Science, 2004, 305: 972–974
2 Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. Nature, 2012, 488: 294–303
3 Gray H B. Powering the planet with solar fuel. Nat Chem, 2009, 1: 7
4 Yu H M, Yi B L. Hydrogen for energy storage and hydrogen production from electrolysis (in Chinese). Eng Sci, 2018, 20: 58–65 [俞红梅, 衣宝廉. 电解制氢与氢储能. 中国工程科学, 2018, 20: 58–65]
5 Li X G. Status and development of hydrogen preparation, storageand transportation (in Chinese). Chin Sci Bull, 2022, 67: 425–436 [李星国. 氢气制备和储运的状况与发展. 科学通报, 2022, 67: 425–436]
6 Jiao Y, Zheng Y, Jaroniec M, et al. Design of electrocatalysts for oxygen- and hydrogen-involving energy conversion reactions. Chem Soc Rev, 2015, 44: 2060–2086
7 Carmo M, Fritz D L, Mergel J, et al. A comprehensive review on PEM water electrolysis. Int J Hydrogen Energy, 2013, 38: 4901–4934
8 Chong L, Gao G, Wen J, et al. La- and Mn-doped cobalt spinel oxygen evolution catalyst for proton exchange membrane electrolysis. Science, 2023, 380: 609–616
9 Lei Z, Wang T, Zhao B, et al. Recent progress in electrocatalysts for acidic water oxidation. Adv Energy Mater, 2020, 10: 2000478
10 Kibsgaard J, Chorkendorff I. Considerations for the scaling-up of water splitting catalysts. Nat Energy, 2019, 4: 430–433
11 Zhang J H, Yue Q. Progress on the anode catalysts for proton exchange membrane water electrolysis (in Chinese). Chin Sci Bull, 2022, 67: 2889–2905 [张佳豪, 岳秦. 质子交换膜电解水阳极析氧催化剂. 科学通报, 2022, 67: 2889–2905]

12 Jain A, Ong S P, Hautier G, et al. The Materials Project: A materials genome approach to accelerating materials innovation. APL Mater, 2013, 1: 011002
13 Rao R R, Kolb M J, Giordano L, et al. Operando identification of site-dependent water oxidation activity on ruthenium dioxide single-crystal surfaces. Nat Catal, 2020, 3: 516–525
14 Singh A K, Zhou L, Shinde A, et al. Electrochemical stability of metastable materials. Chem Mater, 2017, 29: 10159–10167
15 Gunasooriya G T K K, Nørskov J K. Analysis of acid-stable and active oxides for the oxygen evolution reaction. ACS Energy Lett, 2020, 5: 3778–3787
16 Hubert M K A, Patel A M, Gallo A, et al. Acidic oxygen evolution reaction activity–stability relationships in Ru-based pyrochlores. ACS Catal, 2020, 10: 12182–12196
17 Kötz R, Lewerenz H J, Stucki S. XPS studies of oxygen evolution on Ru and RuO_2 anodes. J Electrochem Soc, 1983, 130: 825–829
18 Hodnik N, Jovanovič P, Pavlišič A, et al. New insights into corrosion of ruthenium and ruthenium oxide nanoparticles in acidic media. J Phys Chem C, 2015, 119: 10140–10147
19 Lin C, Li J L, Li X, et al. *In-situ* reconstructed Ru atom array on α-MnO_2 with enhanced performance for acidic water oxidation. Nat Catal, 2021, 4: 1012–1023
20 Man I C, Su H, Calle-Vallejo F, et al. Universality in oxygen evolution electrocatalysis on oxide surfaces. ChemCatChem, 2011, 3: 1159–1165
21 Rossmeisl J, Qu Z W, Zhu H, et al. Electrolysis of water on oxide surfaces. J Electroanal Chem, 2007, 607: 83–89
22 Rong C, Dastafkan K, Wang Y, et al. Breaking the activity and stability bottlenecks of electrocatalysts for oxygen evolution reactions in acids. Adv Mater, 2023, 35: 2211884
23 Koper M T M. Theory of multiple proton–electron transfer reactions and its implications for electrocatalysis. Chem Sci, 2013, 4: 2710–2723
24 Zeng F, Mebrahtu C, Liao L, et al. Stability and deactivation of OER electrocatalysts: A review. J Energy Chem, 2022, 69: 301–329
25 Wang Q, Cheng Y, Tao H B, et al. Long-term stability challenges and opportunities in acidic oxygen evolution electrocatalysis. Angew Chem Int Ed, 2023, 62: e202216645
26 Ying J, Chen J B, Xiao Y X, et al. Recent advances in Ru-based electrocatalysts for oxygen evolution reaction. J Mater Chem A, 2023, 11: 1634–1650
27 Shi Z, Li J, Wang Y, et al. Customized reaction route for ruthenium oxide towards stabilized water oxidation in high-performance PEM electrolyzers. Nat Commun, 2023, 14: 843
28 Roy C, Rao R R, Stoerzinger K A, et al. Trends in activity and dissolution on RuO_2 under oxygen evolution conditions: Particles versus well-defined extended surfaces. ACS Energy Lett, 2018, 3: 2045–2051
29 Liu C, Shviro M, Bender G, et al. Degradation effects at the porous transport layer/catalyst layer interface in polymer electrolyte membrane water electrolyzer. J Electrochem Soc, 2023, 170: 034508
30 Oh H S, Nong H N, Reier T, et al. Electrochemical catalyst–support effects and their stabilizing role for IrO_x nanoparticle catalysts during the oxygen evolution reaction. J Am Chem Soc, 2016, 138: 12552–12563
31 Klyukin K, Zagalskaya A, Alexandrov V. Role of dissolution intermediates in promoting oxygen evolution reaction at RuO_2 (110) surface. J Phys Chem C, 2019, 123: 22151–22157
32 Kötz R, Stucki S, Scherson D, et al. *In-situ* identification of RuO_4 as the corrosion product during oxygen evolution on ruthenium in acid media. J Electroanal Chem Interfacial Electrochem, 1984, 172: 211–219
33 Cherevko S, Zeradjanin A R, Topalov A A, et al. Dissolution of noble metals during oxygen evolution in acidic media. ChemCatChem, 2014, 6: 2219–2223
34 Binninger T, Mohamed R, Waltar K, et al. Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts. Sci Rep, 2015, 5: 12167
35 Geiger S, Kasian O, Mingers A M, et al. Catalyst stability benchmarking for the oxygen evolution reaction: The importance of backing electrode material and dissolution in accelerated aging studies. ChemSusChem, 2017, 10: 4140–4143
36 Li A, Kong S, Guo C, et al. Enhancing the stability of cobalt spinel oxide towards sustainable oxygen evolution in acid. Nat Catal, 2022, 5: 109–118
37 Hou L, Li Z, Jang H, et al. Electronic and lattice engineering of ruthenium oxide towards highly active and stable water splitting. Adv Energy Mater, 2023, 13: 2300177
38 Liu H, Zhang Z, Fang J, et al. Eliminating over-oxidation of ruthenium oxides by niobium for highly stable electrocatalytic oxygen evolution in acidic media. Joule, 2023, 7: 558–573
39 Huang K, Lin C, Yu G, et al. Ru/Se-RuO_2 composites via controlled selenization strategy for enhanced acidic oxygen evolution. Adv Funct Mater, 2023, 33: 2211102
40 Miao X, Zhang L, Wu L, et al. Quadruple perovskite ruthenate as a highly efficient catalyst for acidic water oxidation. Nat Commun, 2019, 10:

3809
41 Qin Y, Yu T, Deng S, et al. RuO_2 electronic structure and lattice strain dual engineering for enhanced acidic oxygen evolution reaction performance. Nat Commun, 2022, 13: 3784
42 Hao S, Liu M, Pan J, et al. Dopants fixation of ruthenium for boosting acidic oxygen evolution stability and activity. Nat Commun, 2020, 11: 5368
43 Wu Z Y, Chen F Y, Li B, et al. Non-iridium-based electrocatalyst for durable acidic oxygen evolution reaction in proton exchange membrane water electrolysis. Nat Mater, 2022, 22: 100–108
44 Wen Y, Liu C, Huang R, et al. Introducing Brønsted acid sites to accelerate the bridging-oxygen-assisted deprotonation in acidic water oxidation. Nat Commun, 2022, 13: 4871
45 Jin H, Liu X, An P, et al. Dynamic rhenium dopant boosts ruthenium oxide for durable oxygen evolution. Nat Commun, 2023, 14: 354
46 Zhu W, Song X, Liao F, et al. Stable and oxidative charged Ru enhance the acidic oxygen evolution reaction activity in two-dimensional ruthenium-iridium oxide. Nat Commun, 2023, 14: 5365
47 Wang Y, Yang R, Ding Y, et al. Unraveling oxygen vacancy site mechanism of Rh-doped RuO_2 catalyst for long-lasting acidic water oxidation. Nat Commun, 2023, 14: 1412
48 Jeon D, Kim D Y, Kim H, et al. Electrochemical evolution of Ru-based polyoxometalates into Si,W-codoped RuO_x for acidic overall water splitting. Adv Mater, 2024, 36: 2304468
49 Zhou G, Wang P, Hu B, et al. Spin-related symmetry breaking induced by half-disordered hybridization in $Bi_xEr_{2-x}Ru_2O_7$ pyrochlores for acidic oxygen evolution. Nat Commun, 2022, 13: 4106
50 Harzandi A M, Shadman S, Nissimagoudar A S, et al. Ruthenium core–shell engineering with nickel single atoms for selective oxygen evolution via nondestructive mechanism. Adv Energy Mater, 2021, 11: 2003448
51 Lin Y, Tian Z, Zhang L, et al. Chromium-ruthenium oxide solid solution electrocatalyst for highly efficient oxygen evolution reaction in acidic media. Nat Commun, 2019, 10: 162
52 Wen Y, Chen P, Wang L, et al. Stabilizing highly active Ru sites by suppressing lattice oxygen participation in acidic water oxidation. J Am Chem Soc, 2021, 143: 6482–6490
53 Zhang L, Jang H, Liu H, et al. Sodium-decorated amorphous/crystalline RuO_2 with rich oxygen vacancies: A robust pH-universal oxygen evolution electrocatalyst. Angew Chem Int Ed, 2021, 60: 18821–18829
54 He J, Zhou X, Xu P, et al. Regulating electron redistribution of intermetallic iridium oxide by incorporating Ru for efficient acidic water oxidation. Adv Energy Mater, 2021, 11: 2102883
55 Galyamin D, Torrero J, Rodríguez I, et al. Active and durable R_2MnRuO_7 pyrochlores with low Ru content for acidic oxygen evolution. Nat Commun, 2023, 14: 2010
56 Chen L, Li Y, Liang X. Ar/H_2/O_2-controlled growth thermodynamics and kinetics to create zero-, one-, and two-dimensional ruthenium nanocrystals towards acidic overall water splitting. Adv Funct Mater, 2021, 31: 2007344
57 Zhao Z L, Wang Q, Huang X, et al. Boosting the oxygen evolution reaction using defect-rich ultra-thin ruthenium oxide nanosheets in acidic media. Energy Environ Sci, 2020, 13: 5143–5151
58 Cui X, Ren P, Ma C, et al. Robust interface Ru centers for high-performance acidic oxygen evolution. Adv Mater, 2020, 32: 1908126
59 Yan H, Jiang Z, Deng B, et al. Ultrathin carbon coating and defect engineering promote RuO_2 as an efficient catalyst for acidic oxygen evolution reaction with super-high durability. Adv Energy Mater, 2023, 13: 2300152
60 Ge R, Li L, Su J, et al. Ultrafine defective RuO_2 electrocatayst integrated on carbon cloth for robust water oxidation in acidic media. Adv Energy Mater, 2019, 9: 1901313
61 Wohlfahrt-Mehrens M, Heitbaum J. Oxygen evolution on Ru and RuO_2 electrodes studied using isotope labelling and on-line mass spectrometry. J Electroanal Chem Interfacial Electrochem, 1987, 237: 251–260

补充材料

表S1 酸性介质中不同钌基氧化物催化剂析氧活性和稳定性对比

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 “钌基氧化物酸性析氧电催化剂”

Ruthenium-based oxides as electrocatalysts for acidic oxygen evolution

Rendian Wan, Guangxing Huang, Qingxun Liu & Bote Zhao*

School of Environment and Energy, South China University of Technology, Guangzhou 510006, China
* Corresponding author, E-mail: botezhao@scut.edu.cn

The problems of energy scarcity, cost volatility and climate change are accelerating the move away from fossil fuels. Diversifying energy sources, investing in renewable energy sources, such as solar and wind power, can combat both the energy and climate crises. Hydrogen is a clean energy carrier that could be produced by water electrolysis. Electricity can be generated from off-grid power generators, such as solar and wind power. The oxygen evolution reaction (OER) is a key half reaction for hydrogen production by water electrolysis. The sluggish kinetics of the OER, caused by a complex multistep electron transfer process result in a high overpotential, inevitably limiting the energy conversion efficiency of water electrolysis. Thus, the development of highly active and stable OER electrocatalysts is an urgent task.

Proton exchange membrane (PEM) electrolysis, a promising technology for green hydrogen production, has more advantages (e.g., higher current density, operating pressure, gas purity, and system compactness) compared to alkaline water electrolysis using an alkaline solution as electrolyte. However, the acidic operating environment imposes more stringent requirements on the stability of the catalyst. To date, the commercially available oxygen evolution reaction (OER) catalysts for PEM electrolysis are mainly iridium (Ir)-based materials. To achieve large-scale application of hydrogen production from water, relatively low-cost electrocatalysts are pursued to replace Ir in acidic media. In comparison with Ir-based materials, the ruthenium (Ru)-based oxide catalysts have the advantage of much lower cost but competitive OER activity. Thus, the Ru-based oxide catalysts are one of the most promising candidates for acidic OER in PEM water electrolysis. However, Ru-based oxide catalysts usually suffer from poor electrochemical stability in acidic media. The development of efficient and stable Ru-based oxide catalysts for acidic OER has received increasing attention.

This review covers the theoretical stability, OER mechanism, and theoretical activity of Ru-based oxide catalysts. We start with the price analysis of metallic Ru and Ir within a five-year range. Theoretical stability, including chemical stability and electrochemical stability, is then discussed based on Pourbaix diagrams. The OER mechanisms commonly used in acidic media are reviewed, including adsorbate evolution mechanism (AEM), lattice oxygen-mediated mechanism (LOM), and oxide path mechanism (OPM). Furthermore, the theoretical OER activity of RuO_2 compared with IrO_2 and other oxides is also discussed. To unravel the origin of the poor electrochemical stability for Ru-based oxide catalysts in acidic media, this review further delves into the fundamental understanding of degradation mechanisms, including anodic dissolution (or anodic oxidation with subsequent chemical dissolution), transient dissolution, LOM-derived dissolution, and poor electrical contact between catalysts and substrate. Based on the understanding of the degradation mechanisms, we further summarize and discuss the design strategies used to improve the activity and stability of Ru-based oxide catalysts, such as doping/substitution, phase design, heterostructure engineering, electrochemical lithiation, morphology control, surface coating, support design, and defect engineering. The different stabilization ways (e.g., inhibition of over-oxidation and stabilization of lattice oxygen or inhibition of lattice oxygen participation during OER) to overcome the stability issue are also addressed. Finally, we propose the critical challenges and perspectives regarding the use of Ru-based oxide catalysts for acidic OER. These challenges include finding guidelines for the rational design of Ru-based oxide compositions as promising OER electrocatalysts and managing the activity/stability trade-off of Ru-based oxide electrocatalysts. We believe that by addressing these challenges, a new generation of commercial Ru-based oxide catalysts for acidic OER can be developed.

water electrolysis, ruthenium-based oxides, degradation mechanism, catalyst design strategy

doi: 10.1360/TB-2024-0233